
Valence Tautomerism in Dinuclear Cobalt Dioxolene Complexes with Non-Innocent Behaving Bridging Ligands

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**“If I have seen further, it is by standing on the
shoulders of giants.”**

-Isaac Newton

Kurzzusammenfassung

Zu den drei großen anorganischen Verbindungsklassen schaltbarer und bistabiler Verbindungen zählen neben Spincrossover-Verbindungen und gemischtvalenten Verbindungen die Valenztautomere. Beim Valenztautomerismus handelt es sich um einen durch einen äußeren Zwang induzierten intramolekularen Elektronentransfer zwischen einem Elektronen-Donor- und Elektronen-Akzeptor-Fragment, der reversibel verlaufen kann. In den meisten Fällen bilden ein Metallzentrum und ein organischer Ligand das entsprechende Redoxpaar. Dabei werden zwei diskrete Redoxisomere mit unterschiedlichen Ladungsverteilungen sowie unterschiedlichen physikalischen, optischen und spektroskopischen Eigenschaften generiert.

Damit ein thermisch induzierter Valenztautomerismus (VT) auftreten kann, müssen diese Komplexverbindungen bestimmte Voraussetzungen erfüllen. Der organische Ligand muss ein nicht-unschuldiges Verhalten hinsichtlich seiner Redox Eigenschaften aufweisen. Die Valenzorbitale der Donor- und Akzeptor-Fragmente müssen energetisch sehr ähnlich sein. Die intramolekulare Kopplung muss stark genug sein, um einen Elektronentransfer zu ermöglichen, zugleich aber schwach genug, um zwei diskrete Zustände zu erhalten und deren elektronischen Strukturen nicht durch Delokalisierung oder Mischung der Orbitale zu verwischen.

Aufgrund ihrer Fähigkeit, auf äußere Einflüsse mit einer Änderung ihrer Eigenschaften zu reagieren, stellen Valenztautomere ideale Kandidaten für stark miniaturisierte elektronische Bauelemente dar. Dinukleare Verbindungen bieten dabei die zusätzliche Möglichkeit, bis zu drei verschiedene Zustände zu adressieren und damit komplexere *Logic Gates* zu realisieren. Als besonders geeignetes Modellsystem haben sich Cobalt-Dioxolen-Verbindungen herauskristallisiert. Ihre Valenzorbitale liegen energetisch sehr ähnlich beieinander, und durch geschickt gewählte Liganden kann beim VT-Übergang zusätzlich ein Spincrossover-Phänomen auftreten, das die entropische Triebkraft verstärkt und den Übergang begünstigt. Darüber hinaus lässt sich der VT-Übergang in diesem System gut mittels Magnetometrie verfolgen, was bei anderen Metallzentren selten auftritt.

Die vorliegende Arbeit untersucht systematisch an einem Piperazin-basierten Brückenliganden die Auswirkung verschiedener Modifikationen auf den valenztautomeren Übergang und dessen Übergangsprofil. Die elektronische Modifikation der Dioxolen-Liganden, die sterische und elektronische Modifikation des Brückenliganden, Packungseffekte und Gitterlösungsmittelleffekte durch Variation der Anionen sowie die Auswirkung einer veränderten elektronischen Kommunikation innerhalb der Brückeneinheit wurden dabei untersucht. In einem ersten Schritt wurde der Einfluss tetrahalogenierter Dioxolene auf den VT-Übergang untersucht, das Redoxpotential des Catecholats/Semichinonat-Paares moduliert und eine systematische Anionenstudie zur Untersuchung von Packungseffekten durchgeführt. Anschließend wurde der Brückenligand mit elektronendonierenden bzw. elektronenziehenden Substituenten modifiziert, um das Co(II)/Co(III)-Redoxpotential gezielt einzustellen. Durch ein abgestimmtes Zusammenspiel sterischer Reste am Brückenliganden konnte Co(II)-Semichinonat Radikalzustand bevorzugt stabilisiert werden. In Kombination mit einem elektronisch moderat eingestellten 4,5-Dichlorocatecholat gelang es erstmals, einen dinuklearen VT-Komplex mit einem unschuldigen Brückenliganden herzustellen, der einen vollständigen und reversiblen Übergang zeigt. Im letzten Schritt wurde der aliphatische Brückenligand mit geringer elektronischer Kommunikation der Cobalt-Zentren durch eine aromatische Pyrazin-Einheit mit erhöhter elektronischer Kommunikation ersetzt. Erste Ergebnisse belegen, dass auch mit dem neuen System Valenztautomerismus realisiert werden kann.

Abstract

Valence tautomers represent one of the three major classes of inorganic switchable and bistable compounds, alongside spin-crossover compounds and mixed-valence compounds. Valence tautomerism describes an intramolecular electron transfer between an electron-donor and an intramolecular electron transfer between an electron-donor and an electron-acceptor fragment, induced by an external stimulus, which can proceed reversibly. In most cases, a metal centre and an organic ligand constitute the corresponding redox pair. This gives rise to two discrete redox isomers with distinct charge distributions as well as distinct physical, optical, and spectroscopic properties.

For thermally induced valence tautomerism to occur, the complex compounds involved must meet certain requirements. The organic ligand must exhibit non-innocent behaviour with respect to its redox properties. The valence orbitals of the donor and acceptor fragments must be energetically very similar. The intramolecular coupling must be strong enough to allow electron transfer, yet weak enough to preserve two discrete states and prevent their electronic structures from being obscured by delocalization or orbital mixing.

Owing to their ability to respond to external stimuli with a change in their properties, valence tautomers are ideal candidates for highly miniaturized electronic devices. Dinuclear compounds additionally offer the possibility of addressing up to three distinct states, enabling the realization of more complex logic gates. Cobalt-dioxolene compounds have emerged as a particularly suitable model system. Their valence orbitals lie energetically very close to one another, and through judicious choice of ligands, a spin-crossover phenomenon can additionally occur at the valence tautomeric transition. Furthermore, the valence tautomeric transition in this system can be conveniently monitored by magnetometry, which is rarely the case of other metal centres.

The present work systematically investigates, using a piperazine-based bridging ligand, the effects of various modifications on the valence tautomeric transition and its transition profile. The electronic modification of the dioxolene ligands, the steric and electronic modification of the bridging ligand, packing effects and lattice solvent effects through variation of the counter-anions, as well as the effect of altered electronic communication within the bridging unit were examined. In a first step, the influence of tetrahalogenated dioxolenes on the valence tautomeric transition was studied, the redox potential of the catecholate/semiquinonate pair was modulated, and a systematic anion study was conducted to investigate packing effects. Subsequently, the bridging ligand was modified with electron-donating and electron-withdrawing substituents to fine-tune the Co(II)/Co(III) redox potential. Through a carefully balanced interplay of steric substituents on the bridging ligand, the Co(II)semiquinonate radical state could be preferentially stabilised. In combination with an electronically moderately tuned 4,5-dichlorocatecholate, it was possible for the first time to prepare a dinuclear valence tautomeric complex bearing an innocent bridging ligand that undergoes a complete and reversible transition. In the final step, the aliphatic bridging ligand, which affords low electronic communication between the cobalt centres, was replaced by an aromatic pyrazine unit providing enhanced electronic communication. Preliminary results demonstrate that valence tautomerism can likewise be realised with the new system.

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List of Abbreviations

bq	benzoquinone
Br ₄ cat	Tetrabromocatecholate
χ	Magnetic Susceptibility
cat	catecholate
Cl ₄ cat	Tetrachlorocatecholate
CSD	Crystal Structure Database
CV	Cyclic Voltammetry
Δ	Ligand Field Splitting Energy
dbcat/dbucat/dtbcac	Di-tert-butyl-catecholate
dbsq/dbusq	Di-tert-butyl-semiquinonate
ΔE_p	Peak-to-Peak Separation
DFT	Density Functional Theory
ΔG	Change in Free Gibbs Energy
ΔH	Change in Enthalpy
diox	Dioxolene
DOSY	Diffusion Ordered Spectroscopy
ΔS	Change in Entropy
ΔV	Change in Volume
$E_{1/2}$	Half-Wave Potential
E_m	Half-Step Potential
EPR	Electron Pair Resonance
E_p	Peak Potential
ESI ⁺	Electron Spray Ionisation (positive)
Fc	Ferrocene
Fc ⁺	Ferrocenium
GFA	Guanidine Functionalised Aromatic System
H _{ab}	Electronic Coupling Parameter
HS	High-Spin
HSAB	Hard Soft Acids Bases
IR	Infrared
IVCT	Intervalence Charge Transfer
K _c	Comproportionation Constant

λ	Reorganisation Energy
LIESST	Light-induced excited spin-state trapping
LIVT	Light-induced-valence tautomerism
LMCT	Ligand-to-Metal Charge-Transfer
LS	Low-Spin
LUMO	Lowest Unoccupied Molecular Orbital
MAS	Magic Angle Spinning
MLCT	Metal-to-Ligand Charge-Transfer
MMCT	Metal-to-Metal Charge Transfer
MOS	Metric Oxidation State
MV	Mixed-valent
NIR	Near-Infrared
NMR	Nuclear Magnetic Resonance
P	Spin Pairing Energy
p	pressure
SCO	Spin-crossover
sq	semiquinonate
T	Temperature
$T_{1/2}$	Transition Temperature
UV-Vis	Ultraviolet-Visible
VT	Valence tautomerism
X ₄ cat	Tetrahalogenated Catecholate
XRD	X-ray Diffraction

1. Introduction

1.1 Switchable and bistable molecules

Molecular switches and bistable systems occupy a central role in chemistry and biology alike. Their defining feature is the existence of at least two thermodynamically accessible states, separated by a sufficiently small energy barrier to allow reversible interconversion upon external stimulation. These states may differ, for instance, in their electronic, geometric, or spin configuration. A special class of molecular switches are bistable systems, in which both states correspond to local energy minima, enabling the system to retain its switched state even after the stimulus is removed, a prerequisite for information storage at the molecular level. These stimuli include temperature¹⁻³, irradiation⁴⁻⁶, pressure^{7,8}, electric fields⁹, coordination effects¹⁰⁻¹², or pH changes.^{13,14}

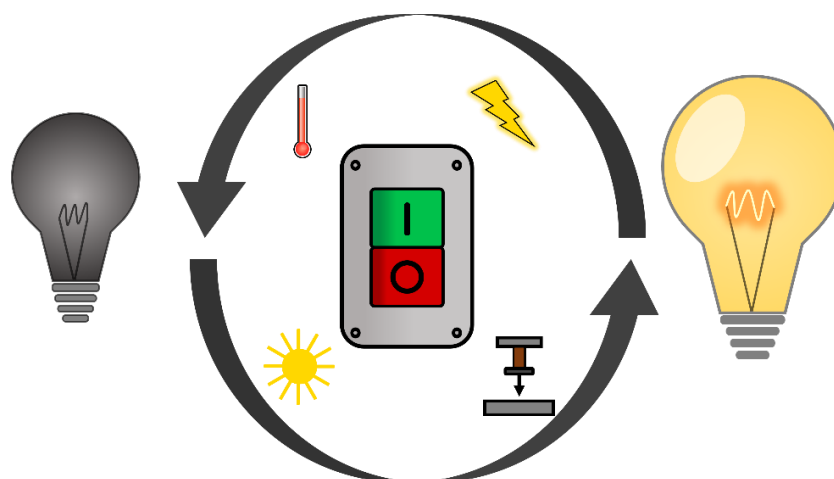


Figure 1: Bistable molecules reacting to external stimuli switching between an inactive and active state accompanied by changing their structural, optical, magnetic properties and more.

A classic example of a naturally occurring, light-switchable system is retinal, embedded within the protein rhodopsin in the rod cells of the retina. Upon exposure to light, retinal undergoes a cis-trans isomerisation of the C11-C12 double bond. This photoisomerisation of retinal induces a conformational change in the surrounding protein, ultimately triggering a nerve signal that is transmitted via the optic nerve to the brain, thereby enabling visual perception.^{15,16}

Beyond photoswitchable systems, numerous redox-active molecular switches exist in nature. Cytochromes and iron-sulphur clusters, for instance, reversibly interconvert between Fe(II) and Fe(III) oxidation states, and thereby form the basis of electron transport in the mitochondrial respiratory chain. While cytochromes operate via redox switching, haemoglobin represents a complementary example in which oxygen binding to the central iron atom induces a coupled spin transition, formally corresponding to a transition from high-spin Fe(II) in deoxyhaemoglobin to an intermediate Fe(II) centre in the oxygenated form, with partial superoxide character of the bound oxygen. This process plays a crucial role in oxygen transport and regulation within the human body.¹⁷⁻²⁰

pH-sensitive systems are also widespread in nature. Anthocyanins, common plant pigments, display a pronounced pH-dependent colour change. In red cabbage, for example, they shift from red under acidic to blue under basic conditions. This phenomenon arises from pH-dependent protonation and tautomerisation of the chromophore, which alter its conjugation and thus its optical absorption.^{21,22}

In summary, molecular switching behaviour is a fundamental feature of biological systems, where it fulfils essential functions in signal transduction, electron transfer, energy conversion, and the perception of environmental stimuli.²³ The ability to reversibly switch between distinct molecular states is a prerequisite for the maintenance and regulation of life processes. The underlying principles of these natural systems have inspired the rational design of artificial molecular switches. These

systems promise to play a transformative role in the miniaturisation of electronic devices, as discussed in the following chapter.

1.2 Electronic Miniaturisation: Molecular Switches

Higher, faster, stronger - a well-known paraphrase of the Olympic motto - has long symbolised the ideal of continuous human progress. This pursuit of peak performance within ever tighter constraints finds a direct parallel in the trajectory of modern technology, which is driven by the need to achieve greater performance while simultaneously reducing size, weight and energy consumption. Moore's law states that the number of transistors in an integrated circuit doubles approximately every two years. While this prediction held remarkably well for several decades, physical limitations of silicon-based technologies have made it increasingly difficult to sustain, providing a strong incentive for the exploration of alternative approaches to miniaturisation.^{24,25}

A historical example illustrates this clearly. IBM's first commercially successful computer, the 305 RAMAC (*Random Access Method of Accounting and Control*), contained one of the earliest hard drives capable of real-time data storage. Yet its modest capacity of roughly four megabytes (4 000 000 bytes) required a storage unit measuring approximately $150 \times 170 \times 60$ cm, and the entire system weighed close to one metric ton.²⁶ In contrast, the global volume of digital data is expected to reach around 530 zettabytes (530 000 000 000 000 000 000 bytes) by 2029, a scale that places enormous demands on processing speed and device miniaturisation.²⁷

Efforts toward electronic miniaturisation therefore focus on producing components that occupy less space while maintaining or ideally enhancing their functional performance. At the smallest conceivable scale, molecular systems offer a promising route forward. Individual molecules occupy just a few cubic nanometres, several orders of magnitude below the dimensions of current silicon-based components. Molecular switches are particularly attractive candidates because they can respond to external stimuli by reversibly changing their physical or chemical properties, allowing them to function as logic gates at the level of individual molecules. Their nanometre-scale dimensions would, in principle, allow functional units far smaller than those achievable with silicon-based technologies. They are of interest for a wide range of applications, including sensing, actuation, display technologies and molecular logic operations. Systems containing several metal centres can be especially powerful when these centres can be addressed independently, as this allows a single molecule to encode multiple distinct states.^{28,29}

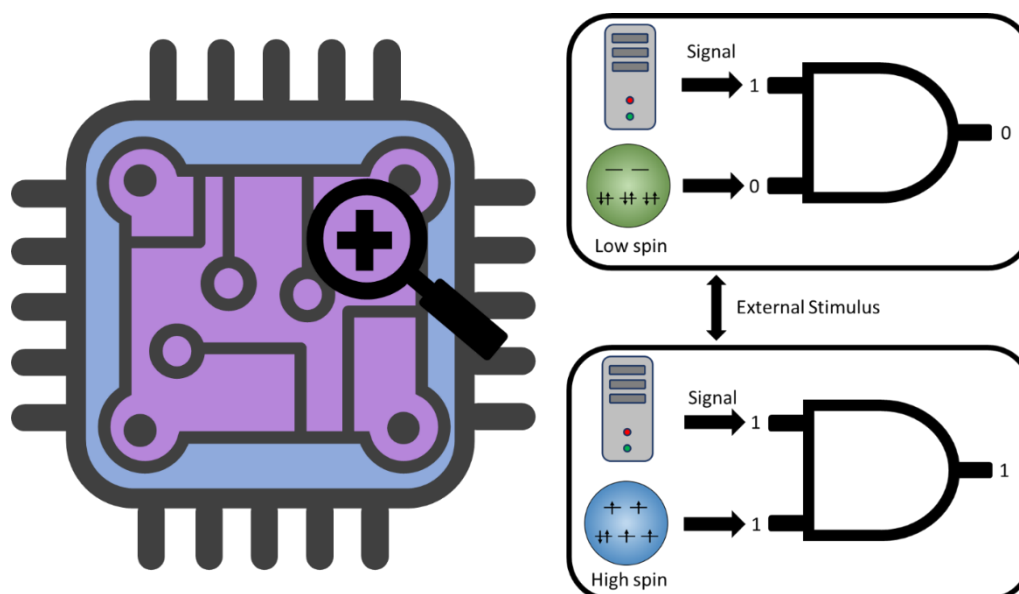


Figure 2: Conceptual illustration of a molecular-electronic hybrid logic element. The spin switchable molecule acts as a magnetically readable binary input. Its diamagnetic low-spin state corresponds to 0, while the paramagnetic high-spin state corresponds to 1. Upon external stimulation, the spin-state changes the AND-gate output from 0 to 1 in conjunction with the electronic input.

Transition-metal complexes form one of the most versatile families of molecular switches. Their electronic, optical, structural and magnetic properties can change abruptly and reversibly when stimulated by temperature variations, light, pressure, electric fields or chemical influences. Because these changes are often large and easily detectable, such complexes are well suited for use in highly miniaturised electronic architectures.³⁰

Among the established switching motifs within this field are spin-crossover compounds (SCO), mixed-valence systems such as Prussian blue analogues, and valence-tautomeric complexes (VT). Each of these families embodies a distinct mechanism that enables electronically bistable or multistable molecular behaviour and has become a central topic in the development of molecule-based switching materials. Although spin-crossover compounds, mixed-valence systems, and valence tautomers are rooted in different physical mechanisms, including spin-state changes, electron delocalisation, and redox-driven electron transfer, they share the common feature of a bistable electronic ground state. The following sections introduce each in turn before focusing on valence tautomerism, which constitutes the central topic of this work.

1.3 Spin-Crossover: Switching the Spin-State

Spin-crossover (SCO) compounds represent one of the most extensively studied classes of switchable molecules in inorganic chemistry. These compounds undergo a reversible transition between a low-spin (LS) state, characterised by maximum electron pairing, and a high-spin (HS) state with the maximum number of unpaired electrons.

The phenomenon was first reported by Cambi *et al.* in the early 1930s, who observed anomalous temperature-dependent magnetic behaviour in iron(III) dithiocarbamate complexes. Although initially misinterpreted as an equilibrium between two magnetic isomers, this observation was later recognised as the first documented example of spin-crossover behaviour. Since then, SCO has developed into a highly active research field. The focus has shifted progressively from the synthesis of novel SCO complexes and the pursuit of room-temperature transitions, through the study of multistep transition profiles and chiral SCO systems, to the current emphasis on practical applications.^{31–34}

Octahedrally coordinated $3d^4$ – $3d^7$ transition metal ions can populate the five ligand-field-split $3d$ orbitals (t_{2g} and e_g^*) in two distinct ways, depending on the relative magnitudes of the ligand field splitting energy (Δ) and the spin pairing energy (P). When $\Delta \gg P$, electrons preferentially occupy the lower-lying t_{2g} orbitals, maximising pairing and yielding the LS configuration. Conversely, when $\Delta \ll P$, electrons are distributed according to Hund's rule, populating all available orbitals singly to give the HS configuration. SCO behaviour arises in the intermediate regime, where Δ is approximately equal to P , such that both spin states are thermally accessible and an external stimulus can drive the interconversion between them.^{35,36}

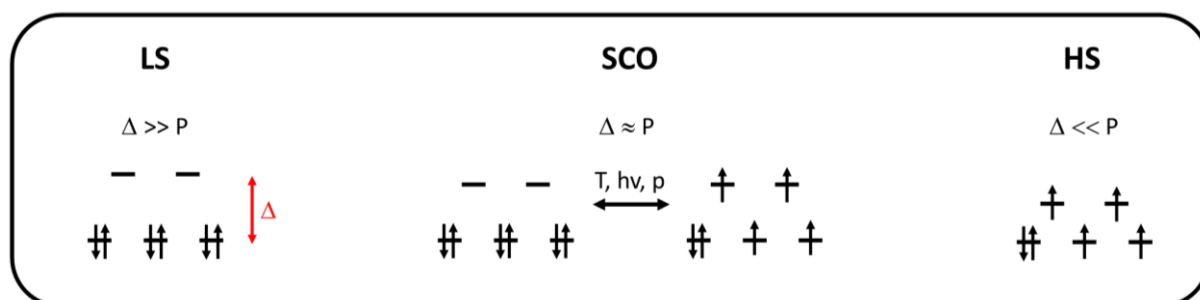


Figure 3: Schematic representation of the three limiting electronic configurations for an octahedral d^6 Fe(II) ion. In the strong ligand field regime ($\Delta > P$), a low-spin configuration is favoured, whereas weak ligand fields ($\Delta < P$) stabilize the high-spin state. In the intermediate case, where Δ and P are of comparable magnitude, external stimuli such as temperature, Light irradiation or pressure can induce reversible switching between the low-spin and high-spin states, resulting in spin crossover behaviour.

This sensitivity to ligand field strength explains why SCO behaviour is almost exclusively observed in $3d$ transition metal complexes. Moving from $3d$ to $4d$ and $5d$ metal ions, the ligand field splitting energy increases by approximately 50% per row, while the spin pairing energy does not increase correspondingly. As a result, the condition $\Delta \gg P$ is generally fulfilled for $4d$ and $5d$ metals, which therefore adopt exclusively LS configurations under typical coordination environments. Tetrahedral coordination also precludes SCO, as the ligand field splitting in tetrahedral complexes is approximately $4/9$ of that in analogous octahedral systems, invariably favouring the HS state.³⁴

The thermodynamic basis of SCO behaviour follows directly from the Gibbs free energy ($\Delta G = \Delta H - T\Delta S$). The LS state is enthalpically favoured due to stronger metal-ligand orbital overlap, shorter bond lengths, and larger ligand field splitting. It is therefore stabilised at low temperatures. The HS state, by contrast, is entropically favoured as a result of its greater number of accessible electronic and vibrational microstates. Consequently, the HS state becomes thermodynamically preferred at elevated temperatures, and thermal SCO proceeds from LS to HS upon heating.^{37,38}

The two spin states differ markedly in their electronic configuration, which manifests directly in their structural properties. Population of the antibonding e_g^* orbitals in the HS state weakens the metal-ligand bonds, resulting in significantly longer bond lengths compared to the LS state. In iron(II) complexes, HS Fe-N bond lengths are typically around 10% longer than their LS counterparts. Where the spin transition results in an asymmetric population of the e_g^* orbitals, the resulting degeneracy is lifted and a structural distortion occurs to minimise the total energy of the system, in accordance with the Jahn-Teller theorem.³⁹

These structural, along with optical and magnetic differences between spin states, enable characterisation by a wide range of techniques including SQUID magnetometry, UV-Vis, Mössbauer, NMR, IR spectroscopy and X-ray diffraction (XRD). SCO compounds can be switched reversibly through a range of external stimuli. While temperature-induced transitions have been studied most extensively, owing to the convenience of monitoring magnetic susceptibility by SQUID magnetometry, other stimuli include pressure, electric fields, light irradiation, most notably via light-induced excited spin-state trapping (LIESST), changes in the coordination environment, and host-guest interactions.^{35,40–42}

SQUID magnetometry in particular allows detailed analysis of transition profiles through the temperature dependence of their magnetic properties. Several characteristic profiles are observed. Gradual transitions (a) arise in compounds with negligible cooperativity and are commonly encountered in solution, as probed by measurements such as Evans NMR method⁴³, and in the solid state when intermolecular interactions within the crystal lattice are weak. Abrupt transitions (b), by contrast, result from strong cooperativity, in which the transition of one metal centre lowers the barrier for neighbouring sites. Hysteretic behaviour (c), in which the LS-to-HS and HS-to-LS transitions occur at different temperatures, emerges due to exceptionally strong cooperativity, such that the system exhibits kinetic bistability. Two-step and multistep transition (d) profiles are also observed, arising either from crystallographically or chemically inequivalent metal sites in mononuclear compounds or, in di- and polynuclear complexes, from electronic communication between metal centres, whereby the spin transition of one centre disfavours or delays the transition of a neighbouring centre. Finally, incomplete transitions (e), in which a residual fraction of one spin state persists across the entire temperature range, are also frequently encountered.^{34,44,45}

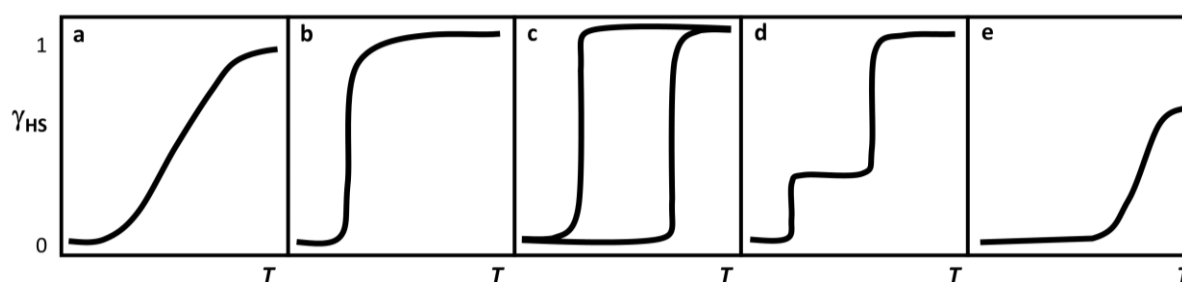


Figure 4: Schematic representation of common SCO transition profiles shown as the HS fraction as a function of temperature: a) gradual, b) abrupt, c) hysteretic, d) multistep, and e) incomplete SCO behaviour, adapted from ³⁴.

While SCO involves a change in spin state at a formally constant metal oxidation state, a related but mechanistically distinct class of switchable compounds exists. In such mixed-valence systems, the degree of electron delocalisation between redox-active centres determines the physical and spectroscopic properties of the compound and forms the conceptual basis for the bistable behaviour discussed in the following section.

1.4 Mixed-Valence Complexes: From Localisation to Delocalisation

Mixed-valence (MV) compounds contain a single element in two formally different oxidation states within the same molecule. Depending on the degree of electronic coupling between redox-active centres, an electron or hole may be fully localised on one centre, symmetrically delocalised across both, or in an intermediate situation where thermally or optically induced electron transfer between centres becomes possible.⁴⁶

The concept was originally developed for transition metal complexes in which two metal centres of the same type are connected by a bridging ligand. It has since been extended to include systems with organic redox centres, inverted mixed-valence systems in which organic redox centres are bridged by a transition metal unit, and compounds in which electron transfer involves the bridging unit itself. Examples such as radical anions of di- and polynitroaryl compounds are now also recognized as mixed-valence systems, although some of these compounds were first described before the concept of mixed valence was formally established.^{46–49}

The most historically significant example of a synthetic transition metal MV complex is the Creutz-Taube ion, a dinuclear ruthenium complex bridged by pyrazine. Originally synthesised as a kinetically stable model for degenerate inner-sphere electron transfer, electrochemical measurements revealed electronic communication between the two ruthenium centres through the bridging ligand. A characteristic long-wavelength absorption band in the near-infrared region was subsequently identified as an intervalence charge transfer (IVCT) band, and the absence of hyperfine coupling in EPR spectroscopy confirmed that the complex is a fully delocalised species, with a formal oxidation state of +2.5 at each ruthenium centre.^{50–55}

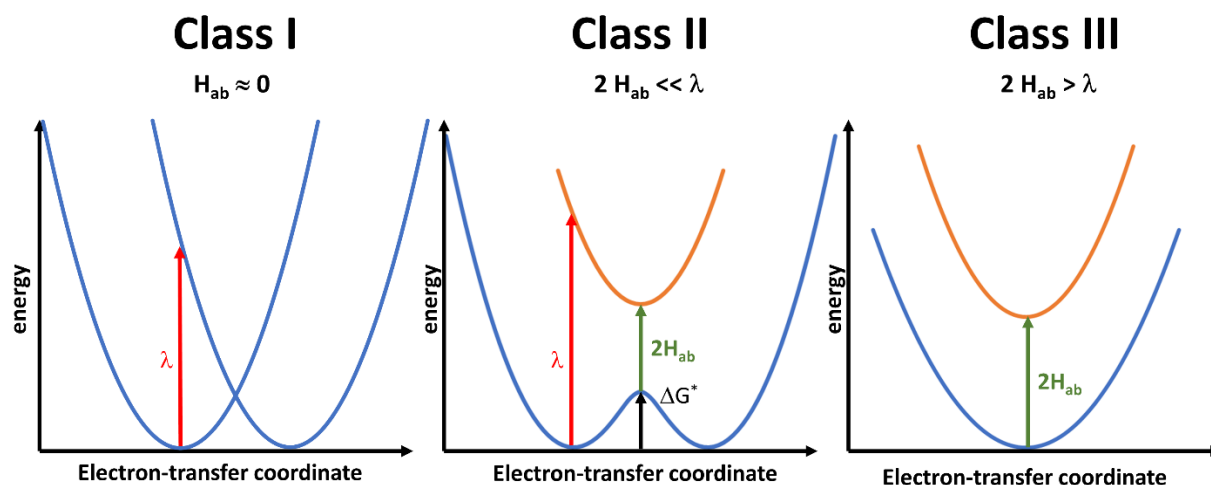


Figure 5: Schematic representation of the potential energy surfaces of Robin-Day classes I-III for mixed-valence systems along the electron-transfer coordinate. Adapted from ⁴⁶.

The Robin-Day classification provides the principal framework for categorising MV compounds according to their degree of electronic coupling.⁵⁶ Class I compounds possess decoupled redox centres with fully localised charges and no meaningful electronic communication. Class II compounds exhibit moderate electronic coupling, characterised by a double-well adiabatic ground-state potential energy surface with an activation barrier for thermal electron transfer. In these systems, the electronic coupling parameter $2H_{ab}$, defined as the energy splitting between the ground state and excited adiabatic potential energy surfaces, is smaller than the reorganisation energy λ , which encompasses both inner-sphere contributions arising from structural changes upon electron transfer and outer-sphere contributions from solvent reorganisation, as described by Marcus theory.^{46,57,58} Class III compounds display strong electronic coupling, where $2H_{ab} \geq \lambda$, resulting in a single potential energy minimum and complete charge delocalisation across both redox centres. The original three-class

system has since been extended by the intermediate class II/III, in which very small activation barriers and fast electron transfer rates can give rise to contradictory results across spectroscopic methods operating on different timescales.⁵⁹

The degree of electronic coupling is experimentally accessible through several complementary techniques. Electrochemically, the comproportionation constant K_c ⁵⁴, derived from the separation of the two redox potentials, quantifies the thermodynamic stability of the mixed-valence state. Spectroscopically, the energy, bandwidth, and intensity of the IVCT band serve as diagnostic criteria for Robin-Day classification and allow estimation of H_{ab} via Hush theory.^{54,60,61} Structurally, X-ray diffraction can reveal differences in metal-ligand bond lengths between the two redox centres, providing a direct indication of charge localisation.⁶² For iron systems on the Mössbauer timescale, localised and delocalised systems can often be distinguished by the presence of one or two distinct metal ion environments.⁴⁶

From the perspective of bistable and switchable molecules, Class I systems are of limited interest owing to their localised and non-interconverting character. Class III systems, by contrast, are attractive candidates for molecular electronic components due to their delocalised ground states, in which the concept of a discrete electron transfer event no longer applies. Class II and class II/III systems are of particular relevance for switching applications, as the localised charge distribution can, in principle, be toggled between states by an external stimulus, making them viable candidates for logic elements in electronic miniaturisation.^{46,63}

Unlike SCO compounds, in which switching involves a change in spin state without a formal change in metal oxidation state, and classical MV complexes, in which electron transfer occurs between two metal centres of the same type, valence tautomeric complexes represent a third and mechanistically distinct class of bistable molecules, in which intramolecular electron transfer occurs between a metal centre and a redox-active ligand rather than between two metal centres of the same type. This phenomenon is examined in detail in the following section.

1.5 Valence Tautomerism: Intramolecular Electron Transfer Between Redox Isomers

Valence tautomerism (VT) is a phenomenon in which a metal complex bearing a redox-active organic ligand undergoes reversible intramolecular electron transfer between the electron donating part and the electron accepting one upon external stimulation, generating two distinct redox isomers with different charge distributions, spin states, and physical, optical, and spectroscopic properties.^{64,65}

1.5.1 Historical Origins and Early Observations of Valence Tautomerism

The term valence tautomerism was originally applied to purely organic systems involving intramolecular rearrangements without changes in atomic connectivity, such as the equilibrium between cyclooctatetraene and bicyclo[4,2,0]octa-2,4,7-triene⁶⁶, or sigmatropic [3,3]-rearrangements in barbalone derivatives.⁶⁷

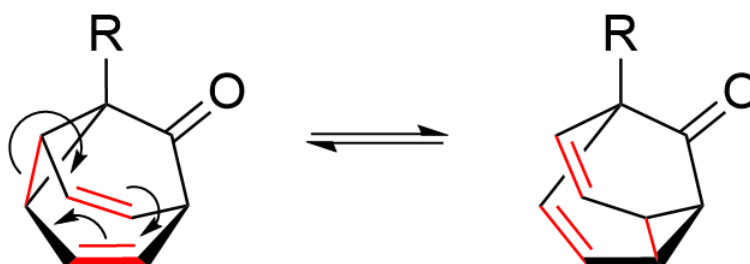


Figure 6: Sigmatropic [3,3]-rearrangement of barbalone derivatives with the participating bonds highlighted in red. Adapted from literature.⁶⁷

In 1980, Buchanan and Pierpont extended this concept to coordination chemistry, thereby establishing the field of inorganic valence tautomerism. They reported the tautomeric catecholate-semiquinonate interconversion via metal-ligand electron transfer in $\text{Co}(3,5\text{-dbcats})(3,5\text{-dbsq})(\text{bpy})$, demonstrating that metal complexes bearing redox-active, non-innocent ligands can undergo reversible intramolecular electronic reorganisations in response to external stimuli, such as temperature, accompanied by pronounced changes in physical and spectroscopic properties.⁶⁸

To place VT within the broader context of bistable inorganic systems, it is important to distinguish it conceptually from the related phenomena discussed in the preceding sections. In SCO compounds, only the spin state at a single metal centre changes, while its formal oxidation state remains constant. In classical mixed-valence complexes, electron transfer occurs between two redox centres of the same element. VT, by contrast, involves a genuine change in oxidation state through intramolecular electron transfer between a metal centre and a redox-active ligand, generating two true redox isomers.^{34,46,69}

1.5.2 Redox-Active Ligands and Non-Innocent Behaviour

Redox-active non-innocent ligands play a central role in VT chemistry. In 1966, Jørgensen introduced the classification of ligands as innocent or non-innocent, defining innocent ligands as those that allow unambiguous assignment of the metal oxidation state, and non-innocent ligands as those whose redox state cannot be directly inferred.⁷⁰ The simplest example is nitric oxide (NO), which can be formally described as NO^+ , $\text{NO}^\bullet$ or NO^- depending on the coordination environment, as illustrated by $[\text{Fe}(\text{NO})(\text{H}_2\text{O})_5]^{2+}$, best described as a $\text{Fe}(\text{III})(\text{NO}^-)$ species. The different binding modes of the nitrosyl ligand can be distinguished by the M-N-O bond angle, which is linear for NO^+ , bent for $\text{NO}^\bullet$, and strongly bent for NO^- (**Figure 7**).^{71,72}

It is important to note that the potential for non-innocent behaviour is an intrinsic feature of certain ligands. However, whether this behaviour is expressed strongly depends on the electronic structure of the metal centre and the overall coordination environment. Accordingly, it is more precise to speak of non-innocent behaviour rather than classifying a ligand as inherently non-innocent.⁷³

Unrecognised non-innocent behaviour has historically led to misassignment of unusual oxidation states at metal centres. A well-known example is the mononuclear gallium complex initially described as $[\text{Ga}^{\text{II}}(\text{tbu-dab}^2)(\text{tbu-dab})]$ but later correctly reformulated as $[\text{Ga}^{\text{III}}(\text{tbu-dab}^*)(\text{tbu-dab}^2)]$ (tBu-dab = 1,4-di-*tert*-butyl-1,4-diazabutadiene).⁷⁴ Established ligand classes known to exhibit non-innocent behaviour include catecholates/semiquinonates/quinones (1,2-diheterolenes), α -diimines, tetrapyrrole macrocycles, α -dithiolenes, and oxide/superoxide/peroxide systems, among others can be seen in **Figure 7**.⁷²

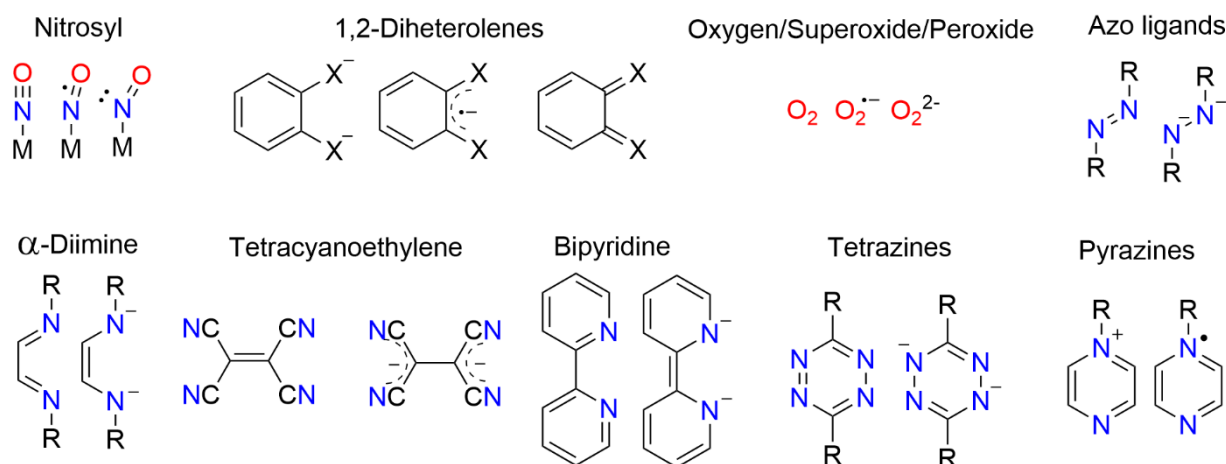


Figure 7: Selected examples of ligands exhibiting non-innocent behaviour, adapted from literature.^{71,72,75}

In the context of VT, dioxolene ligands are by far the most extensively investigated, as their redox processes occur at readily accessible potentials and their π^* orbitals are energetically close to the d orbitals of first-row transition metals, enabling facile metal-ligand electron transfer.⁷⁶ The dioxolene redox series encompasses three oxidation states, the dianionic catecholate (cat^{2-}), the monoanionic semiquinonate radical anion ($\text{sq}^{\bullet-}$), and the neutral benzoquinone (bq) (**Figure 8**).^{71,77}

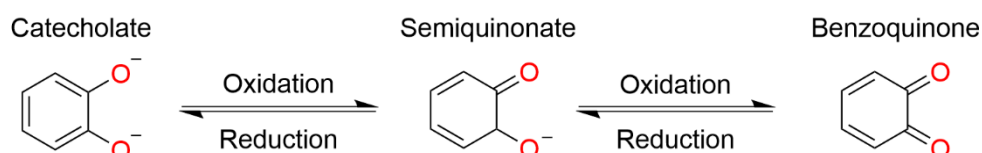


Figure 8: The three formal redox states of the dioxolene ligand system: catecholate, semiquinonate, and benzoquinone.⁷⁸

The structural signatures of these three forms are well established. In the catecholate form, the six-membered ring is aromatic with C-O bond lengths of approximately 1.35 Å and C-C bond lengths intermediate between single and double bonds. In the quinone form, aromaticity is lost, C-O bonds shorten to double bond character, and the ring displays alternating single and double C-C bonds. The semiquinonate is intermediate between these two extremes. These bond length changes provide a reliable structural indicator of the ligand oxidation state (**Figure 9**). For a more quantitative assignment, a metric oxidation state (MOS) can be calculated from a least-squares fitting of the five most sensitive bond parameters against a reference database of structurally characterised compounds in the CSD.⁷⁹

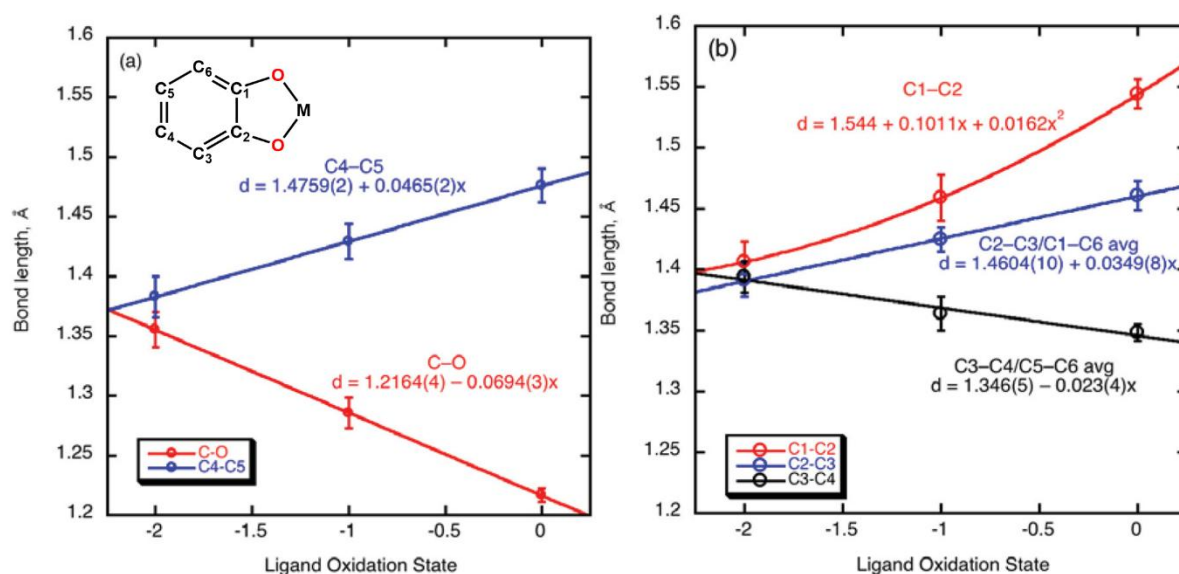


Figure 9: Correlation between characteristic bond distances and the oxidation state of catecholate-type ligands: a) C-O and C4-C5 bonds with the numbering scheme; b) C1-C2, C2-C3/C1-C6, and C3-C4/C5-C6 bonds.⁷⁹

While dioxolenes dominate VT research, other redox-active ligand classes have been employed, including *o*-iminobenzoquinonates, verdazyls, α -diimines, amidophenolates, bis(pyridylamino)isoindolines, and guanidino-substituted-benzodioxoles (**Figure 10**).^{64,80–87} However, the number of confirmed VT examples with non-dioxolene ligands remains considerably smaller.

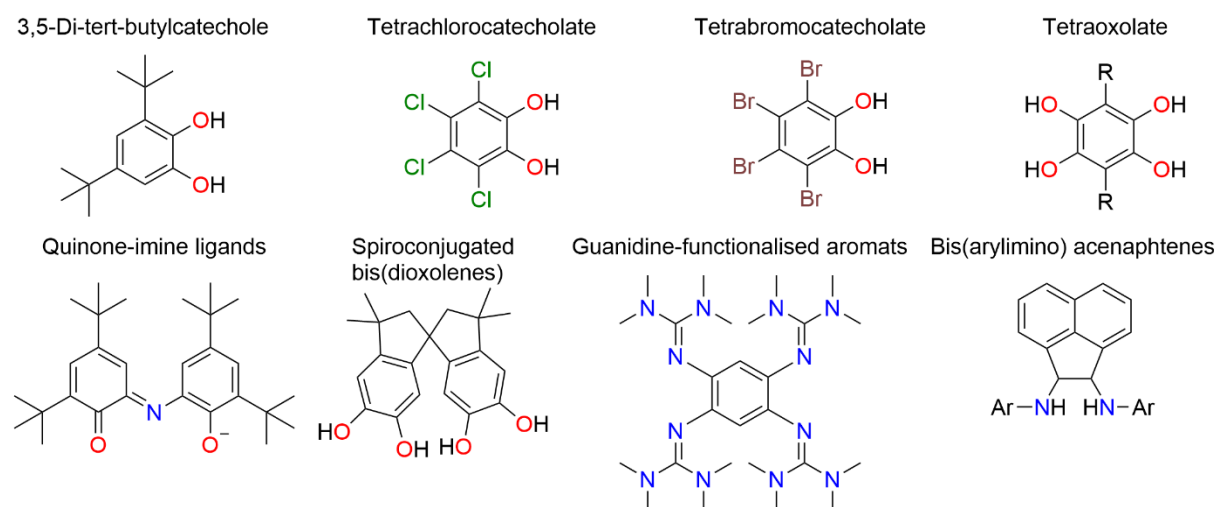


Figure 10: Selected examples of redox-active ligands from the literature relevant to valence tautomerism.^{81,88–92}

1.5.3 Valence Tautomerism: General Remarks

For thermally induced VT to occur, several conditions must be simultaneously fulfilled. First, the organic ligand must exhibit non-innocent behaviour and possess at least two accessible redox states. Second, the frontier orbitals of the donor and acceptor fragments must be energetically similar, such that the redox processes of metal oxidation and ligand reduction are thermodynamically comparable.⁶⁴ Third, the intramolecular electronic coupling must be sufficiently strong to allow electron transfer, yet not so strong that complete delocalisation and orbital mixing destroy the discrete electronic structures of the two redox isomers.⁷⁵ Fourth, as in SCO, the transition must be thermodynamically accessible. One redox isomer must be enthalpically more stable, while the other must be entropically favoured, such that the Gibbs free energy balance changes sign within an experimentally accessible temperature range.⁶⁹

1.5.4 The Cobalt-Dioxolene System

The cobalt-dioxolene system is by far the most extensively studied VT system, for two principal reasons. First, the redox potentials of the Co(III)/Co(II) couple and the $\text{cat}^{2-}/\text{sq}^{\bullet-}$ couple are naturally well matched, such that metal-centred oxidation and ligand-centred reduction are thermodynamically comparable.⁸⁰ Second, and uniquely among VT-active metals, the intramolecular electron transfer in cobalt-dioxolene complexes is typically accompanied by a spin-state change. The LS Co(III)cat state ($t_{2g}^6 e_g^{*0}$, $S = 0$) converts to the HS Co(II)sq state ($t_{2g}^5 e_g^{*2}$, $S = 3/2$), which greatly increases the entropy of the high-temperature tautomer through both electronic spin multiplicity and vibrational contributions, thereby providing a strong thermodynamic driving force for the transition.^{64,69,93}

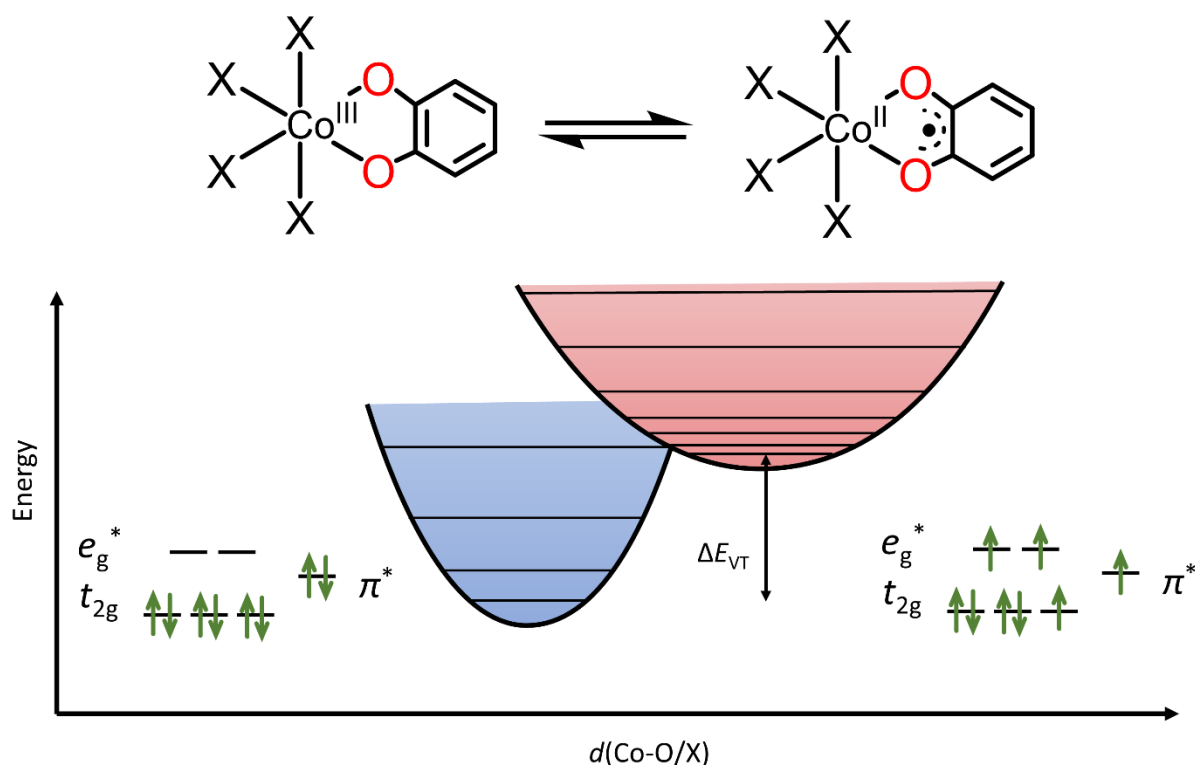


Figure 11: Schematic representation of the valence tautomeric transition between the LS Co(III)cat and HS Co(II)sq states of a cobalt dioxolene complex, showing the corresponding electronic configurations and potential energy wells as a function of the Co-donor bond distance, adapted from literature.⁶⁹

The remaining coordination sites are typically occupied by an imine- or amine-based ancillary ligand, whose ligand field strength can be tuned to adjust the Co(III)/Co(II) redox potential and thereby control the charge distribution and transition temperature. In the LS Co(III)cat tautomer the metal centre is in a high oxidation state, short Co-N and Co-O bond lengths arising from the strong metal-ligand orbital overlap, resulting in a pronounced charge separation between the electron-rich catecholate and the electron-poor metal ion and rendering the complex highly ionic in character. Upon thermally induced electron transfer to the HS Co(II)sq tautomer, the Co-N bond lengths elongate by up to 0.23 Å as the antibonding e_g^* orbitals become populated, the catecholate converts to the semiquinonate radical, the spin state changes from LS to HS, and the charge distribution becomes significantly less polarised. The two tautomers are therefore readily distinguished by magnetic susceptibility measurements with χ_{MT} values of approximately $0 \text{ cm}^3 \text{ K mol}^{-1}$ for the diamagnetic LS Co(III)cat form and paramagnetic with higher values for HS Co(II)sq.^{68,94}

1.5.5 Thermodynamics of Valence Tautomerism

The thermodynamics of VT follow directly from the Gibbs free energy $\Delta G = \Delta H - T\Delta S$. The LS Co(III)cat state is enthalpically favoured ($\Delta H_{VT} < 0$) due to stronger metal-ligand orbital overlap, shorter bond lengths, and a lower total energy of the coordination sphere, and is therefore the ground state at low temperatures. The HS Co(II)sq state is entropically favoured ($\Delta S_{VT} > 0$), as it possesses higher spin degeneracy and increased structural degrees of freedom compared to the LS state. Additional entropic contributions arise from broader potential energy surfaces and lower vibrational frequencies, which result in a greater number of accessible vibrational microstates. With increasing temperature, the entropic term $T\Delta S_{VT}$ eventually overcomes the enthalpic term, and the HS Co(II)sq tautomer becomes thermodynamically preferred. At the transition temperature $T_{1/2}$, the Gibbs free energies of the two tautomers are equal and both are equally populated. Since $\Delta G_{VT} = 0$ at $T_{1/2}$, the transition temperature is directly related to the thermodynamic parameters by $T_{1/2} = \Delta H_{VT} / \Delta S_{VT}$, both of which can be determined experimentally from solution variable-temperature magnetic susceptibility via the Evans NMR method or UV-Vis data.^{43,69,76,95}

The relative thermodynamic stability of the two tautomers can be expressed in terms of the free energies of the individual redox processes. The free energy of metal-centred oxidation ($\text{Co(II)} \rightarrow \text{Co(III)}$, ΔG_m) and ligand-centred oxidation ($\text{cat}^{2-} \rightarrow \text{sq}^*$, ΔG_L) are related to the overall VT free energy by $\Delta G_{VT} = \Delta G_L - \Delta G_m$. For thermally induced VT, ΔG_{VT} must be positive at low temperatures and negative at high temperatures, requiring close energetic matching of the two redox processes.⁶⁹ This balance can be tuned through the ancillary ligand and through substitution of the dioxolene. Electron-donating substituents on the ancillary ligand stabilise Co(III) by increasing the ligand field and raising the Co(III)/Co(II) redox potential, while electron-withdrawing substituents have the opposite effect.⁹⁶ Sterically demanding groups near the metal centre favour longer bond lengths and thereby stabilise the HS state.⁹⁷ On the dioxolene, electron-withdrawing substituents raise the $\text{cat}^{2-} / \text{sq}^*$ redox potential and stabilising Co(III)cat, whereas electron-donating substituents lower it and promote electron transfer to give Co(II)sq.^{69,89,98}

VT transitions display a variety of temperature-dependent profiles analogous to those observed in SCO, ranging from gradual Boltzmann-type equilibria in solution, where only the thermal population distribution is involved, to abrupt cooperative transitions with hysteresis in the solid state, driven by lattice cooperativity and intermolecular interactions. Incomplete, multistep, and temperature-invariant behaviours are also observed. Of particular importance is the pronounced sensitivity of VT to the solvent environment. In solution, the outer-sphere reorganisation energy, which arises from reorientation of solvent molecules around the complex in response to the change in charge distribution, contributes significantly to both the thermodynamics and kinetics of the transition. This is illustrated by the solvatochromic behaviour of VT complexes, where UV-Vis spectroscopy reveals preferential population of the Co(III)cat tautomer in polar solvents and the Co(II)sq tautomer in non-polar media. Consequently, VT transition temperatures in solution are strongly solvent-dependent, and can differ substantially from the solid-state values for the same compound.^{64,69}

1.5.6 Alternative Switching Stimuli in Valence Tautomerism

Beyond thermal stimulation, VT can be induced by light irradiation, pressure, electrochemical perturbation, and changes in the coordination environment. Light-induced valence tautomerism (LIVT) is achieved by irradiation of the ligand-to-metal charge-transfer (LMCT) absorption band of the LS Co(III)cat tautomer, populating an excited LMCT state that can relax into the metastable HS Co(II)sq tautomer rather than returning directly to the LS ground state. The reverse transition can be induced by excitation of the metal-to-ligand charge-transfer (MLCT) band of the HS Co(II)sq form (**Figure 12**). In solution, the photoinduced HS Co(II)sq tautomer typically reconverts to the LS ground state on the nanosecond timescale with Arrhenius-type behaviour. In the solid state, LIVT is generally only observable at low temperatures and often yields incomplete photoconversion due to sample opacity and spectral overlap of the two tautomers, leading to a photostationary state.^{64,81,99–101}

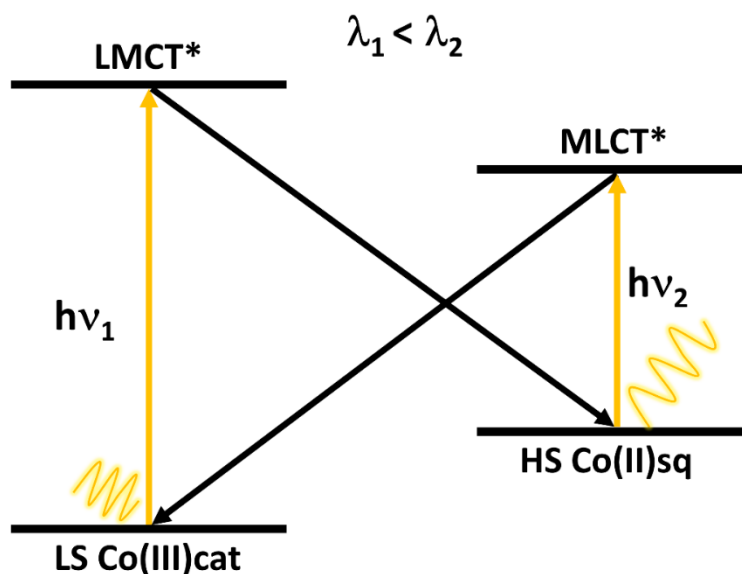


Figure 12: Simplified Jablonski diagram illustrating light-induced valence tautomerism. Photoexcitation of the LS Co(III)cat state leads to a LMCT excited state, followed by relaxation to the HS Co(II)sq state and the inverted effect with excitation into an excited MLCT state from the HS Co(II)sq state with relaxation. Adapted from literature.¹⁰²

Pressure-induced VT is considerably less explored, with only a limited number of examples in the literature.^{103,104} Unlike thermal VT, which is entropy-driven, pressure-induced transitions are governed by the volumetric difference between the two tautomers. Application of pressure stabilises the tautomer with the smaller molecular volume and higher packing density. In classical cobalt-dioxolene systems, this corresponds to the LS Co(III)cat form, which features shorter Co-N bond lengths and a more compact coordination sphere. The extended Gibbs free energy expression under applied pressure, $\Delta G = \Delta H - T\Delta S + p\Delta V$, shows that if the volume change associated with formation of the low-spin state is negative ($\Delta V < 0$), increasing pressure thermodynamically stabilises this state.^{64,105}

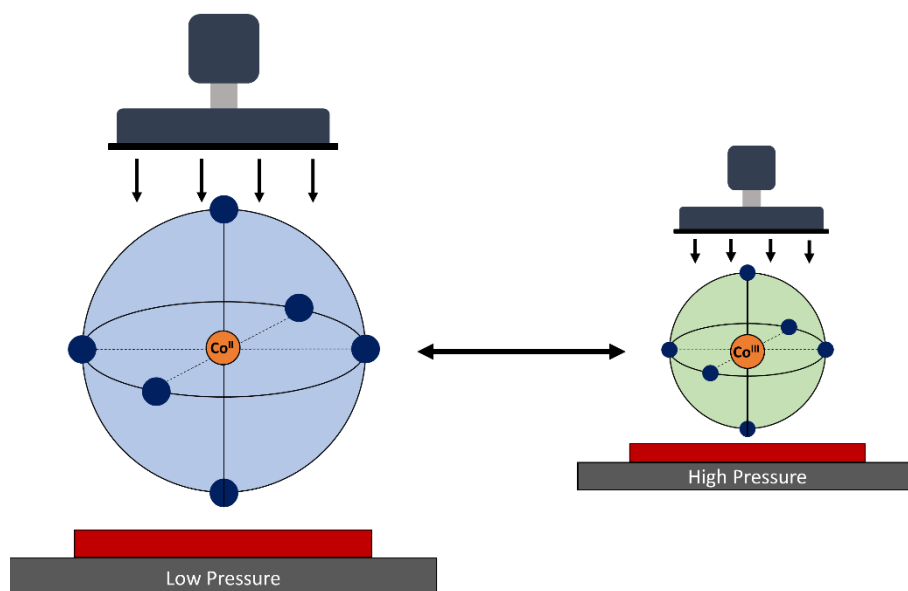


Figure 13: Schematic illustration of pressure-induced valence tautomerism, highlighting the preferential stabilisation of the LS Co(III)cat state under applied pressure.

1.5.7 Examples of Mononuclear Cobalt-Dioxolene VT Complexes in Literature

In mononuclear cobalt-dioxolene complexes two main motifs have been employed which can be differentiated by their ratio of cobalt to dioxolenes. Complexes can have a 1:1 ratio according to the general formula $[\text{Co}(\text{N}_4\text{L})(\text{diox})]^+$ or $[\text{Co}(\text{N}_2\text{L})_2(\text{diox})]^+$ with N_4L being a tetradentate nitrogen donor ancillary ligand and N_2L a bidentate one. Additionally a 1:2 ratio of cobalt to dioxolene after the scheme $[\text{Co}(\text{N}_2\text{L})(\text{sq})(\text{diox})]$ or *trans*- $[\text{Co}(\text{NL})_2(\text{sq})(\text{diox})]$ is known in the literature (**Figure 14**). Interestingly complexes of the ratio 1:2 have 1 dioxolene that can take part in the valence tautomeric transition and a temperature-invariant semiquinonate radical that does not take part in the VT transition. The 1:1 motif yields cationic complexes, while the 1:2 motif typically yields neutral species. This structural difference also manifests in the magnetic properties of the LS Co(III)cat state as complexes of the 1:1 motif are fully diamagnetic, while those of the 1:2 motif retain a small paramagnetic moment arising from the radical character of the temperature-invariant semiquinonate.

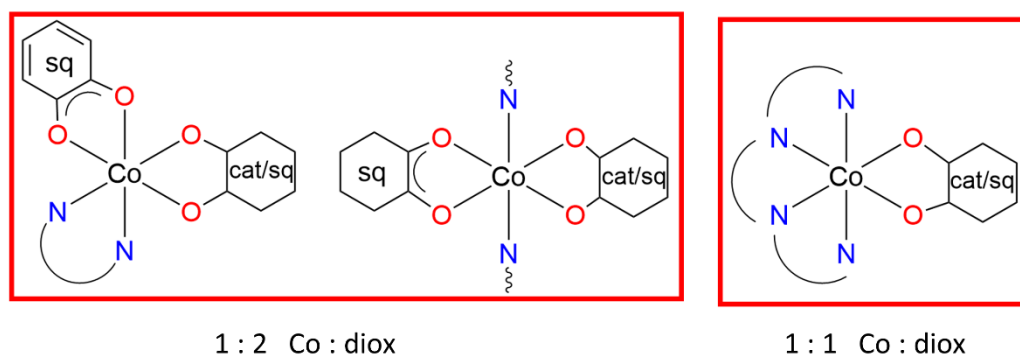


Figure 14: Schematic representation of the mononuclear cobalt-dioxolene motifs found in literature, differentiated by the cobalt-to-dioxolene ratio.

From the classical thermally induced valence tautomeric systems to more recent unconventional switching phenomena, numerous mononuclear cobalt-dioxolene complexes have significantly advanced the understanding of intramolecular electron transfer processes. Selected examples are discussed in the following.

The first unambiguous evidence for thermally induced VT was established in 1980 by Pierpont and Buchanan in mononuclear cobalt-dioxolene complexes. They investigated the complex $\text{Co}(3,5\text{-dbcat})(3,5\text{-dbsq})(\text{bpy})$ (3,5-di-tert-butylcatecholate, 3,5-di-tert-butyl-semiquinonate, 2,2'-bipyridine). X-ray structural analysis confirmed the presence of a Co(III) species in the solid state, in which one dioxolene ligand is coordinated in the catecholate form and the other in the semiquinonate form - recognisable, among other things, by characteristic C–O bond lengths of approx. 1.35 Å (catecholate) and approx. 1.30 Å (semiquinone), respectively, as well as by the short Co–N distances, which are typical of Co(III). In toluene solution, however, magnetic, EPR and NMR spectroscopic measurements reveal a temperature-dependent equilibrium between this Co(III) form and a Co(II) species, $\text{Co}(3,5\text{-dbsq})_2(\text{bpy})$, which arises through intramolecular electron transfer from the catecholate ligand to the metal centre. The magnetic moment increases from approx. 1.9 μ_{B} in the solid state at room temperature to up to 3.75 μ_{B} in solution at room temperature, increasing to 4.26 μ_{B} at 333 K, reflecting the increasing population of the Co(II) tautomer with rising temperature. This work thus laid the conceptual foundation for understanding thermally switchable VT complexes based on cobalt-dioxolene.⁶⁸

Building on these foundations, Hendrickson *et al.* systematically demonstrated in 1993 how the equilibrium state of valence tautomerism can be controlled by specifically varying the ancillary diamine ligand. In the complex series $\text{Co(L)}(3,5\text{-dbsq})(3,5\text{-diox})$ with $\text{L} = 4,4'\text{-diphenyl-2,2'-bipyridine (dpbpy)}$, $4,4'\text{-dimethyl-2,2'-bipyridine (dmbpy)}$, $1,10\text{-phenanthroline (phen)}$, $2,2'\text{-bipyrimidine (bpym)}$ or $2,2'\text{-bipyrazine (bpz)}$, the reduction potential of the diamine ligand determined which tautomer is preferentially present in the solid state at room temperature. Ligands that are more easily reduced (more positive reduction potential) stabilise the Co(II) form by accepting electron density into their π^* orbital, while ligands that are more difficult to reduce favour the Co(III) form. Particularly noteworthy was the phen complex, which is considered the first example of a VT complex, exhibiting the $\text{Co(II)} - \text{Co(III)}$ transition even in the solid state. Below 200 K, the complex exists as a LS Co(III) tautomer with $\mu_{\text{eff}} = 1.7 \mu_{\text{B}}$. Upon warming, the transformation occurs abruptly at 200 K to a HS Co(II) tautomer with $\mu_{\text{eff}} = 5.1 \mu_{\text{B}}$, with a hysteresis of approximately 5 K, indicative of a cooperative phase transition. The presence of toluene solvate molecules is crucial here, as in its absence, the transformation does not occur, which underscores the pronounced sensitivity of VT complexes to the crystalline environment.¹⁰⁶

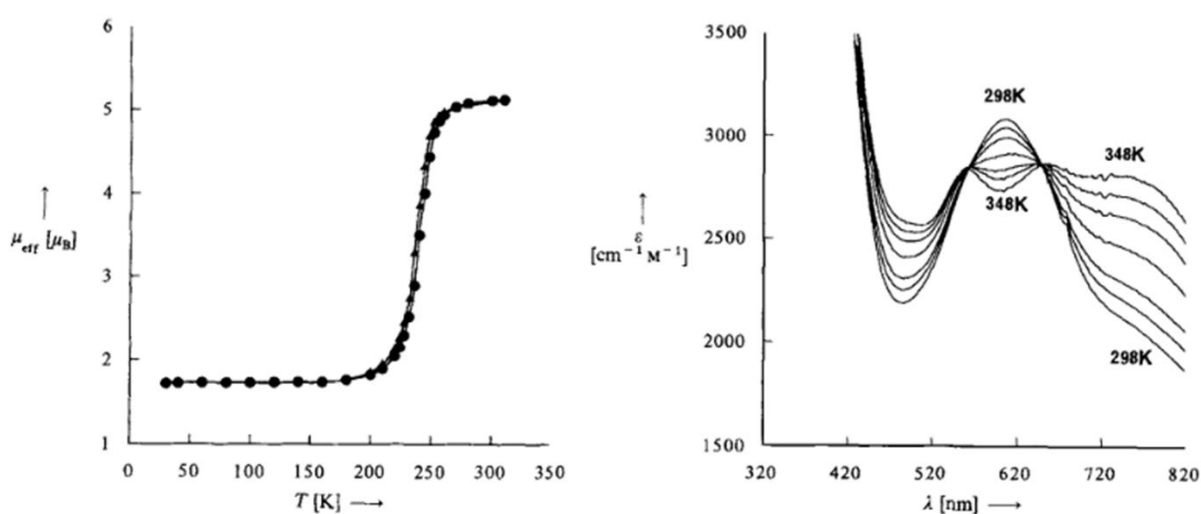


Figure 15: Left: Temperature dependence of the effective magnetic moment of a polycrystalline sample of the Co(phen) complex illustrating thermally induced VT with a transition temperature around 200 K. Right: Temperature-dependent electronic absorption spectra of the Co(dpbbpy) in toluene, showing changes in molar extinction coefficient upon heating showing VT behaviour.¹⁰⁶

In 2008, Beni *et al.* adopted a more systematic approach to controlling the charge distribution and photoswitchable properties of cobalt-dioxolene complexes. In the series $[\text{Co}(\text{Me}_n\text{tpa})(\text{diox})]\text{PF}_6$ ($n=0\text{-}3$), the tripodal tpa ligand (tris(2-pyridylmethyl)amine) was sterically modified by the successive introduction of methyl groups into the 6-position of the pyridine rings, which gradually shifted the redox properties of the metal centre and thus determined the charge distribution in the cobalt-dioxolene fragment at room temperature. While the less substituted complexes ($n = 0,1$) represented diamagnetic Co(III) cat species in the solid state, the fully methylated complex ($n=3$) existed as a paramagnetic Co(II)sq species, and the doubly methylated complex ($n=2$) exhibited entropy-driven incomplete VT interconversion starting near room temperature (**Figure 16**). The free energy difference ΔG was found to decrease systematically with increasing methylation, shifting from positive values for the unmethylated complex to negative values for the fully methylated analogue, in quantitative agreement with the observed charge distributions. Irradiation experiments at 9 K induced a small fraction of the metastable Co(II) state in each of the Co(III) species ($n=0\text{-}2$). The relaxation kinetics of the photoinduced phases correlated qualitatively with the free energy differences, but were significantly influenced by intermolecular $\pi\text{-}\pi$ interactions in the crystal lattice as well as by the solvent molecule used in crystallisation.⁹⁷

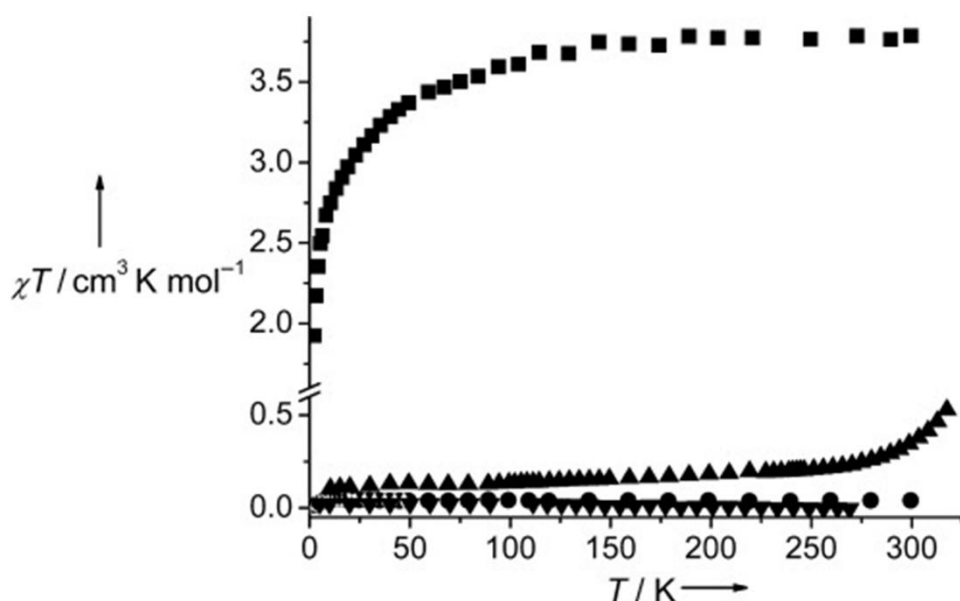


Figure 16: χT vs. T (2–300 K) for a series of tpa-based cobalt-dioxolene complexes with different degrees of methylation. Complexes with 0 and 1 methyl group (downward triangles and circles) are temperature-independent and remain in the LS Co(III)cat state over the entire temperature range. The dimethylated derivative (upward triangles) exhibits a weak, incomplete valence tautomeric transition at elevated temperatures (<250 K), predominantly remaining in the LS Co(III)cat state. The trimethylated complex (squares) is temperature-independent and stabilised in the HS Co(II)sq state.⁹⁷

A recent study by Boskovic *et al.*, published in 2024, revisits the $[\text{Co}(\text{Me}_n\text{tpa})(\text{diox})]^+$ complex family and extends the structural characterisation of valence tautomerism to atomic resolution using variable-temperature and high-pressure single-crystal X-ray diffraction. For the doubly methylated complex ($n=2$), a two-step thermally induced HS Co(II)sq to LS Co(III)cat transformation at 155 K and 95 K was observed. This was attributed to the presence of two crystallographically independent molecules A and B in the asymmetric unit. Molecule B undergoes the transition at 155 K, accompanied by a shortening of the mean Co–N bond lengths, followed by molecule A at 95 K. The triply methylated complex on the other hand, showed no thermal VT, as expected. Under hydrostatic pressure, the two complexes behave fundamentally differently. $[\text{Me}_2\text{tpa}]$ undergoes a single-step, simultaneous conversion of both independent molecules between 0.43 and 1.30 GPa, while $[\text{Me}_3\text{tpa}]$, despite its thermal inactivity, exhibited pressure-induced VT between 2.60 and 3.10 GPa, as the external pressure overcomes the steric barrier of the trimethylated ligand and makes the smaller-volume LS-Co(III)cat tautomer accessible. DFT calculations confirmed that compression shifts the relative spin-state energy ΔE towards the LS Co(III)cat tautomer.¹⁰⁵

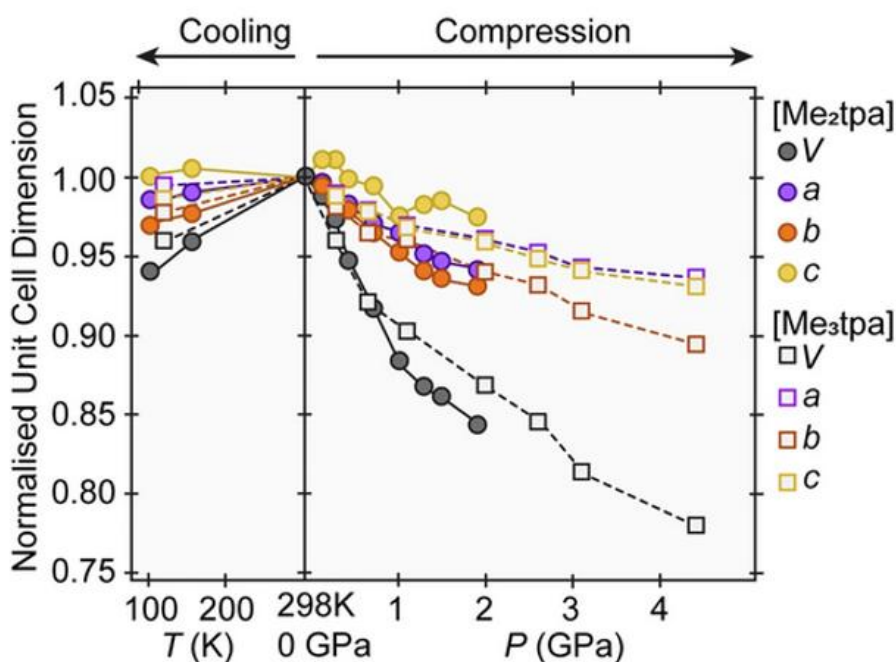


Figure 17: Relative changes in normalised unit cell dimensions of $[Me_3tpa]$ (squares) and $[Me_2tpa]$ (circles) at variable pressure and temperature.¹⁰⁵

Metzger *et al.* provided a conceptually significant extension of the VT paradigm in 2023 with the first documented example of valence tautomerism from a LS Co(III) catecholate to a LS Co(II)sq state. In all previously known cobalt-dioxolene VT complexes, thermally induced interconversion always led to the formation of a HS Co(II)sq tautomer. In complex $[Co(L-N_4^tBu_2)(Cl_2cat)]^+$, however, a low-spin Co(II)sq state is formed upon heating. The key factor is the tetraazamacrocyclic auxiliary ligand $L-N_4^tBu_2$, whose sterically bulky *tert*-butyl substituents elongate the axial Co-N bonds, thereby raising the Co(III)/Co(II) redox potential, while at the same time the electron-deficient 4,5-dichlorocatecholate ligand raises the redox potential of the coordinated dioxolene compared to the analogous di-*tert*-butyl-system, thereby stabilising the Co(III)cat ground state. VT in solution was unequivocally demonstrated by temperature-dependent NMR, IR and UV-Vis-NIR spectroscopy, as well as by singular value decomposition of the electronic absorption spectra. The characteristic absorption band of the LS Co(II)sq tautomer at approximately 1100 nm increases with rising temperature and decreasing solvent polarity.¹⁰⁷

1.5.8 Examples of Dinuclear Cobalt-Dioxolene VT Complexes in Literature

Dinuclear VT complexes are of particular interest as they can, in principle, access three distinct electronic states through a two-step transition: the fully oxidised $\text{Co(III)cat-Co(III)cat}$ state, the mixed-valent $\text{Co(III)cat-Co(II)sq}$ state, and the fully reduced Co(II)sq-Co(II)sq state, thereby enabling ternary molecular switching and more complex logic operations (**Figure 18**). Two principal structural motifs exist in the literature, distinguished by the nature of the bridging unit: complexes in which the metal centres are connected via a non-redox-active ancillary ligand, and those in which a redox-active ligand serves as the bridge. Complexes in which the metal centres are bridged via an ancillary ligand have received comparatively little attention, with only a small number of examples reported, most of which exhibit incomplete or single-step transitions.^{69,108,109}

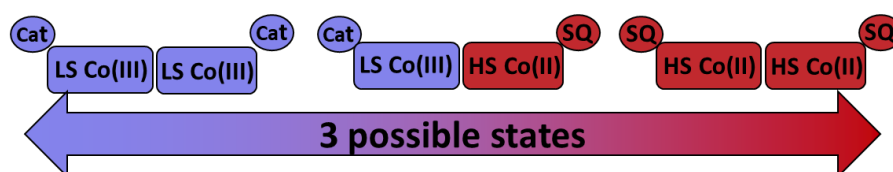


Figure 18: Schematic representation of the three possible electronic states in dinuclear cobalt-dioxolene complexes, ranging from the fully LS Co(III)cat state, via the mixed-valence LS Co(III)cat - HS Co(II)sq state, to the fully HS Co(II)sq state.

The use of redox-active bridging ligands has been investigated more extensively, with tetraoxolenes and bis(dioxolene) motifs being the most commonly employed bridging units. The Boskovic group established, using a spiroconjugated bis(dioxolene) bridging unit system, that two factors are critical for two-step VT in dinuclear complexes with a redox-active bridging unit. First, the degree of electronic communication within the bis(dioxolene) ligand, and second, the matching of the redox potentials of the cobalt ion and the dioxolene (**Figure 19**). This relationship was found to hold equally in non-spiroconjugated bis(dioxolene) bridging systems.^{64,69}

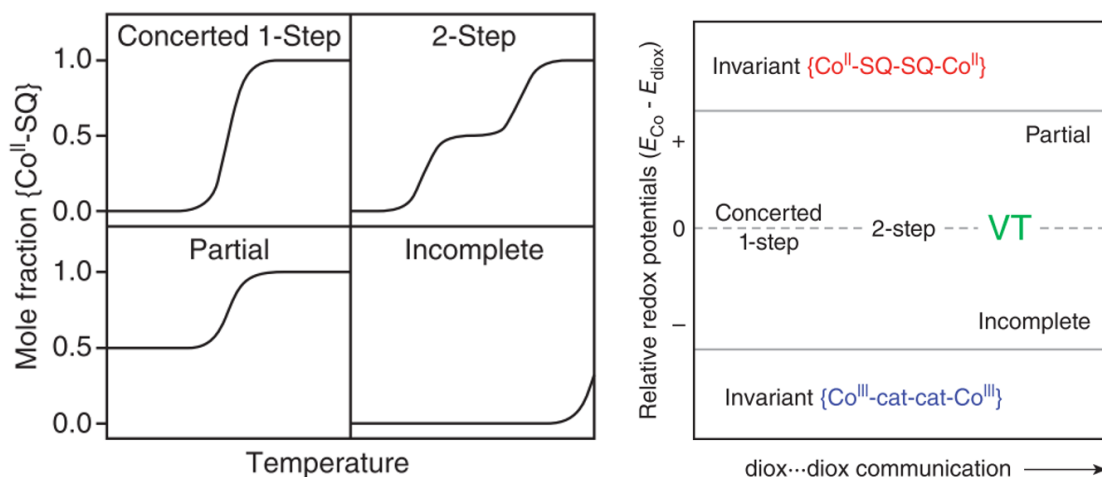


Figure 19: Left: Schematic illustration of dinuclear valence tautomeric transitions in dinuclear cobalt-bis(dioxolene) complexes, depicting possible transition profiles, including concerted one-step, sequential two-step, partial, and incomplete transitions. Right: Highlighting how the nature of the transition profile is governed by the degree of electronic communication between the dioxolene ligands and the relative redox potentials of the cobalt metal and the dioxolene ligand in redox-active ligand bridged dinuclear complexes.⁶⁹

In 2004, Carbonera *et al.* took an important conceptual step forward by achieving VT for the first time in a dinuclear cobalt-tetraoxolene complex, demonstrating not only thermally but also light-induced switchability. The complex $\{\text{Co}(\text{cth})\}_2(\text{dhbq})_3$ (cth: (dl)-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) contained two cobalt centres linked via the bridging tetraoxolene ligand dhbq, and exhibited a LS Co(III)-LS Co(III) ground state below 100 K, which gradually converted to a mixed-valent HS Co(II)-LS Co(III) species upon warming to 175 K, which is demonstrated by the increase in $\chi_{\text{M}}T$ from 0.45 to 2.5 $\text{cm}^3 \text{K mol}^{-1}$ as well as by EPR spectroscopy. Furthermore, the diamagnetic Co(III) state at 10 K could be converted to the paramagnetic Co(II) state by irradiation with light (648 nm), whereby nearly quantitative photoconversion was observed at the surface, while in the bulk material the strong light absorption of the dark violet solid limited the penetration depth to 40% (**Figure 20**). This work extended the concept of VT complexes for the first time to dinuclear systems with a bridging redox-active ligand.¹¹⁰

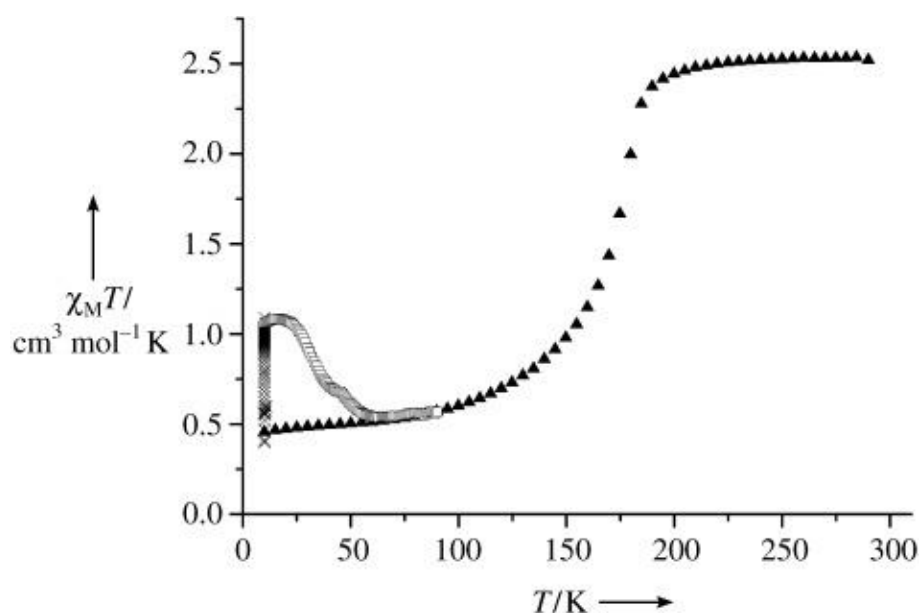


Figure 20: χT vs. T [$\{\text{Co}(\text{cth})\}_2(\text{dhbq})\}(\text{PF}_6)_3$] measured before (triangles) and after (squares) 648 nm irradiation, crosses indicate the time-dependent increase of magnetic moment under irradiation.¹¹⁰

In 2006, Tao *et al.* advanced the system with $(\text{Co}(\text{tpa}))_2(\text{dhbq})_3$, which exhibited a pronounced and reproducible thermal hysteresis of 13 K near room temperature. The VT interconversion occurs between a diamagnetic LS-Co(III)-dhbq³⁻-LS-Co(III) (dhbq = deprotonated 2,5-dihydroxy-1,4-benzoquinone) state at low temperatures and a paramagnetic LS-Co(III)-dhbq²⁻-HS-Co(II) state at higher temperatures, which is clearly demonstrated by X-ray structural analysis, magnetic susceptibility, EPR and IR spectroscopy on three isolated redox states of the complex. The cause of cooperativity and thus the hysteresis lies in the two-dimensional layered structure of the crystal, in which the cationic units are stacked in a head-to-waist mode and interact via staggered π - π interactions of the tpa pyridine rings, as well as edge-to-face interactions between the tpa pyridine rings and the dhbq benzene ring. It is precisely the choice of the tpa ligand with its pyridine rings that enables this intermolecular communication and thus the bistability. Furthermore, at 5 K, irradiation with 532 nm light induced a reversible photoinduced VT, with the light-induced HS Co(II) tautomer remaining metastable up to 38 K.¹¹¹

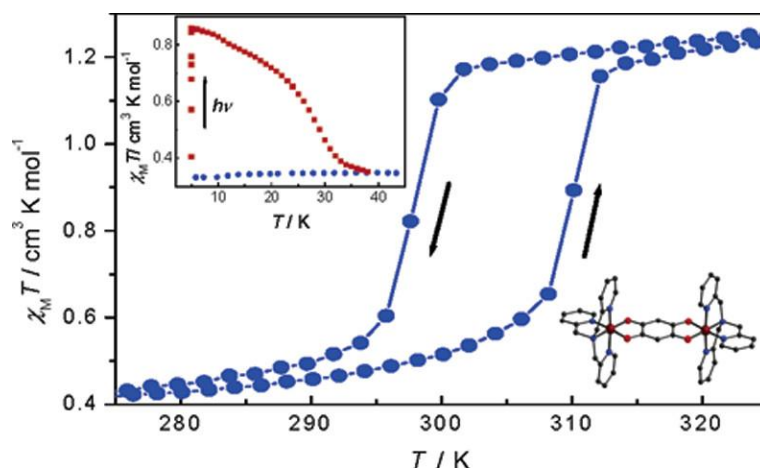


Figure 21: Dinuclear valence tautomerism with a pronounced hysteresis (13 K) centred near room temperature, as well as photoinduced VT at low temperatures.¹¹¹

In the same year, Hearn *et al.* reported on a dinuclear cobalt bis(dioxolene) complex with 4,6-di-2'-pyridylpyrimidine as a bridging bis(diamine) ligand, which showed evidence of all three possible redox states Co(II)Co(II), Co(II)Co(III) and Co(III)Co(III). The VT transitions of the two metal centres are coupled via the ancillary bridging ligand, so that upon cooling, a sequential switching from HS Co(II) to LS Co(III) at one centre is initially observed, followed by the onset of the transition at the second centre at lower temperatures. This was demonstrated by temperature-dependent near-infrared absorption spectroscopy on amorphous thin films, whereby the intensity of the intervalence charge transfer band at 4900 cm⁻¹ was used as a direct measure of the Co(III) content, and a characteristic plateau between 125 and 225 K confirmed the partial stabilisation of the mixed-valent Co(II)Co(III) state. Noteworthy here is the pronounced phase dependence of the VT properties. While the thin film exhibits all three states, only the mixed-valent Co(II)Co(III) state is observed in the amorphous powder. In toluene solution only the transition between Co(II)₂ and Co(III)₂ is accessible, showing how strongly the solid state environment and intermolecular interactions influence the VT equilibrium.¹⁰⁹

In 2013, Alley *et al.* published a conceptually groundbreaking study on a family of the spiroconjugated bis(dioxolene) ligand spiroH₄, in which systematic variations of the Me_ntpa auxiliary ligand (n = 0-3) yielded all four conceivable charge distributions (Co(III)-cat-cat-Co(III), Co(II)-sq-sq-Co(II), Co(III)-cat-sq-Co(III) and Co(III)-sq-sq-Co(III)). The standout result of the study is the Me₂tpa complex [Co₂(spiro)(Me₂tpa)₂]²⁺, which exhibits a two-step thermal interconversion Co(III)-cat-cat-Co(III) to HS Co(II)-sq-cat-LS Co(III) to HS Co(II)-sq-sq-HS Co(II) both in the solid state and in solution. EPR spectroscopic investigations of the mixed-valent species Co(III)-sq-cat-Co(III) provide compelling evidence that the unpaired electron spin is delocalised across both halves of the spiro-bridge ligand at room temperature and only localises on a single cobalt-dioxolene centre at low temperatures.¹¹²

The most in-depth conceptual insight to date into the control of one-step versus two-step VT transitions in dinuclear cobalt bis(dioxolene) complexes was provided by Gransbury *et al.* in 2020 in a combined experimental and DFT study. By introducing the tetrabrominated bridging ligand Br₄spiroH₄, which has redox potentials shifted relative to spiroH₄, and systematically varying the Me_ntpa auxiliary ligand (n = 0, 2, 3), four distinct VT behaviours were realised and rationalised within an isostructural complex family: the temperature-invariant Co(III)-cat-cat-Co(III) state (n = 0), an incomplete VT above 275 K (n = 2 with Br₄spiro), partial single-step VT Co(III)-cat-sq-Co(II) ↔ Co(II)-sq-sq-Co(II) at 190 K (n = 3 with Br₄spiro) and the two-step VT of the reference complex (n = 2 with spiro) (**Figure 22**). The central mechanistic finding of the study is the formulation of two independent, measurable parameters for predicting the VT profile. The electrochemical distance Δ_{diox} between the two ligand-centred redox processes as a measure of intraligand electronic communication, and the distance Δ_{ox-red} between metal and ligand redox potentials as a measure of energetic fit. Using a correlation plot of these two parameters, they demonstrated that two-step VT occurs only when the electronic

communication in the bridging ligand is weak but not zero, and at the same time the redox potentials of cobalt and dioxolenes are well matched.¹¹³

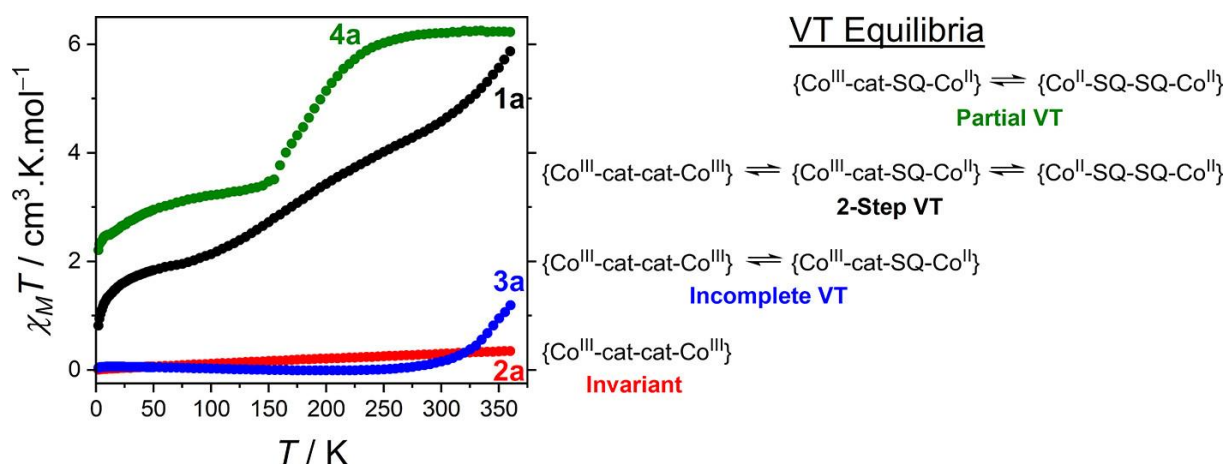


Figure 22: $\chi_M T$ vs. T for the first heating of spiro-conjugated complexes **1a** $\text{Co}_2(\text{Me}_2\text{tpa})(\text{spiro})$ (black) showing a two-step VT transition, **2a** $\text{Co}_2(\text{Me}_2\text{tpa})(\text{Br}_4\text{spiro})$ (red) exhibiting temperature-invariant behaviour staying in the LS $(\text{Co}^{\text{III}}\text{cat})_2$ state, **3a** $\text{Co}_2(\text{Me}_2\text{tpa})(\text{Br}_4\text{spiro})$ (blue) displaying an incomplete VT transition starting from 275 K and **4a** $\text{Co}_2(\text{Me}_3\text{tpa})(\text{Br}_4\text{spiro})$ showing partial single-step VT transition at 190 K.¹¹³

1.5.9 Valence tautomerism Beyond Cobalt

While cobalt-dioxolene complexes dominate the VT literature, valence tautomeric behaviour has been demonstrated in a growing number of complexes based on other transition metals and, more recently, f-block elements. Selected examples are discussed in the following, with particular emphasis on parallels and differences to the cobalt system.^{64,69}

Manganese

The manganese ion exhibits rich redox chemistry and therefore represents a promising candidate for VT. Initial solution studies on $\text{Mn}(\text{dbcat})_2(\text{py})_2$ revealed VT transitions according to the scheme: $\text{Mn}^{\text{IV}}(\text{cat})_2 \rightleftharpoons \text{HS Mn}^{\text{III}}(\text{cat})(\text{sq}) \rightleftharpoons \text{HS Mn}^{\text{II}}(\text{sq})_2$.¹¹⁴

As in the cobalt system, greater vibrational contributions to entropy constitute the primary thermodynamic driving force for VT. However, in contrast to the cobalt system, both dioxolene ligands participate in the VT switching behaviour. Owing to antiferromagnetic coupling between the dioxolene ligand and the metal centre, and the absence of a spin-state change, monitoring by magnetic susceptibility measurements is not straightforward, as all three states exhibit a persistent ground state of $S = 3/2$.⁶⁹

Thermally induced VT in solution and in the solid state was observed in the system $[\text{Mn}(\text{cth})\text{dbdiox}]^+$ between a HS $\text{Mn}^{\text{III}}\text{cat}$ and HS $\text{Mn}^{\text{II}}\text{sq}$ state as well as a VT transition in solution with the dinuclear system $[\text{Mn}_2(\text{bpm})(\text{Br}_4\text{diox})_4]^{2-}$.^{115,116}

Iron

For a long time, thermally induced VT in iron complexes was considered unlikely. This assumption mainly originated from the comparatively small entropic driving force associated with the Fe-based electron transfer process. In contrast to cobalt systems, where the system is commonly accompanied by a spin-switch phenomenon, iron systems generally remain in a high-spin configuration on both sides of the equilibrium. Consequently, the electronic contribution to the entropy gain is substantially smaller. In addition, the structural changes accompanying the electron transfer are less pronounced in iron complexes. The Fe-O bond lengths in HS Fe(II) and Fe(III) differ only marginally, resulting in a significantly reduced vibrational and structural entropy contribution compared to cobalt systems. Another important factor is the observed antiferromagnetic coupling between the HS Fe(II) centre and the semiquinonate radical. As a result, the spin degeneracy does not increase substantially upon

electron transfer, further reducing the thermodynamic driving force for a thermally accessible VT transition.⁶⁴

One of the earlier results was reported for $[\text{Fe}(\text{bispicen})(\text{Cl}_4\text{cat})(\text{Cl}_4\text{sq})]$ (bispicen = *N,N'*-bis(2-pyridylmethyl)1,2-ethanediamine), which undergoes a thermally induced valence tautomeric transition according to the equilibrium $\text{HS Fe(III)}(\text{cat})(\text{sq}) \rightleftharpoons \text{HS Fe(II)}(\text{sq})_2$. The transition was identified by variable-temperature UV-Vis-NIR spectroscopy between 298 and 338 K, where distinct isosbestic points indicated a temperature-dependent equilibrium between two tautomeric species. Magnetic measurements revealed a $S = 2$ ground state, which was assigned to a HS Fe(III) centre antiferromagnetically coupled to a semiquinonate radical ligand. In contrast to cobalt valence tautomers, the electron transfer in this system is therefore not accompanied by a spin-state change.¹¹⁷

A major breakthrough was later achieved by Janetzki *et al.* with the complex $[\text{Fe}(\text{Ph-BIAN})_3](\text{BPh}_4)_2$, which represents the first iron valence tautomer to exhibit an electron transfer process directly coupled to a spin transition. In this system, a thermally induced transition from LS Fe(III)($\text{L}^{\bullet-}$)(L^0)₂ to HS Fe(II)(L^0)₃ was observed and comprehensively confirmed by solid-state structural analysis, magnetic measurements, and Mössbauer spectroscopy. The unique behaviour of this complex was attributed not only to the suitable redox potential of the ligand framework, but also to its ligand field strength, which enables spin crossover at the iron centre. This distinguishes the complex fundamentally from previously reported iron valence tautomers, whose coordination environments generally favour HS configurations on both sides of the equilibrium. Remarkably, this complex also showed indications of light-induced valence tautomeric transitions in solid-state photomagnetic measurements. Such behaviour had previously only been observed for cobalt-dioxolene systems. This complex represented both the first iron complex to combine electron transfer with a spin-state change and the first non-cobalt system showing indications for LIVT.⁸¹

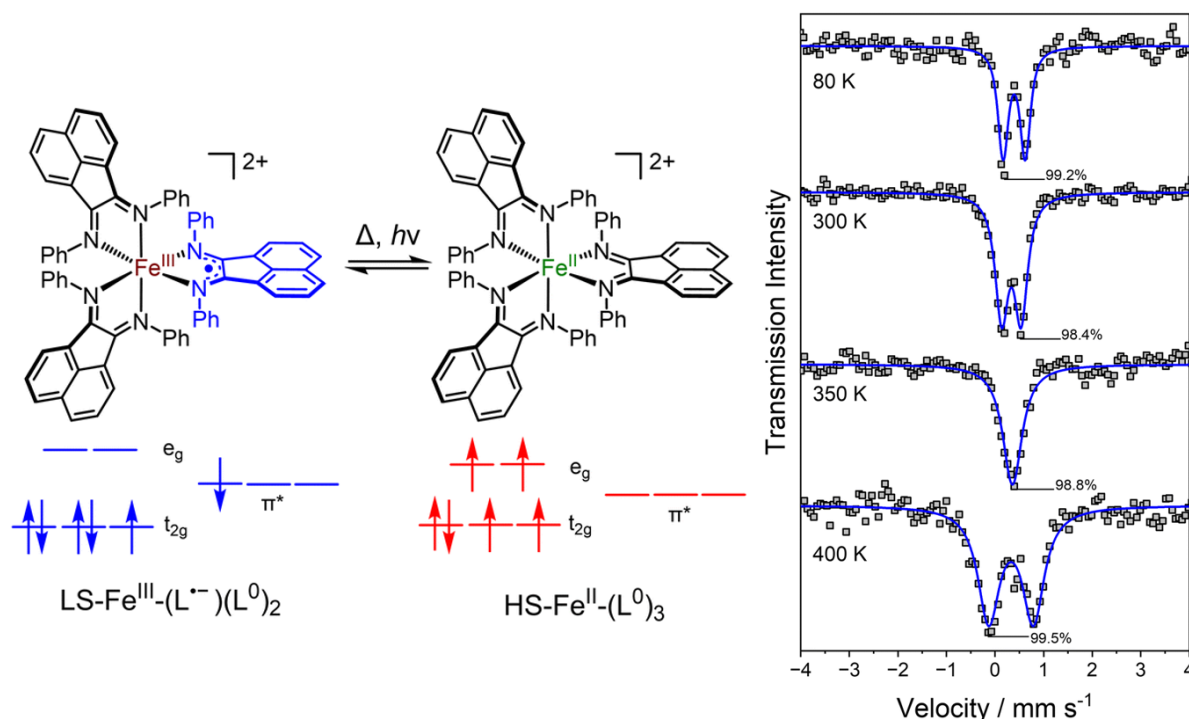


Figure 23: Left: Schematic illustration of the valence tautomeric equilibrium in the solid state and in solution. Right: Temperature-dependent Mössbauer spectra recorded at 80, 300, 350 and 400 K, showing a thermally induced transition from LS Fe(III) ground state to HS Fe(III) and ultimately HS Fe(II) at elevated temperatures.⁸¹

Copper

Although thermally induced valence tautomerism in copper complexes is significantly less common than in cobalt-dioxolene systems, several Cu-based examples have been reported. In particular, copper-dioxolene complexes capable of interconverting between Cu(II)cat and Cu(I)sq states are of considerable interest due to their mechanistic relevance to biological copper-containing oxidoreductases.⁶⁴

In copper VT, the accessibility of the Cu(II)/Cu(I) redox couple is strongly influenced by the pronounced geometric preferences of the two oxidation states. Cu(I), possessing a d^{10} electronic configuration, generally favours tetrahedral coordination geometries, whereas Cu(II), with a d^9 configuration, adopts square-planar or tetragonally distorted geometries as a consequence of the Jahn-Teller theorem, particularly in four-coordinate environments. The substantial structural reorganisation associated with the Cu(I)/Cu(II) interconversion therefore represents a major factor governing the thermodynamics and kinetics of the VT transition.⁹¹

In this context, the nature of the coligands plays a decisive role and can often be rationalised using HSAB considerations. Hard donor ligands such as amines or pyridines preferentially stabilise Cu(II), whereas softer donor ligands including thiolates favour Cu(I).^{118,119}

Classical copper-dioxolene systems nevertheless remained relatively limited, which motivated the development of guanidine-based ligand architectures. Studies on Cu(II) guanidine complexes revealed that these systems frequently exhibit significant distortions away from the expected square-planar geometry towards more tetrahedral coordination environments. Such preorganisation reduces the structural reorganisation energy associated with electron transfer and therefore lowers the activation barrier for intramolecular electron transfer processes.^{120,121}

Typically, guanidine-functionalised aromatic systems (GFA) are employed as neutral electron donors. Depending on their oxidation state, these guanidine fragments can either remain neutral or adopt a doubly oxidised 2+ charge state, resulting in charge distributions opposite to those commonly encountered in classical dioxolene systems. Consequently, the preferred coligands are no longer neutral donors but rather anionic ligands.^{91,122}

In dinuclear Cu-guanidine frameworks (GFAs) the HSAB principles provide a useful guideline for understanding the stabilisation of the different electronic states. Hard anionic ligands such as acetate preferentially stabilise the paramagnetic Cu(II)-GFA⁰-Cu(II) state, whereas softer ligands such as halides favour formation of the diamagnetic Cu(I)-GFA²⁺-Cu(I) state. Thermally induced VT transitions between these two electronic configurations have been observed.^{91,123}

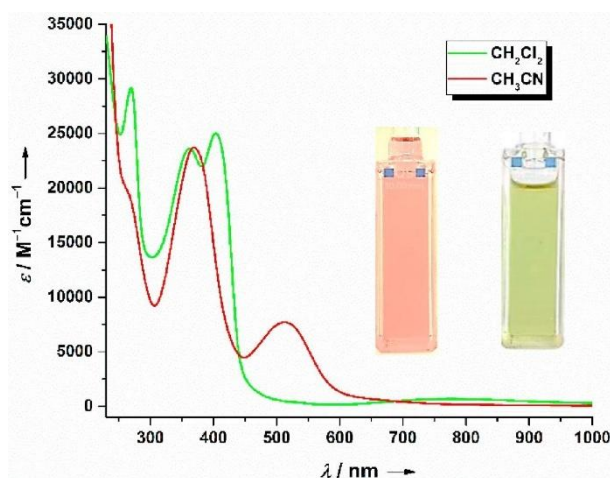


Figure 24: Differences in the UV-Vis spectra and solution colours of a dinuclear copper guanidine-functionalised aromatic system in dichloromethane and acetonitrile.⁹¹

Lanthanides

Lanthanide complexes were long considered unsuitable VT candidates owing to the redox inertness of the trivalent 4f state, the dominance of spin-orbit coupling over crystal-field effects, and the diffuse nature of the 4f orbitals, which limits metal-ligand orbital overlap. Exceptions to the remarkable stability of the trivalent oxidation state are mainly observed for electronically particularly stable configurations such as 4f⁰, 4f⁷, and 4f¹⁴. Despite this apparent redox inertness, extensive synthetic efforts over the past decades have enabled the preparation and isolation of coordination compounds containing nearly all lanthanides in the divalent or tetravalent oxidation state. This progress enabled the investigation of valence tautomeric behaviour in f-element systems. The first examples of valence tautomerism involving lanthanides were identified in inorganic solid-state materials, where the transition was described as a (partial) electron transfer from localized 4f orbitals into a conduction band, formally corresponding to an increase in the lanthanide oxidation state. In contrast, molecular lanthanide valence tautomerism remains exceedingly rare. A major breakthrough was achieved by Dunstan *et al.*, who demonstrated that electron transfer between Sm(II) centres and pyrazine ligands can give rise to genuine molecular VT. The compound SmI₂(pyz)₃ represented the first unambiguous example of complete molecular valence tautomerism in an f-block coordination compound.¹²⁴ Furthermore, it was shown that the valence tautomeric behaviour of these materials can be tuned through the introduction of other metal ions as impurities. Such substitutions influence the cooperativity and exert a form of chemical pressure on the lattice, destabilising the low-temperature phase and thereby modifying the valence tautomeric transition temperature.¹²⁵

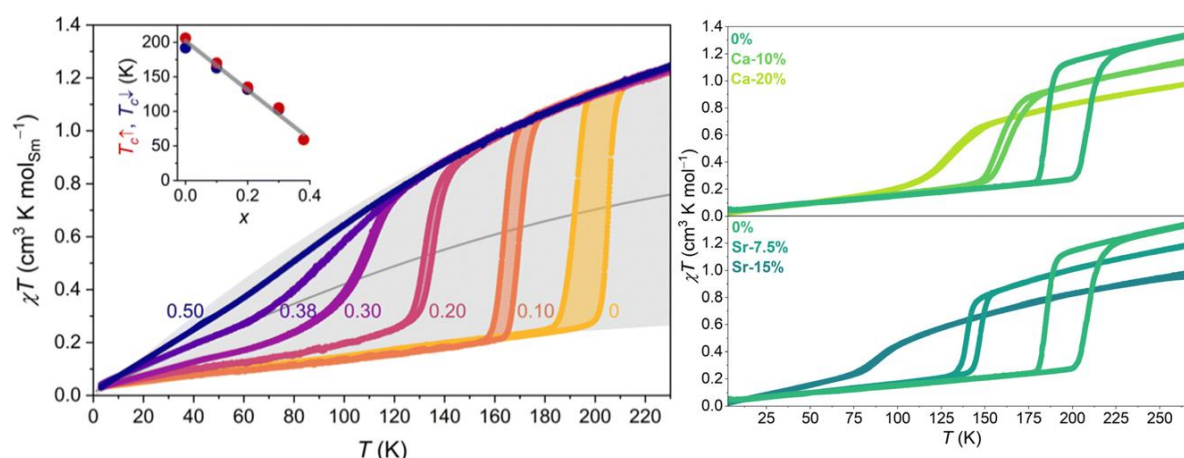


Figure 25: χT vs T for Sm_{1-x}Yb_xI₂(pyz)₃, normalized to the samarium content (1- x), showing the evolution of the phase transition with increasing Yb substitution with the grey line indicating 50% phase conversion. Inset: Linear dependency of the transition temperature on Yb content. Right: χT vs T for Ca- and Sr-substituted samples at different concentrations.^{124,125}

Ruthenium (and Osmium)

Valence tautomeric behaviour in ruthenium and osmium complexes is considerably less developed. To date, only the coexistence of different valence tautomeric forms has been observed, whereas no clear evidence for a thermally induced equilibrium between the electronic states has been reported. Consequently, these systems are generally regarded as electronically bistable rather than genuinely switchable valence tautomers. Interestingly, several ruthenium and osmium examples involve the fully reduced benzoquinone bq, giving rise to electronic formulations such as Ru(III)sq and Ru(II)bq as well as related systems formulated as Ru(II)sq and Ru(I)bq with osmium analogues reported for the latter formulation. In contrast to many first-row transition-metal valence tautomers, the ruthenium complexes remain low-spin in both electronic states. Although distinct valence tautomeric electronic configurations could be identified, no reversible thermally induced valence tautomeric equilibrium has yet been observed for ruthenium or osmium systems.^{126–128}

Nickel

In comparison to cobalt, iron, manganese, or copper systems, examples of VT involving nickel are exceptionally scarce. Only a very limited number of nickel complexes displaying reversible intramolecular electron transfer behaviour have been reported. One of the few known examples represents a predominantly coordination-induced process rather than a classical purely intramolecular thermally driven VT transition. In this system, the addition of DMF to a chloroform solution of $[\text{Ni}(\text{II})(\text{N}_2\text{L})(\text{dbcats})]^+$ induced the formation of the species $[\text{Ni}(\text{III})(\text{N}_2\text{L})(\text{DMF})_2(\text{dbsq})]^+$. The transformation corresponds to an intramolecular electron transfer to the dioxolene ligand from the nickel centre accompanied by coordination of two DMF molecules. Furthermore, upon addition of 200 equiv. of DMF to a dichloromethane solution of the starting complex, a reversible coordination-assisted thermally induced equilibrium was observed according to $\text{LS } [\text{Ni}(\text{III})(\text{N}_2\text{L})(\text{DMF})_2(\text{dbsq})]^+ \rightleftharpoons [\text{Ni}(\text{II})(\text{N}_2\text{L})(\text{dbcats})]^+ + 2 \text{ DMF}$. The equilibrium could be shifted thermally, demonstrating switchable behaviour between the two electronic states. However, because the process involves a change in the coordination number and ligand sphere of the nickel centre, this example does not strictly fulfil the classical definition of VT. Nevertheless, the system is noteworthy and is included here for completeness in the broader discussion of VT behaviour across different transition metals.^{64,69,129,130}

2. Aim of the Work

The rapidly growing global demand for data storage and processing represents one of the defining technological challenges of the present era. The global volume of digital data is projected to reach approximately 530 zettabytes by 2029, a figure that will be further amplified by the rapid expansion of artificial intelligence, large language models and machine learning applications, which place exceptional demands on processing speed, energy efficiency, and device miniaturisation. As outlined in the preceding chapters, one promising strategy to address these demands is the development of functional molecular components capable of operating as logic elements at the nanoscale. Among the most compelling candidates for this purpose are valence tautomeric complexes, which can reversibly switch between distinct electronic states in response to external stimuli, and whose nanometre-scale dimensions offer the prospect of functional units far smaller than those achievable with conventional silicon-based technologies.^{27,131,132}

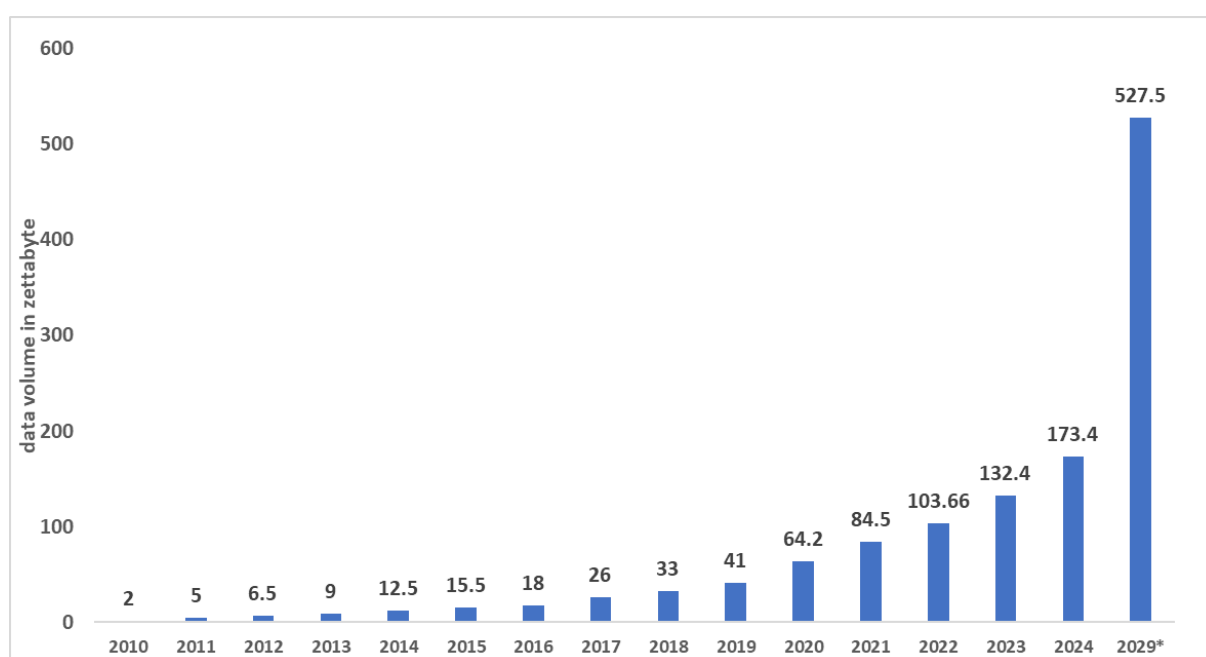


Figure 26: Annual global data volume generated and replicated between 2010 and 2024, including the projected data growth for 2029.²⁷

Since the discovery of VT in cobalt-dioxolene systems by Buchanan and Pierpont in 1980, the field has developed rapidly over four and a half decades. From the initial characterisation of thermally induced transitions, research has progressed through the establishment of abrupt and hysteretic switching behaviour, electronic and steric control of transition temperatures in mononuclear complexes, photo- and pressure-induced transitions, multi-stimulus-responsive systems, and extension to manganese, iron, copper, and lanthanide ions. Despite this progress, VT remains the most recently established and least developed of the three principal classes of bistable inorganic switching phenomena.^{64,68}

Of particular relevance to the present work is the development of dinuclear VT systems, which can, in principle, access three distinct electronic states through a two-step transition, thereby enabling ternary molecular switching and more complex logic operations. Two structural motifs have been pursued in the literature: bridging cobalt centres via a redox-active bis(dioxolene) ligand, and bridging via a redox-innocent ancillary ligand. The redox-active bridging approach has been investigated extensively. The work of Boskovic and co-workers established a predictive model based on two key parameters. First, the degree of electronic communication within the bis(dioxolene) ligand and the energetic matching of the cobalt and dioxolene redox potentials. This model was validated across both

the initial spiroconjugated system on which it was developed and non-spiroconjugated redox-active bridging systems.^{69,92,113}

In contrast, the motif of bridging via a redox-innocent ancillary ligand has received comparatively little attention and remains underrepresented in the literature. The few reported examples exhibit only highly gradual and incomplete VT transitions. One notable example, reported by Hearn *et al.* showed evidence for sequential two-step switching only indirectly, through near-infrared intervalence charge transfer measurements on amorphous thin films, without a complete magnetic transition being observed. M. Diehl demonstrated in his doctoral thesis (2015) within the Rentschler group that a dicationic dinuclear cobalt complex bridged by a piperazine-based bis(tetradentate) ancillary ligand exhibits VT behaviour that is strongly dependent on the choice of counteranion and lattice solvent. The complex with a perchlorate anion remained in the LS Co(III)cat state up to 380 K, while the sulphate analogue displayed an incomplete VT transition above 320 K, reaching a χ_{MT} value of $1.26 \text{ cm}^3 \text{ K mol}^{-1}$ at 380 K. These findings suggest that packing effects and intermolecular interactions play a decisive role in the solid-state VT behaviour of innocent-bridged dinuclear systems, but the underlying principles have not yet been systematically investigated.^{75,88,108,109}

The present work builds directly on Diehl's initial findings and exploits the particular advantages of the innocent bridging ligand motif. In contrast to systems based on redox-active bridging units, the use of a redox-innocent bridge greatly simplifies the synthesis and coordination chemistry, as the bridging ligand does not participate in the electron transfer process, and commercially available catecholates with well-defined redox properties can be employed without the complications of mixed-valence contamination or aerobic oxidation. The dicationic nature of the complex furthermore provides a direct handle on solid-state packing through counteranion exchange, enabling systematic modulation of intermolecular interactions and lattice solvent content.

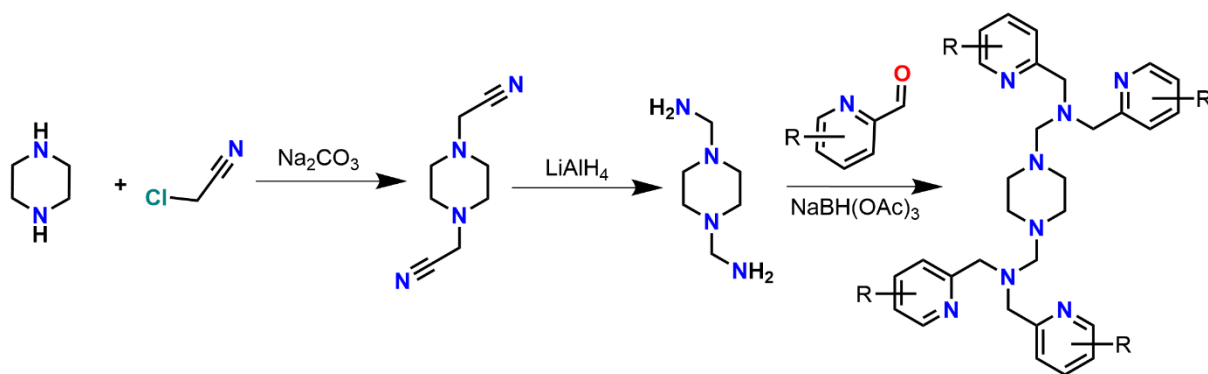


Figure 27: Reaction scheme illustrating the three-step synthesis of the bis-tetradentate, innocently behaving ancillary ligand, with emphasis on the final reductive amination step. In this step, the substitution pattern of the ancillary ligand can be readily tuned via the choice of commercially available aldehydes, enabling straightforward structural diversification.^{75,89}

The system offers four adjustable parameters, each targeting a distinct aspect of the VT transition. First, the counteranion can be varied to modulate packing effects and intermolecular interactions in the solid state, with the aim of increasing cooperativity and transition completeness. Second, the dioxolene substituents can be varied using substituted catecholates to tune the catecholate / semiquinonate redox potential and thereby optimise the energetic matching with the Co(III)/Co(II) couple. Third, the substituents on the pyridyl arms of the ancillary ligand can be modified through a reductive amination in the final step of the ligand synthesis, allowing systematic electronic and steric manipulation of the cobalt redox potential. Fourth, the aliphatic piperazine bridging unit can be replaced by an aromatic or olefinic bridge to introduce electronic communication between the two cobalt-dioxolene centres, with the aim of accessing genuine two-step VT behaviour through intramolecular cooperativity.

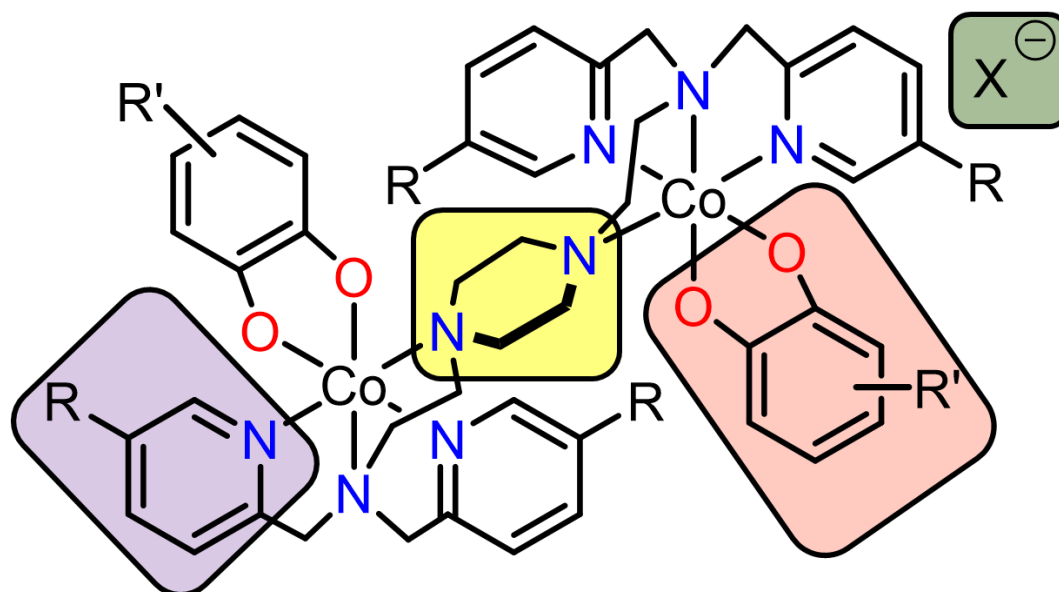


Figure 28: The four tuneable parameters in M. Diehl's system controlling distinct aspects of valence tautomeric transitions: dioxolene ligand substitution (red), ancillary innocent ligand substitution (blue), choice of counter anion (green), and the nature of the bridging unit between metal centres (yellow).

These four parameters define the research strategy of the present work. Whether the principles of electronic and steric substituent control established for mononuclear cobalt-dioxolene complexes can be transferred directly to the dinuclear innocent-bridging motif remains to be demonstrated. The extent to which packing effects, counteranion choice, and lattice solvent content govern the completeness and cooperativity of VT transitions in such systems is not yet completely understood. Furthermore, whether two-step switching behaviour, which was previously only achieved with redox-active bridging ligands, can be realised in innocent bridged systems through either sequential phase transitions or enhanced communication via a conjugated bridge represents an open and significant question in the field.

To address these questions, a series of novel dinuclear cobalt-dioxolene complexes was synthesised and comprehensively characterised by SQUID magnetometry, UV-Vis spectroscopy, X-ray diffraction, cyclic voltammetry, and complementary spectroscopic methods. The result aims to demonstrate that the innocent bridging ligand motif, long underrepresented in the dinuclear VT literature, represents a viable and synthetically versatile strategy for the design of bistable molecular switching systems with tuneable transition profiles.

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3. Outline of the Thesis

This dissertation is structured around four independently adjustable parameters of the parent dinuclear cobalt-dioxolene system, as illustrated in the following figure, each targeting a distinct aspect of the valence tautomeric transition. It builds on the foundational work of Diehl on dinuclear cobalt-dioxolene complexes and systematically investigates four adjustable parameters of this parent system to advance the understanding of valence tautomeric behaviour in the innocent-bridged dinuclear motif. These four parameters are counteranion and lattice solvent packing effects, dioxolene substitution, ancillary ligand substitution, and bridging unit substitution.

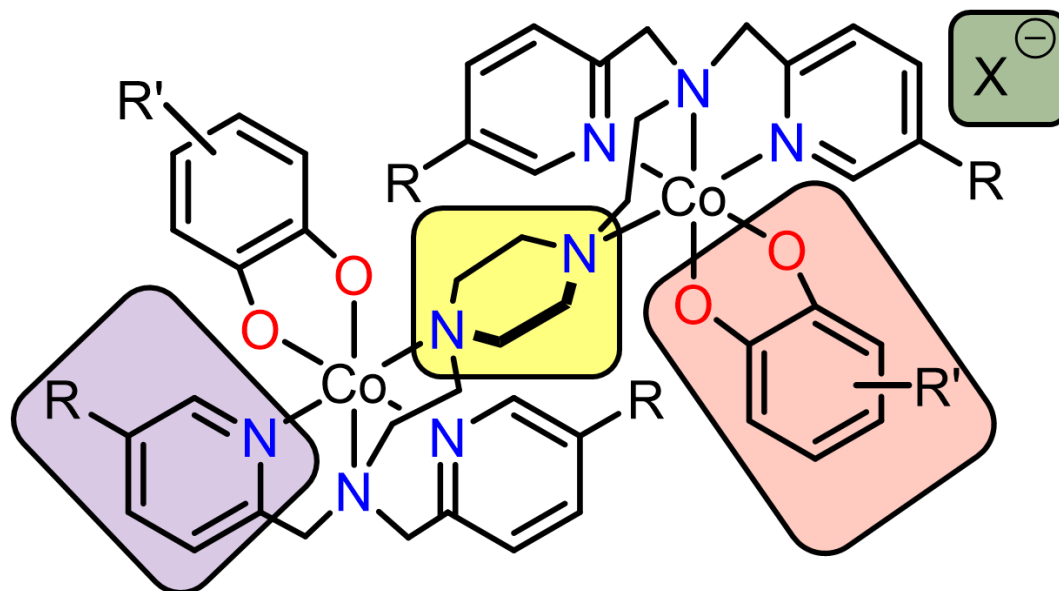


Figure 29: The four tuneable parameters in M. Diehl's system controlling distinct aspects of valence tautomeric transitions: dioxolene ligand substitution (red), ancillary innocent ligand substitution (blue), choice of counter anion (green), and the nature of the bridging unit between metal centres (yellow).

In chapter 1, the influence of dioxolene electronics and counteranion choice on the VT behaviour is investigated through a series of eight dinuclear cobalt complexes bearing tetrahalogenated catecholate ligands and varying counter anions. The impact of electron-deficient catecholates on the Co(III)/Co(II) redox potential and transition temperature is examined, and the role of solid-state packing through counteranion and lattice solvent variation is explored.

Chapter 2 addresses the transferability of ancillary ligand electronic effects to the dinuclear innocent-bridged motif. A series of complexes incorporating electron-withdrawing and electron-donating substituents at the *meta* position of the pyridyl arms of the bridging ligand is presented. The influence of these modifications on the Co(III)/Co(II) redox potential and on the VT transition temperature is investigated in both solution and solid state.

In chapter 3, the interplay of steric and electronic substituent effects is exploited to achieve complete and reversible VT in a dinuclear innocent-bridged system. A sterically demanding ortho-methylated bridging ligand is combined with systematically varied electron-withdrawing catecholate substituents, and the resulting complexes are characterised by single-crystal X-ray diffraction, UV-Vis spectroscopy, variable-temperature solid state ¹³C MAS NMR spectroscopy, and SQUID magnetometry.

Chapter 4 examines the effect of replacing the aliphatic piperazine bridging unit with an aromatic pyrazine bridge, with the aim of increasing electronic communication between the two cobalt-dioxolene centres and approaching the two-step VT transition regime. The synthesis of the modified bridging ligand and the corresponding dinuclear cobalt complex is described, and preliminary magnetic and spectroscopic characterisation of the pyrazine-bridged system is presented.

4. Chapter 1: Dioxolene Electronics and Counteranion Effects on Dinuclear Cobalt VT

This chapter presents an improved purification procedure for the bis(tetradentate) bridging ligand and reports the first dinuclear cobalt-dioxolene complexes bearing tetrahalogenated catecholate ligands described in the literature. A series of eight complexes was fully characterised by single-crystal X-ray diffraction, UV-Vis spectroscopy, cyclic voltammetry, IR spectroscopy, mass spectrometry, Evans NMR spectroscopy, and SQUID magnetometry. All complexes adopt the LS Co(III)cat configuration at low temperatures and remain diamagnetic. Complexes bearing sulfate counter-anions exhibit a thermally induced valence tautomeric transition at approximately 340 K. X-ray diffraction measurements reveal that the introduction of halogen substituents does not give rise to halogen-halogen or halogen-hydrogen interactions. Solution-state measurements, however, show that introduction of electron-withdrawing substituents on the catecholate moiety hinders VT. The sulfate anion promotes VT by co-crystallising with a large number of solvent molecules, thereby establishing an extensive intermolecular hydrogen-bonding network that softens the crystal lattice and facilitates the tautomeric transition.

The results are presented as a scientific article published in ACS Omega (Doi: <https://doi.org/10.1021/acsomega.5c05045>).

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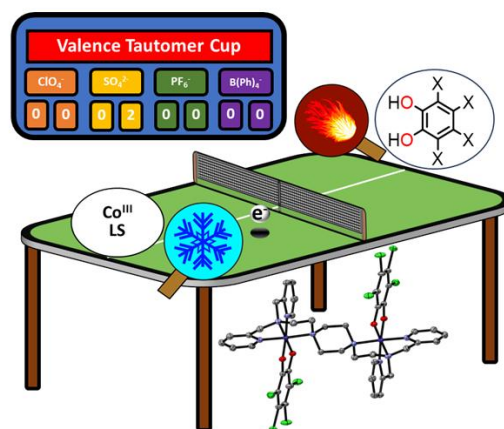
Author contribution:

The synthesis and characterisation of ligands and complexes was carried out by Tim Hieke. Synthesis and preliminary analytical evaluation of the perchlorate and sulfate complexes were performed as part of a master's thesis; final evaluation as well as the synthesis and characterisation of the remaining complexes were completed during the doctoral research. Single-crystal X-ray diffraction measurements, structure solution, and refinement were performed by [REDACTED]. The manuscript was written by Tim Hieke and revised with input from all authors. [REDACTED] provided overall supervision of the experimental work and the manuscript preparation. All authors have read and approved the final version of the manuscript.

Manuscript: Switchable Valence States in Dinuclear Cobalt Complexes: The Role of Halogenated Catecholates and Counterions

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Graphical Abstract



Abstract

We present the synthesis and comprehensive characterisation of a series of eight dinuclear cobalt complexes, **C1–C8**, with the general formula $[\text{Co}_2(\text{L})(\text{X}_4\text{cat})_2]^{2+}(\text{A})_{1-2}$, wherein $\text{X} = \text{Br}$ or Cl , $\text{A} = \text{SO}_4^{2-}$, ClO_4^- , PF_6^- , or $\text{B}(\text{Ph})_4^-$, and L denotes a redox inactive bis-tetradentate bridging ligand. Single-crystal X-ray diffraction at 120 K confirms a low-spin Co(III) configuration in all compounds. SQUID magnetometry also shows that the complexes remain diamagnetic below room temperature. However, the complexes bearing sulphate anions, **C1** and **C5**, exhibit a distinct thermally induced valence tautomeric transition above room temperature, marked by an increase in magnetic moment. The temperature of this transition is strongly influenced by the electronic properties of the catecholate (cat) ligands, with electron-deficient tetrahalogenated catecholates stabilising the low-spin state. In addition, counterions and solvent molecules are found to modulate intermolecular interactions in the solid state. Comparative cyclic voltammetry with previously reported di-*tert*-butyl catecholate (dbucat) complex **C9** highlights the influence of ligand electronics on redox potentials with electron-deficient catecholates shifting redox processes to higher potentials. These results highlight the tunability of cobalt valence tautomerism and redox behaviour through strategic ligand and counterion selection.

Introduction

Bistable molecules are at the forefront of next-generation materials, offering tuneable properties crucial for advanced applications. These include molecular-scale memory elements capable of switching between distinct states under external stimuli, as well as adaptive sensors that respond dynamically to environmental changes such as temperature shifts or chemical exposure. Such innovations hold immense potential for smart materials in fields ranging from environmental monitoring to biomedical diagnostics.^{1–7} Among bistable systems, metal complexes featuring open-shell ions are particularly intriguing, as changes in their electronic structure can induce significant modifications in their physical properties. Three key classes of bistable metal complexes exhibit this multi-stability: (i) spin-crossover (SCO) complexes (ii) Prussian-blue analogues and (iii) valence tautomeric (VT) complexes. While SCO compounds—especially those based on Fe(II), Fe(III), and Co(II)—have been extensively studied for decades,^{6–13} research into valence tautomerism has gained

momentum only in recent years.^{14–18} Understanding and controlling these bistable systems is essential for unlocking their full potential in molecular electronics, data storage, and responsive materials.

Prussian Blue analogues represent a versatile class of bistable materials. It is evident that Fe/Co Prussian blue analogues are particularly noteworthy as exemplary systems for metal-to-metal charge transfer (MMCT). These analogues exhibit remarkable switchable magnetic and optical properties, thus making them valuable models for research in this field. These systems have been the focus of significant research over the past two decades, owing to their noteworthy physico-chemical properties that are being investigated for their use in potential molecular electronic devices.^{19–23}

Valence tautomerism was first identified in 1980 by Buchanan and Pierpont on mononuclear cobalt-dioxolene complexes.²⁴ Unlike in spin crossover (SCO) systems, valence tautomeric (VT) behaviour requires the presence of redox-active, non-innocent ligands, of which dioxolenes are a prominent example. For a complex to exhibit valence tautomerism, it needs to contain both an electron donor and an electron acceptor, typically the metal centre and the redox-active ligand. The interaction results in simultaneous changes in the oxidation states of both components, fundamentally altering the electronic structure of the complex. The defining feature for valence tautomerism therefore is an intramolecular electron transfer between a metal ion and an organic ligand^{16,25–28}. This close interplay enables reversible electronic transitions that can be triggered by external stimuli such as temperature,^{29–31} pressure^{18,32} or light^{33,34}. The ability to control these transformations makes valence tautomeric systems highly attractive for applications in molecular electronics, stimuli-responsive materials, and switchable functional devices.

Cobalt complexes are the most extensively studied VT systems due to the intrinsic link between their redox transitions and associated spin state changes.^{35–38} This feature provides a distinct magnetic contrast between states, making SQUID magnetometry a powerful tool for monitoring VT transitions. While valence tautomerism has been observed in other transition metals, including those of manganese,^{39–42} iron,^{43,44} and copper,^{45–47} these often lack an accompanying spin-state change, precluding magnetic detection.¹⁷ In such cases, alternative spectroscopic techniques, particularly UV-Vis spectroscopy, are used to probe the characteristic optical changes associated with valence tautomerism.⁴¹

Compared to mononuclear systems, dinuclear cobalt complexes offer a wider range of electronic states.^{35,48,49} In most reported examples, redox-active ligands act as bridging units, facilitating electronic communication between metal centers. In contrast, complexes featuring innocent bridging ligands remain largely unexplored, with only a few examples described in the literature.^{16,50–52}

Furthermore, the majority of reported studies focus on di-*tert*-butyl-substituted catecholates, while tetrahalogenated analogues remain relatively unexplored. Although halogen substituents - being strongly electron withdrawing - can suppress dioxolene oxidation to semiquinone (sq) and destabilise the VT equilibrium, they also increase the air stability of the resulting complexes¹⁶. Only a handful of mononuclear cobalt complexes bearing tetrachlorinated (Cl₄-cat)^{38,53–57} or tetrabrominated catecholates (Br₄-cat)^{41,58,59} have been reported, and cases of reversible switching behaviour among them are extremely rare.

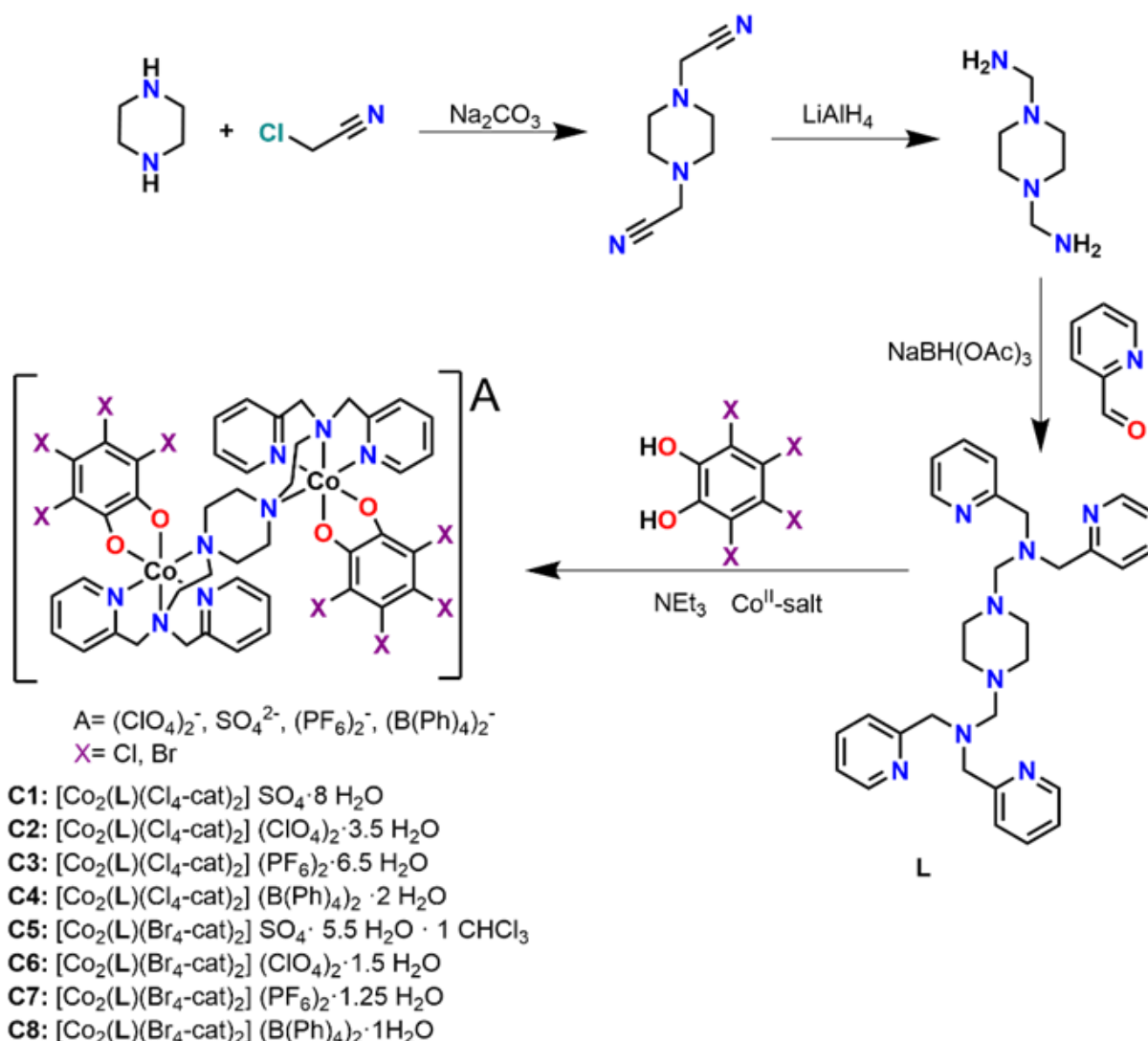
To the best of our knowledge, no dinuclear cobalt complexes with tetrahalogenated catechols have been reported to date. In this study, we present the synthesis and characterization of a family of eight cobalt complexes featuring tetrahalogenated catechol ligands. These complexes vary in the choice of catechol ligand and the uncoordinated counterions. The primary goal was to investigate the effect of electronic and structural modifications on valence tautomerism (VT) and redox properties. Additionally, we took advantage of this cationic complex family in the tunability of VT behaviour through counterion selection and thus varying lattice solvent effects, which modulate intermolecular interactions, which are critical to VT transitions. To assess the impact of electron-withdrawing halogen substituents, we compare these new complexes to our previously reported di-*tert*-butyl catecholate

analogues. This comparative approach quantifies the influence of electron-withdrawing versus electron-donating groups on the redox properties and VT behaviour of cobalt complexes.

Results and Discussion

Ligand Synthesis

The bridging ligand used for complexes **C1–C8** was synthesized according to our previously reported procedure,⁶⁰ as shown in **Scheme 1**. However, the final purification step was modified to improve both the yield and purity of the product. Instead of the original washing step with acetone, a double recrystallisation was carried out using 10 mL of acetone. The ligand was obtained as yellow crystals with a final yield of 85% and was fully characterised by a number of techniques including infrared spectroscopy (**Figures S1–S3**), ¹H (**Figures S12–S14**), ¹³C NMR spectroscopy (**Figure S15**) and 2D-NMR techniques (**Figure S16–S18**). 2D NMR allowed us to assign ¹³C signals more precisely.



Scheme 1: Reaction scheme of the multi-step ligand synthesis of the bis-tetradentate ligand *N, N, N', N'*-Tetra-2-picolyl-1,4-bis(2-aminoethyl)piperazine (**L**) and complex synthesis of **C1–C8**.

Complex Synthesis

The detailed synthetic procedures for the complexes **C1–C8** can be found in the experimental section. In general, the cobalt(II)-salt (0.2 mmol, 2.0 eq.), **L** (0.1 mmol, 1.0 eq.) and the corresponding tetrahalogenated catechol (0.2 mmol, 2.0 eq.) were dissolved in 15 mL of the respective solvent. When using cobalt(II) chloride, a mixture of acetonitrile and methanol (20 mL, 1:1) was used. A solution of triethylamine (0.4 mmol, 4.0 eq.) in 1 mL of the solvent used was added dropwise and an immediate colour change to green was observed. After heating for an hour under reflux, the reaction mixture was cooled down to room temperature and filtered. Single crystals, suitable for X-ray diffraction analyses, were obtained by slow evaporation of the mother liquor over one to 15 days. When hexafluorophosphate or tetraphenylborate salts were used, the precipitates were recrystallized to obtain single crystals suitable for X-ray diffraction.

Single crystals were used for structural determination and further analytical studies. The bulk identity was verified using infrared spectroscopy, which identified characteristic bands of the anions (perchlorate, sulphate, tetraphenyl borate, and hexafluorophosphate) at their specific wavenumbers, along with the C–O vibrations of catechols at approximately 1425 cm^{-1} (**Figures S4–S11**). High-resolution mass spectrometry confirmed the presence of the dicationic fragment $[M]^{2+}$ for all complexes (**C1–C8**), with the observed isotopic patterns precisely matching theoretical calculations, verifying the formation of dinuclear cobalt compounds (**Figures S22–S37**). Elemental analysis further confirmed the bulk purity of the samples and revealed that air exposure led to the replacement of lattice solvents with water molecules, resulting in the formation of hydrated complexes.

Crystal Structures Description

The structures of **C1–C8** have been determined by single crystal X-ray diffraction at 120 K. **Figure 1** shows the structures of the complexes $[\text{Co}_2(\text{L})(\text{Cl}_4\text{cat})_2]\text{SO}_4$, **C1–Cl–SO₄**, and $[\text{Co}_2(\text{L})(\text{Br}_4\text{cat})_2]\text{SO}_4$, **C5–Br–SO₄**, while the remaining structures can be found in the ESI. (**Figures S38–S45**)

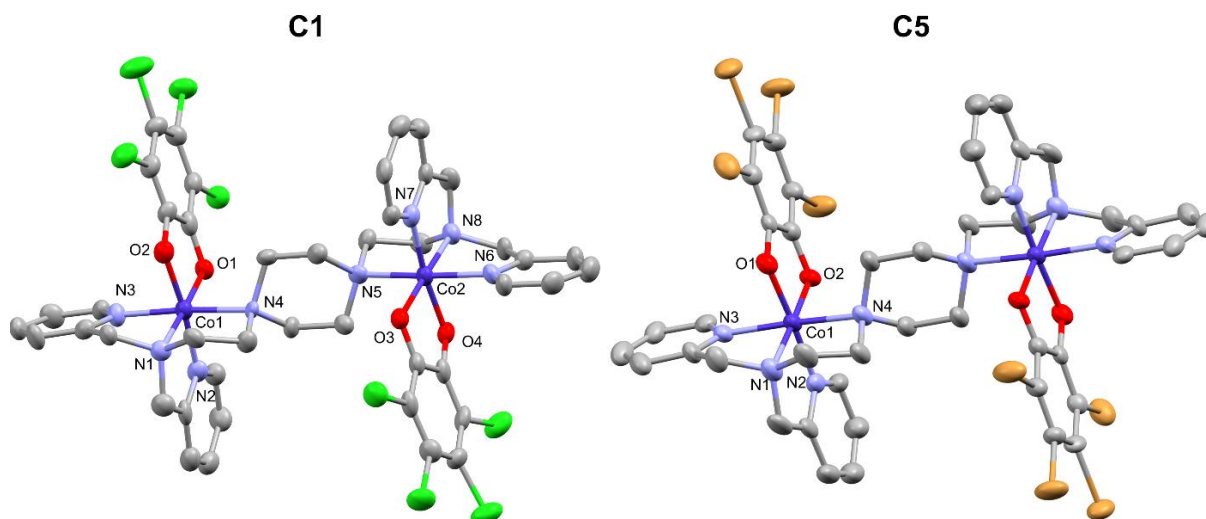


Figure 1: Complex structures of $[\text{Co}_2(\text{L})(\text{Cl}_4\text{cat})_2]\text{SO}_4$, **C1–Cl–SO₄**, and $[\text{Co}_2(\text{L})(\text{Br}_4\text{cat})_2]\text{SO}_4$, **C5–Br–SO₄** at 120 K. Lattice solvent molecules, anions and hydrogen atoms are omitted for clarity. The probability level for the displacement of the ellipsoid is 50%. Colour code: carbon (grey), cobalt (dark blue), nitrogen (light blue), oxygen (red), chloride (green), bromide (brown).

Complexes **C1–Cl–SO₄**, **C4–Cl–BPh₄** crystallised in the centrosymmetric $P 2_1/c$ space group, **C8–Br–BPh₄** in the monoclinic $P 2_1/n$ space group, while complexes **C2–Cl–ClO₄**, **C3–Cl–PF₆**, **C5–Br–SO₄**, **C6–Br–ClO₄** and **C7–Br–PF₆** crystallised in the triclinic $P\bar{1}$ space group with only one molecule in the unit cell. The molecular structure of the isostructural complexes shows a dinuclear cobalt complex in which the two metal centres are coordinated by a bis-tetradentate bridging ligand. The coordination sphere of each

cobalt ion is completed by the bidentate, deprotonated *ortho*-dioxolene ligand. In detail, the N_4O_2 coordination environment of each cobalt centre is composed as follows: Two nitrogen atoms originate from pyridine units, another from an aliphatic tertiary amine, while the fourth comes from the piperazine heterocycle. The two *ortho* oxygen atoms of the deprotonated catechol ligand complete the coordination. The octahedral coordination geometry around each cobalt ion is only slightly distorted, likely due to the rigidity of the bridging ligand. The metal donor bond lengths are 1.8708 – 1.912 Å for Co-O, and 1.902 – 1.957 Å for Co-N for the three nitrogen donor atoms of the capping sidearms. The bond lengths of Co-N for the piperazine nitrogen donor are always significantly longer with metal donor distances of 2.0376 - 2.107 Å. Details can be found in **Table 1**. The expected metal donor bond distances are 1.926 - 1.955 Å for Co - N and 1.877 -1.880 Å for Co-O in similar low spin Co(III) complexes as well as 2.125 - 2.243 Å for Co-N and 1.988 -2.171 Å for Co-O in similar high spin Co(II) complexes⁶¹. The software program *SHAPE 2.1*⁶² was utilised to conduct continuous shape measurements. The cobalt centres of complexes **C1-8** exhibited little deviations from the ideal octahedral coordination geometry, suggesting a small distortion. The coordination environments exhibit *SHAPE* indices ranging from 0.23856 to 0.41186. The closer the index is to 0, the closer the coordination environment is to the ideal geometry. It is possible to discern the small distortions in the structures of the compounds, as can be seen by the nitrogen atom of the piperazine. This atom always exhibits longer bond distances in comparison to the other metal-nitrogen bonds. The complete *SHAPE* calculations are listed in **Tables S20-29**. The “metrical oxidation states” (MOS) for each of the attached catecholates were calculated based on all C-O and C-C ring distances in the dioxolene ligand.⁶³ The values which were obtained for the catecholates range from -1.69 to -1.91 which corresponds to catecholate ligands. The complete values for the MOS can be found in **Tables S30**. The metal donor distances clearly show that the cobalt ions are in the low spin d^6 state^{64,65}. This is in accordance also with the C-C bond lengths of the catechols which vary between 1.375 and 1.438 Å and indicate aromatic C-C bonds as expected for catecholates. Thus, at 120 K the cobalt ions for all complexes are trivalent and the non-innocent ligand is in its catecholate state. All bond lengths, together with the bond angles, are listed in **Tables S5-S19**.

The intermolecular interactions for each of the eight complexes are investigated in detail. Complex **C5-Br-SO₄** shows π - π interactions between aromatic pyridines with a centroid-to-centroid distance of 3.820 Å, a parallel shift of 1.743 Å and an angle of 0° between both pyridine planes (**Figure S53**). The remaining complexes do not exhibit any π - π interactions between aromatic compounds. However, every complex is dicationic in nature and therefore crystallises with its respective anion: **C1-Cl-SO₄**, **C5-Br-SO₄**: sulphate, **C2-Cl-ClO₄**, **C6-Br-ClO₄**: perchlorate, **C3-Cl-PF₆**, **C7-Br-PF₆**: hexafluorophosphate, **C4-Cl-BPh₄**, **C8-Br-BPh₄**: tetraphenylborate. Moreover, all single crystals of the complexes are grown from the mother liquor and contain lattice solvent molecules: **C1-Cl-SO₄** · 11 MeOH, **C2-Cl-ClO₄** · 3 H₂O · 1 MeCN, **C3-Cl-PF₆** · 2MeOH · 2 MeCN, **C4-Cl-BPh₄** · 1 MeCN, **C5-Br-SO₄** · 4 MeOH · 2 H₂O, **C6-Br-ClO₄** · 2 MeCN, **C7-Br-PF₆** · 1 MeOH · 1 MeCN, **C8-Br-BPh₄** · 4 MeCN. Complex **C1-Cl-SO₄**, with 11 methanol molecules, has the largest number of solvent molecules per complex ion, and it is therefore not surprising that it also has the strongest hydrogen bond network (**Figure S54**), especially considering that the sulphate anion is doubly negatively charged. For the analogue Br₄-cat complex, **C5-Br-SO₄**, with 4 methanol molecules, this interaction is already less pronounced (**Figure S56**). In contrast, as expected, the complexes bearing MeCN solvent molecules (**C4-Cl-BPh₄**, **C6-Br-ClO₄**, **C8-Br-BPh₄**) don't show any hydrogen bonding interactions. For the other complexes the hydrogen bonding network is found to be small to moderate. Worth noting in this context is the H...F interaction for the hexafluorophosphate anions being close to non-acidic CH groups of the complex cations in **C3-Cl-PF₆** and **C7-Br-PF₆** (**Figures S57-S58**).

The flexibility of the crystal lattice, which allows volume expansion during tautomeric valence transitions, plays a crucial role in their behaviour. Complexes with minimal lattice solvent have a rigid structure. In **C1-Cl-SO₄** and **C5-Br-SO₄**, by contrast, several methanol molecules fill empty spaces in the packing and engage in extensive intermolecular interactions. This allows the formation of a rich hydrogen bonding network which makes the lattice more flexible and facilitates valence tautomeric

transitions as will be discussed in more detail below. In detail, **C1-Cl-SO₄** shows a herringbone structure when viewed along the a-axis (**Figure S59**), but resembles a star-shaped motif when viewed in the a-b plane because of the alternating orientations of the complexes along the c-axis (**Figure 2**). The same cation packing motif is found for **C3-Cl-PF₆**.

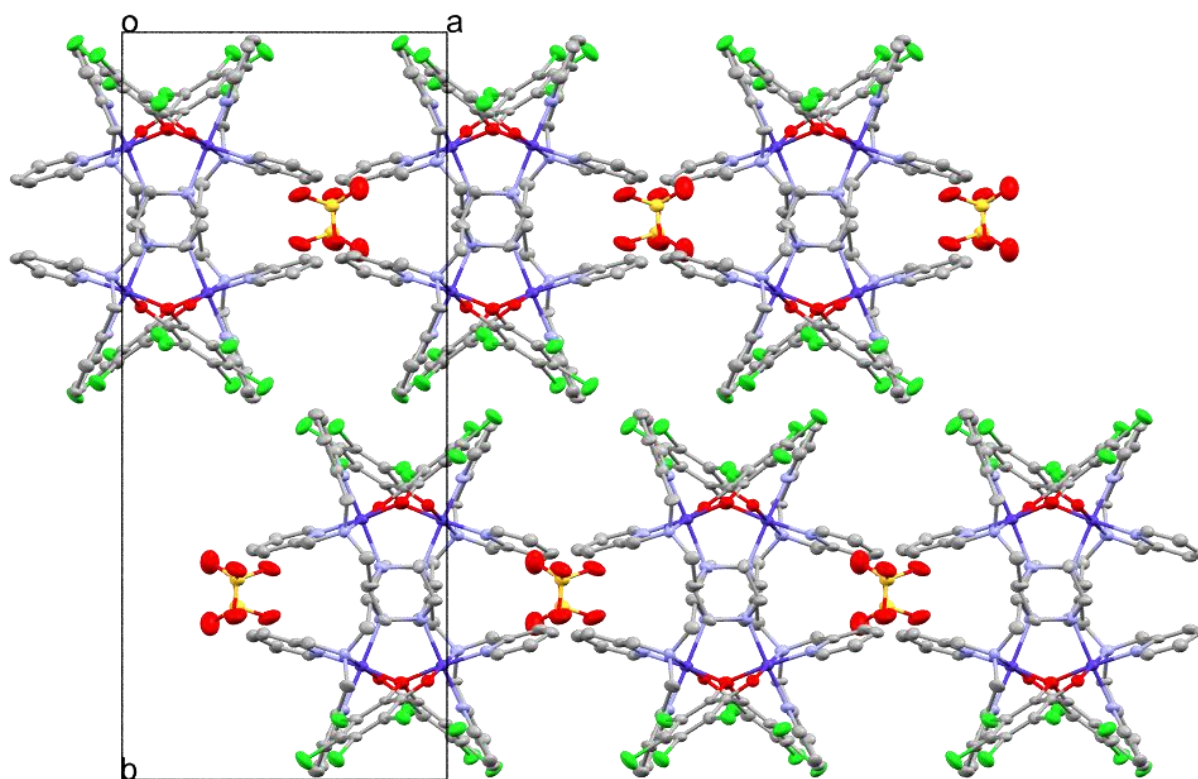


Figure 2: Crystal packing of **C1-Cl-SO₄** viewed along the c axis of the crystal. Lattice solvent molecules and hydrogen atoms are omitted for clarity.

Table 1: Metal-Donor bond lengths of complexes **C1-C8** in Å at 120 K

Co-X	C1-Cl-SO ₄	C2-Cl-ClO ₄	C3-Cl-PF ₆	C4-Cl-BPh ₄	C5-Br-SO ₄	C6-Br-ClO ₄	C7-Br-PF ₆	C8-Br-BPh ₄
Co1-O1	1.881(6)	1.898(4)	1.8816(14)	1.8708(13)	1.912(5)	1.898(5)	1.8722(18)	1.8773(13)
Co1-O2	1.898(6)	1.871(4)	1.8966(15)	1.8909(15)	1.893(5)	1.882(4)	1.8918(18)	1.8745(13)
Co1-N1	1.933(8)	1.936(4)	1.9399(16)	1.9454(17)	1.957(6)	1.942(5)	1.937(2)	1.9460(15)
Co1-N2	1.924(7)	1.910(4)	1.9081(18)	1.9200(18)	1.925(7)	1.902(6)	1.915(2)	1.9170(16)
Co1-N3	1.922(8)	1.916(4)	1.9171(17)	1.9173(19)	1.937(6)	1.923(6)	1.914(2)	1.9251(15)
Co1-N4	2.043(7)	2.048(4)	2.0479(17)	2.0555(17)	2.05F(6)	2.107(6)	2.047(2)	2.0376(15)
Co2-O3	1.889(6)	1.895(4)	-	-	-	-	-	-
Co2-O4	1.895(6)	1.873(4)	-	-	-	-	-	-
Co2-N5	2.045(8)	1.938(4)	-	-	-	-	-	-
Co2-N6	1.919(8)	1.921(4)	-	-	-	-	-	-
Co2-N7	1.926(8)	1.914(4)	-	-	-	-	-	-
Co2-N8	1.928(7)	2.045(4)	-	-	-	-	-	-

Electrochemistry

Cyclic voltammograms were obtained for solutions of compounds **C2-Cl-ClO₄**·3.5 H₂O, **C6-Br-ClO₄**·1.5 H₂O and our previously reported **C9** [Co₂(L)(dbucat)₂](ClO₄)₂·1.5 H₂O⁶⁰ (Figure 3) due to solubility problems with the complexes **C1-Cl-SO₄** and **C5-Br-SO₄**. It is evident from the results of the UV-Vis and Evans method discussed in the later part of the manuscript that all complexes **C2-Cl-ClO₄**, **C6-Br-ClO₄** and **C9-dbucat-ClO₄** are in the LS-Co(III)-cat state at room temperature in acetonitrile solution. Electrochemical studies were carried out on 1 mM dry acetonitrile solutions with 0.1 M n-Bu₄PF₆ using a glassy carbon working electrode and a silver wire pseudo-reference electrode. As an internal reference, all measurements were calibrated against the ferrocene/ferrocenium (Fc/Fc⁺) redox couple by adding ferrocene after the last measurement of a series. The half-wave potentials (*E*_{1/2}) and peak-to-peak separations (ΔE_p) are given in Table 2, together with the peak potentials (*E*_p) for the irreversible processes.

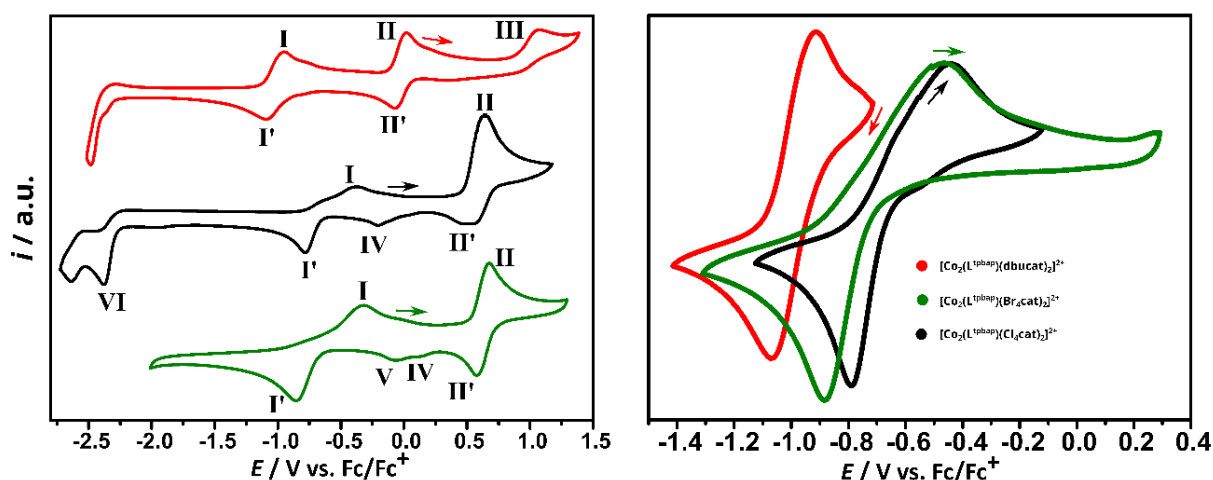


Figure 3: Cyclic voltammograms (left) and comparison of redox process (I/I') (right) for compounds [Co₂(L)(Br₄cat)₂](ClO₄)₂ · 1.5 H₂O **C6** (green), [Co₂(L)(Cl₄cat)₂](ClO₄)₂ · 3.5 H₂O **C2** (black) and the previously reported [Co₂(L)(dbucat)₂](ClO₄)₂ · 1.5 H₂O **C9** (red) (1.0 mM with 0.1 M n-Bu₄PF₆ in acetonitrile obtained with a scan rate of 100 mV s⁻¹) with a glassy carbon working electrode, a silver wire reference electrode, referenced internally against the redox pair ferrocene/ferrocenium (Fc/Fc⁺).

Table 2: Cyclic voltammetry data for **C9-dbucat-ClO₄**·1.5 H₂O, **C2-Cl-ClO₄**·3.5 H₂O and **C6-Br-ClO₄**·1.5 H₂O in acetonitrile. *E*_m is the experimentally determined average potential between the potentials of the corresponding anodic and cathodic events of a reversible or quasi-reversible electrochemical event while *E*_p is the peak potential of an irreversible electrochemical event.

Compound	Cyclic Voltammetry data <i>E</i> _m or <i>E</i> _p /V (ΔE_p /mV) vs. Fc/Fc ⁺ .					
	I/I'	II/II'	III	IV	V	VI
C9-dbucat-ClO₄ 1.5 H ₂ O	-1.022 (147)	-0.027 (91)	1.070	-	-	-
C2-Cl-ClO₄ ·3.5 H ₂ O	-0.578 (408)	0.574 (139)	-	-0.206	-	-2.378
C6-Br-ClO₄ ·1.5 H ₂ O	-0.585 (537)	0.591 (95)	-	0.160	-0.065	-

The previously reported **C9-dbucat-ClO₄**·1.5 H₂O and **C2-Cl-ClO₄**·3.5 H₂O were suitable for measuring over the entire acetonitrile solvent window, whereas the stability of complex **C6-Br-ClO₄**·1.5 H₂O only allowed us to measure in the range of -2 to 1.5 V vs. Fc/Fc⁺. Each complex showed distinct redox processes denoted as (I/I') and (II/II'), corresponding respectively to the redoxpair of Co(II) / Co(III) and to the redoxpair catecholate / semiquinonate, which were assigned according to the literature^{59,66,67}. During the initial cycle of the cyclic voltammetry experiments, the peak that corresponds to the oxidation of Co(II) to Co(III) was absent. Only after the first reduction process (I)

did (I') appear, confirming that this redox process is cobalt centred, since at room temperature the cobalt centres should be in the trivalent oxidation state. The scan rate investigation (**Figure S83-S85**) reveals that all redox processes are quasi-reversible, as the peak potentials are shifted away from each other with increasing scan rates. Furthermore, the differences in peak potentials are significantly greater than 59 mV, confirming the quasi-reversible nature. In the case of the previously reported complex **C9-dbucat-ClO₄ · 1.5 H₂O** the redox process (III) is attributed to the irreversible oxidation of the semiquinonate to the quinonate. The irreversibility of the redox process (III) can be attributed to the weak coordination of quinones, which consequently leads to dissociation⁶⁶. Within the measured potential range, complexes **C2-Cl-ClO₄·3.5 H₂O** and **C6-Br-ClO₄·1.5 H₂O** do not show a redox process (III). Furthermore, as expected, the potentials of the redox processes (I/I') and (II/II') occur at more anodic voltages as expected for the electron-withdrawing chloro and bromo substituents bearing catecholates (**Figure**).

The lack of electron density in the catecholates due to the negative inductive effects of the halogen substituents in the case of the tetrahalogenated catecholate complexes promotes the reduction process and hinders the oxidation process. As a result, process (III) becomes inaccessible for both complexes **C2-Cl-ClO₄·3.5 H₂O** and **C6-Br-ClO₄·1.5 H₂O**. However, both **C2-Cl-ClO₄·3.5 H₂O** and **C6-Br-ClO₄·1.5 H₂O** show the irreversible reduction processes (IV) and (V), which might be ligand-based. These processes occur only after the oxidation process (II) at the elevated potential and do not appear when the window is narrowed down to scan in the region where process (I/I') occur, as can be seen in the scan-rate studies (**Figure S83-S85**). In addition, the redox process (VI) represents an irreversible reduction event. The reduction events at these negative potentials are not of any relevant interest to the current studies. However, at these negative potentials and, taking into account the presence of electron-withdrawing substituents, the reduction can either be due Co(II) being reduced to Co(I) species or, most likely, an irreversible ligand reduction.⁶⁸ It has been demonstrated that the shapes of the redox process (I/I') differ for the tetrahalogenated and the di-*tert*-butyl catecholate cyclic voltammograms. It is evident that the peak difference is intensified for the tetrahalogenated catecholates. A larger peak separation is generally associated with higher barriers to electron transfers due to lower kinetics, and therefore the need for more extreme potentials. It appears that tetrahalogenated catecholates stabilise the LS-Co(III)-cat state more strongly, resulting in a slower electron transfer and, consequently, a broader peak separation. In contrast, the complex with di-*tert*-butyl-catecholate demonstrates a reduced peak separation, indicative of a faster and electrochemical reversible process.⁶⁹

Another interesting value determined by cyclic voltammetry is the potential gap between redox processes I/I' and II/II'. It is evident that these processes are associated with the Co(II)/Co(III) and the cat/sq redox processes. This is precisely what occurs during the VT transition. It can thus be concluded that, in order to minimise the energy required to overcome the activation barrier of the switching behaviour, the potential gap must be reduced to the smallest possible level. **C9-dbucat-ClO₄** exhibits the narrowest gap, with a difference of 996 mV, while **C2-Cl-ClO₄** demonstrates a wider gap of 1152 mV and **C6-Br-ClO₄** shows a gap of 1176 mV. It is evident that the electron-donating force on the catecholate diminishes the potential gap, thereby favouring the VT behaviour.

Magnetic Characterization

The temperature dependent magnetic susceptibility for complexes **C1-C8** was measured in polycrystalline samples in a SQUID magnetometer from 200 to 380 K, as shown as the $\chi_M T$ product in **Figure 4**. In all cases the complexes remain diamagnetic below 300 K, as expected for a $\text{Co}^{\text{III}}_2(\text{cat})_2$ species. This is further supported by the metal to ligand donor distances observed in the X-ray structure data at low temperatures. The complexes **C2-C4** and **C6-C8** retain their diamagnetic character up to 380 K and show no evidence of switching behaviour. The individual magnetic susceptibility measurements for each complex are given in the Supporting Information (**Figures S86-S93**).

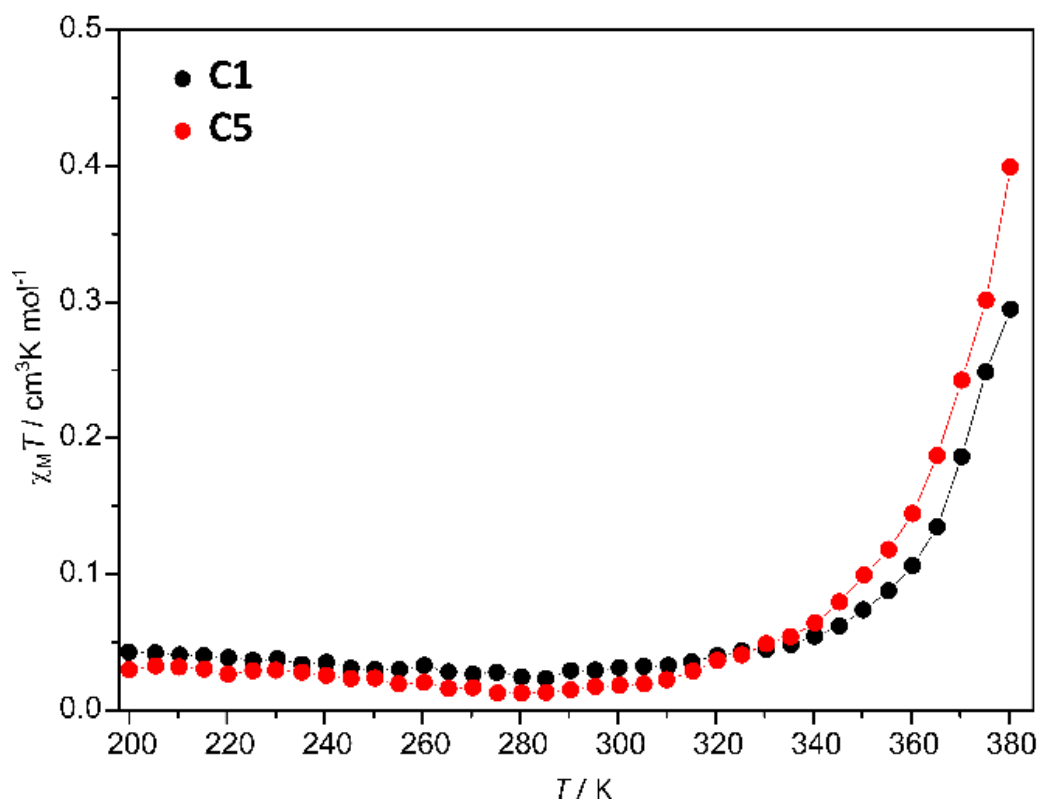


Figure 4: Temperature dependent magnetic susceptibility of compounds **C1-Cl-SO₄** and **C5-Br-SO₄** over the temperature window of 200 K to 380 K.

In the case of complexes **C1-Cl-SO₄** and **C5-Br-SO₄**, a gradual subtle increase in magnetic moment occurs above room temperature, indicating the transition from the low spin (LS) $\text{Co}^{\text{III}}(\text{cat})$ entity to the high spin (HS) $\text{Co}^{\text{II}}(\text{sq})$ configuration.^{16,51,70} The small increase in the magnetic moment to $0.294 \text{ cm}^3 \text{K mol}^{-1}$ and $0.399 \text{ cm}^3 \text{K mol}^{-1}$ at 380 K for **C1-Cl-SO₄·8 H₂O** and **C5-Br-SO₄·5.5 H₂O · CHCl₃** respectively is attributed to this transition, although the transition is incomplete. According to the spin-only values, a peak spin-only $\chi_M T$ value of $2.25 \text{ cm}^3 \text{K mol}^{-1}$ at elevated temperature is expected for an HS $\text{Co}(\text{II})$ (with a spin value of 3/2) and a semiquinone radical (with a spin value of 1/2).⁷¹ Due to orbital angular momentum of the $^4\text{T}_1$ state in $\text{Co}(\text{II})$ even higher magnetic moments can be observed.^{16,71-73} It is worth noting that the complexes **C2-C4** and **C6-C7** also show a small increase in the magnetic moment above room temperature, but the increase is too small and the slope is too weak to allow a valence tautomerism transition to be established. For the complexes **C1-Cl-SO₄** and **C5-Br-SO₄** we observe higher onset temperature of the transition in comparison to $[\text{Co}_2(\text{L})(\text{dbucat})_2]\text{SO}_4$ ⁶⁰, as expected for a change from electron-donating to electron-withdrawing tetrahalogen substituents in the catechols, and since chlorine is more electronegative than bromine, even more so for the latter (**Figure 4**). This delay clearly shows that the electron-deficient tetrahalogenated catechols are reluctant to participate in intramolecular electron transfer compared to the di-*tert*-butyl catechols. Compared to the di-*tert*-butyl catechols. Thus, while the transition begins at around 340 K for the complexes with the

tetrahalogenated catechols, it does not begin for the di-tert-butyl catechol complexes. To understand why only the complexes **C1-Cl-SO₄** and **C5-Br-SO₄** exhibit a significant VT, while this is not the case for the others, we have to go back to the discussion of the crystal packing, which differs in the series of complexes with different counteranions. The valence tautomeric transition from the LS Co(III) to the HS Co(II) state is always accompanied by a change in the volume of the crystal lattice. The changes in metal-ligand bond lengths are significant because antibonding *eg** orbitals are occupied upon transition from the LS to the HS state. The Co-N and Co-O bond lengths can increase by up to 0.15 Å.⁵⁶ For this to happen, the crystal lattice needs to be flexible and less rigid. The complexes **C1-Cl-SO₄**·8 H₂O and **C5-Br-SO₄**·5, 5 H₂O · 1 CHCl₃ are the only ones with only a single counterion for the divalent sulphate ion, which makes intermolecular cation-anion interactions quite different from those of the complexes with two monovalent anions. The looser packing of the molecules in the crystal is reflected in the larger number of solvent molecules found in the unit cell. As mentioned above, the crystal packing for **C1-Cl-SO₄** and **C5-Br-SO₄** has up to eight water molecules as lattice solvents, making the lattice more flexible than for the compounds with the other anions.

The ligand field strength, which was altered by the various substituted catechols was clearly visible in the oxidation potential studies by cyclic voltammetry and can also be seen in the magnetic data. When the complexes with the same counterion, **C9-dbucat-ClO₄**, **C2-Cl-ClO₄** and **C6-Br-ClO₄**, are compared, a temperature shift of the valence tautomeric transition is observed for the three catechols with varying electron-withdrawing substituents due to the different resulting ligand field strengths.

Solution Studies

To eliminate packing effects affecting VT behaviour, electronic properties of the complexes in solution were investigated. Solution stability and structural integrity in solution were investigated by DOSY-NMR (**Figure S19-S21**). The observation of a single signal in the DOSY spectrum indicates that the cationic fragment of the complex diffuses as a unit and does not dissociate further. Electronic absorption spectra (**Figure 5**) were recorded for **C2-Cl-ClO₄**, **C6-Br-ClO₄** and **C9-dbucat-ClO₄** at room temperature in acetonitrile. The spectra of **C2-Cl-ClO₄** and **C6-Br-ClO₄** are very similar and exhibit three absorption bands only differing in its intensities were the tetrabrominated catecholate complex shows higher intensities while in **C9-dbucat-ClO₄** the bands are shifted to lower energies due to the electron-rich di-tert-butyl catecholates. The first two absorption bands at 233 nm and 319 nm for **C2-Cl-ClO₄**, 236 nm and 318 nm for **C6-Br-ClO₄** and 299 nm and 378 nm for **C9-dbucat-ClO₄** are ligand based π - π^* transitions from the pyridine and catecholate fragments. Both complexes also exhibit a weak transition at 654 nm for **C2-Cl-ClO₄**, 652 nm for **C6-Br-ClO₄** which is shifted for **C9-dbucat-ClO₄** to 781 nm which has been described in the literature as symmetry forbidden Co(III)cat LMCT.⁶⁶ All three UV-VIS spectra are characteristic for low spin Co(III)-cat species.⁵⁹

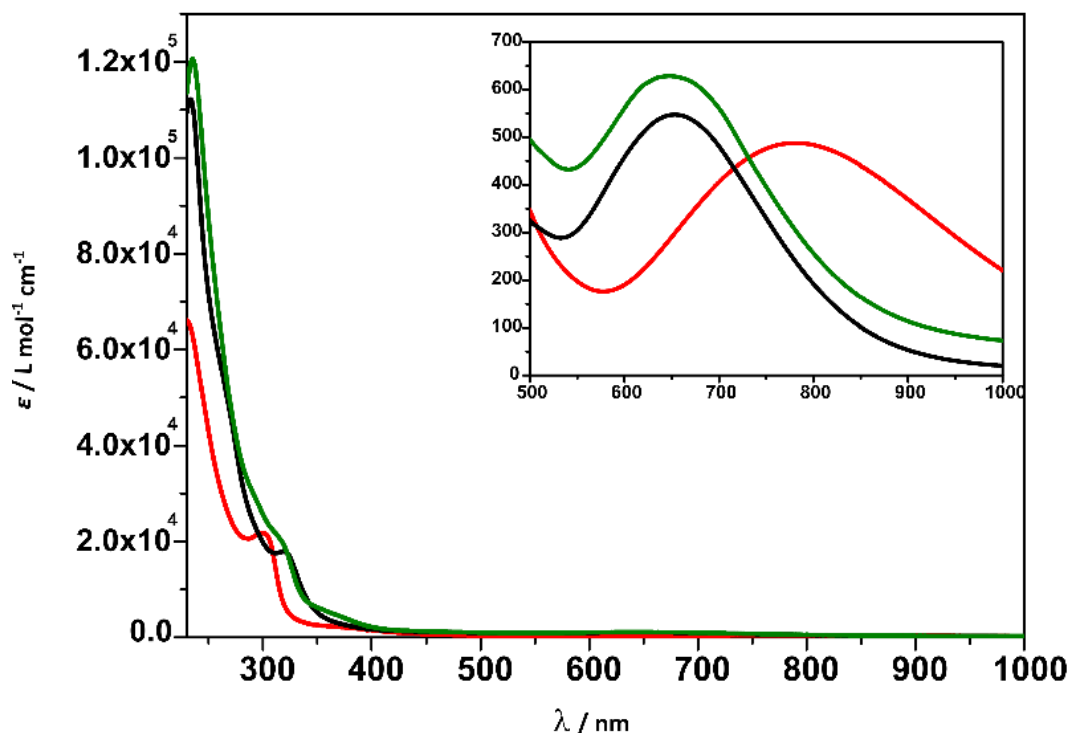


Figure 5: UV-VIS absorption spectra for acetonitrile solutions of **C2-Cl-CIO₄** (black) 0.1 mM, **C6-Br-CIO₄** (green) 0.01 mM and **C9-dbucat-CIO₄** (red) 0.01 mM with a zoomed-in section from 500 to 1000 nm at 1 mM concentration for all complexes.

The paramagnetic behaviour of **C9-dbucat-CIO₄** was probed in solution using the variable temperature Evans ¹H-NMR method between 298 and 343 K in 5 K steps. Measurements were performed in deuterated acetonitrile at a concentration of 6 mM. The Evans method has a relative error of approximately 5-10 %.^{74–76} As shown in **Figure S100** and detailed in **Table S31**, the complex stays diamagnetic with no significant paramagnetic shifts until 318 K. Above this temperature, a prominent shift emerges, and at the maximum temperature of 343 K the $\chi_M T$ value reaches a maximum of 0.478 cm³K mol⁻¹, indicating a valence tautomeric transition in solution. In contrast, Evans method measurement of **C3-Cl-PF₆** and **C7-Br-PF₆** under the same conditions (6 mM in acetonitrile) did not show any evidence of a paramagnetic shift. (**Figures S101-102**) These results suggest that the tetrahalogenated complexes do not undergo valence tautomeric transitions in acetonitrile solution. Unfortunately, due to solubility problems the complexes could not be measured in alternative solvents that might favour the less polar Co(II)-semiquinonate state.⁷⁷

Conclusion and Outlook

We have synthesized a family of eight novel dinuclear cobalt complexes **C1-C8** featuring a non-redox active bridging ligand and tetrahalogenated redox-active dioxolene co-ligands. Single crystal X-ray diffraction at 120 K confirmed that all complexes adopt low spin Co(III) states, consistent with the diamagnetic behaviour observed in SQUID measurements up to room temperature. Above room temperature, complexes **C1-Cl-SO₄** and **C5-Br-SO₄**, containing sulphate counterions, exhibit a temperature-dependent increase in $\chi_M T$, suggesting an incomplete valence tautomeric (VT) transition within the accessible temperature range. To the best of our knowledge, these are the first reported VT active dinuclear cobalt complexes with tetrahalogenated catechols. Electrochemical studies on **C2-Cl-CIO₄**, **C6-Br-CIO₄** and the previously reported **C9-dbucat-CIO₄** reveal significant shifts in the oxidation potentials highlighting the influence of catechol substitution on redox properties. Complementary UV-Vis spectroscopy shows a bathochromic shift in LMCT absorption for the di-*tert*-butyl substituted catecholate, further supporting ligand field modulation. Investigations are currently underway to build on this preliminary evidence for valence tautomeric transitions in this system by

fine-tuning the design of the ligand to achieve a complete transition in this system, centred around room temperature.

Materials and Methods

The commercially available chemicals were used without any further purification methods and were purchased from Sigma, Alfa Aesar, Acros Organics, VWR and Fisher Chemicals. Anhydrous and degassed acetonitrile was purchased from Acros Organics and used for CV measurements. All reactions were carried out aerobic conditions with HPLC grade solvents unless otherwise stated. Dry THF was obtained from a solvent purification system (MBRAUN MG-SPS-800). Infrared spectra were recorded at room temperature in a range of 4000 – 450 cm^{-1} using a Bruker ALPHA II ATR-IR with the Software *OPUS* and plotted using *Origin V7.5*. Crystallographic characterization of suitable single crystals of the compounds were measured on a *STOE IPDS 2T* or on a *STOE STADIVARI* at the Johannes Gutenberg-University Mainz at 120 K. Solving and refinement of the crystal structures was done by *ShelXT*⁷⁸ and *ShelXL*⁷⁹ in combination with *Olex 2*.⁸⁰ The resolved are deposited at the CCDC database with reference numbers CCDC 2444030-37. HRes ESI mass spectra were recorded on *Agilent 6200 series TOF/6500 series G-TOF* (11.0.203.0) at Johannes Gutenberg-University Mainz in acetonitrile or methanol. For cyclic voltammetry measurements a PGSTAT potentiostat with a TSC 1600 was used with an already built-in platinum counter electrode as a vessel wall from *rdh* instruments. The working electrode was a glassy carbon electrode which was polished before every measurement using aluminium oxide polishing paste with grain sizes of 0.1 μm and 0.05 μm from *Buehler* for at least half an hour on a microfiber cloth in figures of 8's. The pseudo reference electrode was a silver wire electrode. Every measurement was referenced against ferrocene/ferrocenium by adding ferrocene at end of the measurement. Tetrabutylammonium hexafluorophosphate was used in a concentration of 0.1 M as the conducting salt. The magnetic measurements were done with a *Quantum Design MPMS XL Squid magnetometer*. The samples were prepared in a gelatine capsule without eicosane and placed in a plastic straw and the magnetic data were obtained from a temperature range of 200-380 K under an applied magnetic field of 0.1 T in the heating mode. Measurements were performed over a length of 4 cm with 24 data points, every data point was measured three times and an average was made. Magnetic contributions of the holder were experimentally determined by a test run of an empty capsule and subtracted from the measured susceptibility data. Molar susceptibility was calculated using *julX 1.4.1* made by Bill using the molecular weight of the sample for complexes **C1**, **C2**, **C5** and **C6**.⁸¹ While complexes **C3**, **C4**, **C7** and **C8** were measured with a *MPMS3 Squid magnetometer*. The samples were prepared in plastic capsules without eicosane placed in a brass holder and the magnetic data were obtained from a temperature range of 200-380K under an applied magnetic field of 0.1 T in the heating mode. Measurements were performed over a length of 4 cm with 24 data points, every data point was measured three times and an average was made. Magnetic contributions of the holder and capsule were experimentally determined by a test run of an empty capsule at the exact same position with the exact same brass sample holder and subtracted from the measured susceptibility data with the software *Squidlab*.⁸² The elemental analysis (CHN) was performed at the Department of Chemistry at the Johannes Gutenberg-University Mainz on an *Elementar vario EL Cube*. NMR spectra as well as the Evans method NMR studies were conducted using an *Avance III HD 300* ($\nu(^1\text{H}) = 400.13 \text{ MHz}$ $\nu(^{13}\text{C}) = 100.1 \text{ MHz}$); *Avance II 400* ($\nu(^1\text{H}) = 400.13 \text{ MHz}$ $\nu(^{13}\text{C}) = 100.1 \text{ MHz}$); *Bruker DRX 400* ($\nu(^1\text{H}) = 400.13 \text{ MHz}$ $\nu(^{13}\text{C}) = 100.1 \text{ MHz}$). All samples were dissolved in suitable deuterated solvents and the given chemical shift refers to the signal against trimethylsilane as an external reference. The obtained spectra were evaluated by *MestReNova x64* made by the company *Mestrelab Research*.

Experimental

Caution: While no issues were encountered during the course of this work, nonetheless, it is important to note that perchlorate salts have the potential to be explosive, so careful handling is advised.

Syntheses were performed similar to **C1-Cl-SO₄**, the complete synthetic procedures can be found in the ESI.

[Co₂(L)(Cl₄cat)₂] SO₄ · 11 MeOH [**C1-Cl-SO₄**]

To a solution of CoSO₄ · 7 H₂O (56 mg, 0.2 mmol, 2.0 eq.), **L** (54 mg, 0.1 mmol, 1.0 eq.) and tetrachlorocatechol (Cl₄cat) (50 mg, 0.2 mmol, 2.0 eq.) in 15 mL methanol triethylamine (40 mg, 0.4 mmol, 4.0 eq.) was added dropwise. A suspension immediately formed, consisting of an orange precipitate in a green solution. The reaction mixture was refluxed for one hour. After the reaction mixture had cooled down to room temperature, it was filtered. After one day of slow evaporation green crystals suitable for X-ray diffraction were obtained. The product obtained was filtered, washed three times with 5 mL of ice-cold methanol and air dried. The desired complex was obtained in low yields (green plates, 33 mg, 0.038 mmol, 37.5 %). IR $\tilde{\nu}$ [cm⁻¹]: 3610(w), 3170(broad) 3071(w), 3011(w), 2947(w), 1664(w), 1608(w), 1433(ss), 1376(m), 1321(w), 1291(w), 1252(m), 1220(w), 1137(m), 1082(m), 1052(m), 1021(m), 1001(w), 970(m), 945(w), 866(w), 841(w), 824(w), 809(m), 798(s), 772(s), 729(m), 716(m), 693(m), 665(m), 647(w), 611(m), 592(m), 550(m), 531(m), 490(m), 473(m), 457(m), 434(m). Elemental Analysis: Found: C, 37.77%; H, 4.11%; N, 7.96%. Calc. for C₄₄H₄₀Cl₈Co₂N₈O₈S · 8 H₂O: C, 38.12%; H, 4.07%; N, 8.08%. Mass spectrometry [m/z]: 572.964 [**C1**]²⁺ (calc. = 572.964).

[Co₂(L)(Cl₄cat)₂](ClO₄)₂ · 3 H₂O · 1 MeCN [**C2-Cl-ClO₄**]

(Green plates, 30 mg, 0.022 mmol, 22.3 %). IR $\tilde{\nu}$ [cm⁻¹]: 3548(m), 3073(m), 2962(m), 1638(m), 1609(m), 1462(m), 1434(s), 1376(s), 1327(m), 1291(m), 1251(s), 1224(m), 1079(ss), 1039(s), 1023(s), 1002(m), 972(s), 954(s), 931(m), 893(m), 865(s), 839(m), 827(m), 810(s), 798(s), 766(s), 731(m), 716(m), 693(m), 665(m), 646(m), 623(s), 595(s), 556(m), 530(m), 488(s), 472(m), 455(s), 434(s). Elemental Analysis: Found: C, 37.33%; H, 3.15%; N, 8.27%. Calc. for C₄₄H₄₀Cl₁₀Co₂N₈O₁₂ · 3.5 H₂O, C, 37.53%; H, 3.36%; N, 7.96% Mass spectrometry [m/z]: 572.964 [**C2**]²⁺ (calc. = 572.964), 1244.880 [**C2+ClO₄**]⁺ (calc. = 1244.877).

[Co₂(L)(Cl₄cat)₂](PF₆)₂ · 2 MeOH · 2 MeCN [**C3-Cl-PF₆**]

(Green powder 68 mg, 0.047 mmol, 47.3%). IR $\tilde{\nu}$ [cm⁻¹]: 2954(w), 1639(w), 1610(w), 1435(s), 1377(w), 1293(w), 1251(m), 1025(w), 975(m), 955(w), 838(ss), 811(s), 800(m), 766(m), 717(m), 694(w), 666(w), 597(m), 558(s), 456(m), 433(m). Elemental Analysis: Found: C, 34.19%; H, 3.72%; N, 7.34% Calc. for C₄₄H₄₀Cl₈Co₂F₁₂N₈O₄P₂ · 6.5 H₂O C, 34.02%; H, 3.44%; N, 7.21% Mass spectrometry [m/z]: 572.964 [**C3**]²⁺ (calc. = 572.964).

[Co₂(L)(Cl₄cat)₂](B(Ph)₄)₂ · 1 MeCN [**C4-Cl-BPh₄**]

(Green powder 56 mg, 0.031 mmol, 31.4%). IR $\tilde{\nu}$ [cm⁻¹]: 3052(w), 1609(m), 1579(w), 1478(m), 1435(s), 1376(m), 1290(m), 1251(m), 1160(m), 1058(w), 1025(m), 975(m), 943(w), 866(m), 812(m), 800(m), 767(m), 734(s), 705(s), 665(w), 612(m), 598(m), 562(w), 470(w), 434(m). Elemental Analysis: Found: C, 60.34%; H, 4.74%; N, 6.43% Calc. for C₉₂H₈₂B₂Cl₈Co₂N₈O₄ · 2 H₂O: C, 60.62%; H, 4.76%; N, 6.15% Mass spectrometry [m/z]: 572.964 [**C4**]²⁺ (calc. = 572.964).

[Co₂(L)(Br₄cat)₂]SO₄ · 2 H₂O · 4 MeCN [**C5-Br-SO₄**]

(Green needles 19 mg, 0.012 mmol, 12.0%). IR $\tilde{\nu}$ [cm⁻¹]: 3606(m), 3090 (broad), 3065(m), 3007(m), 2958(s), 1650(m), 1607(m), 1459(m), 1425(ss), 1348(s), 1320(m), 1290(m), 1264(s), 1235(s), 1207(s), 1138(s), 1082(s), 1051(s), 1037(s), 1020(s), 998(s), 968(m), 956(s), 930(s), 865(s), 841(m), 823(s), 767(ss), 743(s), 728(s), 715(s), 681(s), 665(s), 647(s), 608(s), 580(s), 563(s), 534(s), 519(s), 497(s), 477(s), 460(s), 453(s), 429(s). Elemental Analysis: Found: C, 29.67%; H, 3.17%; N, 6.36%, Calc. for

$C_{44}H_{40}Br_8Co_2N_8O_8S \cdot 5.5 H_2O \cdot 1 CHCl_3$: C, 29.76%; H, 2.89%; N, 6.17%. Mass spectrometry [m/z]: 750.761 [C5]²⁺ (calc. = 750.761)

[Co₂(L)(Br₄cat)₂](ClO₄)₂ · 2 MeCN [C6-Br-ClO₄]

(Green needles 19 mg, 0.011 mmol, 11.2%). IR $\tilde{\nu}$ [cm⁻¹]: 3617(m), 3542(m), 2940(m), 1632(m), 1608(m), 1462(m), 1428(s), 1378(m), 1346(m), 1326(m), 1292(m), 1261(s), 1233(s), 1211(m), 1079(ss), 1038(s), 1022(s), 1001(s), 979(m), 954(s), 930(s), 893(s), 864(s), 839(m), 826(s), 765(ss), 745(s), 730(s), 715(s), 686(m), 665(m), 647(m), 623(s), 589(s), 566(s), 533(s), 492(s), 476(s), 460(s), 451(s), 429(s). Elemental Analysis: Found: C, 30.22%; H, 2.49%; N, 6.47%, Calc. for $C_{44}H_{40}Br_8Cl_2Co_2N_8O_{12} \cdot 1.5 H_2O$: C, 30.59%; H, 2.51%; N, 6.49%. Mass spectrometry [m/z]: 750.762 [C6]²⁺ (calc. = 750.761), 1600.470 [C6+ClO₄]⁺ (calc. = 1600.470).

[Co₂(L)(Br₄cat)₂](PF₆)₂ · 1 MeOH · 1 MeCN [C7-Br-PF₆]

(Green plates, 56 mg, 0.031 mmol, 31.3 %). IR $\tilde{\nu}$ [cm⁻¹]: 3658(w), 3065 (w), 2958 (w), 1637(w), 1609(m), 1571(w), 1462(m), 1427(s), 1346(m), 1293(m), 1260(m), 1231(m), 1163(w), 1098(w), 1084(w), 1063(w), 1052(w), 1038(w), 1024(m), 1003(w), 933(m), 823(s), 764(s), 745(s), 716(m), 665(m), 626(m), 587(m), 556(s), 534(m), 479(m), 452(m), 429(m). Elemental Analysis: Found: C, 29.50%; H, 2.75%; N, 6.35%, Calc. for $C_{44}H_{40}Br_8Co_2F_{12}N_8O_4P_2 \cdot 1.25 H_2O$: C, 29.13%; H, 2.36%; N, 6.18%. Mass spectrometry [m/z]: 750.762 [C7]²⁺ (calc. = 750.761).

[Co₂(L)(Br₄cat)₂](B(Ph)₄)₂ · 4 MeCN [C8-Br-BPh₄]

(Green powder, 190 mg, 0.089 mmol, 88.7 %). IR $\tilde{\nu}$ [cm⁻¹]: 3052(w), 2998(w), 2982(w), 1608(w), 1578(w), 1479(m), 1428(ss), 1345(w), 1290(w), 1261(m), 1232(m), 1160(w), 1058(w), 1027(w), 999(w), 935(m), 865(w), 842(w), 765(s), 733(s), 705(ss), 665(w), 611(s), 591(m), 565(w), 536(w), 465(w), 451(w), 429(w). Elemental Analysis: Found: C, 50.98%; H, 3.97%; N, 5.43%, Calc. for $C_{92}H_{82}Br_8Co_2N_8O_4 \cdot 1 H_2O$: C, 51.15%; H, 3.92%; N, 5.19%. Mass spectrometry [m/z]: 750.761 [C8]²⁺ (calc. = 750.761).

[Co₂(L)(dbucat)₂](ClO₄)₂ · 1.5 H₂O [C9-dbucat-ClO₄]

Was prepared as previously reported.⁶⁰

Conflict of Interest

The authors have no conflict of interest to declare.

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4.1 ESI: Switchable Valence States in Dinuclear Cobalt Complexes: The Role of Halogenated Catecholates and Counterions

Department Chemie, Johannes Gutenberg-Universität Mainz, 55128 Mainz, Germany

4.1.1 IR-Spectra

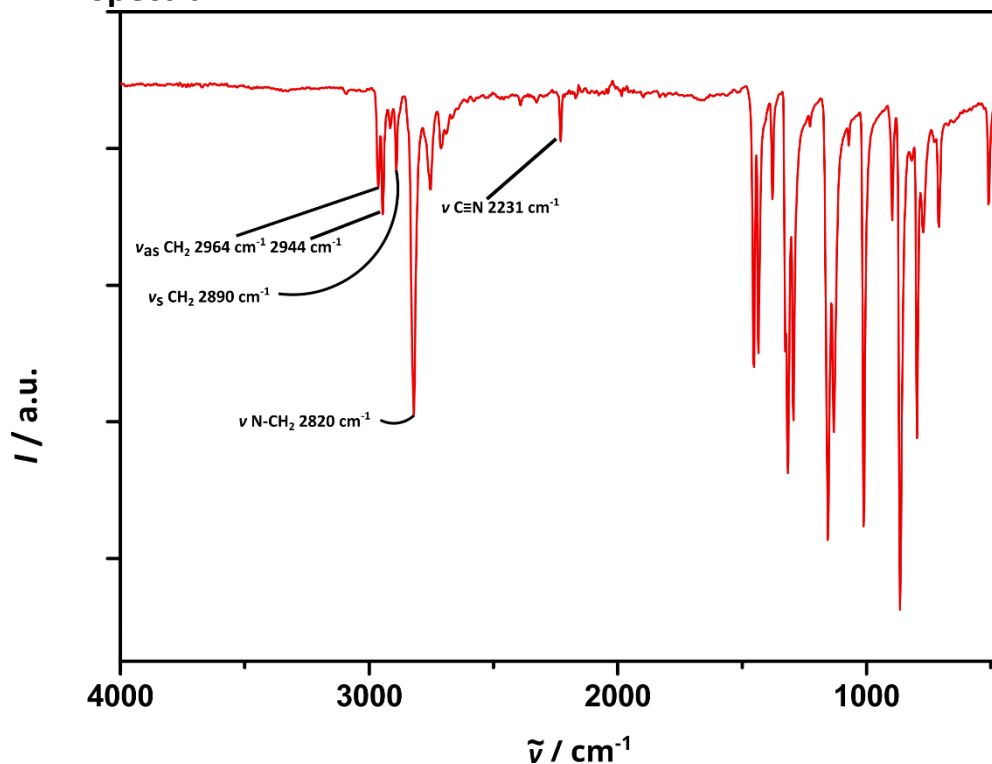


Figure S1: ATR-IR-spectrum of *N, N'*-Bis(cyanomethyl)piperazine at room temperature.

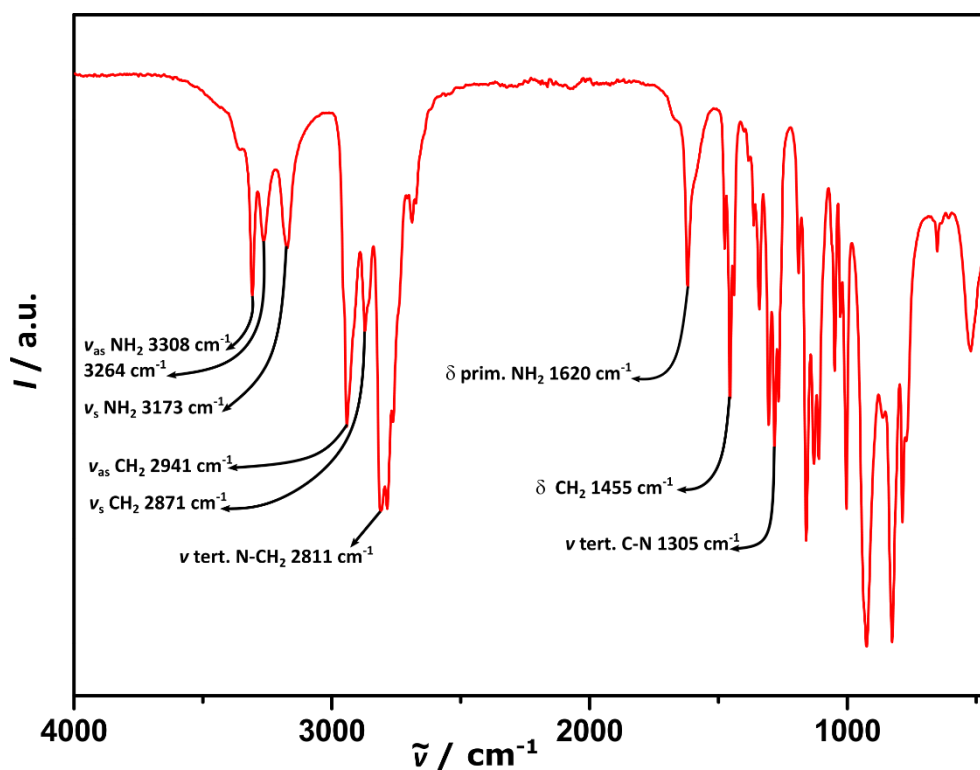


Figure S2: ATR-IR-spectrum of *N, N'*-bis(aminoethyl)piperazine at room temperature.

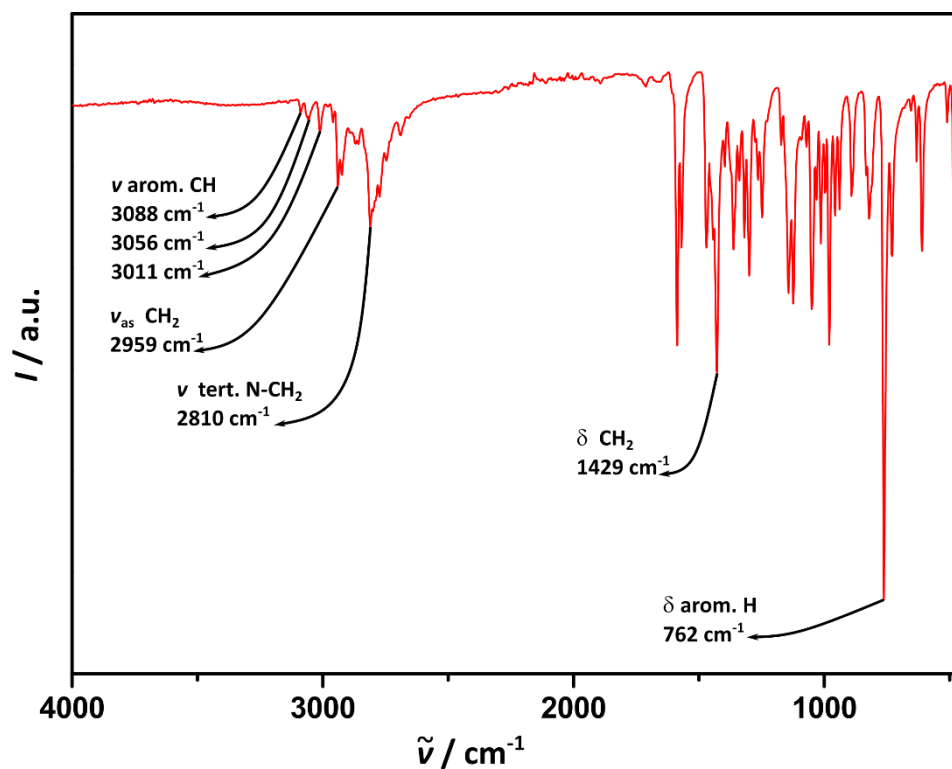


Figure S3: ATR-IR of *N, N, N', N'*-Tetra-2-picolyl-1,4-bis(2-aminoethyl)piperazine (*L*) at room temperature.

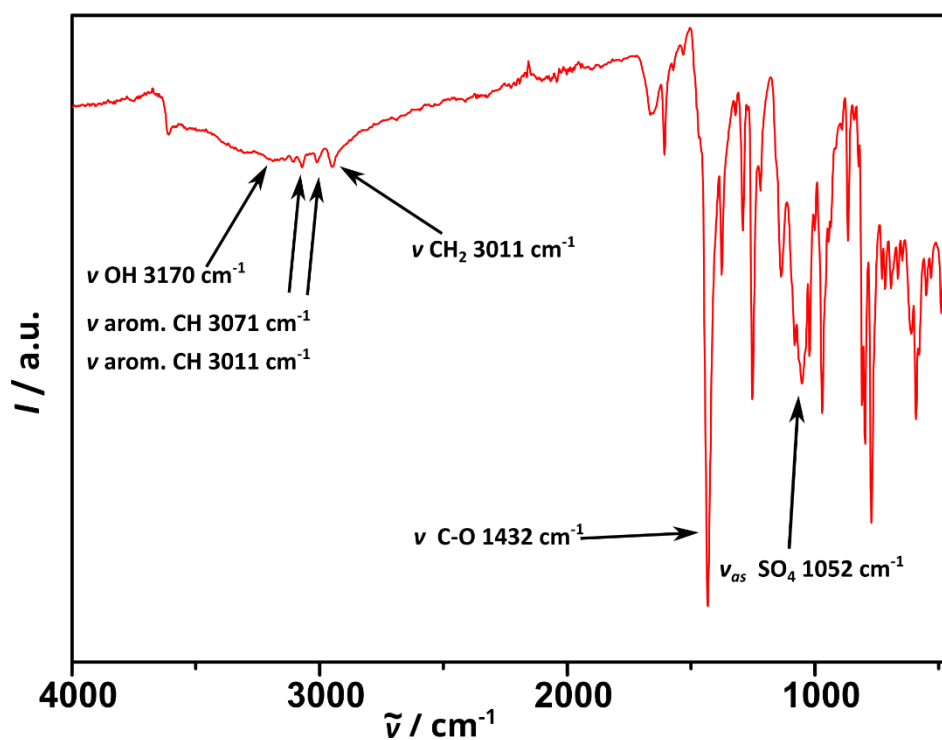


Figure S4: ATR-IR of $[\text{Co}_2(\text{L})(\text{Cl}_4\text{-cat})_2]\text{SO}_4 \cdot 8 \text{ H}_2\text{O}$ (**C1** · 8 H_2O) at room temperature.

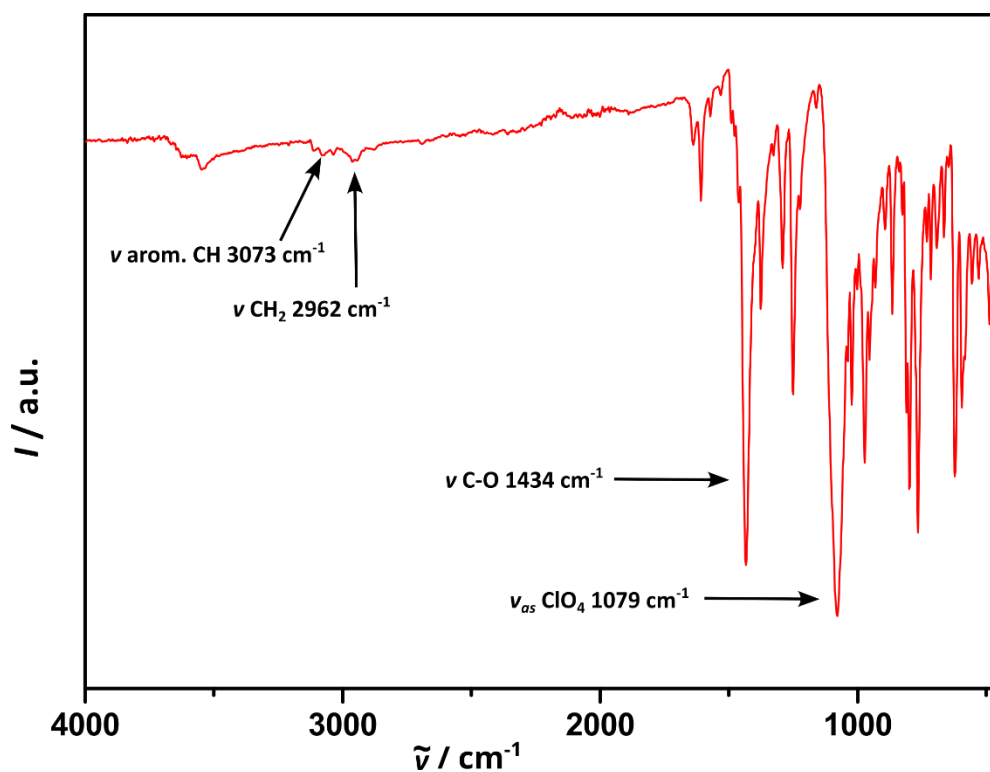


Figure S5: ATR-IR of $[\text{Co}_2(\text{L})(\text{Cl}_4\text{-cat})_2] (\text{ClO}_4)_2 \cdot 3.5 \text{ H}_2\text{O}$ (**C2** · 3.5 H_2O) at room temperature.

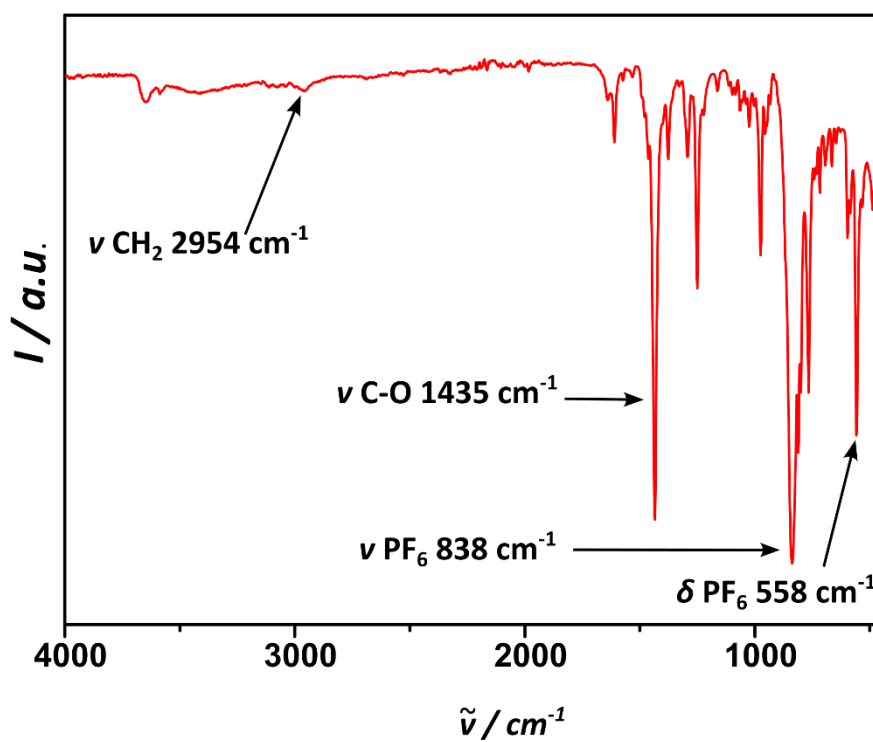


Figure S6: ATR-IR of $[\text{Co}_2(\text{L})(\text{Cl}_4\text{-cat})_2] (\text{PF}_6)_2 \cdot 6.5 \text{ H}_2\text{O}$ (**C3** · 6.5 H_2O) at room temperature.

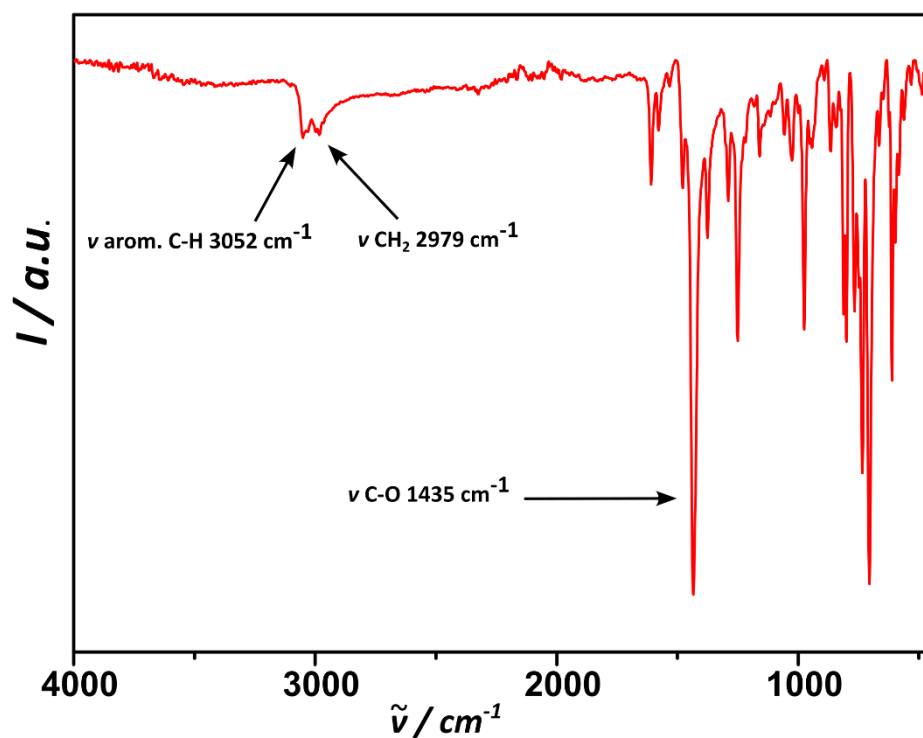


Figure S7: ATR-IR of $[\text{Co}_2(\text{L})(\text{Cl}_4\text{-cat})_2] (\text{B}(\text{Ph})_4)_2 \cdot 2 \text{ H}_2\text{O}$ (**C4** · 2 H_2O) at room temperature.

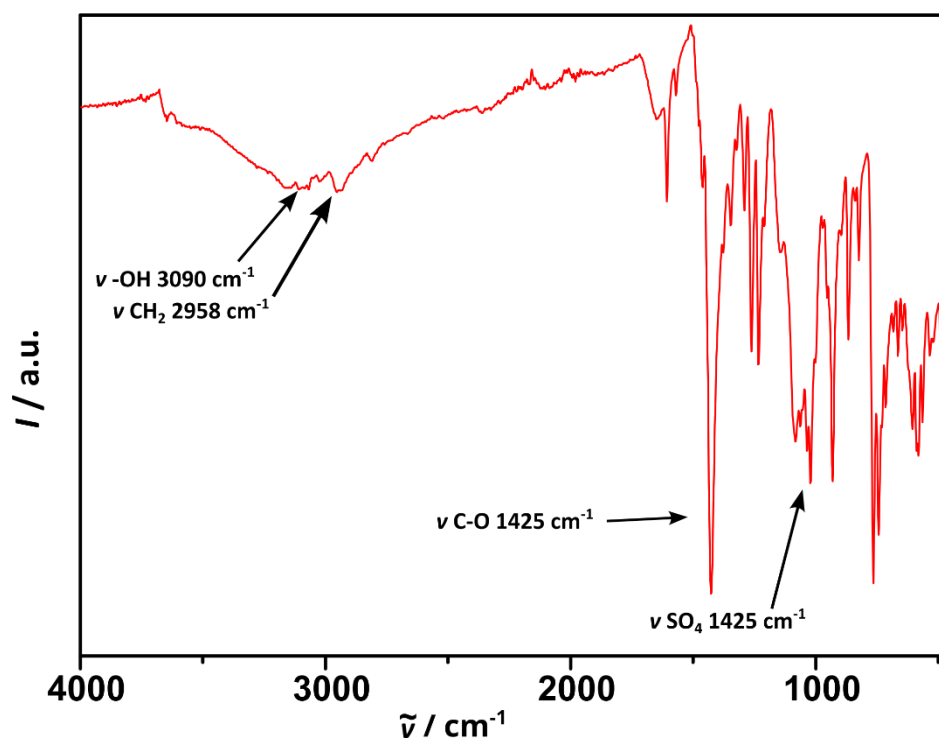


Figure S8: ATR-IR of $[\text{Co}_2(\text{L})(\text{Br}_4\text{-cat})_2]\text{SO}_4 \cdot 5.5 \text{ H}_2\text{O} \cdot 1 \text{ CHCl}_3$ (**C5** · 5.5 $\text{H}_2\text{O} \cdot 1 \text{ CHCl}_3$) at room temperature.

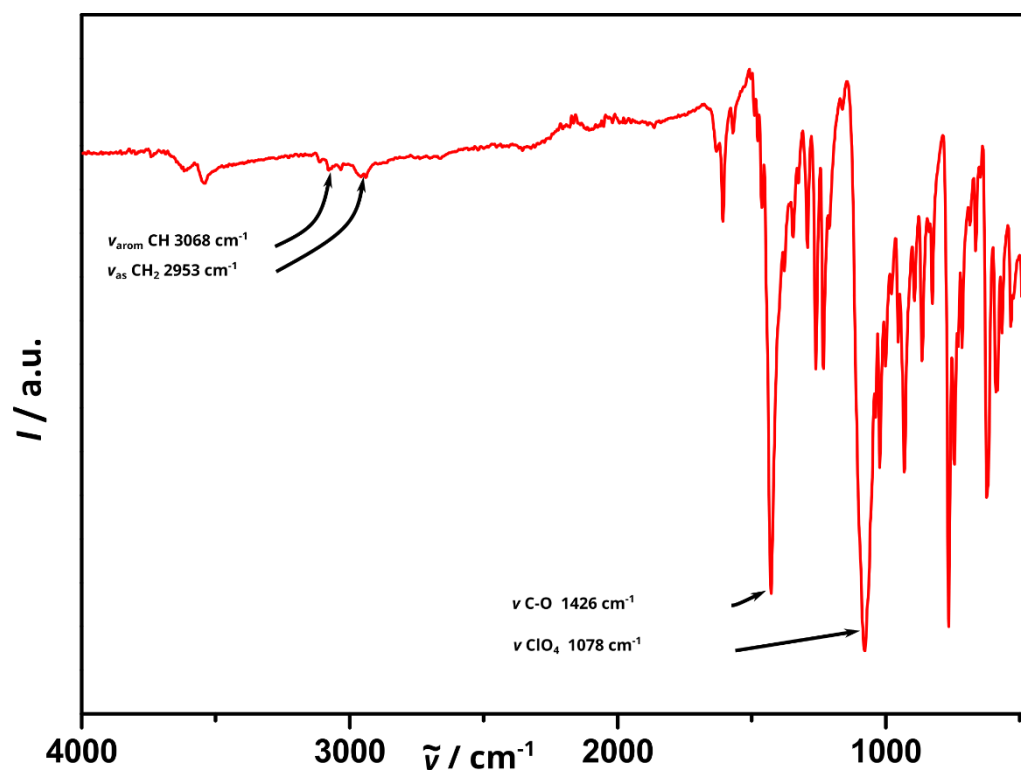


Figure S9: ATR-IR of $[Co_2(L)(Br_4-cat)_2] (ClO_4)_2 \cdot 1.5 H_2O$ (C6 · 1.5 H_2O) at room temperature.

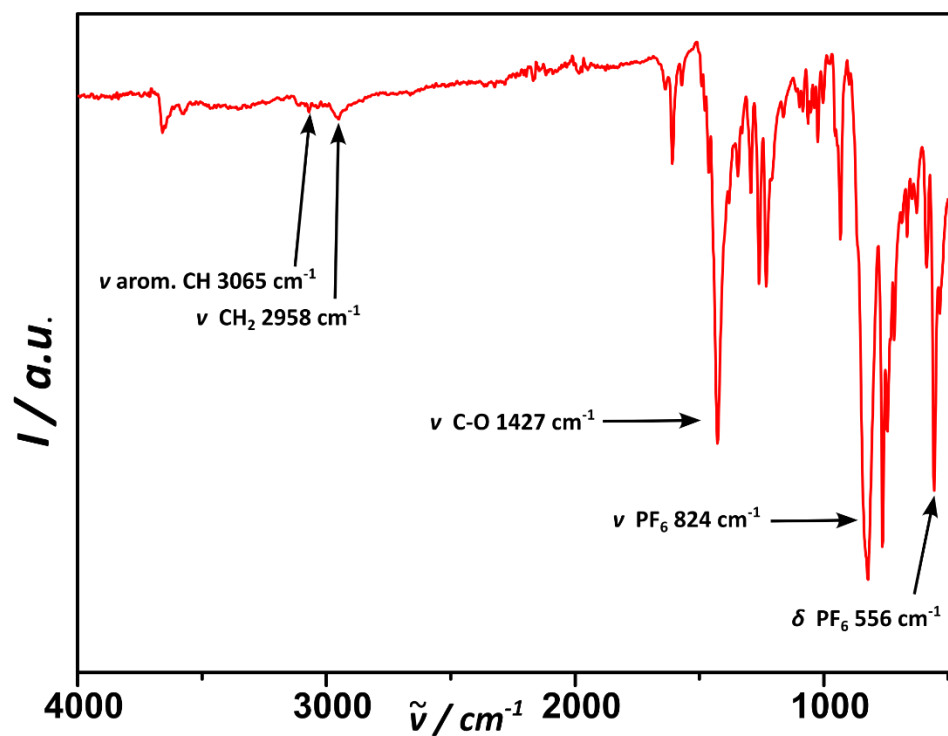


Figure S10: ATR-IR of $[Co_2(L)(Br_4-cat)_2] (PF_6)_2 \cdot 1.5 H_2O$ (C7 · 1.25 H_2O) at room temperature.

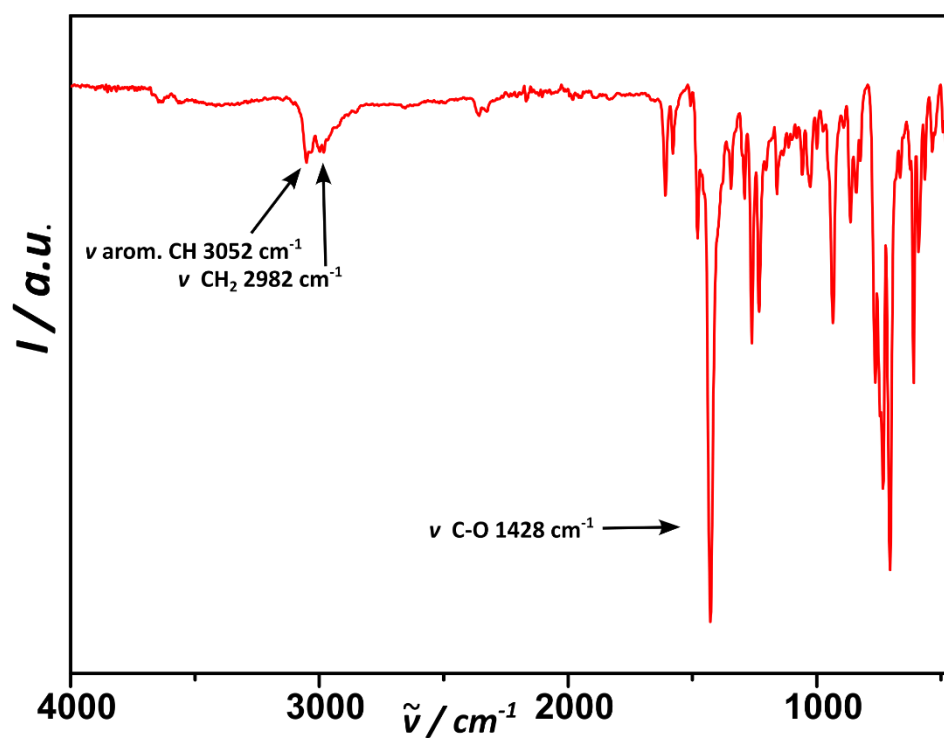


Figure S11: ATR-IR of $[Co_2(L)(Br_4-cat)_2](B(Ph)_4)_2 \cdot 1 H_2O$ (C8 · 1H₂O) at room temperature.

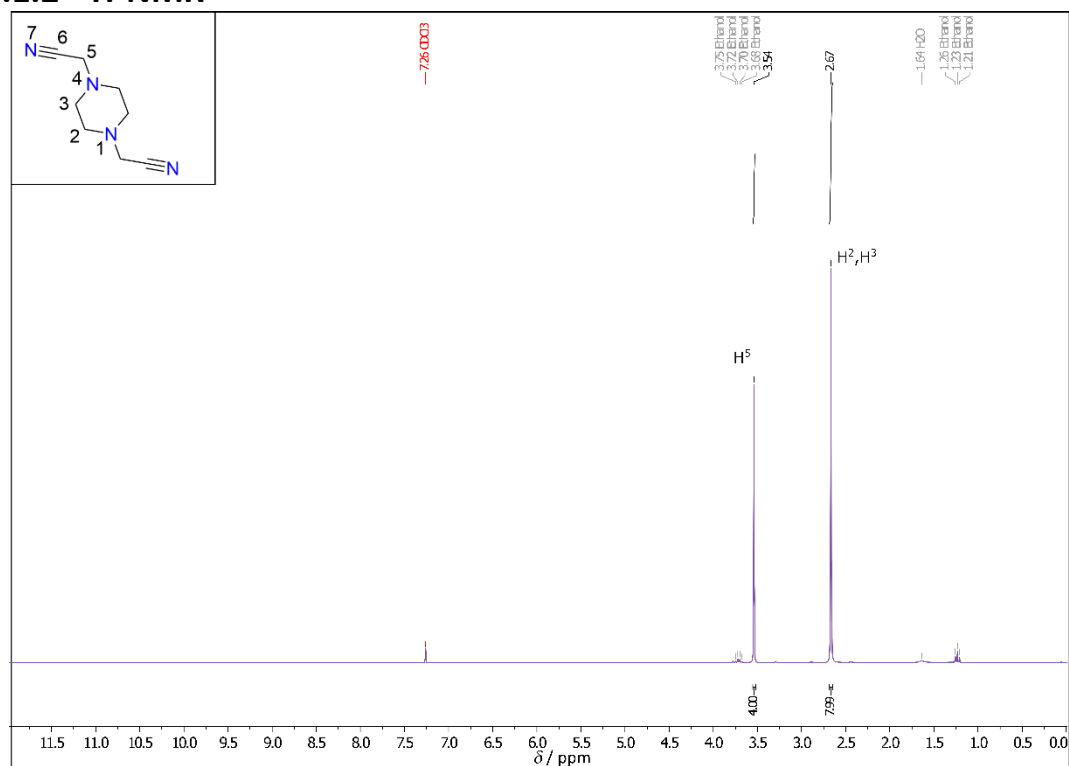
4.1.2 ^1H -NMR

Figure S12: ^1H -NMR-Spectrum of *N, N'*-bis(cyanomethyl)piperazine in CDCl_3 [400 MHz].

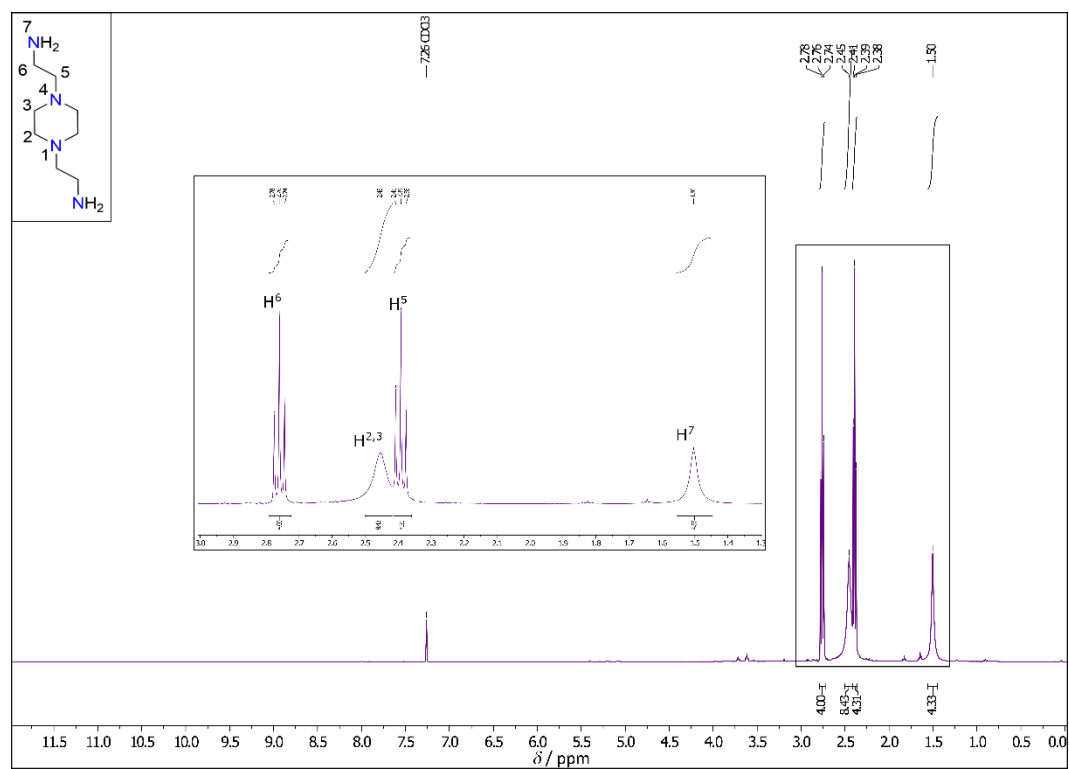
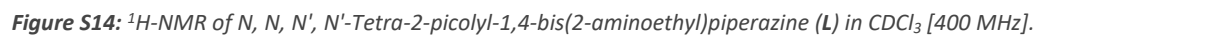


Figure S13: ^1H -NMR-Spectrum of *N, N'*-bis(aminoethyl)piperazine in CDCl_3 [400 MHz].



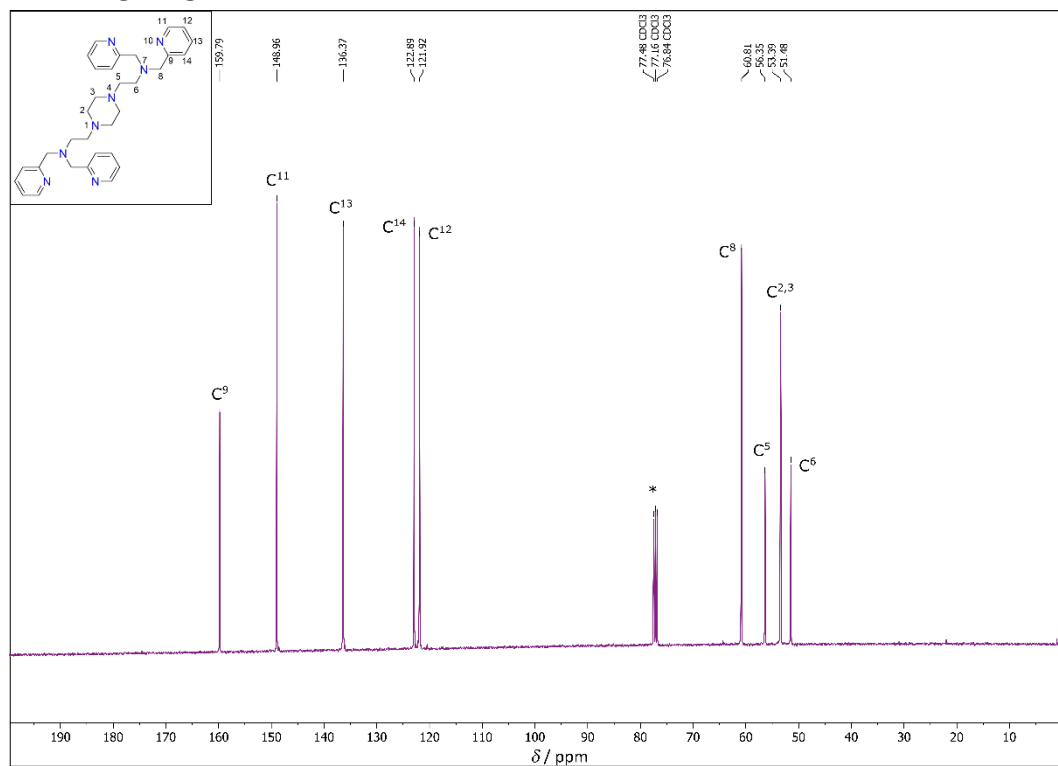
4.1.3 ^{13}C -NMR

Figure S15: ^{13}C -NMR of *N, N', N'*-Tetra-2-picolyl-1,4-bis(2-aminoethyl)piperazine (**L**) in CDCl_3 [101 MHz].

4.1.4 COSY-NMR

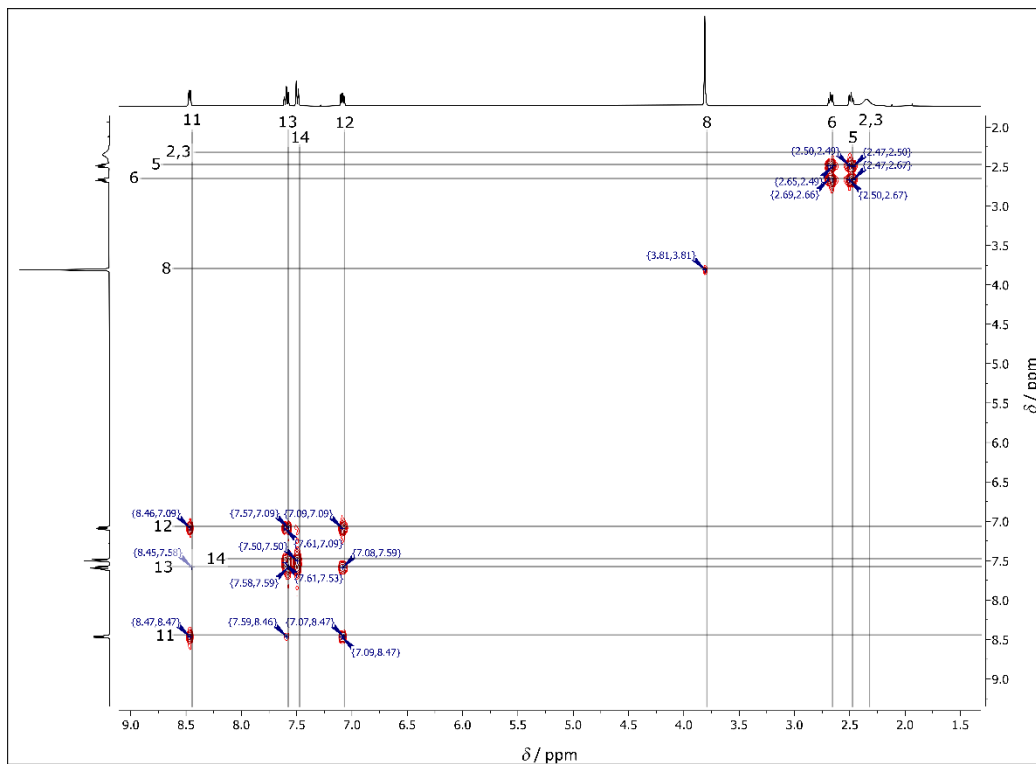


Figure S16: COSY spectrum of *N, N', N'*-Tetra-2-picolyl-1,4-bis(2-aminoethyl)piperazine (**L**) in CDCl_3 .

4.1.5 HMBC-NMR

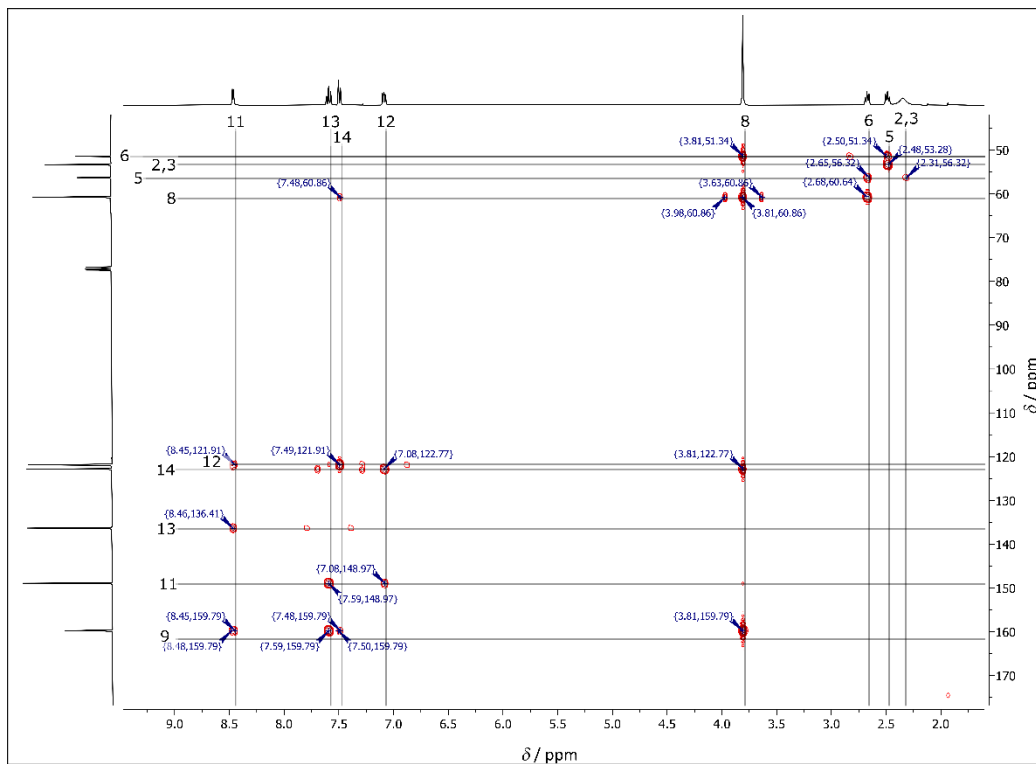


Figure S17: HMBC spectrum of *N, N', N', N'*-Tetra-2-picolyl-1,4-bis(2-aminoethyl)piperazine (**L**) in CDCl_3 .

4.1.6 HSQC-NMR

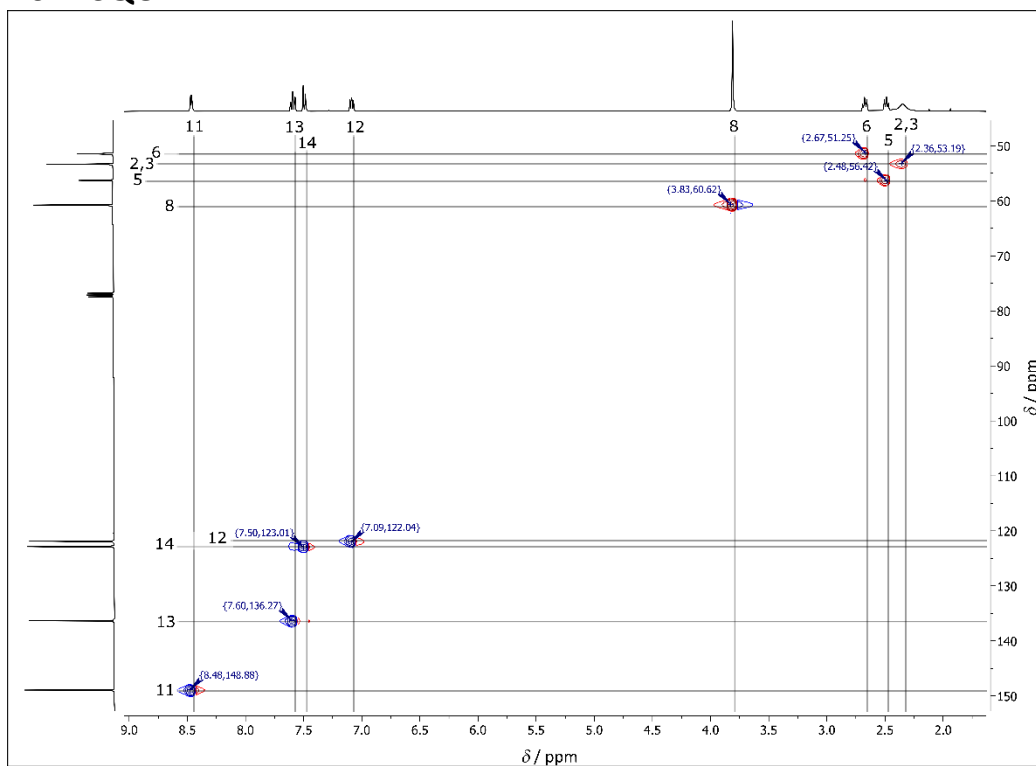


Figure S18: HSQC spectrum of *N, N', N', N'*-Tetra-2-picolyl-1,4-bis(2-aminoethyl)piperazine (**L**) in CDCl_3 .

4.1.7 DOSY- ^1H -NMR-Spectra

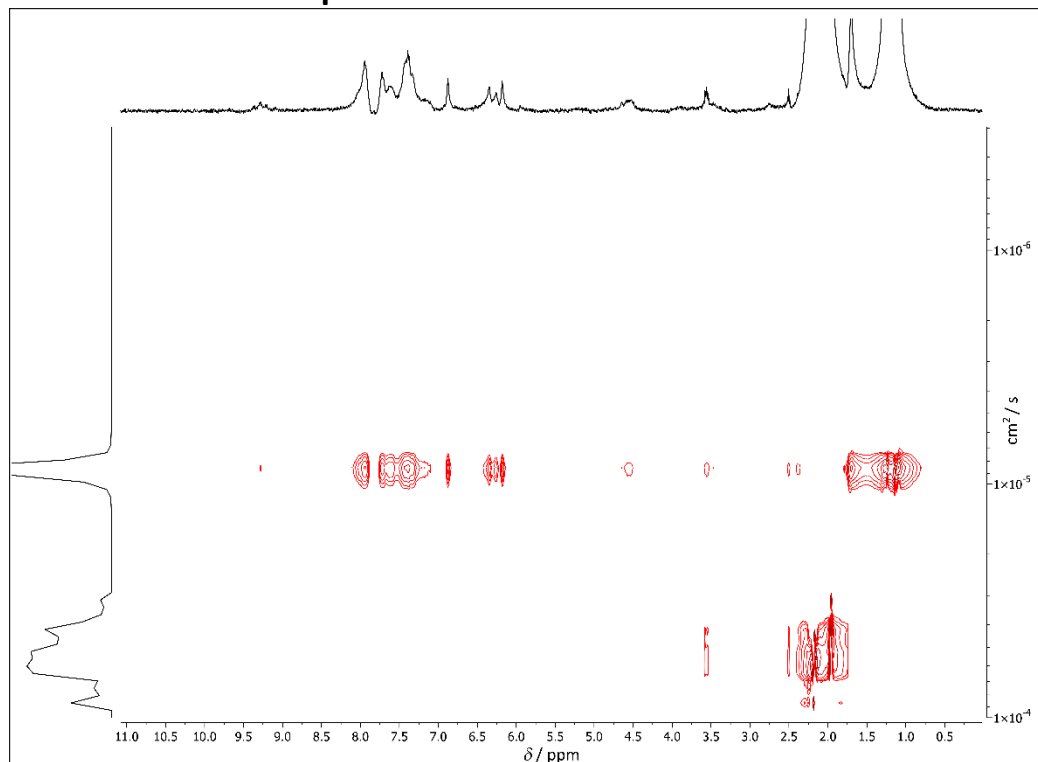


Figure S19: ^1H -DOSY-NMR of previously reported $[\text{Co}_2(\text{L})(\text{dbucat})_2] (\text{ClO}_4)_2 \cdot 1.5 \text{H}_2\text{O}$ [1] in acetonitrile [400 MHz] ($D = 7.90 \cdot 10^{-6} \text{ cm}^2 \text{s}^{-1}$)

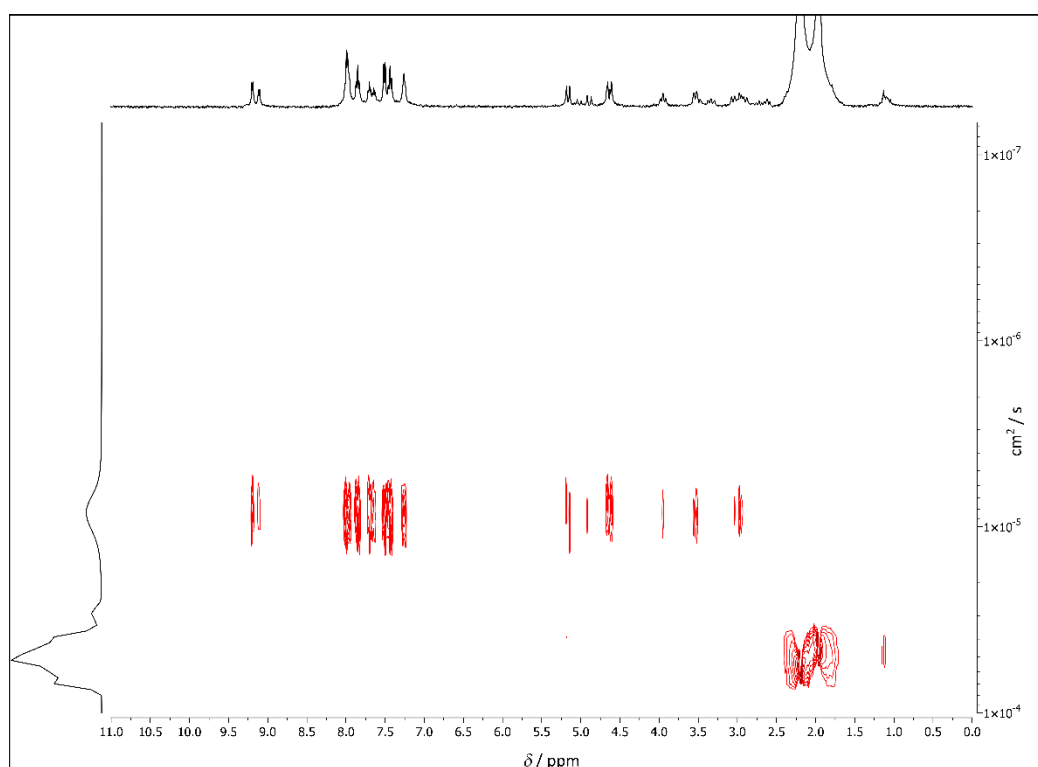


Figure S20: ^1H -DOSY-NMR of $\text{C2} \cdot 3.5 \text{H}_2\text{O}$ in acetonitrile [400 MHz] ($D = 8.49 \cdot 10^{-6} \text{ cm}^2 \text{s}^{-1}$).

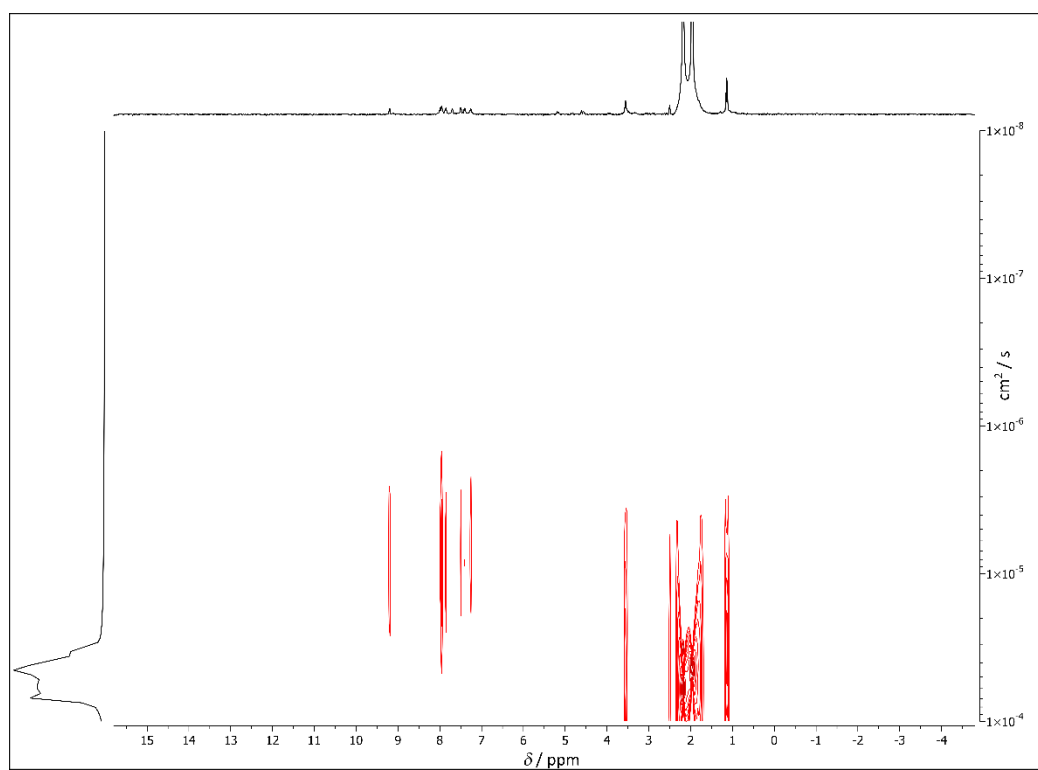


Figure S21: ^1H -DOSY-NMR of $\text{C6} \cdot 1.5 \text{H}_2\text{O}$ in acetonitrile [400 MHz] ($D = 8.49 \cdot 10^{-6} \text{ cm}^2\text{s}^{-1}$).

4.1.8 Complex Synthesis

Caution: While no issues were encountered during the course of this work, nonetheless, it is important to note that perchlorate salts have the potential to be explosive, so careful handling is advised.

[Co₂(L)(Cl₄cat)₂] SO₄ · 11 MeOH [C1]

To a solution of CoSO₄ · 7 H₂O (56 mg, 0.2 mmol, 2.0 eq.), L (54 mg, 0.1 mmol, 1.0 eq.) and tetrachlorocatechol (Cl₄cat) (50 mg, 0.2 mmol, 2.0 eq.) in 15 mL methanol triethylamine (40 mg, 0.4 mmol, 4.0 eq.) was added dropwise. A suspension immediately formed, consisting of an orange precipitate in a green solution. The reaction mixture was refluxed for one hour. After the reaction mixture had cooled down to room temperature, it was filtered. After one day of slow evaporation green crystals suitable for X-ray diffraction were obtained. The product obtained was filtered, washed three times with 5 mL of ice-cold methanol and air dried. The desired complex was obtained in low yields (green plates, 33 mg, 0.038 mmol, 37.5 %). IR $\tilde{\nu}$ [cm⁻¹]: 3610(w), 3170(broad), 3071(w), 3011(w), 2947(w), 1664(w), 1608(w), 1433(ss), 1376(m), 1321(w), 1291(w), 1252(m), 1220(w), 1137(m), 1082(m), 1052(m), 1021(m), 1001(w), 970(m), 945(w), 866(w), 841(w), 824(w), 809(m), 798(s), 772(s), 729(m), 716(m), 693(m), 665(m), 647(w), 611(m), 592(m), 550(m), 531(m), 490(m), 473(m), 457(m), 434(m). Elemental Analysis: Found: C, 37.77%; H, 4.11%; N, 7.96%. Calc. for C₄₄H₄₀Cl₈Co₂N₈O₈S · 8 H₂O: C, 38.12%; H, 4.07%; N, 8.08%. Mass spectrometry [m/z]: 572.964 [C1]²⁺ (calc. = 572.964).

[Co₂(L)(Cl₄cat)₂](ClO₄)₂ · 3 H₂O · 1 MeCN [C2]

To a solution of Co(ClO₄)₂ · 6 H₂O (73 mg, 0.2 mmol, 2.0 eq.), L (54 mg, 0.1 mmol, 1.0 eq.) and tetrachlorocatechol (Cl₄cat) (50 mg, 0.2 mmol, 2.0 eq.) in 15 mL acetonitrile triethylamine (40 mg, 0.4 mmol, 4.0 eq.) was added dropwise. A suspension immediately formed, consisting of an orange precipitate in a green solution. The reaction mixture was refluxed for one hour. After the reaction mixture had cooled down to room temperature, it was filtered. After three days of slow evaporation green crystals suitable for X-ray diffraction were obtained. The product obtained was filtered, washed three times with 5 mL of ice-cold acetonitrile and air dried. The desired complex was obtained in low yields (green plates, 30 mg, 0.022 mmol, 22.3 %). IR $\tilde{\nu}$ [cm⁻¹]: 3548(m), 3073(m), 2962(m), 1638(m), 1609(m), 1462(m), 1434(s), 1376(s), 1327(m), 1291(m), 1251(s), 1224(m), 1079(ss), 1039(s), 1023(s), 1002(m), 972(s), 954(s), 931(m), 893(m), 865(s), 839(m), 827(m), 810(s), 798(s), 766(s), 731(m), 716(m), 693(m), 665(m), 646(m), 623(s), 595(s), 556(m), 530(m), 488(s), 472(m), 455(s), 434(s). Elemental Analysis: Found: C, 37.33%; H, 3.15%; N, 8.27%. Calc. for C₄₄H₄₀Cl₁₀Co₂N₈O₁₂ · 3.5 H₂O, C, 37.53%; H, 3.36%; N, 7.96%. Mass spectrometry [m/z]: 572.964 [C2]²⁺ (calc. = 572.964), 1244.880 [C2+ClO₄]⁺ (calc. = 1244.877).

[Co₂(L)(Cl₄cat)₂](PF₆)₂ · 2 MeOH · 2 MeCN [C3]

To a solution of CoCl₂ · 6 H₂O (48 mg, 0.2 mmol, 2.0 eq.), L (54 mg, 0.1 mmol, 1.0 eq.) and Cl₄cat (50 mg, 0.2 mmol, 2.0 eq.) in 15 mL methanol triethylamine diluted in 1 mL of methanol (40 mg, 0.4 mmol, 4.0 eq.) was added dropwise. A colour change from blue to green was observed. The reaction mixture was refluxed for one hour. After the reaction mixture had cooled down to room temperature, it was filtered. KPF₆ (37 mg, 0.2 mmol, 2.0 eq.) was added to the filtrate during stirring. It was stirred for 15 minutes. A greenish very fine suspension formed. The suspension was centrifuged at 3500 rpm for 20 minutes and filtrated. The green

powder was air dried overnight. The product was obtained as a green powder in moderate yields. Suitable single crystals for single crystal XRD measurements were obtained after repeating the procedure in a 1:1 mixture of 20 mL MeOH:MeCN and slow evaporation of the mother liquor. (green powder 68 mg, 0.047 mmol, 47.3%). IR $\tilde{\nu}$ [cm^{-1}]: 2954(w), 1639(w), 1610(w), 1435(s), 1377(w), 1293(w), 1251(m), 1025(w), 975(m), 955(w), 838(ss), 811(s), 800(m), 766(m), 717(m), 694(w), 666(w), 597(m), 558(s), 456(m), 433(m). Elemental Analysis: Found: C, 34.19%; H, 3.72%; N, 7.34% Calc. for $\text{C}_{44}\text{H}_{40}\text{Cl}_8\text{Co}_2\text{F}_{12}\text{N}_8\text{O}_4\text{P}_2 \cdot 6.5 \text{H}_2\text{O}$ C, 34.02%; H, 3.44%; N, 7.21% Mass spectrometry [m/z]: 572.964 [**C3**] $^{2+}$ (calc. = 572.964).

[Co₂(**L**)(Cl₄cat)₂](B(Ph)₄)₂ · 1 MeCN [**C4**]

To a solution of CoCl₂ · 6 H₂O (48 mg, 0.2 mmol, 2.0 eq.), **L** (54 mg, 0.1 mmol, 1.0 eq.) and Cl₄cat (50 mg, 0.2 mmol, 2.0 eq.) in 15 mL methanol triethylamine diluted in 1 mL of methanol (40 mg, 0.4 mmol, 4.0 eq.) was added dropwise. A colour change from blue to green was observed. The reaction mixture was refluxed for one hour. After the reaction mixture had cooled down to room temperature, it was filtered. The solution was filtrated. NaB(Ph)₄ (69 mg, 0.2 mmol, 2.0 eq.) was added to the filtrate during stirring. It was stirred for 15 minutes. A greenish very fine suspension formed. The suspension was centrifuged at 3500 rpm for 20 minutes and filtrated. The green powder was air dried overnight. The product was obtained as a green powder in low to moderate yields. The product was obtained as a green powder in moderate yields. Suitable single crystals for single crystal XRD measurements were obtained after repeating the procedure in a 1:1 mixture of 20 mL MeOH:MeCN and slow evaporation of the mother liquor. (green powder 56 mg, 0.031 mmol, 31.4%). IR $\tilde{\nu}$ [cm^{-1}]: 3052(w), 1609(m), 1579(w), 1478(m), 1435(s), 1376(m), 1290(m), 1251(m), 1160(m), 1058(w), 1025(m), 975(m), 943(w), 866(m), 812(m), 800(m), 767(m), 734(s), 705(s), 665(w), 612(m), 598(m), 562(w), 470(w), 434(m). Elemental Analysis: Found: C, 60.34%; H, 4.74%; N, 6.43% Calc. for $\text{C}_{92}\text{H}_{82}\text{B}_2\text{Cl}_8\text{Co}_2\text{N}_8\text{O}_4 \cdot 2 \text{H}_2\text{O}$: C, 60.62%; H, 4.76%; N, 6.15% Mass spectrometry [m/z]: 572.964 [**C4**] $^{2+}$ (calc. = 572.964).

[Co₂(**L**)(Br₄cat)₂](SO₄)₂ · 2 H₂O · 4 MeCN [**C5**]

To a solution of CoSO₄ · 7 H₂O (56 mg, 0.2 mmol, 2.0 eq.), (**L**) (54 mg, 0.1 mmol, 1.0 eq.) and Br₄cat (85 mg, 0.2 mmol, 2.0 eq.) in 20 mL of methanol/chloroform (1:1) triethylamine diluted in 1 mL of methanol (40 mg, 0.4 mmol, 4.0 eq.) was added dropwise. A suspension immediately formed, consisting of an orange precipitate in a green solution. The reaction mixture was refluxed for one hour. After the reaction mixture had cooled down to room temperature, it was filtered. After ten days of slow evaporation green crystals suitable for Xray diffraction were obtained. The product obtained was filtered, washed three times with 5 mL of ice-cold methanol and air dried. The desired complex was obtained in low yields. (green needles 19 mg, 0.012 mmol, 12.0%). IR $\tilde{\nu}$ [cm^{-1}]: 3606(m), 3090 (broad), 3065(m), 3007(m), 2958(s), 1650(m), 1607(m), 1459(m), 1425(ss), 1348(s), 1320(m), 1290(m), 1264(s), 1235(s), 1207(s), 1138(s), 1082(s), 1051(s), 1037(s), 1020(s), 998(s), 968(m), 956(s), 930(s), 865(s), 841(m), 823(s), 767(ss), 743(s), 728(s), 715(s), 681(s), 665(s), 647(s), 608(s), 580(s), 563(s), 534(s), 519(s), 497(s), 477(s), 460(s), 453(s), 429(s). Elemental Analysis: Found: C, 29.67%; H, 3.17%; N, 6.36%, Calc. for $\text{C}_{44}\text{H}_{40}\text{Br}_8\text{Co}_2\text{N}_8\text{O}_8\text{S} \cdot 5.5 \text{H}_2\text{O} \cdot 1 \text{CHCl}_3$: C, 29.76%; H, 2.89%; N, 6.17%. Mass spectrometry [m/z]: 750.761 [**C5**] $^{2+}$ (calc. = 750.761)

[Co₂(**L**)(Br₄cat)₂](ClO₄)₂ · 2 MeCN [**C6**]

To a solution of $\text{Co}(\text{ClO}_4)_2 \cdot 6 \text{H}_2\text{O}$ (73 mg, 0.2 mmol, 2.0 eq.), **L** (54 mg, 0.1 mmol, 1.0 eq.) and Br_4cat (85 mg, 0.2 mmol, 2.0 eq.) in 15 mL acetonitrile triethylamine (40 mg, 0.4 mmol, 4.0 eq.) diluted by 1 mL of acetonitrile was added dropwise. A suspension immediately formed, consisting of an orange precipitate in a green solution. The reaction mixture was refluxed for one hour. After the reaction mixture had cooled down to room temperature, it was filtered. After three days of slow evaporation green crystals suitable for X-ray diffraction were obtained. The product obtained was filtered, washed three times with 5 mL of ice-cold acetonitrile and air dried. The desired complex was obtained in low yields (green needles 19 mg, 0.011 mmol, 11.2%). IR $\tilde{\nu}$ [cm^{-1}]: 3617(m), 3542(m), 2940(m), 1632(m), 1608(m), 1462(m), 1428(s), 1378(m), 1346(m), 1326(m), 1292(m), 1261(s), 1233(s), 1211(m), 1079(ss), 1038(s), 1022(s), 1001(s), 979(m), 954(s), 930(s), 893(s), 864(s), 839(m), 826(s), 765(ss), 745(s), 730(s), 715(s), 686(m), 665(m), 647(m), 623(s), 589(s), 566(s), 533(s), 492(s), 476(s), 460(s), 451(s), 429(s). Elemental Analysis: Found: C, 30.22%; H, 2.49%; N, 6.47%, Calc. for $\text{C}_{44}\text{H}_{40}\text{Br}_8\text{Cl}_2\text{Co}_2\text{N}_8\text{O}_{12} \cdot 1.5 \text{H}_2\text{O}$: C, 30.59%; H, 2.51%; N, 6.49%. Mass spectrometry [m/z]: 750.762 [**C6**] $^{2+}$ (calc. = 750.761), 1600.470 [**C6**+ ClO_4] $^+$ (calc. = 1600.470).

[$\text{Co}_2(\text{L})(\text{Br}_4\text{cat})_2$](PF_6) $_2 \cdot 1 \text{ MeOH} \cdot 1 \text{ MeCN}$ [**C7**]

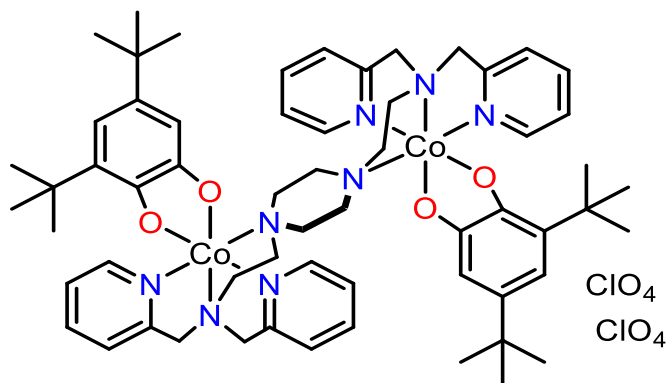
To a solution of $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$ (48 mg, 0.2 mmol, 2.0 eq.), **L** (54 mg, 0.1 mmol, 1.0 eq.) and Br_4cat (85 mg, 0.2 mmol, 2.0 eq.) in 20 mL of methanol : acetonitrile (1:1) triethylamine (40 mg, 0.4 mmol, 4.0 eq.) diluted by 1 mL of acetonitrile was added dropwise. The reaction mixture was refluxed for one hour and afterwards filtrated. KPF_6 (37 mg, 0.2 mmol, 2.0 eq.) was added to the filtrate during stirring. It was stirred for 15 minutes. Single crystals suitable for single crystal XRD measurements were obtained after slow evaporation for two days. The crystals were filtrated and air dried. The product was obtained in moderate yield as green crystals. (green plates, 56 mg, 0.031 mmol, 31.3 %). IR $\tilde{\nu}$ [cm^{-1}]: 3658(w), 3065 (w), 2958 (w), 1637(w), 1609(m), 1571(w), 1462(m), 1427(s), 1346(m), 1293(m), 1260(m), 1231(m), 1163(w), 1098(w), 1084(w), 1063(w), 1052(w), 1038(w), 1024(m), 1003(w), 933(m), 823(s), 764(s), 745(s), 716(m), 665(m), 626(m), 587(m), 556(s), 534(m), 479(m), 452(m), 429(m). Elemental Analysis: Found: C, 29.50%; H, 2.75%; N, 6.35%, Calc. for $\text{C}_{44}\text{H}_{40}\text{Br}_8\text{Co}_2\text{F}_{12}\text{N}_8\text{O}_4\text{P}_2 \cdot 1.25 \text{H}_2\text{O}$: C, 29.13%; H, 2.36%; N, 6.18%. Mass spectrometry [m/z]: 750.762 [**C7**] $^{2+}$ (calc. = 750.761).

[$\text{Co}_2(\text{L})(\text{Br}_4\text{cat})_2$] ($\text{B}(\text{Ph})_4$) $_2 \cdot 4 \text{ MeCN}$ [**C8**]

To a solution of $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$ (48 mg, 0.2 mmol, 2.0 eq.), **L** (54 mg, 0.1 mmol, 1.0 eq.) and Br_4cat (85 mg, 0.2 mmol, 2.0 eq.) in 20 mL of methanol : acetonitrile (1:1) triethylamine (40 mg, 0.4 mmol, 4.0 eq.) diluted by 1 mL of acetonitrile was added dropwise. The reaction mixture was refluxed for one hour and afterwards filtrated. The solution was filtrated. $\text{NaB}(\text{Ph})_4$ (69 mg, 0.2 mmol, 2.0 eq.) was added to the filtrate during stirring. It was stirred for 15 minutes. A greenish very fine suspension formed. The suspension was centrifuged at 3500 rpm for 20 minutes and filtrated. The green powder was air dried overnight. The product was obtained as a green powder in high yields. Suitable single crystals for single crystal XRD measurements were obtained from slow evaporation of the filtrated mother liquor after 1 day. (green powder, 190 mg, 0.089 mmol, 88.7 %). IR $\tilde{\nu}$ [cm^{-1}]: 3052(w), 2998(w), 2982(w), 1608(w), 1578(w), 1479(m), 1428(ss), 1345(w), 1290(w), 1261(m), 1232(m), 1160(w), 1058(w), 1027(w), 999(w), 935(m), 865(w), 842(w), 765(s), 733(s), 705(ss), 665(w), 611(s), 591(m), 565(w), 536(w), 465(w), 451(w), 429(w). Elemental Analysis: Found: C, 50.98%; H, 3.97%; N, 5.43%, Calc. for $\text{C}_{92}\text{H}_{82}\text{Br}_8\text{Co}_2\text{N}_8\text{O}_4 \cdot 1 \text{H}_2\text{O}$: C, 51.15%; H, 3.92%; N, 5.19%. Mass spectrometry [m/z]: 750.761 [**C8**] $^{2+}$ (calc. = 750.761).

$[\text{Co}_2(\text{L})(\text{dbucat})_2] (\text{ClO}_4)_2 \cdot 1.5 \text{ H}_2\text{O}$ [**C9**]

Was prepared as previously reported. (1)



Scheme S1: Structural Scheme of C9.

4.1.9 Mass Spectrometry

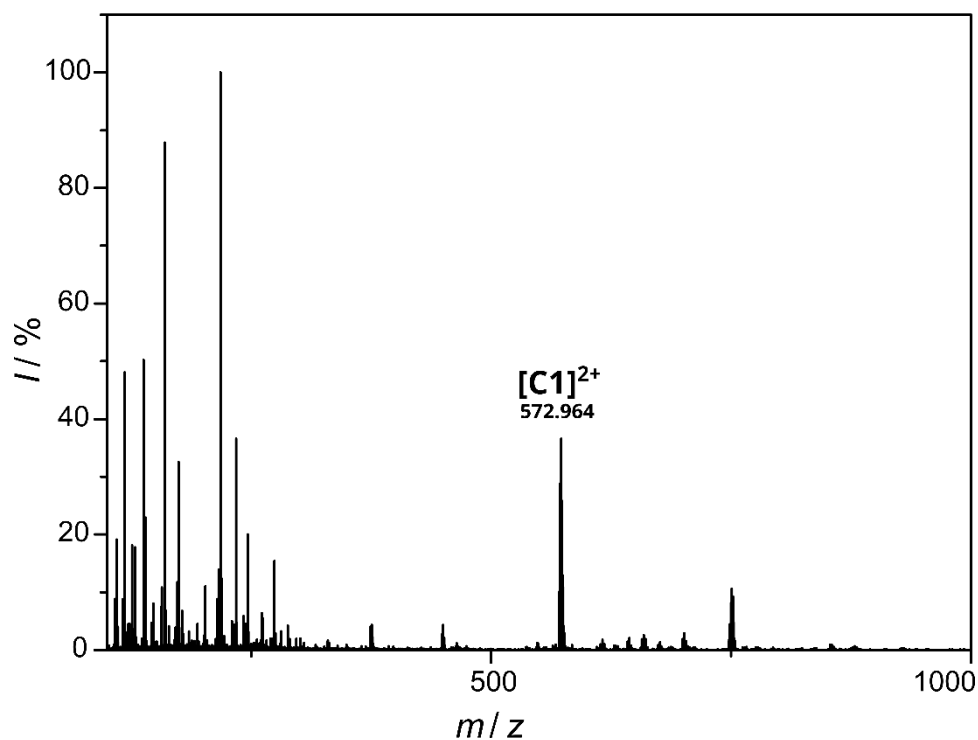


Figure S22: ESI+-MS of $C1 \cdot 8 H_2O$ showing the dicationic $[C1]^{2+}$ fragment without anions at 572.964 m/z .

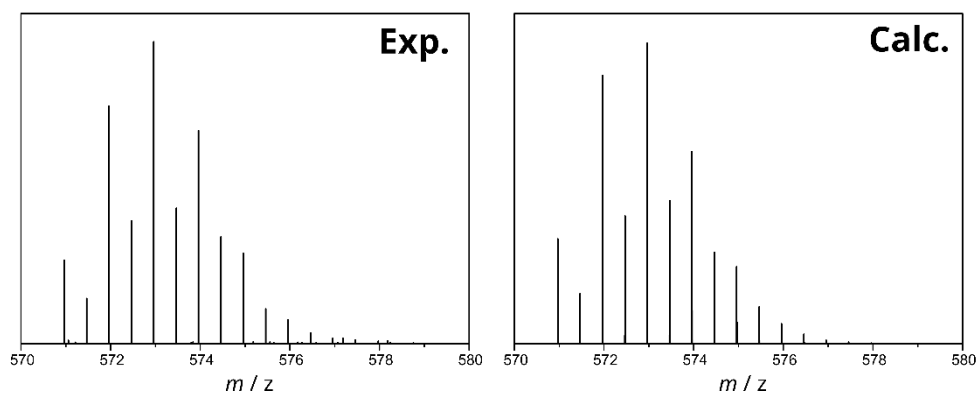


Figure S23: Comparison of the experimentally measured isotopic pattern of $[C1]^{2+}$ at 572.964 m/z with the theoretically calculated isotopic pattern of $[C1]^{2+}$.

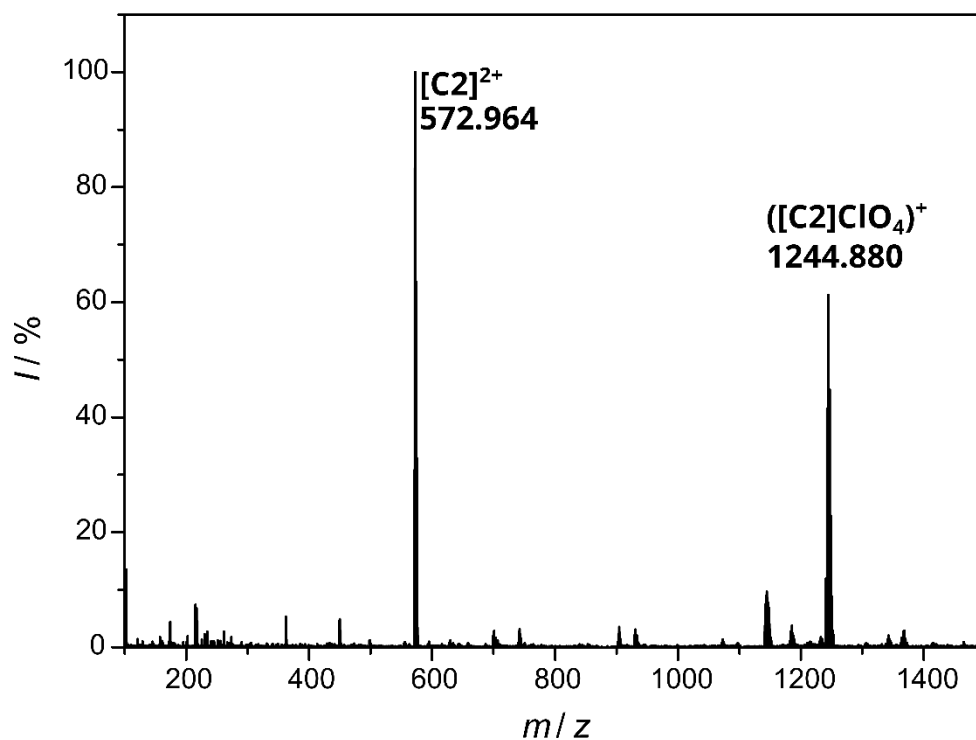


Figure S24: ESI⁺-MS of $C2 \cdot 3.5 H_2O$ showing the dicationic $[C2]^{2+}$ fragment without anions at 572.964 m/z as well as the monocationic $([C2]ClO_4)^+$ signal at 1244.880 m/z.

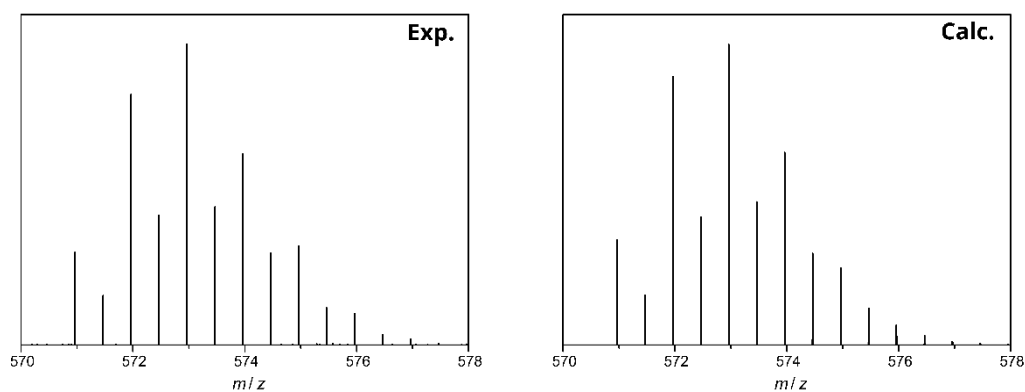


Figure S25: Comparison of the experimentally measured isotopic pattern of $[C2]^{2+}$ at 572.964 m/z with the theoretically calculated isotopic pattern of $[C2]^{2+}$.

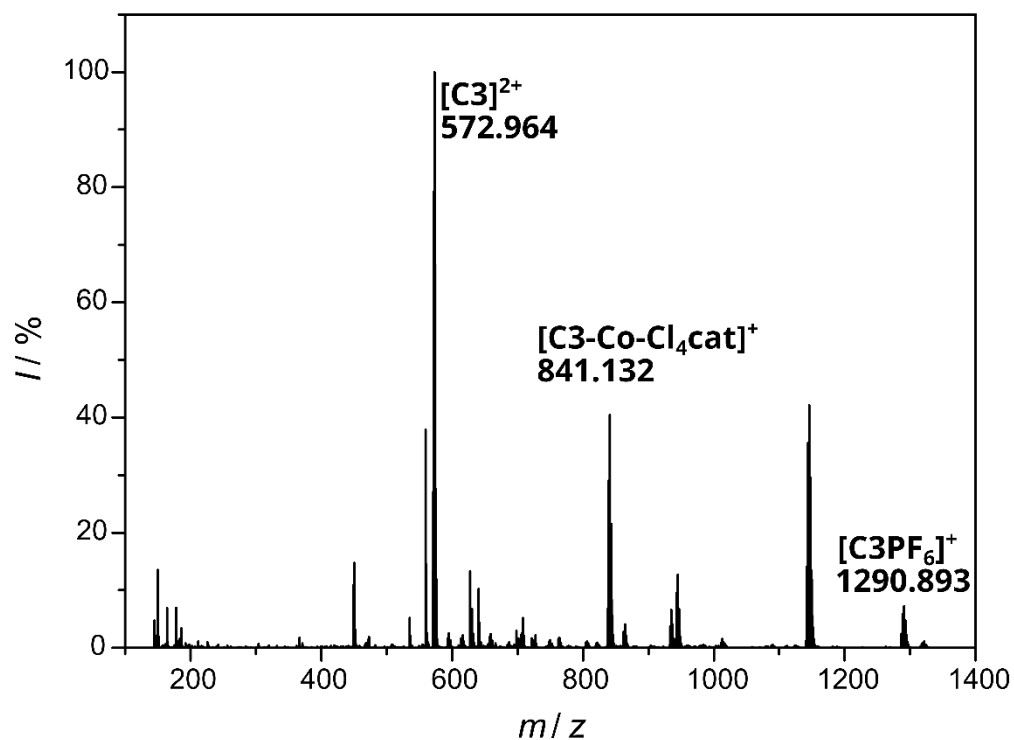


Figure S26: ESI⁺-MS of $\text{C3} \cdot 6.5 \text{H}_2\text{O}$ showing the dicationic $[\text{C3}]^{2+}$ fragment without anions at 572.964 m/z as well as the monocationic $[(\text{C3})\text{-Co-Cl}_4\text{cat}]^+$ signal at 841.132 m/z and the monocationic $[(\text{C3})\text{PF}_6]^+$ at 1290.893 m/z.

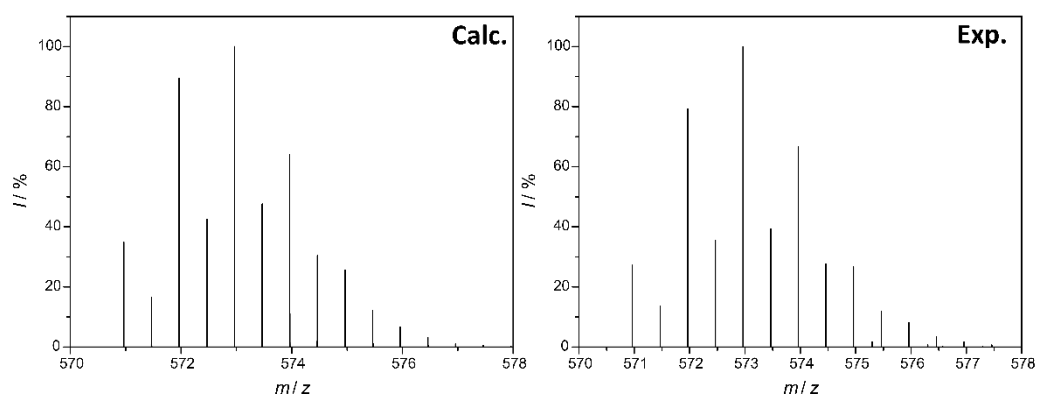


Figure S27: Comparison of the experimentally measured isotopic pattern of $[\text{C3}]^{2+}$ at 572.964 m/z with the theoretically calculated isotopic pattern of $[\text{C3}]^{2+}$.

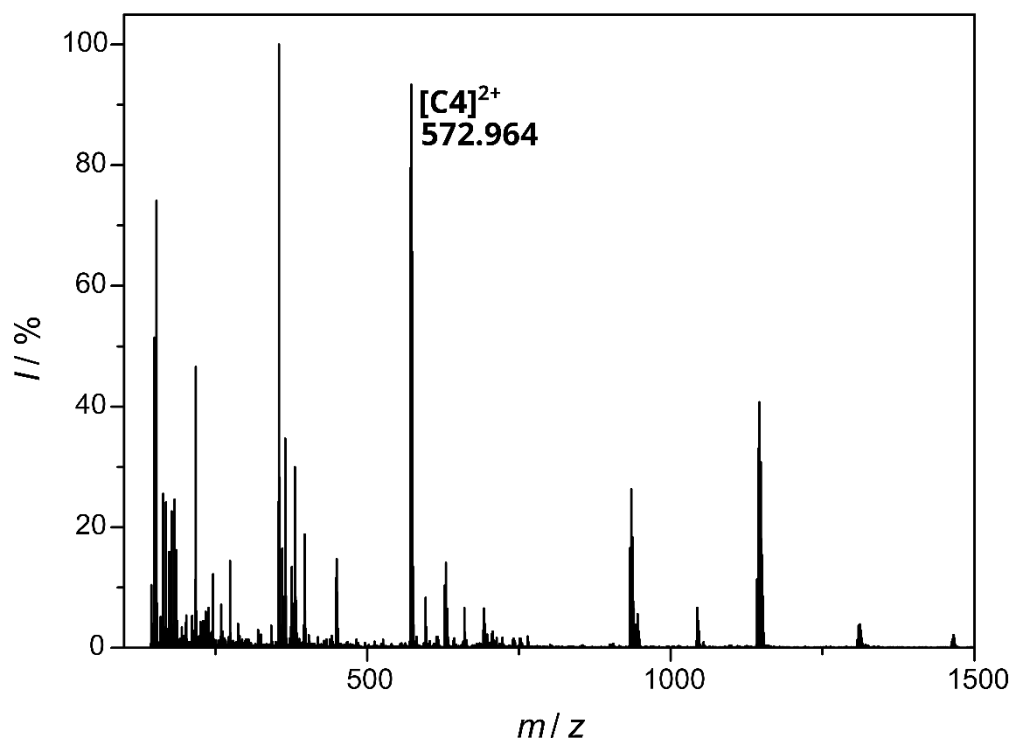


Figure S28: ESI⁺-MS of $C4 \cdot 2 H_2O$ showing the dicationic $[C4]^{2+}$ fragment without anions at 572.964 m/z .

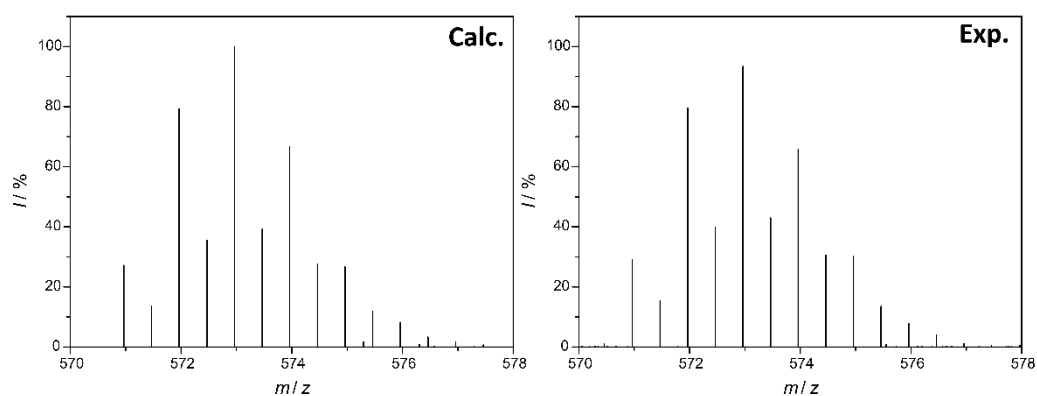


Figure S29: Comparison of the experimentally measured isotopic pattern of $[C4]^{2+}$ at 572.964 m/z with the theoretically calculated isotopic pattern of $[C4]^{2+}$.

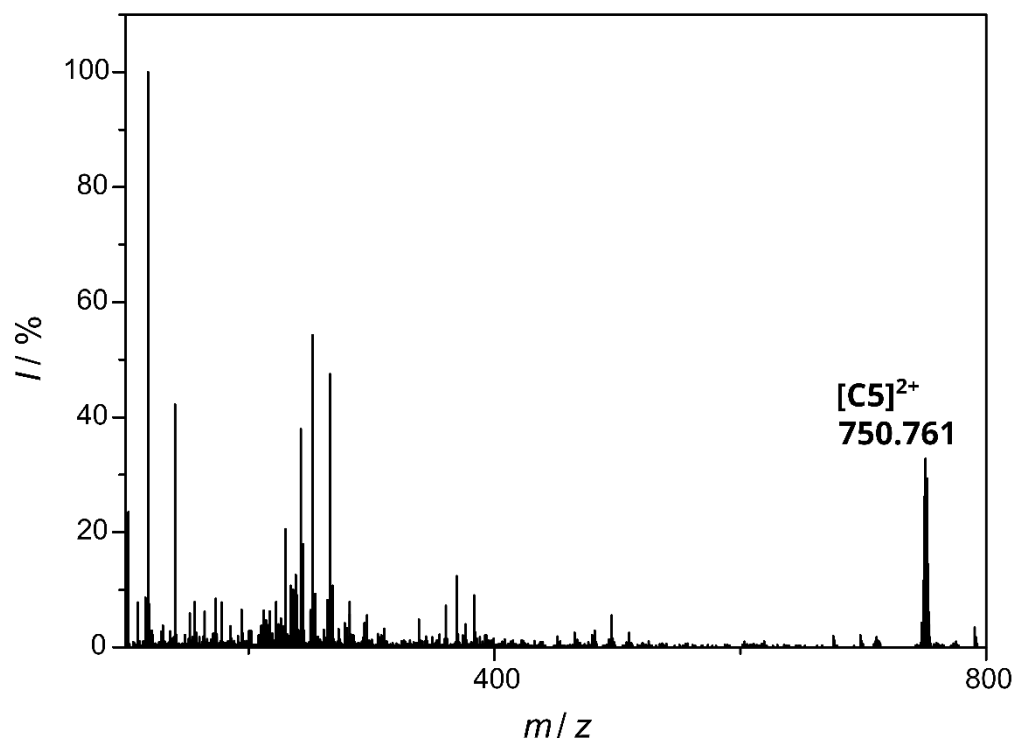


Figure S30: ESI⁺-MS of $C5 \cdot 5.5 H_2O \cdot CHCl_3$ showing the dicationic $[C5]^{2+}$ fragment without anions at 750.761 m/z.

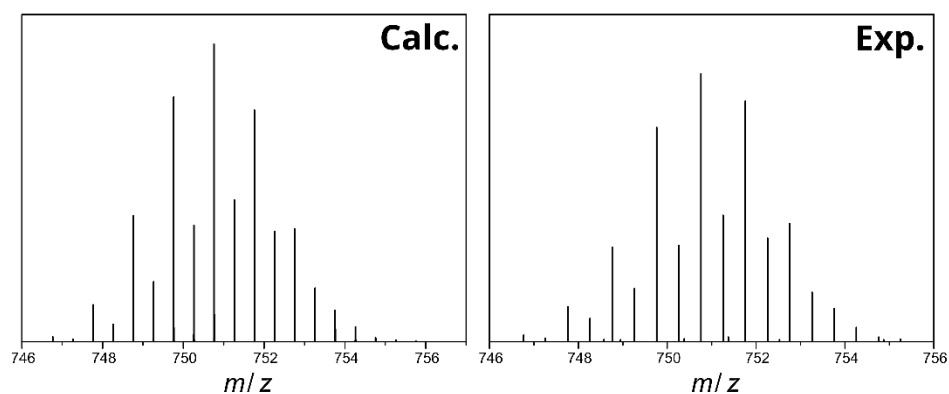


Figure S31: Comparison of the experimentally measured isotopic pattern of $[C5]^{2+}$ at 750.761 m/z with the theoretically calculated isotopic pattern of $[C5]^{2+}$.

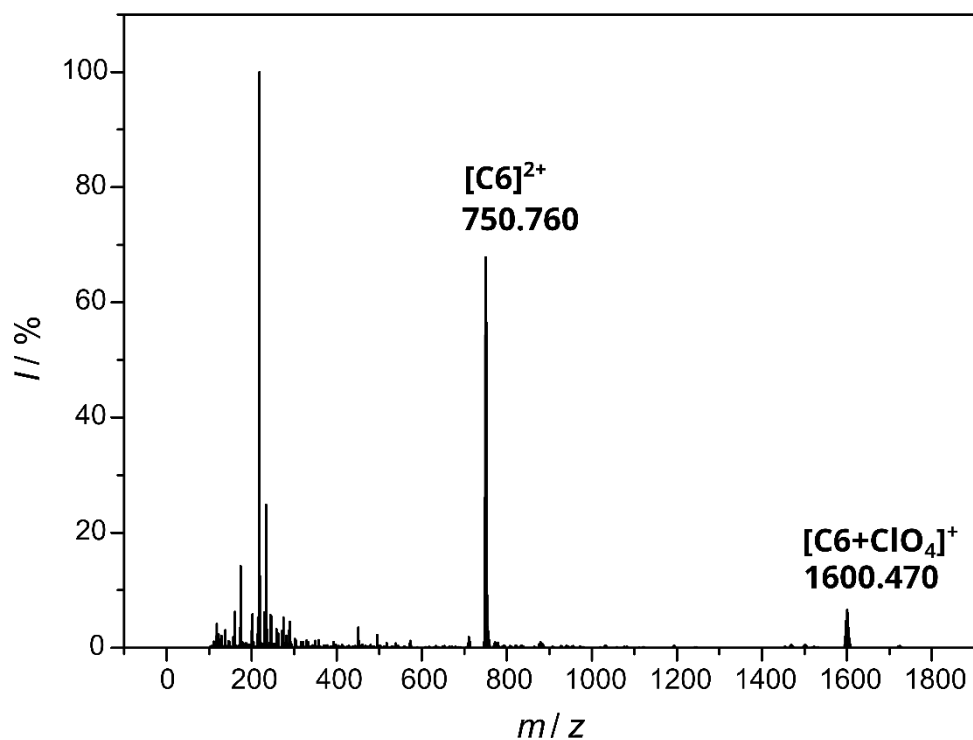


Figure S32: ESI+-MS of $\text{C6} \cdot 1.5 \text{H}_2\text{O}$ showing the dicationic $[\text{C6}]^{2+}$ fragment without anions at 750.761 m/z as well as the monocationic $[(\text{C6})\text{ClO}_4]^+$ signal at 1600.470 m/z .

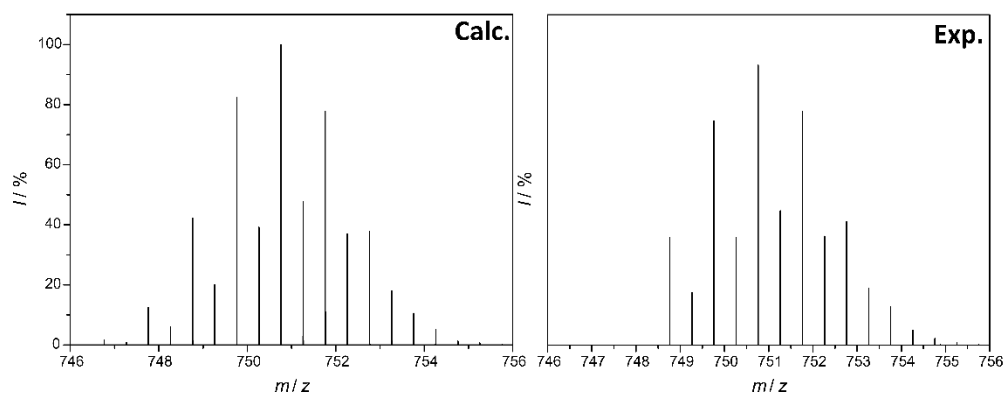


Figure S33: Comparison of the experimentally measured isotopic pattern of $[\text{C6}]^{2+}$ at 750.760 m/z with the theoretically calculated isotopic pattern of $[\text{C6}]^{2+}$.

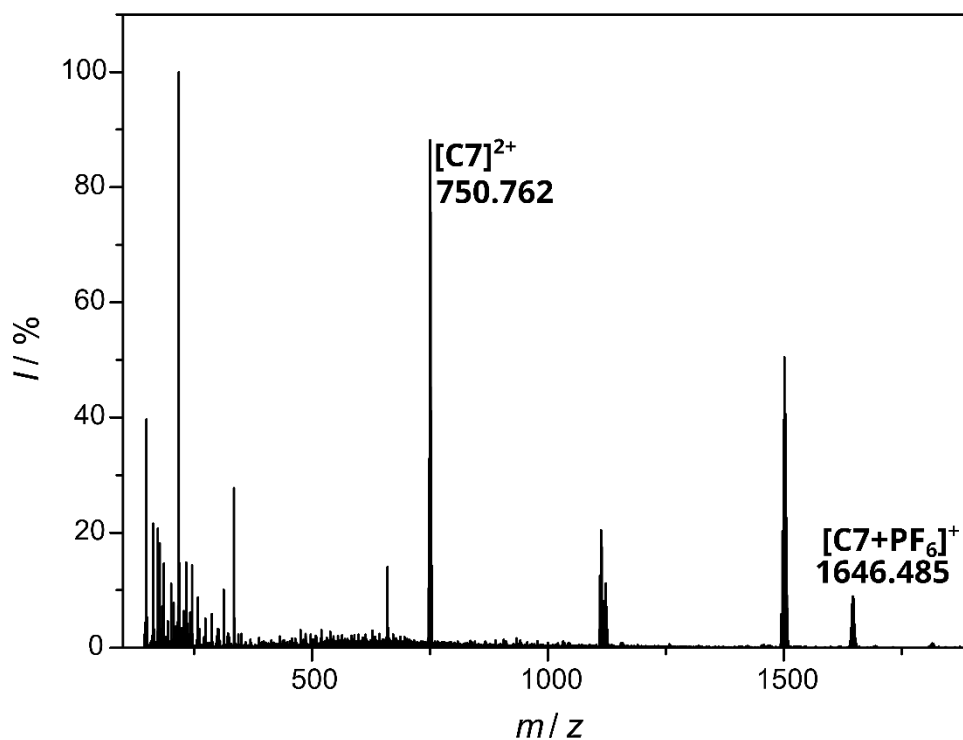


Figure S34: ESI⁺-MS of $C7 \cdot 1.25 H_2O$ showing the dicationic $[C7]^{2+}$ fragment without anions at 750.762 m/z as well as the monocationic $[(C7)PF_6]^+$ signal at 1646.485 m/z.

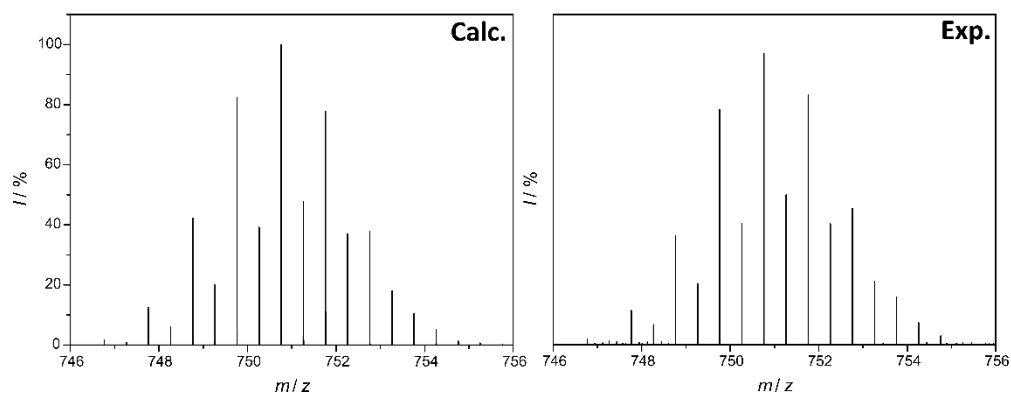


Figure S35: Comparison of the experimentally measured isotopic pattern of $[C7]^{2+}$ at 750.762 m/z with the theoretically calculated isotopic pattern of $[C7]^{2+}$.

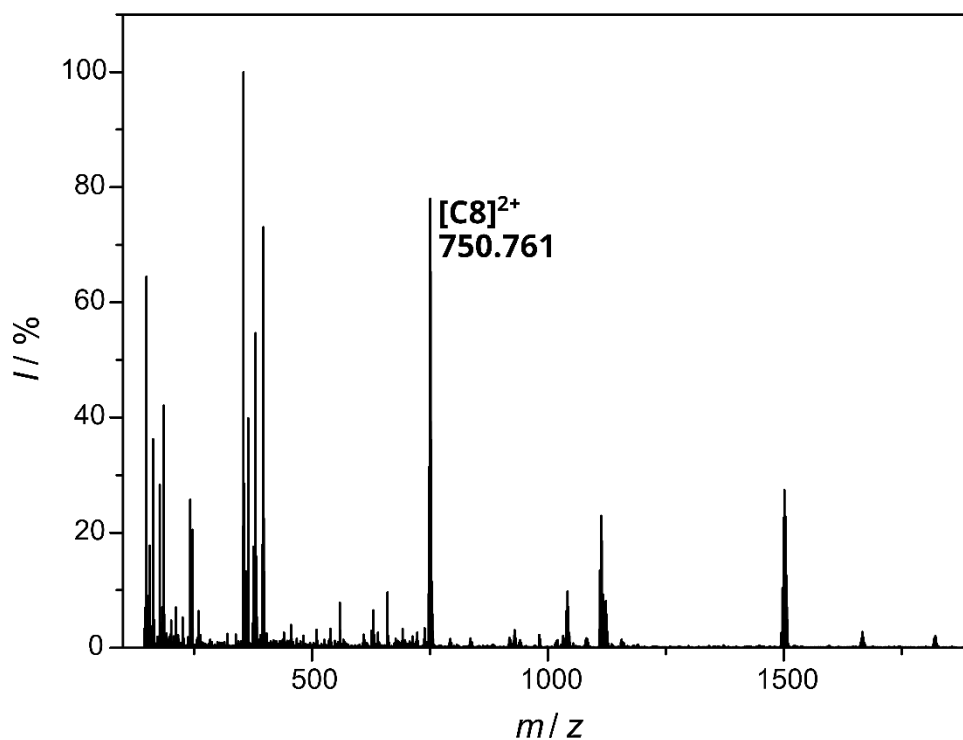


Figure S36: ESI⁺-MS of $C8 \cdot 1 H_2O$ showing the dicationic $[C8]^{2+}$ fragment without anions at 750.761 m/z.

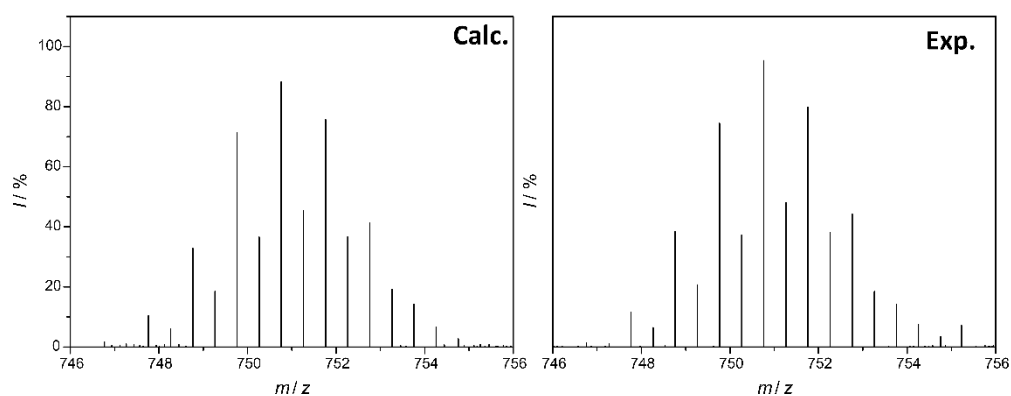


Figure S37: Comparison of the experimentally measured isotopic pattern of $[C8]^{2+}$ at 750.761 m/z with the theoretically calculated isotopic pattern of $[C8]^{2+}$.

4.1.10 Crystallographic Data

Table S1: Crystallographic Data of complexes **C1** and **C2**.

	C1	C2
Empirical formula	C ₅₅ H ₈₄ Cl ₈ Co ₂ N ₈ O ₁₉ S	C ₉₂ H ₉₈ Cl ₂₀ Co ₄ N ₁₈ O ₃₀
Formula weight	1594.82	2880.60
Temperature/K	120.0	120
Crystal system	monoclinic	triclinic
Space group	P2 ₁ /c	P-1
a/Å	12.8328(5)	9.9351(3)
b/Å	29.4246(14)	11.4887(4)
c/Å	19.0165(7)	26.4686(8)
α/°	90	95.276(3)
β/°	93.999(3)	94.497(3)
γ/°	90	97.847(3)
Volume/Å³	7163.1(5)	2967.50(17)
Z	4	1
ρ_{calc}/g/cm³	1.479	1.612
μ/mm⁻¹	0.862	1.080
F(000)	3312.0	1464.0
Crystal size/mm³	0.242 × 0.117 × 0.033	0.31 × 0.14 × 0.01
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	4.196 to 49.998	4.064 to 59.996
Index ranges	-14 ≤ h ≤ 15, -32 ≤ k ≤ 34, -22 ≤ l ≤ 22	-13 ≤ h ≤ 13, -16 ≤ k ≤ 16, -37 ≤ l ≤ 37
Reflections collected	37682	72270
Independent reflections	12512 [R _{int} = 0.0922, R _{sigma} = 0.0794]	17255 [R _{int} = 0.0517, R _{sigma} = 0.0390]
Data/restraints/parameters	12512/0/858	17255/66/789
Goodness-of-fit on F²	1.096	1.104
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.1368, wR ₂ = 0.3310	R ₁ = 0.1048, wR ₂ = 0.2844
Final R indexes [all data]	R ₁ = 0.1844, wR ₂ = 0.3798	R ₁ = 0.1243, wR ₂ = 0.2995
Largest diff. peak/hole / e Å⁻³	3.30/-0.99	4.39/-0.96

Table S2: Crystallographic Data of complexes **C3** and **C4**.

	C3	C4
Empirical formula	C ₅₀ H ₅₄ Cl ₈ Co ₂ F ₁₂ N ₁₀ O ₆ P ₂	C ₉₄ H ₈₃ B ₂ Cl ₈ Co ₂ N ₉ O ₄
Formula weight	1582.43	1825.77
Temperature/K	120.00	120.00
Crystal system	triclinic	monoclinic
Space group	P-1	P2 ₁ /c
a/Å	9.8551(3)	19.6985(3)
b/Å	11.7547(3)	9.9079(3)
c/Å	13.5213(4)	21.3537(4)
α/°	96.438(2)	90
β/°	94.033(2)	98.1760(10)
γ/°	98.114(2)	90
Volume/Å³	1534.98(8)	4125.26(16)
Z	1	2
ρ_{calc}/cm³	1.712	1.470
μ/mm⁻¹	1.035	0.722
F(000)	800.0	1884.0
Crystal size/mm³	0.47 × 0.217 × 0.06	0.24 × 0.177 × 0.06
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	4.364 to 65.222	4.54 to 65.326
Index ranges	-14 ≤ h ≤ 13, -17 ≤ k ≤ 17, -19 ≤ l ≤ 20	-28 ≤ h ≤ 29, -13 ≤ k ≤ 12, -27 ≤ l ≤ 32
Reflections collected	29709	39358
Independent reflections	9623 [R _{int} = 0.0504, R _{sigma} = 0.0350]	12393 [R _{int} = 0.0310, R _{sigma} = 0.0285]
Data/restraints/parameters	9623/118/446	12393/195/581
Goodness-of-fit on F²	1.086	1.043
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0655, wR ₂ = 0.1812	R ₁ = 0.0498, wR ₂ = 0.1289
Final R indexes [all data]	R ₁ = 0.0686, wR ₂ = 0.1863	R ₁ = 0.0637, wR ₂ = 0.1400
Largest diff. peak/hole / e Å⁻³	2.92/-1.94	0.93/-0.57

Table S3: Crystallographic Data of complexes C5 and C6.

	C5	C6
Empirical formula	C ₄₈ H ₅₆ Br ₈ Co ₂ N ₈ O ₁₄ S	C ₄₈ H ₄₆ Br ₈ Cl ₂ Co ₂ N ₁₀ O ₁₂
Formula weight	1758.20	1782.99
Temperature/K	120	120.0
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	10.2674(8)	10.1586(6)
b/Å	10.4742(9)	11.8117(7)
c/Å	14.4507(13)	12.5379(8)
α/°	105.210(7)	94.804(5)
β/°	89.460(7)	96.809(5)
γ/°	100.170(7)	97.067(5)
Volume/Å³	1475.0(2)	1475.07(16)
Z	1	1
ρ_{calc}/cm³	1.979	2.007
μ/mm⁻¹	6.085	6.138
F(000)	862.0	868.0
Crystal size/mm³	0.08 × 0.041 × 0.014	0.1 × 0.043 × 0.01
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	4.034 to 67.734	4.074 to 69.586
Index ranges	-15 ≤ h ≤ 16, -15 ≤ k ≤ 16, -22 ≤ l ≤ 19	-15 ≤ h ≤ 14, -18 ≤ k ≤ 18, -19 ≤ l ≤ 18
Reflections collected	22389	23952
Independent reflections	9903 [R _{int} = 0.0594, R _{sigma} = 0.0937]	10972 [R _{int} = 0.0518, R _{sigma} = 0.0910]
Data/restraints/parameters	9903/99/399	10972/24/371
Goodness-of-fit on F²	1.026	1.026
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0858, wR ₂ = 0.1985	R ₁ = 0.0768, wR ₂ = 0.1814
Final R indexes [all data]	R ₁ = 0.1684, wR ₂ = 0.2405	R ₁ = 0.1578, wR ₂ = 0.2210
Largest diff. peak/hole / e Å⁻³	1.64/-1.15	2.37/-1.21

Table S4: Crystallographic Data of complexes **C7** and **C8**.

	C7	C8
Empirical formula	C ₅₀ H ₅₄ Br ₈ Co ₂ F ₁₂ N ₁₀ O ₆ P ₂	C ₁₀₀ H ₉₂ B ₂ Br ₈ Co ₂ N ₁₂ O ₄
Formula weight	1938.11	2304.61
Temperature/K	120.00	120.00
Crystal system	triclinic	monoclinic
Space group	P-1	P2 ₁ /n
a/Å	10.1114(3)	12.9431(4)
b/Å	11.8311(4)	13.5336(4)
c/Å	13.5809(4)	27.5860(10)
α/°	97.436(2)	90
β/°	93.884(2)	96.206(3)
γ/°	97.718(2)	90
Volume/Å³	1590.41(9)	4803.8(3)
Z	1	2
ρ_{calc}/g/cm³	2.024	1.593
μ/mm⁻¹	5.688	3.731
F(000)	944.0	2304.0
Crystal size/mm³	0.1 × 0.07 × 0.02	0.27 × 0.162 × 0.045
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	4.08 to 65.416	4.228 to 65.472
Index ranges	-14 ≤ h ≤ 13, -15 ≤ k ≤ 17, -20 ≤ l ≤ 20	-17 ≤ h ≤ 18, -18 ≤ k ≤ 18, -37 ≤ l ≤ 36
Reflections collected	32008	49572
Independent reflections	9996 [R _{int} = 0.0379, R _{sigma} = 0.0308]	14818 [R _{int} = 0.0231, R _{sigma} = 0.0242]
Data/restraints/parameters	9996/93/398	14818/0/579
Goodness-of-fit on F²	1.063	1.057
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0417, wR ₂ = 0.1117	R ₁ = 0.0359, wR ₂ = 0.0846
Final R indexes [all data]	R ₁ = 0.0498, wR ₂ = 0.1173	R ₁ = 0.0457, wR ₂ = 0.0895
Largest diff. peak/hole / e Å⁻³	1.05/-1.37	1.18/-1.19

4.1.11 Bond Length Tables

Table S5: Metal-Donor bond lengths of **C1**.

C1	Bond length / Å		Bond length / Å
Co1 O1	1.881(6)	Co2 O3	1.889(6)
Co1 O2	1.898(6)	Co2 O4	1.895(6)
Co1 N1	1.933(8)	Co2 N5	2.045(8)
Co1 N2	1.924(7)	Co2 N6	1.919(8)
Co1 N3	1.922(8)	Co2 N7	1.926(8)
Co1 N4	2.043(7)	Co2 N8	1.928(7)

Table S6: Metal-Donor bond lengths of **C2**.

C2	Bond length / Å		Bond length / Å
Co1 O1	1.898(4)	Co2 O3	1.895(4)
Co1 O2	1.871(4)	Co2 O4	1.873(4)
Co1 N1	1.936(4)	Co2 N5	1.938(4)
Co1 N2	1.910(4)	Co2 N6	1.921(4)
Co1 N3	1.916(4)	Co2 N7	1.914(4)
Co1 N4	2.048(4)	Co2 N8	2.045(4)

Table S7: Metal-Donor bond lengths of **C3** and **C4**.

C3	Bond length / Å	C4	Bond length / Å
Co1 O1	1.8816(14)	Co1 O1	1.8708(13)
Co1 O2	1.8966(15)	Co1 O2	1.8909(15)
Co1 N1	1.9399(16)	Co1 N1	1.9454(17)
Co1 N2	1.9081(18)	Co1 N2	1.9200(18)
Co1 N3	1.9171(17)	Co1 N3	1.9173(19)
Co1 N4	2.0479(17)	Co1 N4	2.0555(17)

Table S8: Metal-Donor bond lengths of C5 and C6.

C5	Bond length / Å	C6	Bond length / Å
Co1 O1	1.912(5)	Co1 O1	1.898(5)
Co1 O2	1.893(5)	Co1 O2	1.882(4)
Co1 N1	1.957(6)	Co1 N1	1.942(5)
Co1 N2	1.925(7)	Co1 N2	1.902(6)
Co1 N3	1.937(6)	Co1 N3	1.923(6)
Co1 N4	2.056(6)	Co1 N4	2.107(6)

Table S9: Metal-Donor bond lengths of C7 and C8.

C7	Bond length / Å	C8	Bond length / Å
Co1 O1	1.8722(18)	Co1 O1	1.8773(13)
Co1 O2	1.8918(18)	Co1 O2	1.8745(13)
Co1 N1	1.937(2)	Co1 N1	1.9460(15)
Co1 N2	1.915(2)	Co1 N2	1.9170(16)
Co1 N3	1.914(2)	Co1 N3	1.9251(15)
Co1 N4	2.047(2)	Co1 N4	2.0376(15)

Table S10: C-C and C-O Bond lengths of the catechols of C1.

C1	Bond length / Å		Bond length / Å
C33 C34	1.383(13)	C39 C40	1.389(12)
C34 C35	1.399(13)	C40 C41	1.407(14)
C35 C36	1.387(14)	C41 C42	1.375(14)
C36 C37	1.418(13)	C42 C43	1.410(14)
C37 C38	1.398(12)	C43 C44	1.418(13)
C38 C33	1.438(13)	C44 C39	1.410(13)
O1 C33	1.327(11)	O3 C39	1.337(11)
O2 C38	1.328(10)	O4 C44	1.319(11)

Table S11: C-C and C-O Bond lengths of the catechols of C2.

C2	Bond length / Å		Bond length / Å
C17 C18	1.418(7)	C39 C44	1.422(8)
C17 C22	1.398(8)	C40 C41	1.395(8)
C18 C19	1.405(7)	C41 C42	1.380(9)
C19 C20	1.381(9)	C42 C43	1.411(7)
C20 C21	1.403(7)	C43 C44	1.393(7)
C21 C22	1.393(7)	C40 C39	1.397(7)
O1 C17	1.336(6)	O3 C39	1.332(6)
O2 C22	1.342(6)	O4 C44	1.332(6)

Table S12: C-C and C-O Bond lengths of the catechols of C3 and C4.

C3	Bond length / Å	C4	Bond length / Å
C17 C18	1.392(3)	C17 C18	1.386(3)
C18 C19	1.397(3)	C17 C22	1.415(3)
C19 C20	1.393(3)	C18 C19	1.395(3)
C20 C21	1.400(3)	C19 C20	1.396(3)
C21 C22	1.396(3)	C20 C21	1.402(3)
C22 C17	1.419(3)	C21 C22	1.390(3)
O1 C17	1.331(2)	O1 C17	1.335(2)
O2 C22	1.332(2)	O2 C22	1.336(2)

Table S13: C-C and C-O Bond lengths of the catechols of C5 and C6.

C5	Bond length / Å	C6	Bond length / Å
C17 C18	1.395(10)	C17 C18	1.409(9)
C17 C22	1.411(10)	C17 C22	1.404(9)
C18 C19	1.401(10)	C18 C19	1.420(9)
C19 C20	1.384(11)	C19 C20	1.381(10)
C20 C21	1.397(10)	C20 C21	1.419(9)
C21 C22	1.399(10)	C21 C22	1.395(9)
O1 C17	1.336(8)	O1 C17	1.328(7)

O2 C22	1.327(9)	O2 C22	1.341(7)
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Table S14: C-C and C-O Bond lengths of the catechols of C7 and C8.

C7	Bond length / Å	C8	Bond length / Å
C17 C18	1.385(4)	C17 C18	1.389(3)
C18 C19	1.399(3)	C17 C22	1.412(2)
C19 C20	1.387(4)	C18 C19	1.398(3)
C20 C21	1.406(4)	C19 C20	1.390(3)
C21 C22	1.387(4)	C20 C21	1.395(3)
C22 C17	1.417(3)	C21 C22	1.387(3)
O1 C17	1.338(3)	O1 C17	1.335(2)
O2 C22	1.332(3)	O2 C22	1.338(2)

4.1.12 Metal-Donor-Bond Angles

Table S15: Metal-Donor bond angles of C1.

C1	Bond Angle /°	C1	Bond Angle /°
O1 Co1 O2	88.3(3)	O3 Co2 O4	87.6(3)
O1 Co1 N4	94.2(3)	O3 Co2 N5	92.3(3)
O1 Co1 N2	94.2(4)	O3 Co2 N6	95.0(4)
O1 Co1 N3	94.2(4)	O3 Co2 N7	94.9(4)
O1 Co1 N1	178.1(4)	O3 Co2 N8	178.3(4)
O2 Co1 N4	92.4(3)	O4 Co2 N5	92.3(3)
O2 Co1 N2	174.2(4)	O4 Co2 N6	85.4(4)
O2 Co1 N3	86.9(4)	O4 Co2 N7	173.4(4)
O2 Co1 N1	90.4(3)	O4 Co2 N8	90.7(4)
N2 Co1 N4	92.6(4)	N6 Co2 N5	172.3(4)
N2 Co1 N1	86.9(4)	N7 Co2 N5	93.7(4)
N3 Co1 N4	171.6(4)	N7 Co2 N6	88.2(4)
N3 Co1 N2	87.7(4)	N7 Co2 N8	86.8(4)
N3 Co1 N1	84.3(4)	N8 Co2 N5	87.9(4)

Table S16: Metal-Donor bond angles of C2.

C2	Bond Angle /°	C2	Bond Angle /°
O1 Co 1N1	91.53(18)	O3 Co2 N5	92.32(17)
O1 Co1 N2	175.81(18)	O3 Co2 N6	175.87(17)
O1 Co1 N3	85.75(18)	O3 Co2 N7	85.56(17)
O1 Co1 N4	92.50(17)	O3 Co2 N8	92.32(16)
O2 Co1 O1	87.92(16)	O4 Co2 O3	87.86(16)
O2 Co1 N1	179.03(18)	O4 Co2 N5	179.38(18)
O2 Co1 N2	93.96(18)	O4 Co2 N6	93.26(17)
O2 Co1 N3	95.17(18)	O4 Co2 N7	95.64(17)
O2 Co1 N4	91.74(17)	O4 Co2 N8	91.89(16)
N1 Co1 N4	89.08(18)	N5 Co2 N8	88.70(17)
N2 Co1 N1	86.5(2)	N6 Co2 N5	86.52(19)
N2 Co1 N3	90.34(19)	N6 Co2 N8	91.63(17)
N2 Co1 N4	91.19(18)	N7 Co2 N5	83.78(19)
N3 Co1 N1	83.99(19)	N7 Co2 N6	90.36(18)

Table S17: Metal-Donor bond angles of C3 and C4.

C3	Bond Angle /°	C4	Bond Angle /°
O1 Co1 O2	87.88(6)	O1 Co1 O2	88.59(6)
O1 Co1 N4	92.41(6)	O1 Co1 N1	178.22(7)
O2 Co1 N1	91.94(7)	O1 Co1 N2	92.90(7)
O2 Co1 N2	175.58(6)	O1 Co1 N3	93.87(7)
O2 Co1 N3	85.46(7)	O1 Co1 N4	93.34(6)
O2 Co1 N4	92.76(7)	O2 Co1 N1	92.27(7)
N1 Co1 N4	88.16(7)	O2 Co1 N2	176.70(7)
N2 Co1 N1	86.78(7)	O2 Co1 N3	86.99(8)
N2 Co1 N3	90.20(7)	O2 Co1 N4	90.08(6)
N2 Co1 N4	91.43(7)	N1 Co1 N4	88.22(7)
N3 Co1 N1	84.00(7)	N2 Co1 N1	86.17(8)
N3 Co1 N4	171.89(7)	N2 Co1 N4	92.77(7)
O1 Co1 O2	87.88(6)	N3 Co1 N1	84.62(8)
O1 Co1 N4	92.41(6)	N3 Co1 N2	89.97(8)

Table S18: Metal-Donor bond angles of C5 and C6.

C5	Bond Angle /°	C6	Bond Angle /°
O1 Co1 N1	92.9(3)	O1 Co1 N1	92.4(2)
O1 Co1 N2	177.5(2)	O1 Co1 N2	176.2(2)
O1 Co1 N3	87.0(2)	O1 Co1 N3	87.0(2)
O1 Co1 N4	90.9(3)	O1 Co1 N4	93.5(2)
O2 Co1 O1	87.2(2)	O2 Co1 O1	87.23(19)
O2 Co1 N1	177.5(2)	O2 Co1 N1	175.9(2)
O2 Co1 N2	93.8(3)	O2 Co1 N2	93.7(2)
O2 Co1 N3	94.0(2)	O2 Co1 N3	93.0(2)
O2 Co1 N4	94.2(2)	O2 Co1 N4	96.7(2)
N1 Co1 N4	88.3(3)	N1 Co1 N4	87.5(2)
N2 Co1 N1	86.0(3)	N2 Co1 N1	86.4(2)
N2 Co1 N3	90.6(3)	N2 Co1 N3	89.3(2)
N2 Co1 N4	91.4(3)	N2 Co1 N4	90.0(2)
N3 Co1 N1	83.5(3)	N3 Co1 N1	82.9(2)

Table S19: Metal-Donor bond angles of C7 and C8.

C7	Bond Angle /°	C8	Bond Angle /°
O1 Co1 O2	87.90(8)	O1 Co1 N1	92.94(6)
O1 Co1 N1	179.28(9)	O1 Co1 N2	175.97(6)
O1 Co1 N2	93.15(9)	O1 Co1 N3	86.11(6)
O1 Co1 N3	95.26(9)	O1 Co1 N4	91.38(6)
O1 Co1 N4	91.96(8)	O2 Co1 O1	88.37(6)
O2 Co1 N1	92.40(9)	O2 Co1 N1	177.99(6)
O2 Co1 N2	175.77(9)	O2 Co1 N2	91.76(6)
O2 Co1 N3	85.51(9)	O2 Co1 N3	95.92(6)
O2 Co1 N4	91.95(8)	O2 Co1 N4	93.91(6)
N1 Co1 N4	88.68(9)	N1 Co1 N4	87.58(6)
N2 Co1 N1	86.50(9)	N2 Co1 N1	86.83(7)
N2 Co1 N4	92.11(9)	N2 Co1 N3	89.87(7)
N3 Co1 N1	84.11(9)	N2 Co1 N4	92.63(6)
N3 Co1 N2	90.31(9)	N3 Co1 N1	82.9(2)
N3 Co1 N4	172.25(9)	N3 Co1 N4	169.78(6)

4.1.13 SHAPE Measurements

Table S20: Continuous shape measurements of **C1** on the Co1 center.

C1 Co1	OC-6	Ideal Structure	CShM =	0.25530
Co	M	10.9739	24.9100	24.2591
N	L1	10.2254	23.1767	23.8554
O	L2	10.5576	25.5064	22.4706
O	L3	9.2435	25.5163	24.8640
N	L5	12.7042	24.3037	23.6542
N	L6	11.7224	26.6433	24.6628
N	L4	11.3902	24.3137	26.0476

Table S21: Continuous shape measurements of **C1** on the Co2 center.

C1 Co2	OC-6	Ideal Structure	CShM =	0.28522
Co	M	7.9189	19.1752	21.9174
N	L1	9.6350	18.5775	21.2644
O	L2	8.4335	18.6896	23.7140
O	L3	8.6392	20.9459	22.1896
N	L5	7.1987	17.4045	21.6451
N	L6	6.2029	19.7728	22.5703
N	L4	7.4044	19.6607	20.1207

Table S22: Continuous shape measurements of **C2** on the Co1 center.

C2 Co1	OC-6	Ideal Structure	CShM =	0.25070
Co	M	5.2538	6.5832	23.6624
O	L1	6.9863	5.7391	23.6963
O	L2	5.9991	8.0740	22.6942
N	L4	4.5086	5.0924	24.6306
N	L6	3.5213	7.4273	23.6285
N	L3	4.8560	5.6999	21.9961
N	L5	5.6516	7.4665	25.3287

Table S23: Continuous shape measurements of **C2** on the Co2 center.

C2 Co2	OC-6	Ideal Structure	CShM =	0.27405
Co	M	6.4582	9.0403	42.0710
N	L1	5.9835	8.3043	40.3532
O	L2	4.7379	9.9049	42.1759
O	L3	5.7280	7.4819	42.9405
N	L5	7.1884	10.5987	41.2015
N	L4	8.1785	8.1758	41.9661
N	L6	6.9329	9.7763	43.7888

Table S24: Continuous shape measurements of **C3** on the Co1 center.

C3 Co1	OC-6	Ideal Structure	CShM =	0.27444
Co	M	-0.2251	6.8457	9.3970
O	L1	-0.9377	5.2924	10.2919
O	L2	-1.9675	7.6723	9.4441
N	L6	0.4876	8.3991	8.5021
N	L4	1.5174	6.0192	9.3499
N	L3	0.1963	7.6366	11.1054
N	L5	-0.6465	6.0548	7.6886

Table S25: Continuous shape measurements of **C4** on the Co1 center.

C4 Co1	OC-6	Ideal Structure	CShM =	0.23856
Co	M	1.7125	4.0381	11.4350
O	L1	0.8383	3.9349	13.1537
O	L2	1.1940	2.2158	11.0618
N	L6	2.5867	4.1414	9.7162
N	L4	2.2310	5.8605	11.8082
N	L3	3.3544	3.4077	12.2322
N	L5	0.0706	4.6686	10.6378

Table S26: Continuous shape measurements of **C5** on the Co1 center.

C5 Co1	OC-6	Ideal Structure	CShM =	0.26684
Co	M	5.5890	1.9207	4.0316
N	L1	5.0486	2.4116	5.8329
O	L2	3.8498	1.1064	3.7317
O	L3	4.9101	3.6159	3.3659
N	L5	6.2679	0.2255	4.6973
N	L4	7.3282	2.7350	4.3315
N	L6	6.1295	1.4298	2.2303

Table S27: Continuous shape measurements of **C6** on the Co1 center.

C6 Co1	OC-6	Ideal Structure	CShM =	0.41186
Co	M	4.6076	7.3116	8.3205
O	L1	2.8618	8.1529	8.2609
O	L2	3.8226	5.7407	9.1419
N	L4	5.3926	8.8826	7.4991
N	L6	6.3534	6.4704	8.3800
N	L3	4.9157	8.0754	10.0757
N	L5	4.2994	6.5479	6.5653

Table S28: Continuous shape measurements of **C7** on the Co1 center.

C7 Co1	OC-6	Ideal Structure	CShM =	0.27241
Co	M	2.6404	3.1036	4.0074
O	L1	3.3790	4.6532	3.1320
O	L2	4.3648	2.2460	3.9443
N	L6	1.9017	1.5540	4.8828
N	L4	0.9159	3.9612	4.0705
N	L3	2.2000	2.3444	2.2919
N	L5	3.0807	3.8628	5.7229

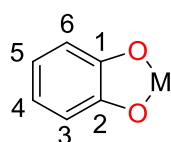
Table S29: Continuous shape measurements of **C8** on the Co1 center.

C8 Co1	OC-6	Ideal Structure	CShM =	0.33435
Co	M	7.4372	-2.1044	14.9051
O	L1	6.2779	-2.3997	16.4146
O	L2	8.0340	-0.4486	15.6873
N	L4	6.8404	-3.7602	14.1229
N	L6	8.5965	-1.8091	13.3956
N	L3	8.8548	-3.0429	15.8102
N	L5	6.0196	-1.1658	14.0000

4.1.14 Metric Oxidation State (MOS)

Table S30: The MOS of the catecholate ligands of C1-C8.

Compound	C-O avg.	C1-C2	C2-C3 avg.	C3-C4 avg.	C4-C5	Calc. MOS
C1 Co1	1.326	1.438	1.391	1.409	1.387	-1.690
C1 Co2	1.3285	1.409	1.4035	1.408	1.375	-1.839
C2 Co1	1.339	1.397	1.4055	1.404	1.382	-1.907
C2 Co2	1.332	1.422	1.395	1.4035	1.380	-1.805
C3	1.3315	1.419	1.394	1.3985	1.393	-1.749
C4	1.3355	1.415	1.388	1.39985	1.396	-1.802
C5	1.331	1.411	1.397	1.399	1.384	-1.809
C6	1.3345	1.404	1.402	1.419	1.382	-1.895
C7	1.335	1.417	1.386	1.403	1.387	-1.844
C8	1.337	1.412	1.388	1.3965	1.391	-1.838



4.1.15 Crystal Structures

4.1.15.1 Complexes

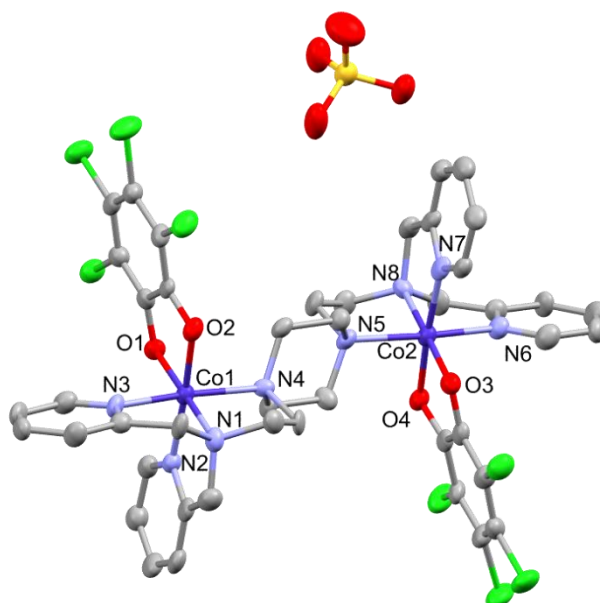


Figure S38: Complex structure of **C1** at 120 K. Lattice solvent molecules and hydrogen atoms are omitted for better visibility. The probability level for the displacement of the ellipsoid is 50%. Colour code: carbon (grey), cobalt (dark blue), nitrogen (light blue), oxygen (red), chloride (green), sulphur (yellow).

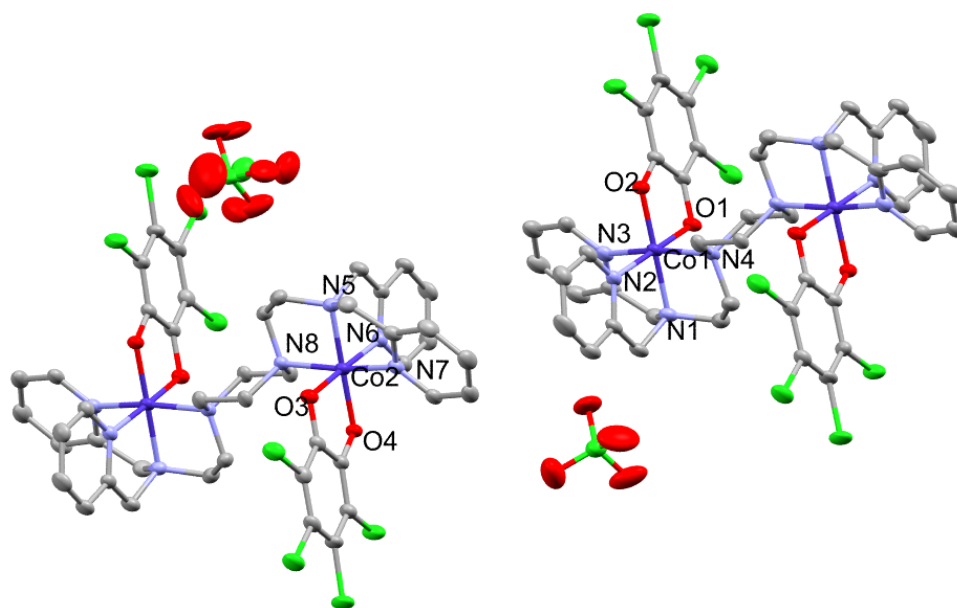


Figure S39: Complex structure of **C2** at 120 K. Lattice solvent molecules and hydrogen atoms are omitted for better visibility. The probability level for the displacement of the ellipsoid is 50%. Colour code: carbon (grey), cobalt (dark blue), nitrogen (light blue), oxygen (red), chloride (green).

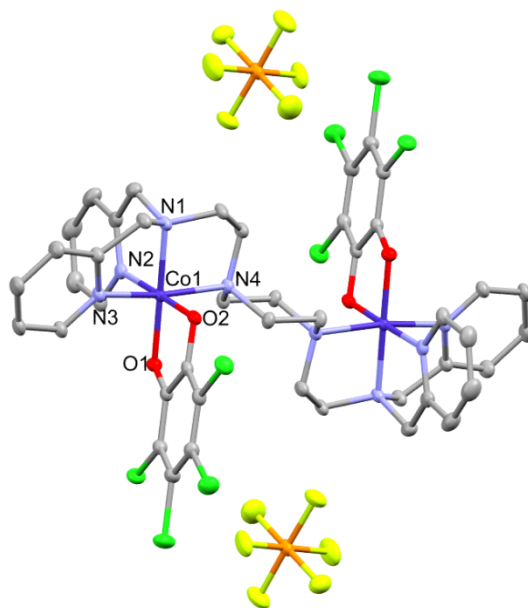


Figure S40: Complex structure of **C3** at 120 K. Lattice solvent molecules and hydrogen atoms are omitted for better visibility. The probability level for the displacement of the ellipsoid is 50%. Colour code: carbon (grey), cobalt (dark blue), nitrogen (light blue), oxygen (red), chloride (green), phosphorous (orange), fluorine (light green).

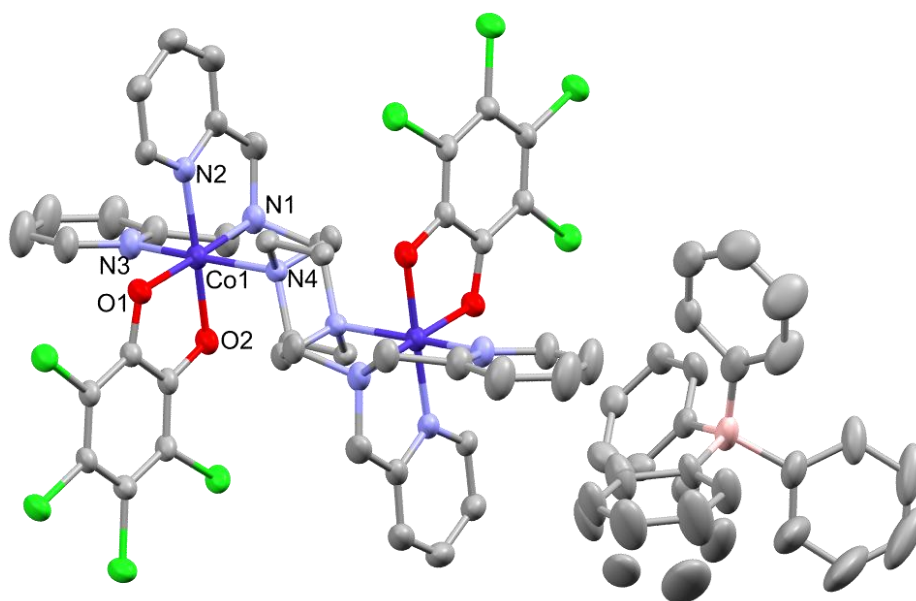


Figure S41: Complex structure of **C4** at 120 K. Lattice solvent molecules and hydrogen atoms are omitted for better visibility. The probability level for the displacement of the ellipsoid is 50%. Colour code: carbon (grey), cobalt (dark blue), nitrogen (light blue), oxygen (red), chloride (green), boron (rosa).

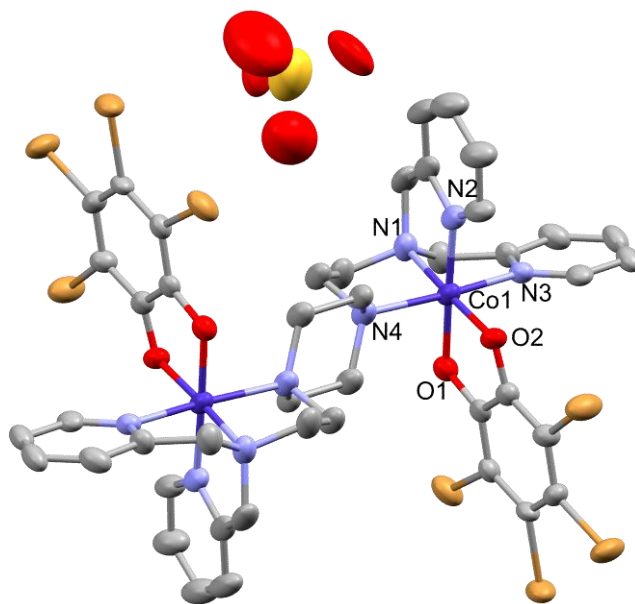


Figure S42: Complex structure of **C5** at 120 K. Lattice solvent molecules and hydrogen atoms are omitted for better visibility. The probability level for the displacement of the ellipsoid is 50%. Colour code: carbon (grey), cobalt (dark blue), nitrogen (light blue), oxygen (red), bromine (brown), sulphur (yellow).

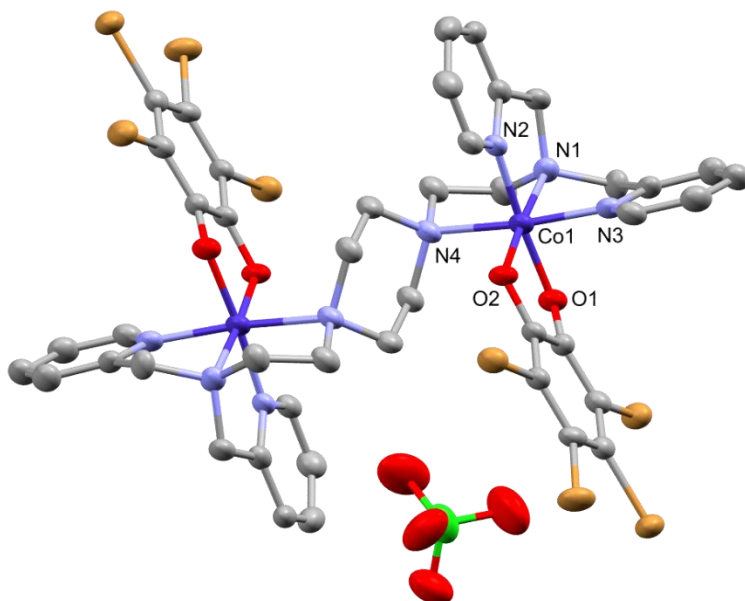


Figure S43: Complex structure of **C6** at 120 K. Lattice solvent molecules and hydrogen atoms are omitted for better visibility. The probability level for the displacement of the ellipsoid is 50%. Colour code: carbon (grey), cobalt (dark blue), nitrogen (light blue), oxygen (red), bromine (brown), chlorine (green).

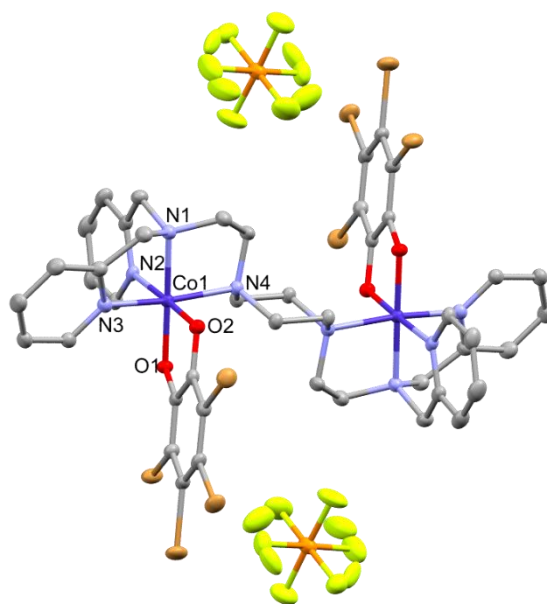


Figure S44: Complex structure of **C7** at 120 K. Lattice solvent molecules and hydrogen atoms are omitted for better visibility. The probability level for the displacement of the ellipsoid is 50%. Colour code: carbon (grey), cobalt (dark blue), nitrogen (light blue), oxygen (red), bromine (brown), phosphorous (orange), fluorine (light green).

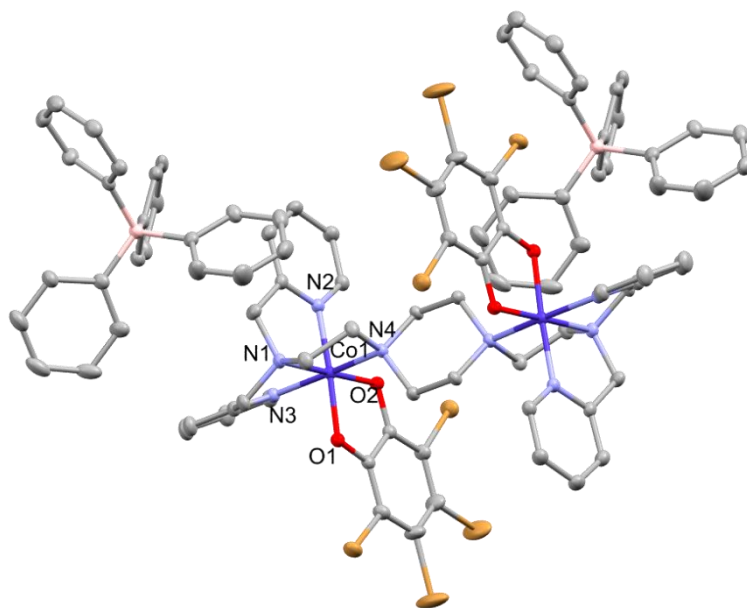


Figure S45: Complex structure of **C8** at 120 K. Lattice solvent molecules and hydrogen atoms are omitted for better visibility. The probability level for the displacement of the ellipsoid is 50%. Colour code: carbon (grey), cobalt (dark blue), nitrogen (light blue), oxygen (red), bromine (brown), boron (pink).

4.1.15.2 Asymmetric unit cells

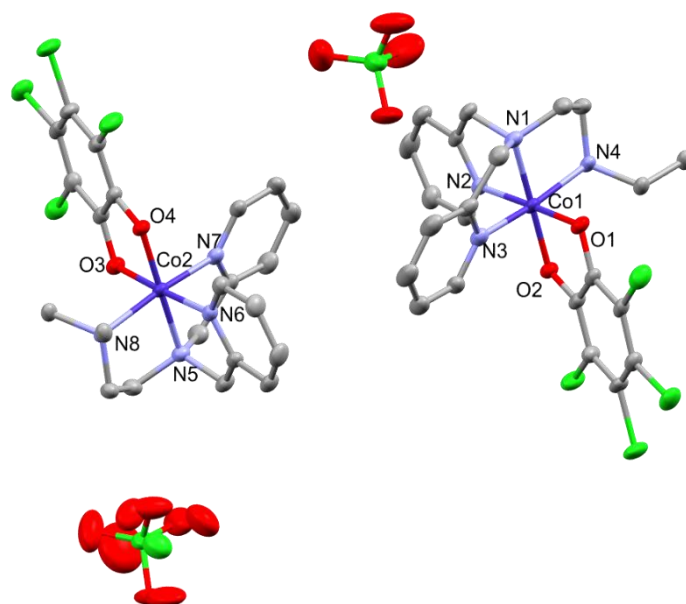


Figure S46: Asymmetric unit cell of **C2** at 120 K. Lattice solvent molecules and hydrogen atoms are omitted for better visibility. The probability level for the displacement of the ellipsoid is 50%. Colour code: carbon (grey), cobalt (dark blue), nitrogen (light blue), oxygen (red), chloride (green).

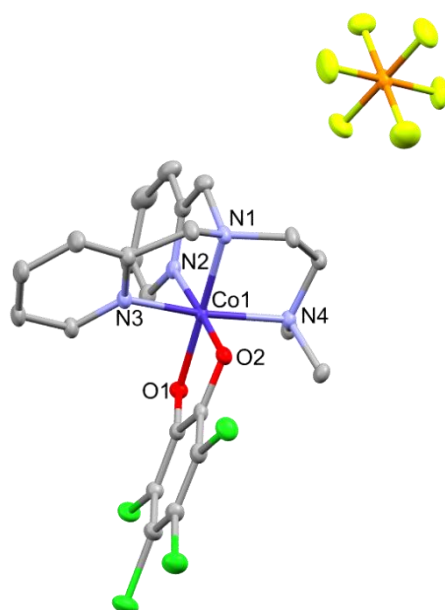


Figure S47: Asymmetric unit cell of **C3** at 120 K. Lattice solvent molecules and hydrogen atoms are omitted for better visibility. The probability level for the displacement of the ellipsoid is 50%. Colour code: carbon (grey), cobalt (dark blue), nitrogen (light blue), oxygen (red), chloride (green), phosphorous (orange), fluoride (light green).

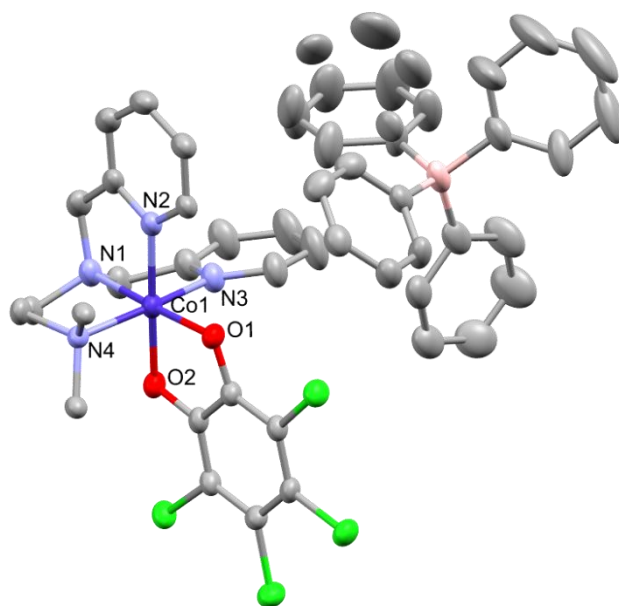


Figure S48: Asymmetric unit cell of **C4** at 120 K. Lattice solvent molecules and hydrogen atoms are omitted for better visibility. The probability level for the displacement of the ellipsoid is 50%. Colour code: carbon (grey), cobalt (dark blue), nitrogen (light blue), oxygen (red), chloride (green), boron (pink).

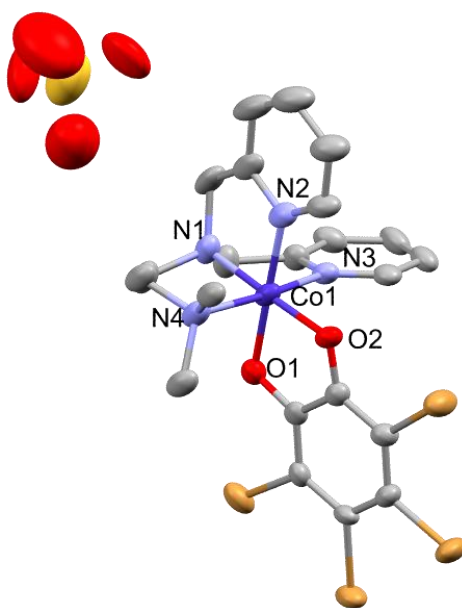


Figure S49: Asymmetric unit cell of **C5** at 120 K. Lattice solvent molecules and hydrogen atoms are omitted for better visibility. The probability level for the displacement of the ellipsoid is 50%. Colour code: carbon (grey), cobalt (dark blue), nitrogen (light blue), oxygen (red), bromine (brown), sulphur (yellow).

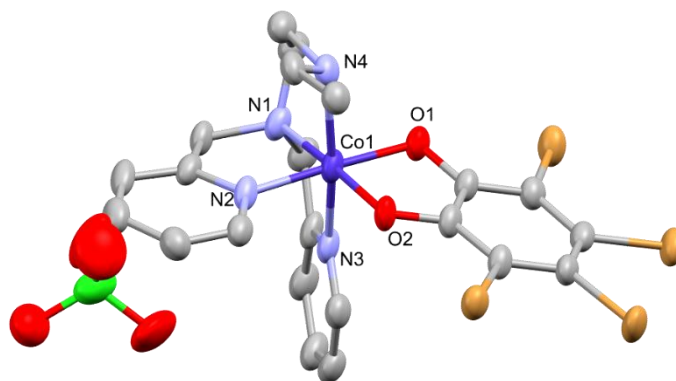


Figure S50: Asymmetric unit cell of **C6** at 120 K. Lattice solvent molecules and hydrogen atoms are omitted for better visibility. The probability level for the displacement of the ellipsoid is 50%. Colour code: carbon (grey), cobalt (dark blue), nitrogen (light blue), oxygen (red), bromine (brown), chlorine (green).

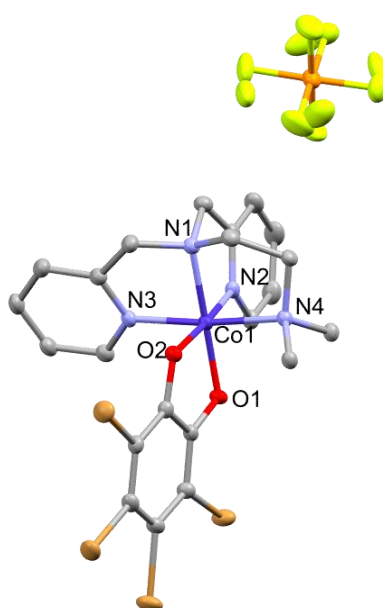


Figure S51: Asymmetric unit cell of **C7** at 120 K. Lattice solvent molecules and hydrogen atoms are omitted for better visibility. The probability level for the displacement of the ellipsoid is 50%. Colour code: carbon (grey), cobalt (dark blue), nitrogen (light blue), oxygen (red), bromine (brown), phosphorous (orange), fluorine (light green).

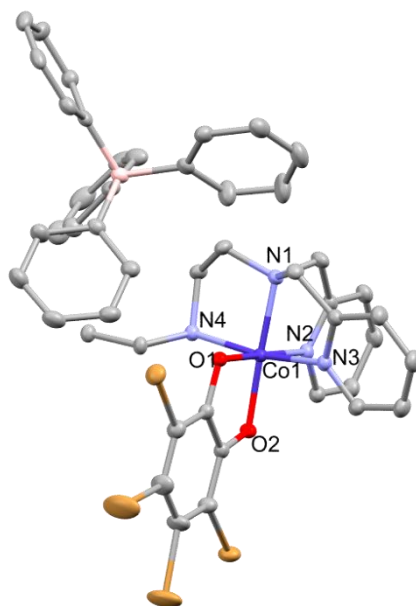


Figure S52: Asymmetric unit cell of **C8** at 120 K. Lattice solvent molecules and hydrogen atoms are omitted for better visibility. The probability level for the displacement of the ellipsoid is 50%. Colour code: carbon (grey), cobalt (dark blue), nitrogen (light blue), oxygen (red), bromine (brown), boron (rosa).

4.1.15.3 π - π interactions

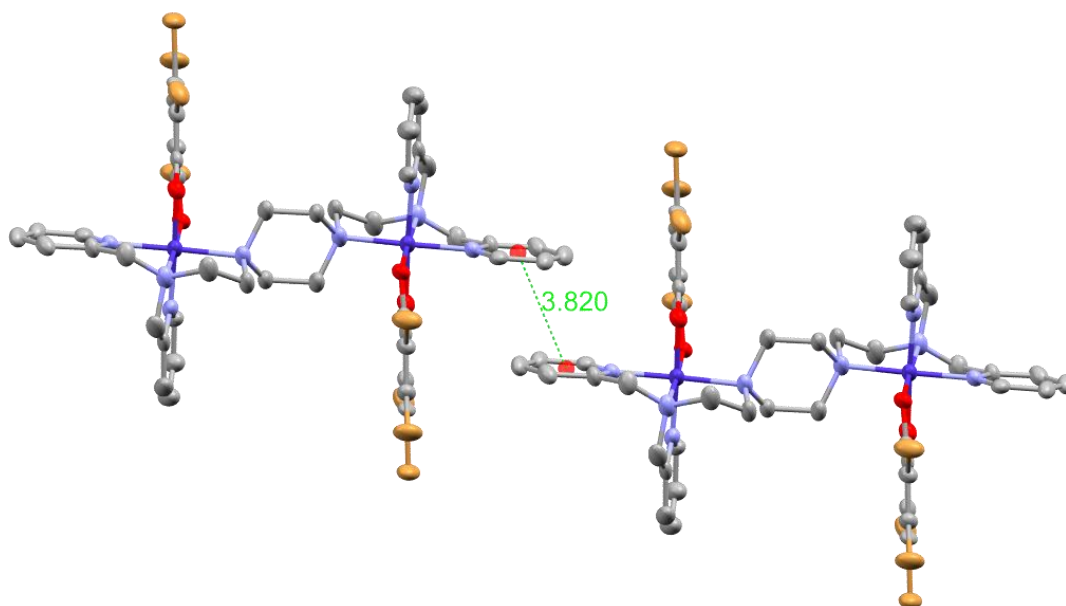


Figure S53: π - π interactions of **C5** with a centroid-to-centroid distance of 3.820 Å, a parallel shift of 1.743 Å and an angle of 0° between both pyridine planes at 120 K. Lattice solvent molecules and hydrogen atoms are omitted for better visibility. The probability level for the displacement of the ellipsoid is 50%. Colour code: carbon (grey), cobalt (dark blue), nitrogen (light blue), oxygen (red), bromine (brown), sulphur (yellow).

4.1.15.4 Hydrogen Bonding Interactions

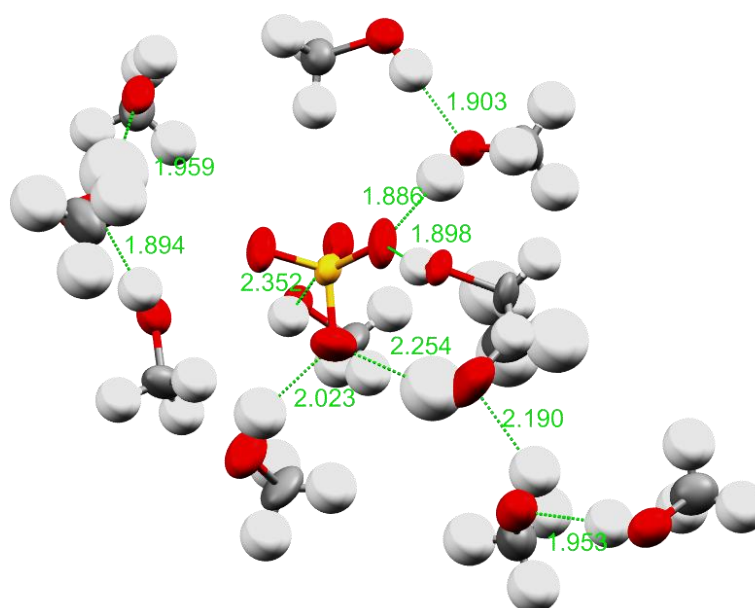


Figure S54: Hydrogen bonding interaction between methanol molecules and the sulphate anion of **C1** at 120 K. Complex fragment was omitted for better visibility. The probability level for the displacement of the ellipsoid is 50%. Colour code: carbon (grey), cobalt (dark blue), nitrogen (light blue), oxygen (red), chloride (green), sulphur (yellow).

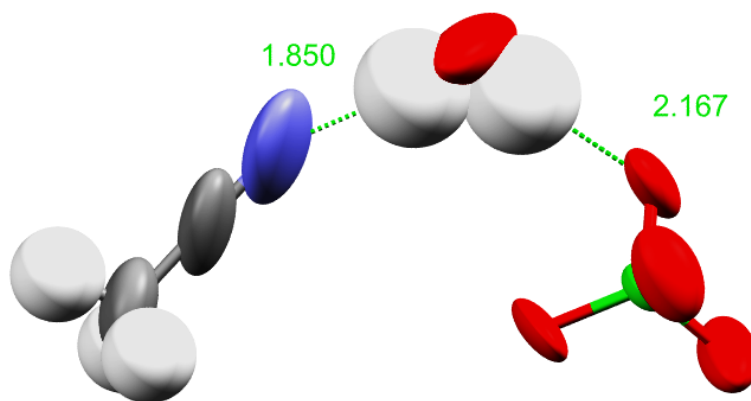


Figure S55: Hydrogen bonding interactions between solvent molecules and anions of **C2** at 120 K. Complex fragment was omitted for better visibility. The probability level for the displacement of the ellipsoid is 50%. Colour code: carbon (grey), cobalt (dark blue), nitrogen (light blue), oxygen (red), chloride (green).

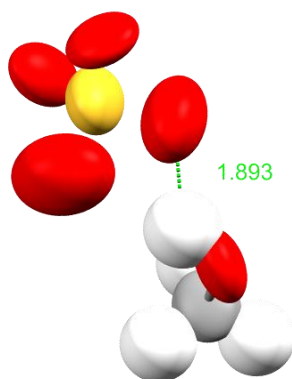


Figure S56: Hydrogen bonding interactions between methanol and sulphate of **C5** at 120 K. Lattice solvent molecules and hydrogen atoms are omitted for better visibility. The probability level for the displacement of the ellipsoid is 50%. Colour code: carbon (grey), cobalt (dark blue), nitrogen (light blue), oxygen (red), bromine (brown), sulphur (yellow).

4.1.15.5 H-F-Bonding Interactions

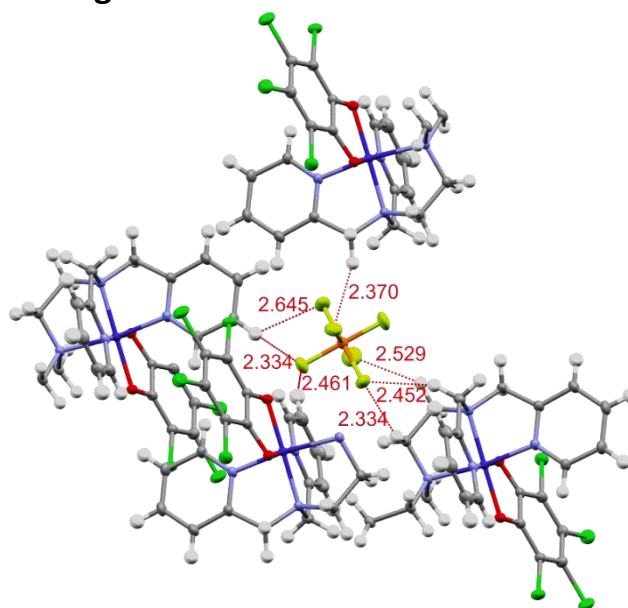


Figure S57: H-F-Bonding interactions of **C3** at 120 K. Lattice solvent molecules and hydrogen atoms are omitted for better visibility. The probability level for the displacement of the ellipsoid is 50%. Colour code: carbon (grey), cobalt (dark blue), nitrogen (light blue), oxygen (red), chloride (green), phosphorous (orange), fluorine (light green).

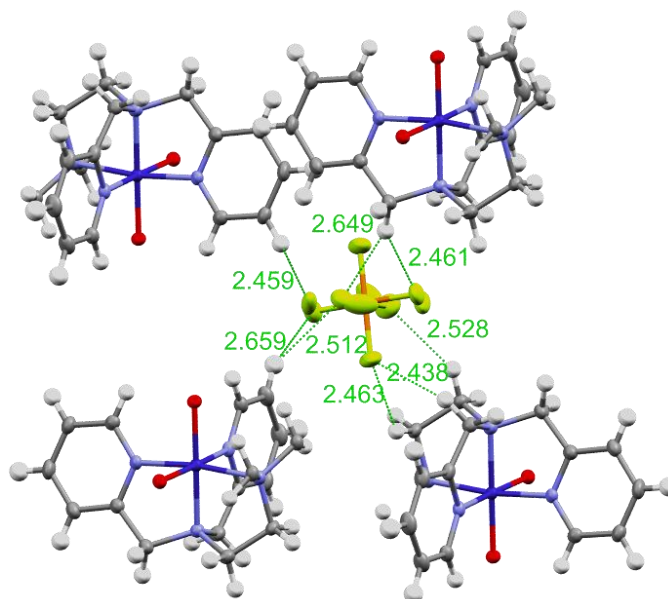


Figure S58: H-F-Bonding interactions of **C7** at 120 K. Lattice solvent are omitted for better visibility. The probability level for the displacement of the ellipsoid is 50%. Colour code: carbon (grey), cobalt (dark blue), nitrogen (light blue), oxygen (red), bromine (brown), phosphorous (orange), fluorine (light green).

4.1.16 Crystallographic planes

In terms of crystal packing, complexes **C3** and **C5-C7** shows a layered structure comprising a complex-anion-complex motif. In **C1** the layers can also be observed, but in the *b*-*c* plane the arrangement in *b* direction as well as in the *c* direction of the complexes are inverted. (**Figure S82**) In the *a*-*b*-plane complex **C1** shows a herringbone pattern but as the packing changes in *c* direction, the 2nd *a*-*b*-plane directly behind shows an inverted herringbone pattern, so that two complexes directly behind each other form a star shaped motif (**Figure S75**).

Complex **C4** also exhibits a herringbone pattern in the *b*-*c*-plane, but here all *b*-*c*-planes are stacked perfectly on top of each other without any inversion like in **C1**. (**Figure S82**) However, due to this herringbone pattern the *a*-*b*-planes are not stacked perfectly, 2 complexes in the *a*-*b*-planes directly behind each other are tilted by 65 degrees angle. (**Figure S77**). Complex **C8** also shows a herringbone pattern in the *a*-*b* plane. But this herringbone pattern is created due to the 2nd *a*-*b* plane behind being inverted (**Figure S81**). The crystallographic parameters, as well as the crystal structures with each plane, asymmetric unit and complete structure are shown in the ESI. (**Figures S53-S97, Tables S2-20**).

C8 also shows a herringbone pattern in the *a*-*b* plane. But this herringbone pattern is created due to the 2nd *a*-*b* plane behind being inverted as well as slightly shifted (**Figure S82**). The crystallographic parameters, as well as the crystal structures with every plane, asymmetric unit and complete structure are shown in the ESI. (**Figures S54-S98, Tables S2-20**).

4.1.16.1 A-B-plane

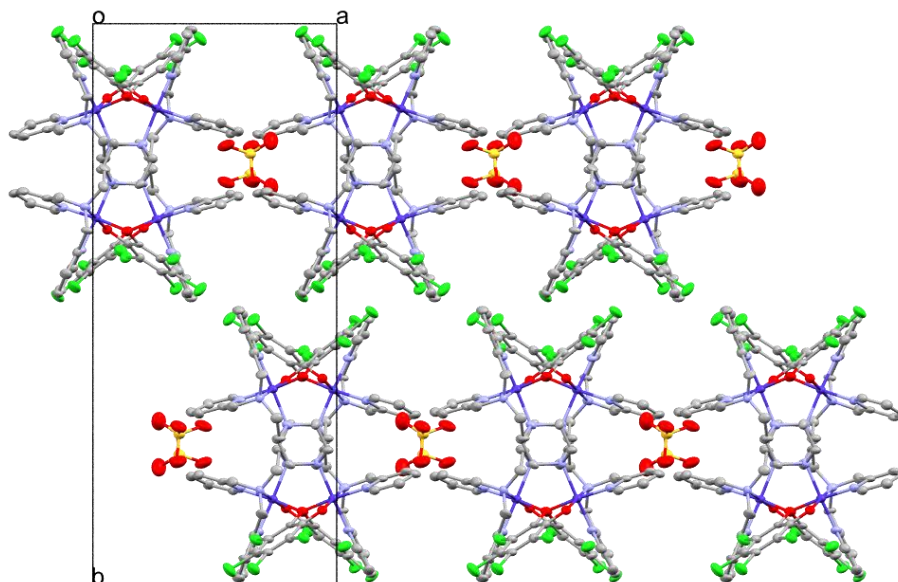


Figure S59: Crystal packing of **C1** view along *c*-axis. Lattice solvent molecules and hydrogen atoms are omitted for better visibility.

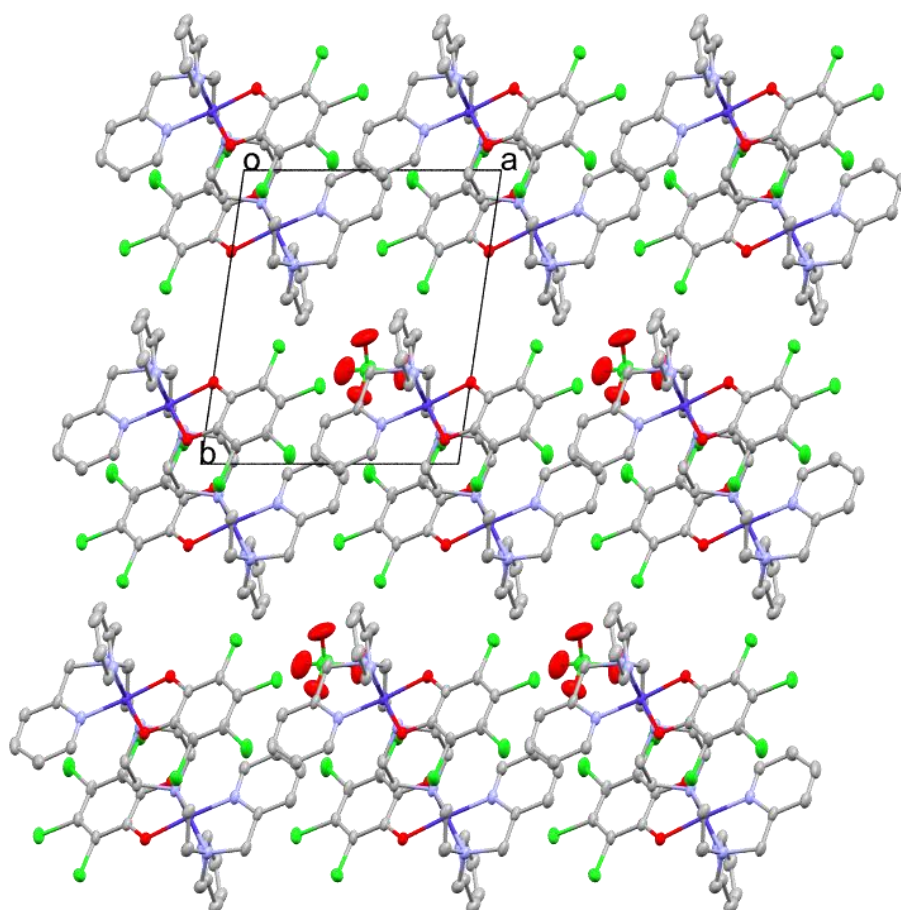


Figure S60: Crystal packing of **C2** view along *c*-axis. Lattice solvent molecules and hydrogen atoms are omitted for better visibility.

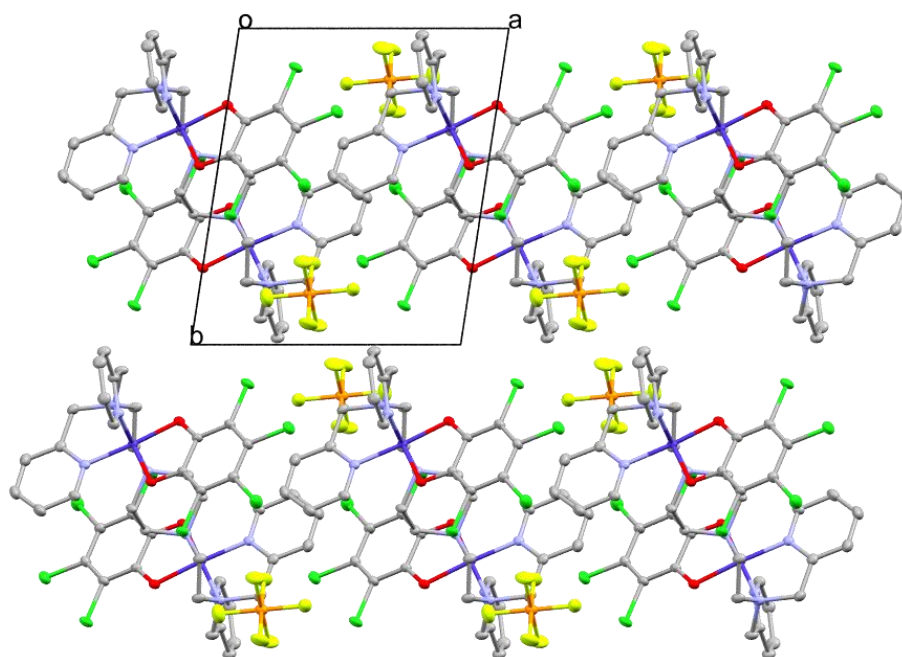


Figure S61: Crystal packing of **C3** view along c-axis. Lattice solvent molecules and hydrogen atoms are omitted for better visibility.

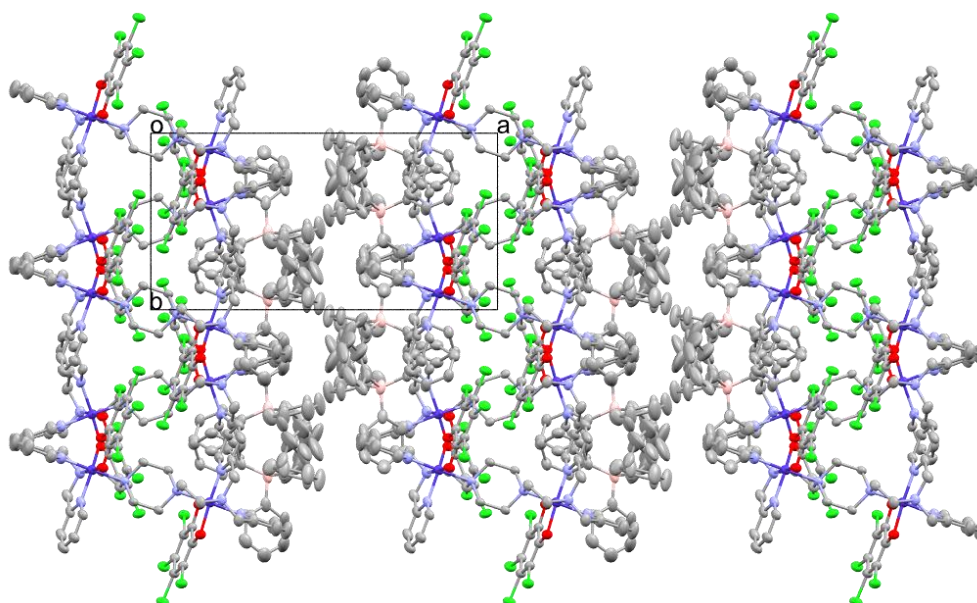


Figure S62: Crystal packing of **C4** view along c-axis. Lattice solvent molecules and hydrogen atoms are omitted for better visibility.

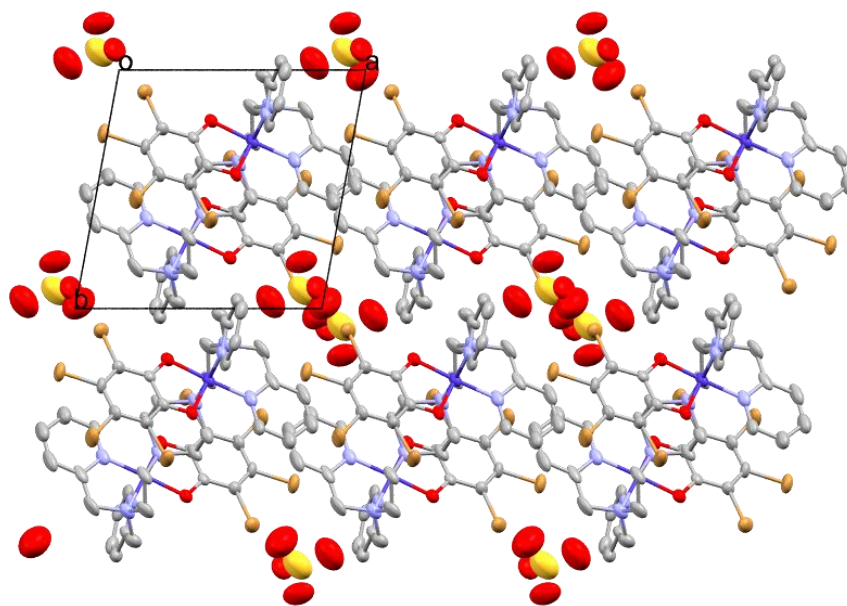


Figure S63: Crystal packing of **C5** view along *c*-axis. Lattice solvent molecules and hydrogen atoms are omitted for better visibility.

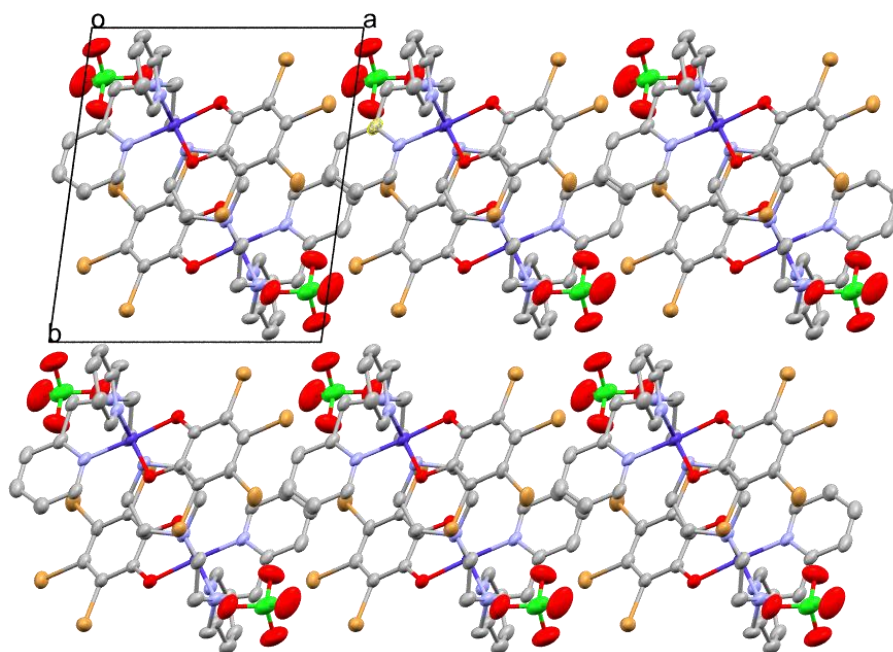


Figure S64: Crystal packing of **C6** view along *c*-axis. Lattice solvent molecules and hydrogen atoms are omitted for better visibility.

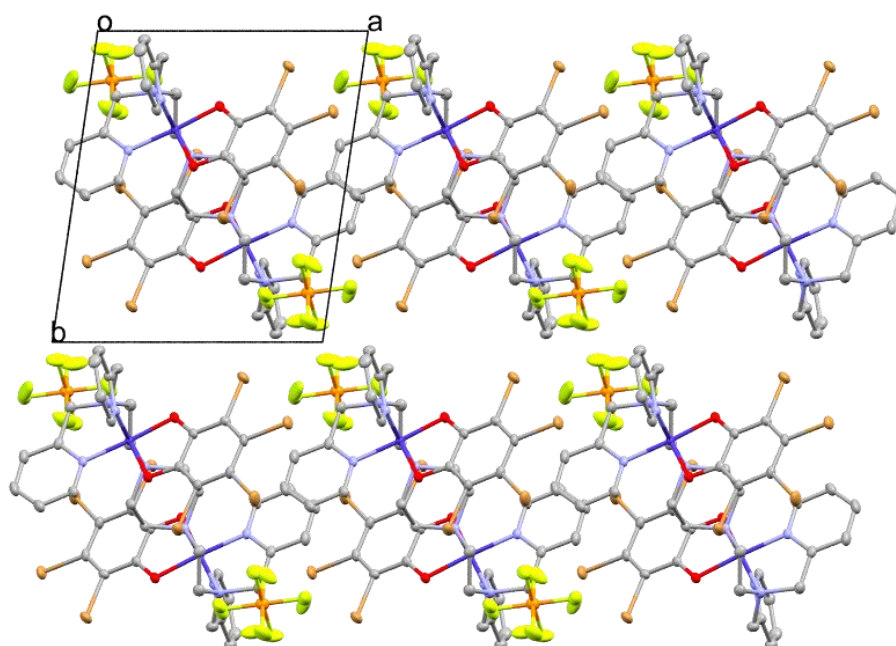


Figure S65: Crystal packing of **C7** view along *c*-axis. Lattice solvent molecules and hydrogen atoms are omitted for better visibility.

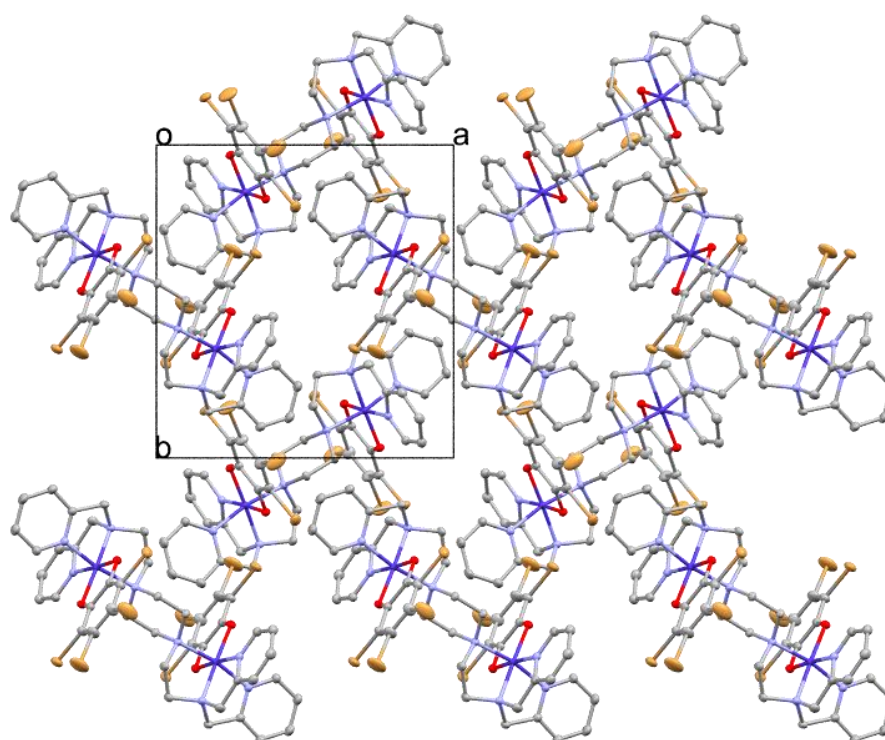


Figure S66: Crystal packing of **C8** view along *c*-axis. Lattice solvent molecules, anions and hydrogen atoms are omitted for better visibility.

4.1.16.2 B-C-Plane

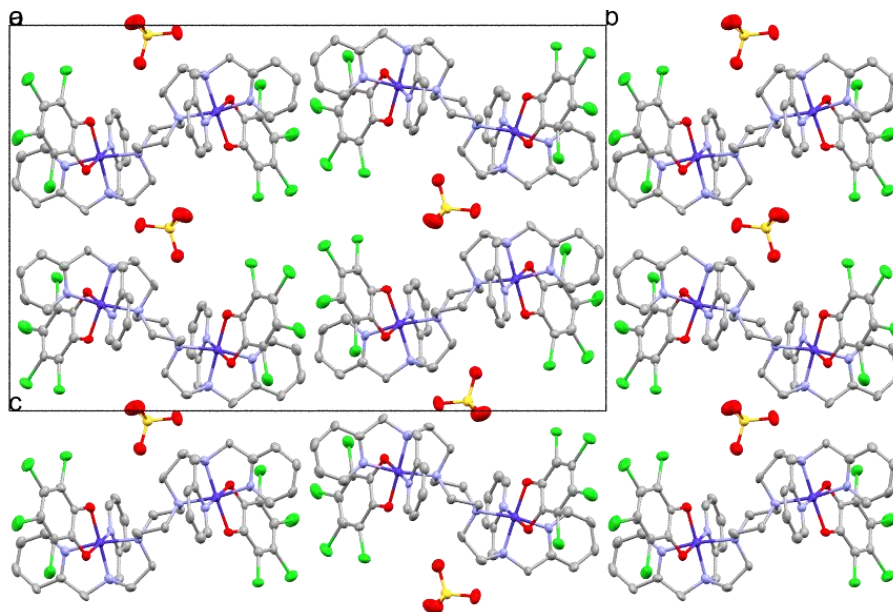


Figure S67: Crystal packing of **C1** view along *a*-axis. Lattice solvent molecules and hydrogen atoms are omitted for better visibility.

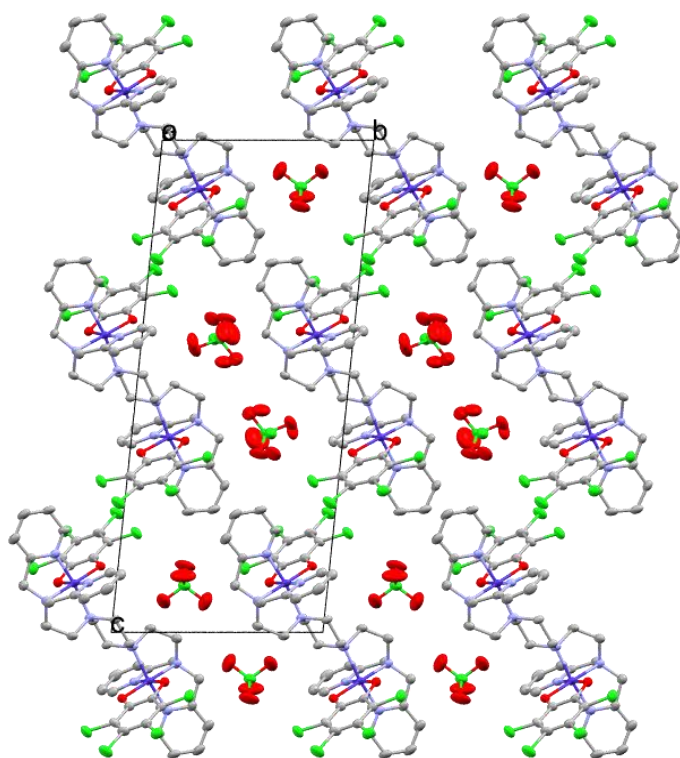


Figure S68: Crystal packing of **C2** view along *a*-axis. Lattice solvent molecules and hydrogen atoms are omitted for better visibility.

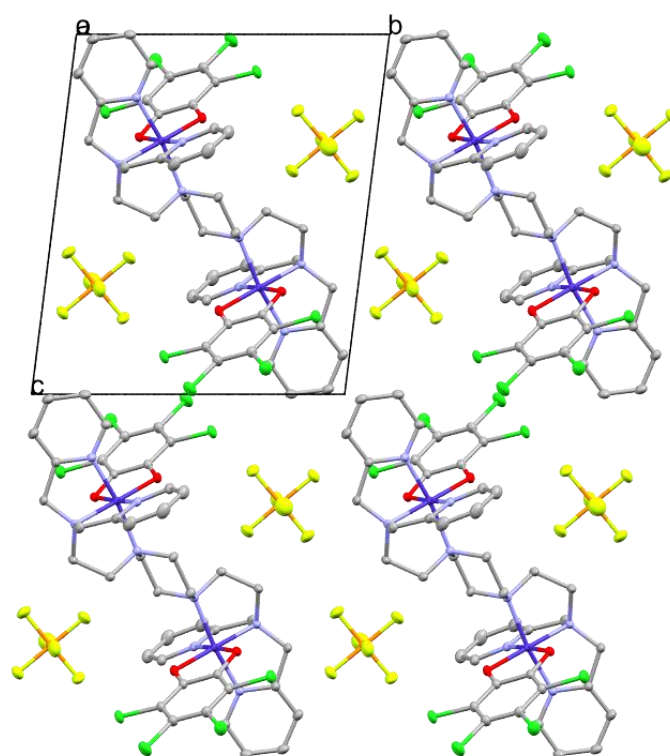


Figure S69: Crystal packing of **C3** view along *a*-axis. Lattice solvent molecules and hydrogen atoms are omitted for better visibility.

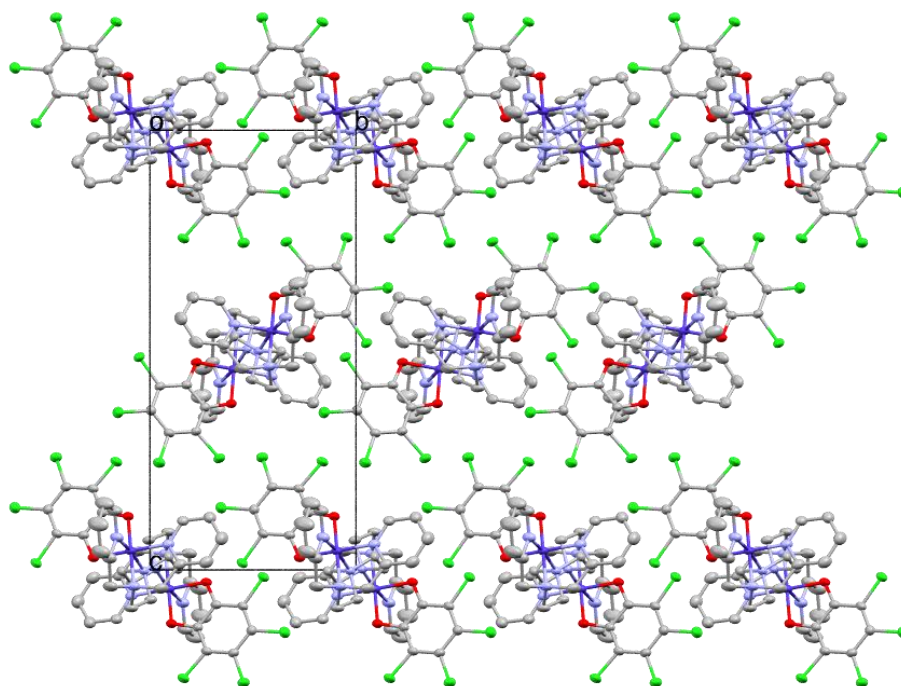


Figure S70: Crystal packing of **C4** view along *a*-axis. Lattice solvent molecules, anions and hydrogen atoms are omitted for better visibility.

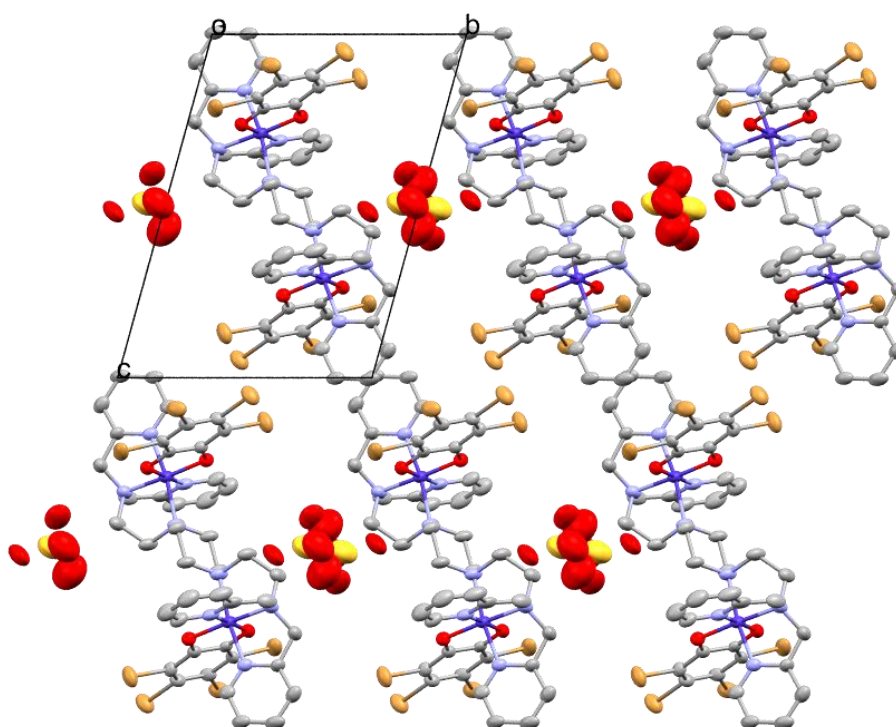


Figure S71: Crystal packing of **C5** view along *a*-axis. Lattice solvent molecules and hydrogen atoms are omitted for better visibility.

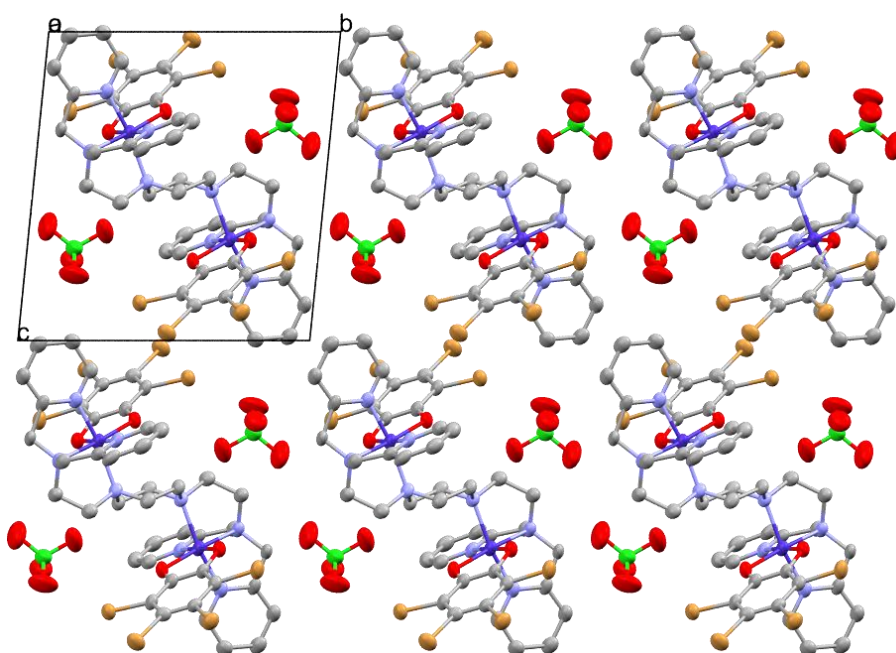


Figure S72: Crystal packing of **C6** view along *a*-axis. Lattice solvent molecules and hydrogen atoms are omitted for better visibility.

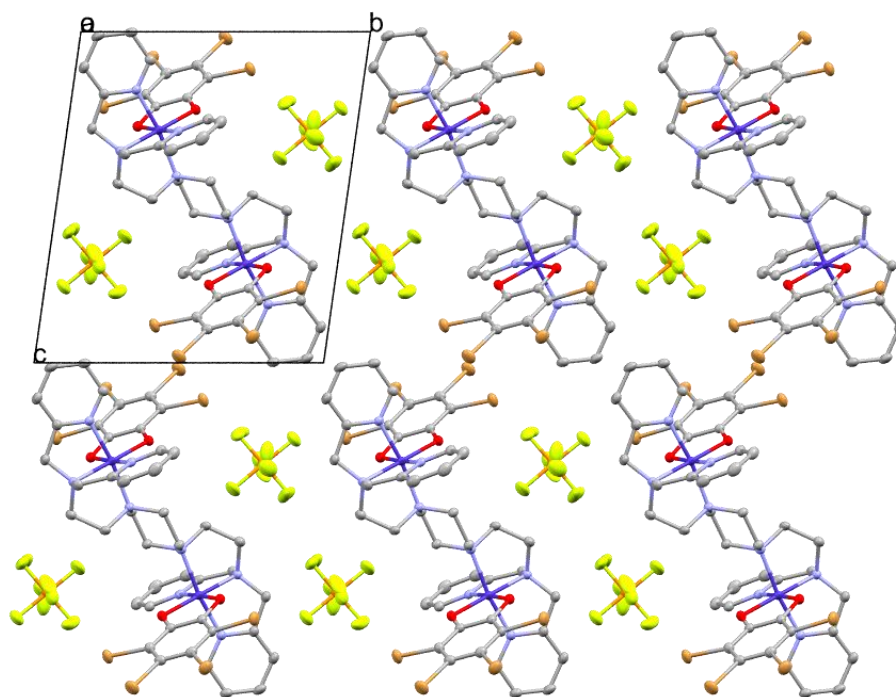


Figure S73: Crystal packing of **C7** view along *a*-axis. Lattice solvent molecules and hydrogen atoms are omitted for better visibility.

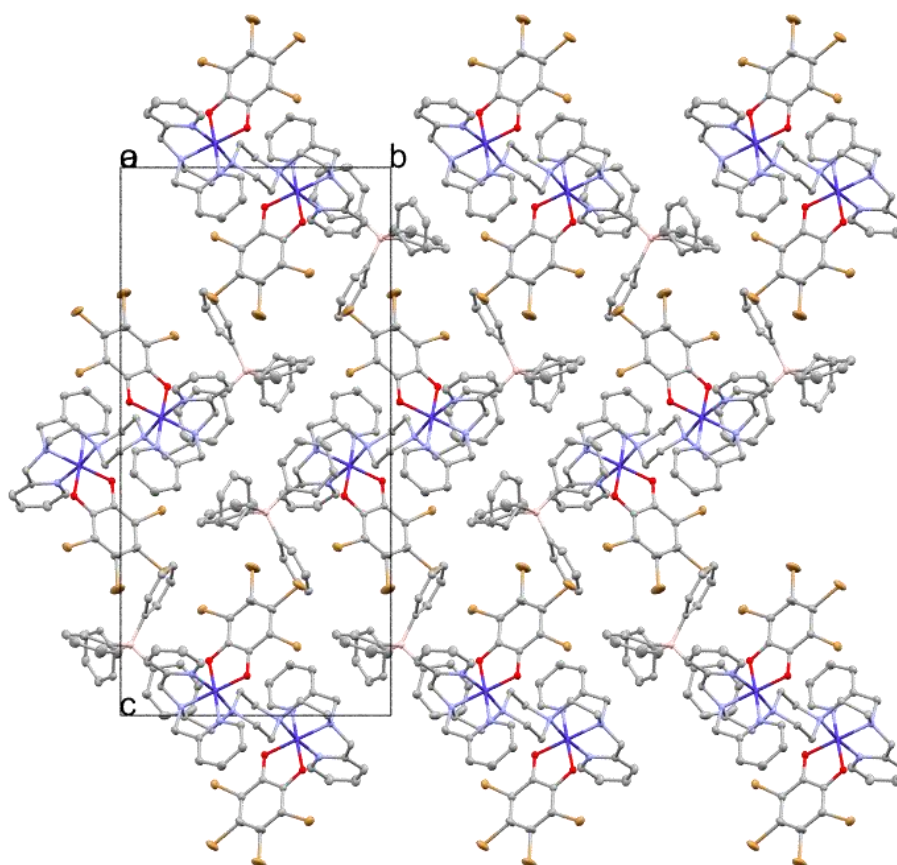


Figure S74: Crystal packing of **C8** view along *a*-axis. Lattice solvent molecules and hydrogen atoms are omitted for better visibility.

4.1.16.3 A-C-Plane

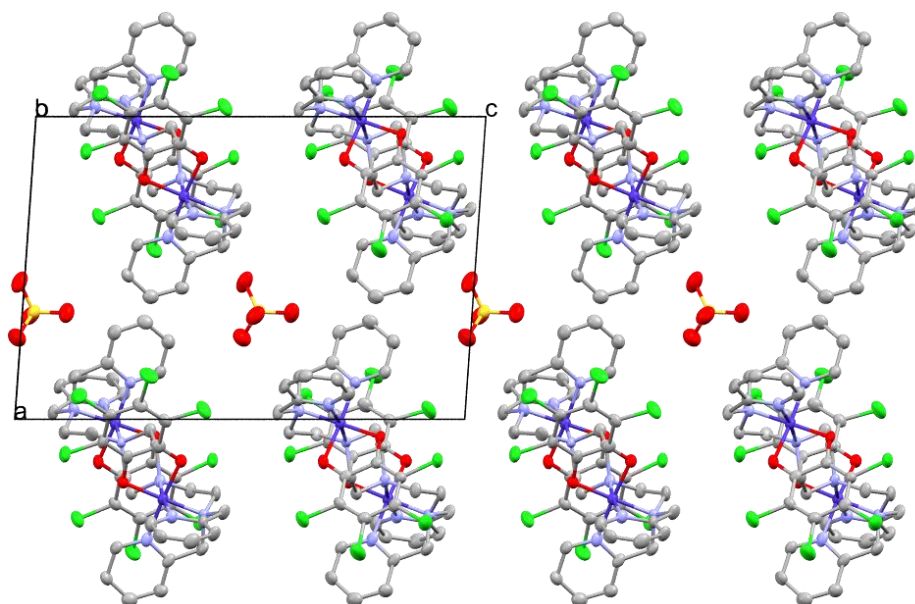


Figure S75: Crystal packing of **C1** view along *b*-axis. Lattice solvent molecules and hydrogen atoms are omitted for better visibility.

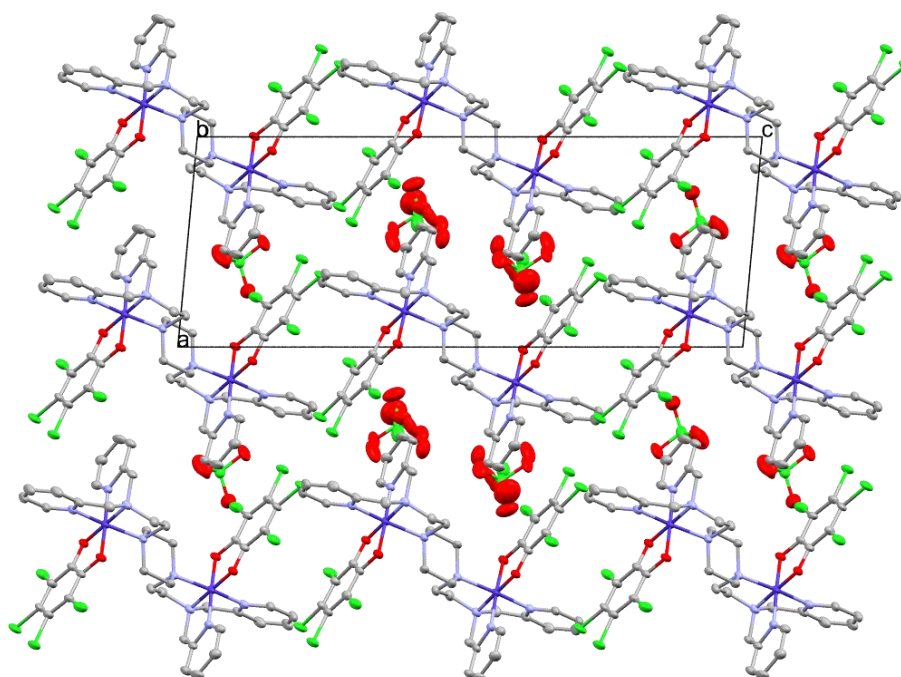


Figure S76: Crystal packing of **C2** view along *b*-axis. Lattice solvent molecules and hydrogen atoms are omitted for better visibility.

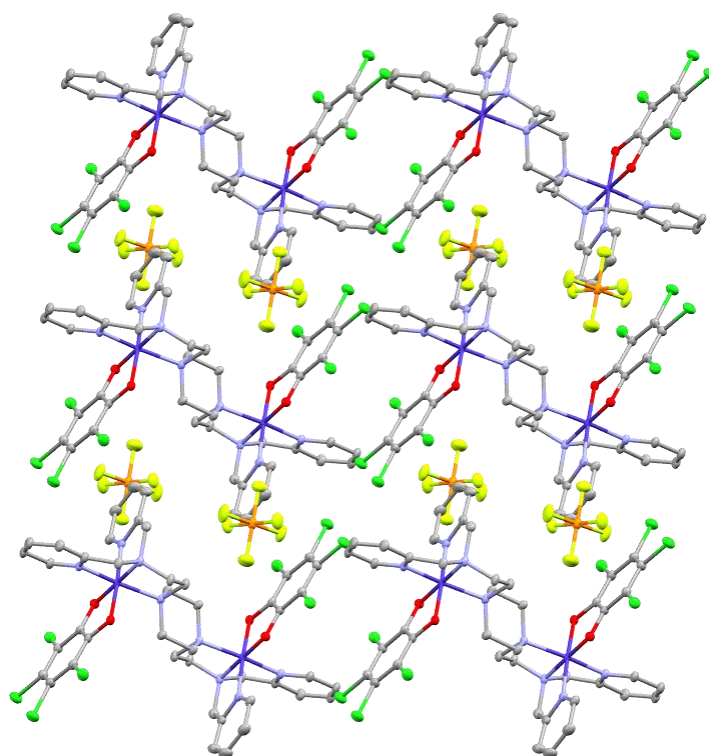


Figure S77: Crystal packing of **C3** view along b-axis. Lattice solvent molecules and hydrogen atoms are omitted for better visibility.

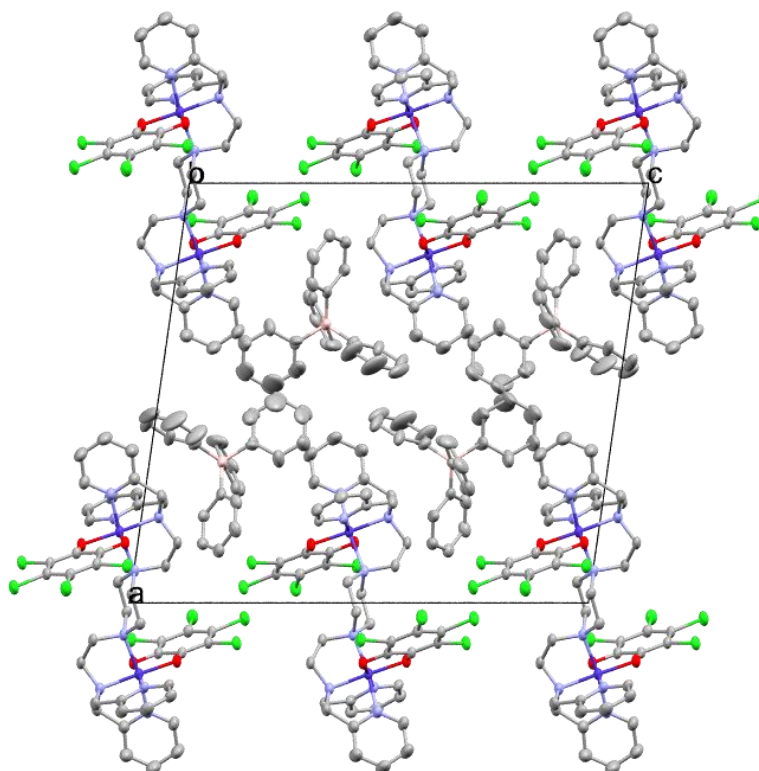


Figure S78: Crystal packing of **C4** view along b-axis. Lattice solvent molecules and hydrogen atoms are omitted for better visibility.

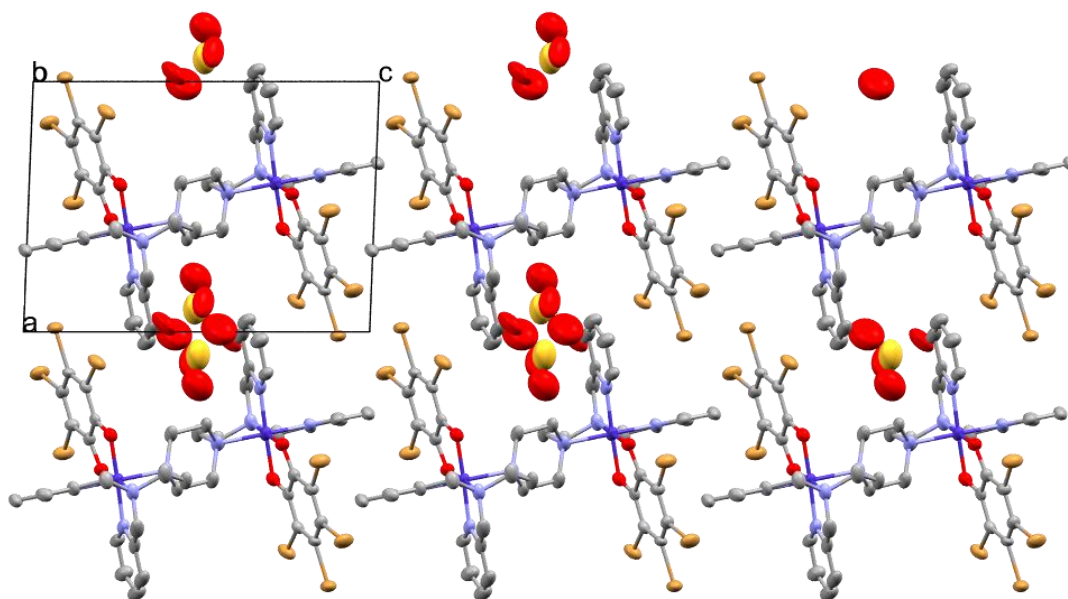


Figure S79: Crystal packing of **C5** view along *b*-axis. Lattice solvent molecules and hydrogen atoms are omitted for better visibility.

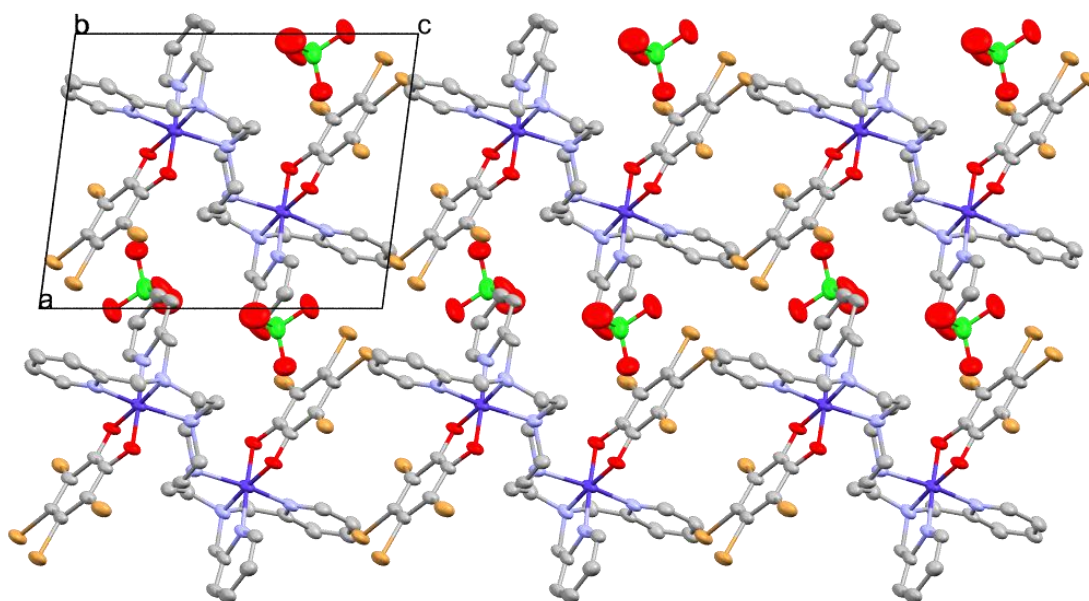


Figure S80: Crystal packing of **C6** view along *b*-axis. Lattice solvent molecules and hydrogen atoms are omitted for better visibility.

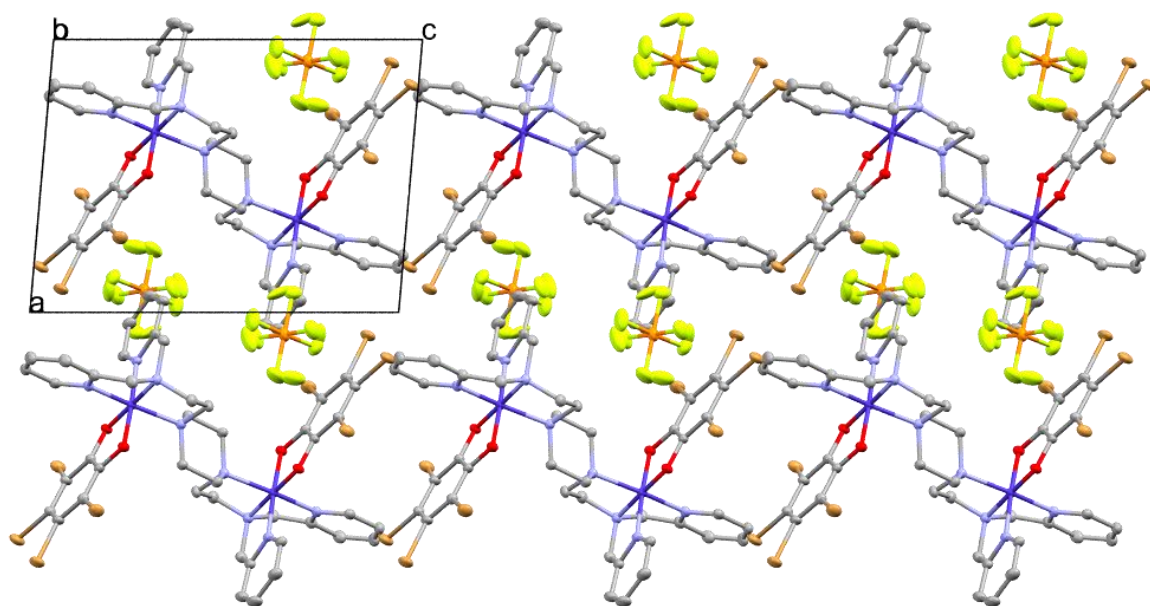


Figure S81: Crystal packing of **C7** view along *b*-axis. Lattice solvent molecules and hydrogen atoms are omitted for better visibility.

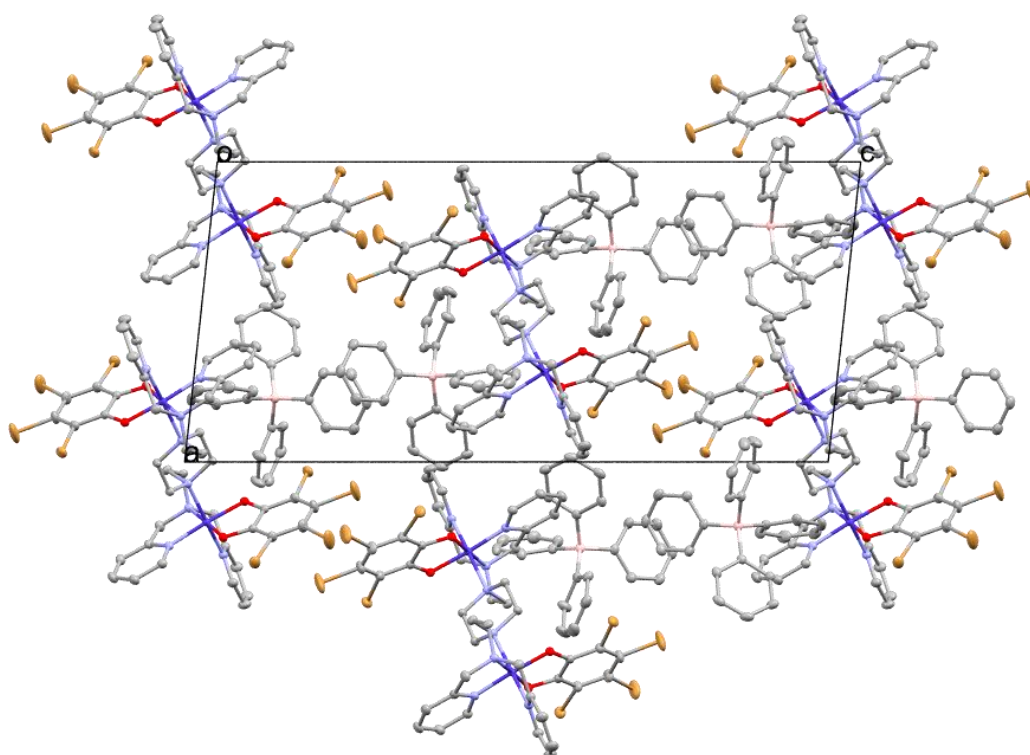


Figure S82: Crystal packing of **C8** view along *b*-axis. Lattice solvent molecules and hydrogen atoms are omitted for better visibility.

4.1.17 Cyclovoltammetric Scan Rate Studies

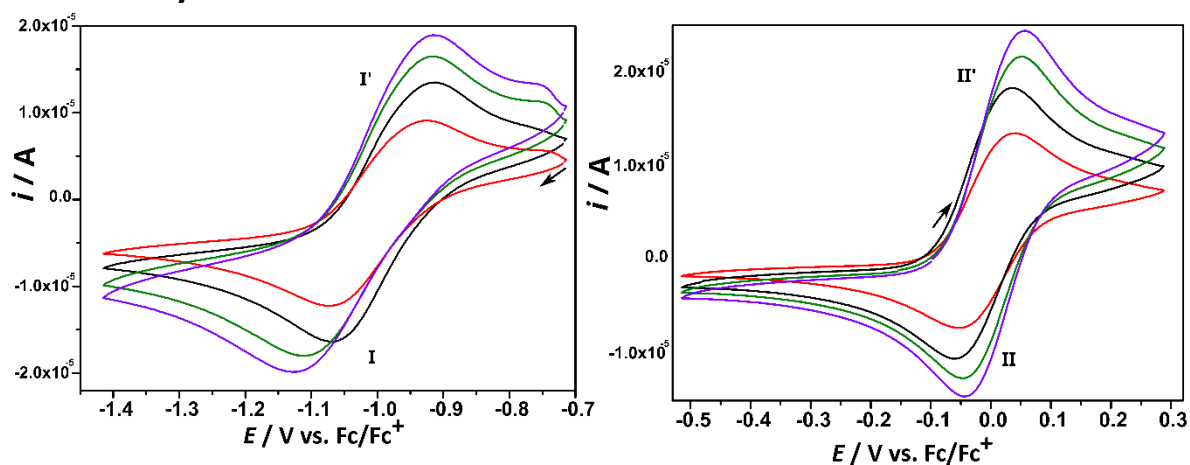


Figure S83: Cyclic voltammogram of previously reported **C9** $[\text{Co}_2(\text{L})(\text{dbucat})_2] (\text{ClO}_4)_2 \cdot 1.5 \text{ H}_2\text{O}$ [1] in acetonitrile ($1 \times 10^{-3} \text{ M}$, 0.1 M $n\text{-Bu}_4\text{PF}_6$) obtained with different scan rates (50 mV s^{-1} (red), 100 mV s^{-1} (black), 150 mV s^{-1} (green), 200 mV s^{-1} (purple)) of redox process (I/I') **left** and redox process (II/II') **right**, measured with a glassy carbon working electrode and a silver wire reference electrode, referenced against the internal redoxpair of Fc/Fc^+ .

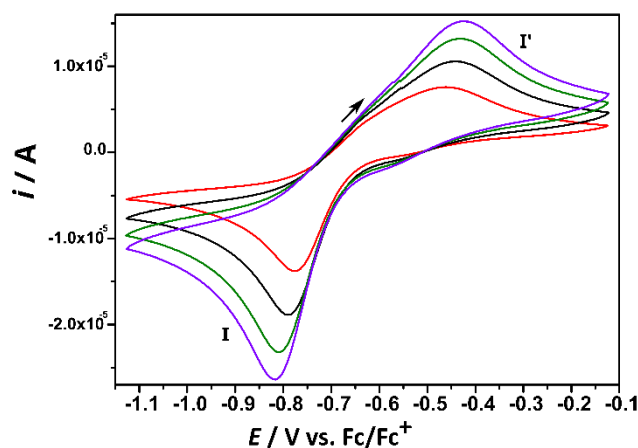


Figure S84: Cyclic voltammogram of **C2** $\cdot 3.5 \text{ H}_2\text{O}$ in acetonitrile ($1 \times 10^{-3} \text{ M}$, 0.1 M $n\text{-Bu}_4\text{PF}_6$) obtained at different scan rates (50 mV s^{-1} (red), 100 mV s^{-1} (black), 150 mV s^{-1} (green), 200 mV s^{-1} (purple)) of redox process (I/I') with a glassy carbon working electrode and a silver wire reference electrode referenced internally against the redoxpair Fc/Fc^+ .

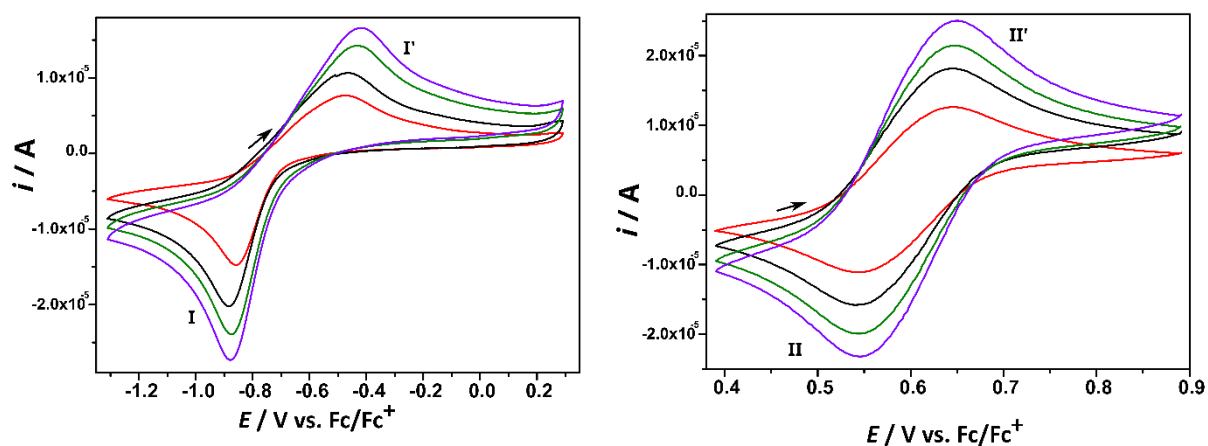


Figure S85: Cyclic voltammogram of $\text{C6} \cdot 1.5 \text{H}_2\text{O}$ in acetonitrile ($1 \times 10^{-3} \text{ M}$, $0.1 \text{ M n-Bu}_4\text{PF}_6$) obtained with different scan rates (50 mV s^{-1} (red), 100 mV s^{-1} (black), 150 mV s^{-1} (green), 200 mV s^{-1} (purple)) of redox process (I/I') **left** and redox process (II/II') **right** with a glassy carbon working electrode and a silver wire reference electrode referenced internally against the redox pair Fc/Fc^+ .

4.1.18 Magnetic Susceptibility Measurements

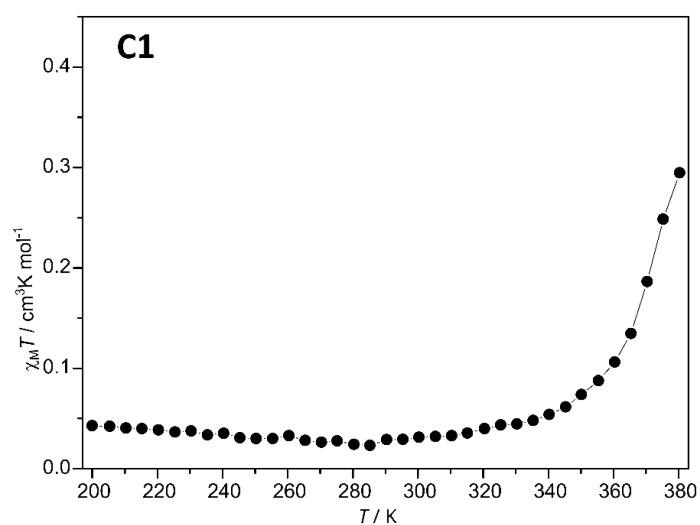


Figure S86: Temperature dependent $\chi_M T$ plot of **C1**· 8 H₂O over the temperature range of 200–380 K.

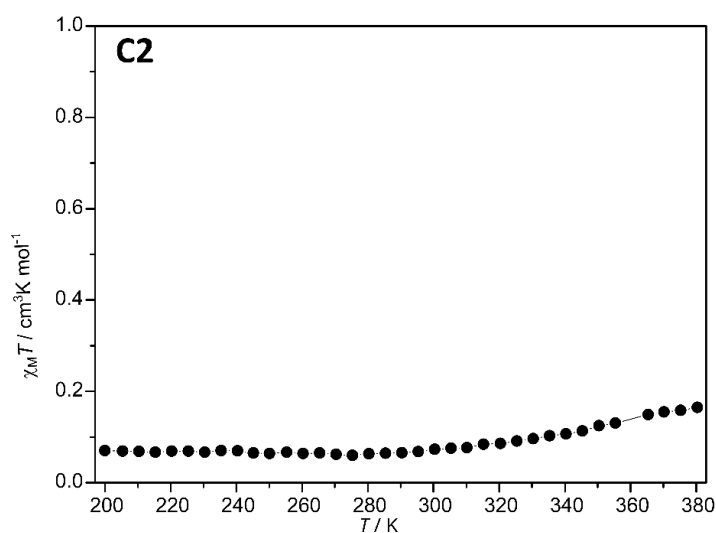


Figure S87: Temperature dependent $\chi_M T$ plot of **C2**· 3.5 H₂O over the temperature range of 200–380 K.

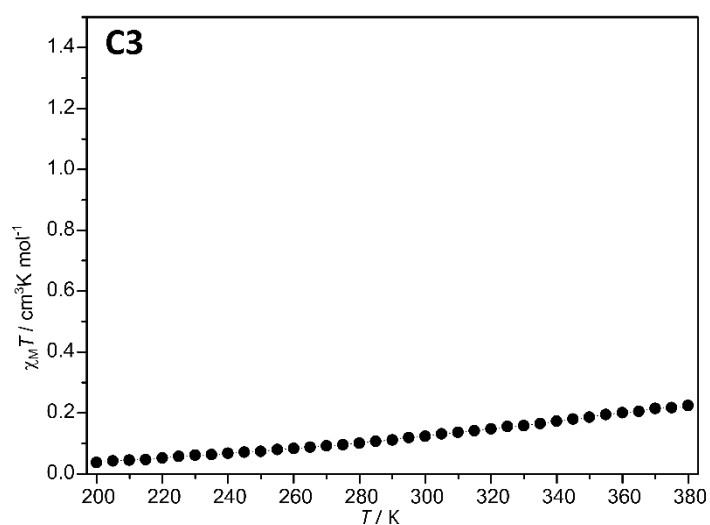


Figure S88: Temperature dependent $\chi_M T$ plot of **C3**· 6.5 H₂O over the temperature range of 200–380 K.

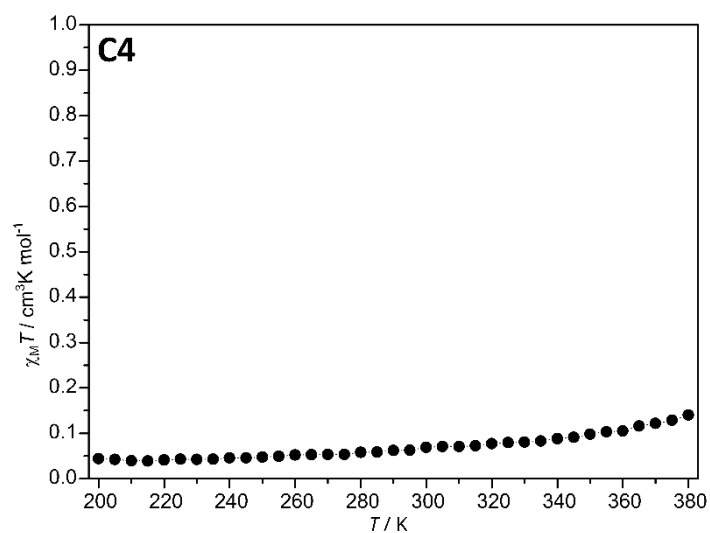


Figure S89: Temperature dependent $\chi_M T$ plot of **C4**· 2 H₂O over the temperature range of 200-380 K.

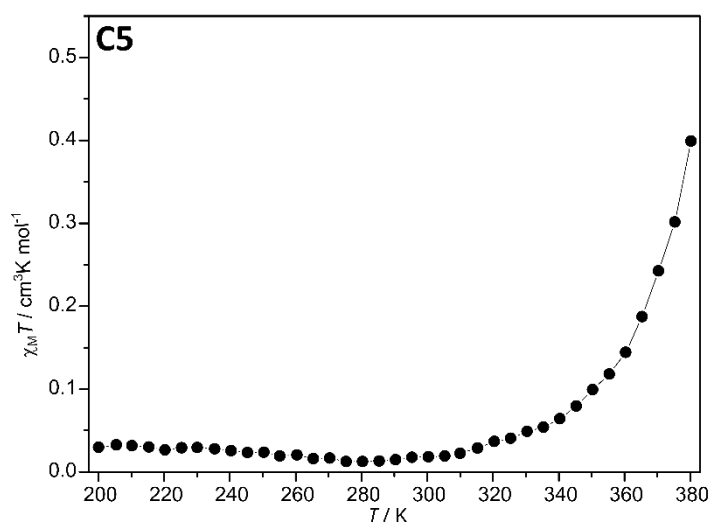


Figure S90: Temperature dependent $\chi_M T$ plot of **C5**· 5.5 H₂O· 1 CHCl₃ over the temperature range of 200-380 K.

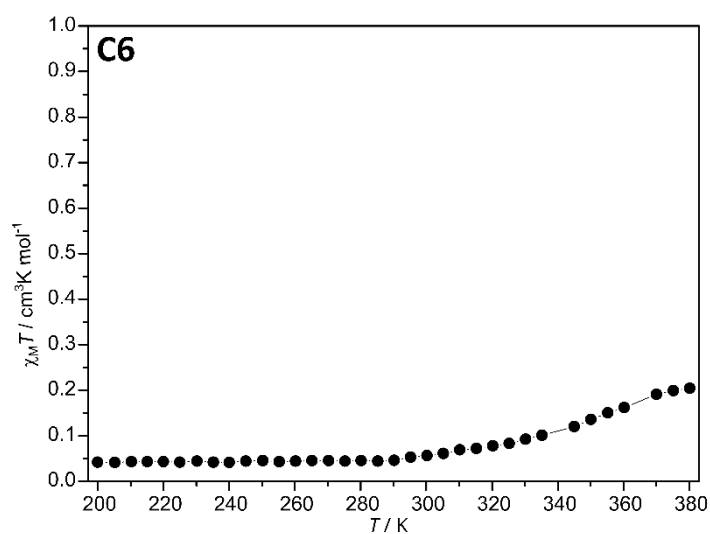


Figure S91: Temperature dependent $\chi_M T$ plot of **C6**· 1.5 H₂O over the temperature range of 200-380 K.

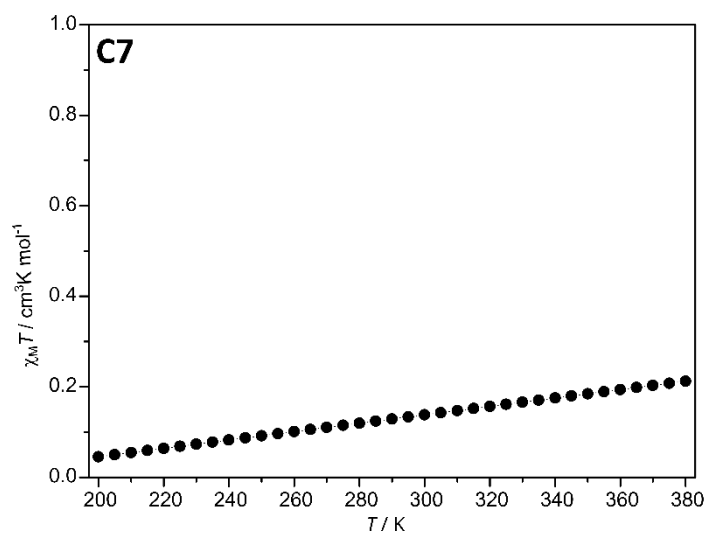


Figure S92: Temperature dependent $\chi_M T$ plot of **C7**· 1.25 H₂O over the temperature range of 200–380 K.

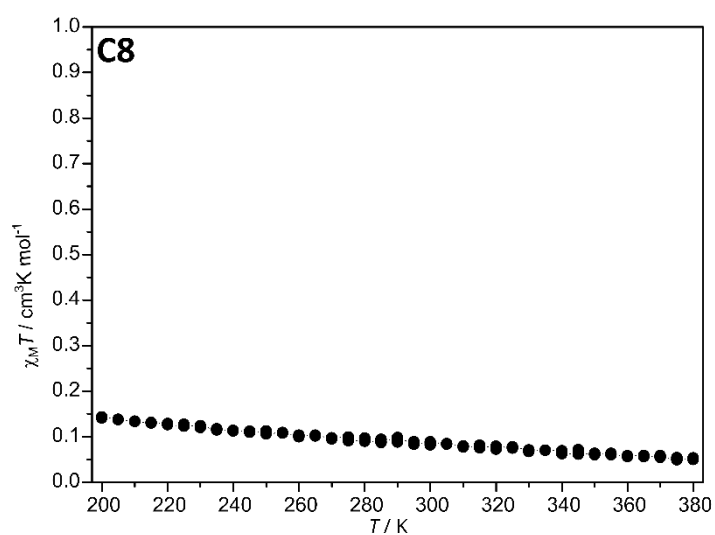


Figure S93: Temperature dependent $\chi_M T$ plot of **C8**· 1 H₂O over the temperature range of 200–380 K.

4.1.19 UV-VIS-Spectroscopy

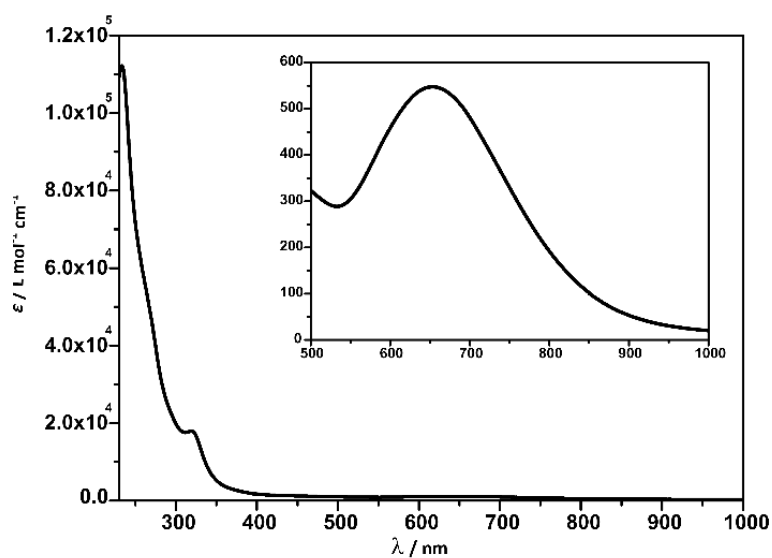


Figure S94: UV-VIS absorption spectra for **C2** 0.1 mM in MeCN with a zoomed-in section from 500 to 1000 nm at a higher concentration of 1mM.

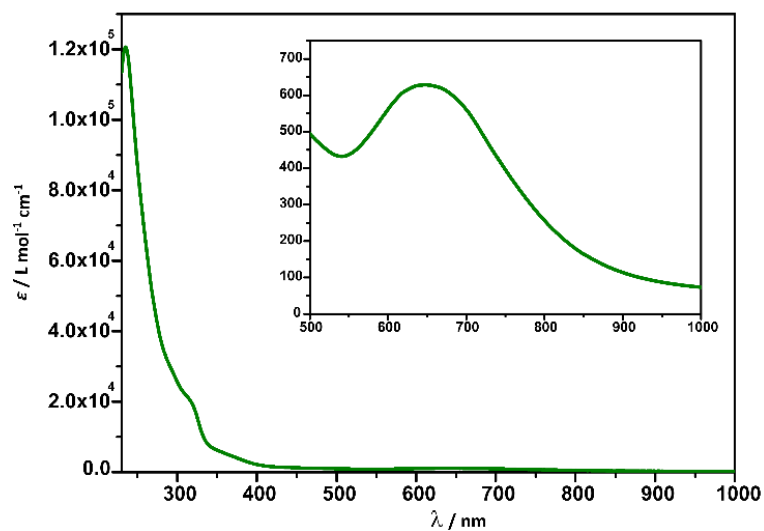


Figure S95: UV-VIS absorption spectra for **C6** 0.01 mM in MeCN with a zoomed-in section from 500 to 1000 nm at a higher concentration of 1mM.

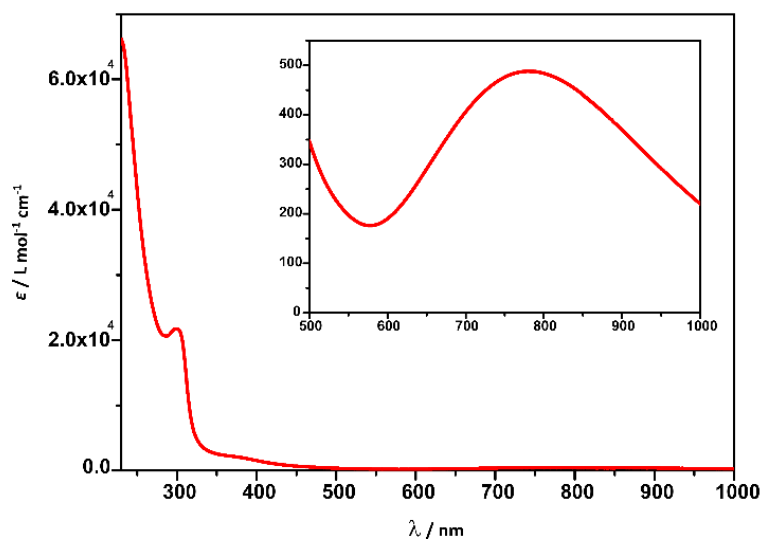


Figure S96: UV-VIS absorption spectra of $[\text{Co}_2(\text{L})(\text{dbucat})_2](\text{ClO}_4)_2 \cdot 1.5 \text{ H}_2\text{O}$ 0.01 mM in MeCN with a zoomed-in section from 500 to 1000 nm at a higher concentration of 1mM.

Table S31: Tabulated molar extinction coefficients in ($\text{L mol}^{-1}\text{cm}^{-1}$) at their respective wavelength in nm for complexes **C2** and **C6**.

C2	C6	$[\text{Co}_2(\text{L})(\text{dbucat})_2](\text{ClO}_4)_2 \cdot 1.5 \text{ H}_2\text{O}$
112185 (233 nm)	120632 (236 nm)	21746 (299 nm)
17921 (319 nm)	20065 (318 nm)	2058 (378 nm)
548 (654 nm)	629 (652 nm)	488 (781 nm)

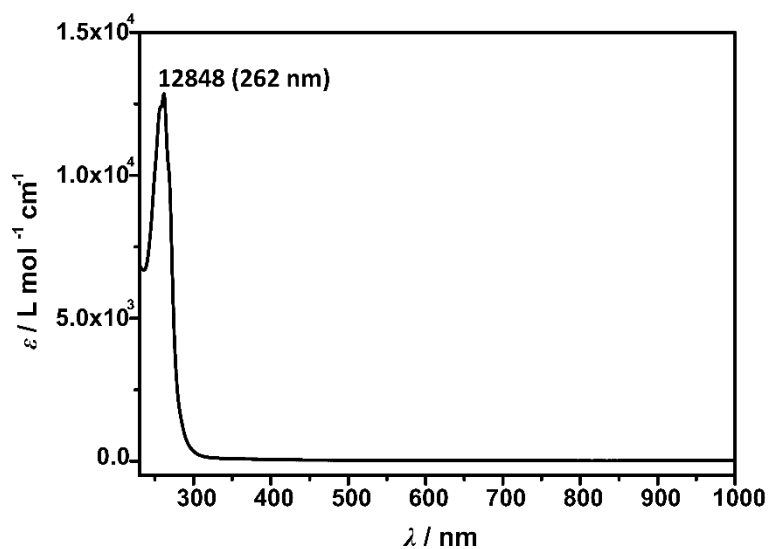


Figure S97: UV-VIS absorption spectra of **L** 0.1 mM in MeCN at RT.

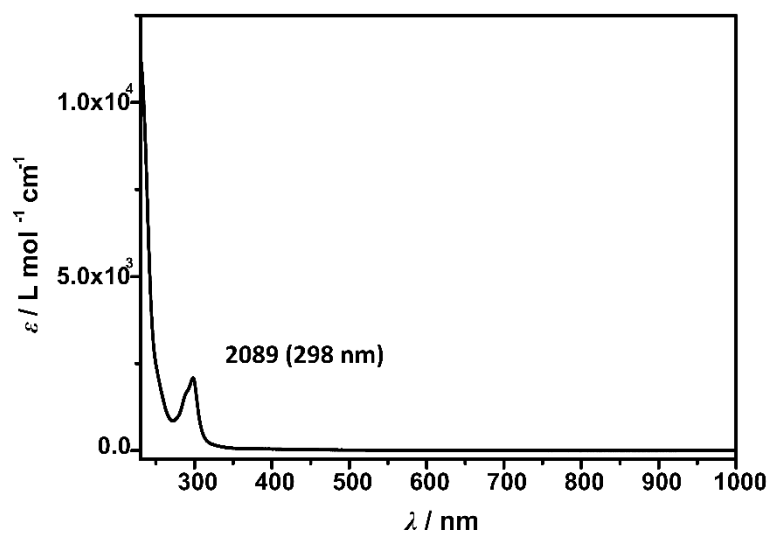


Figure S98: UV-VIS absorption spectra of **Cl4-cat** 0.1 mM in MeCN at RT.

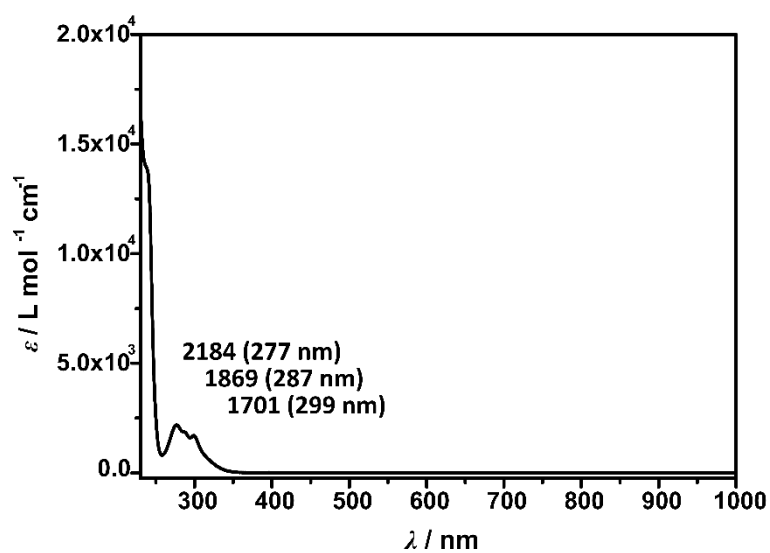


Figure S99: UV-VIS absorption spectra of **Br4-cat** 0.1 mM in MeCN at RT.

4.1.20 Evans Method NMR

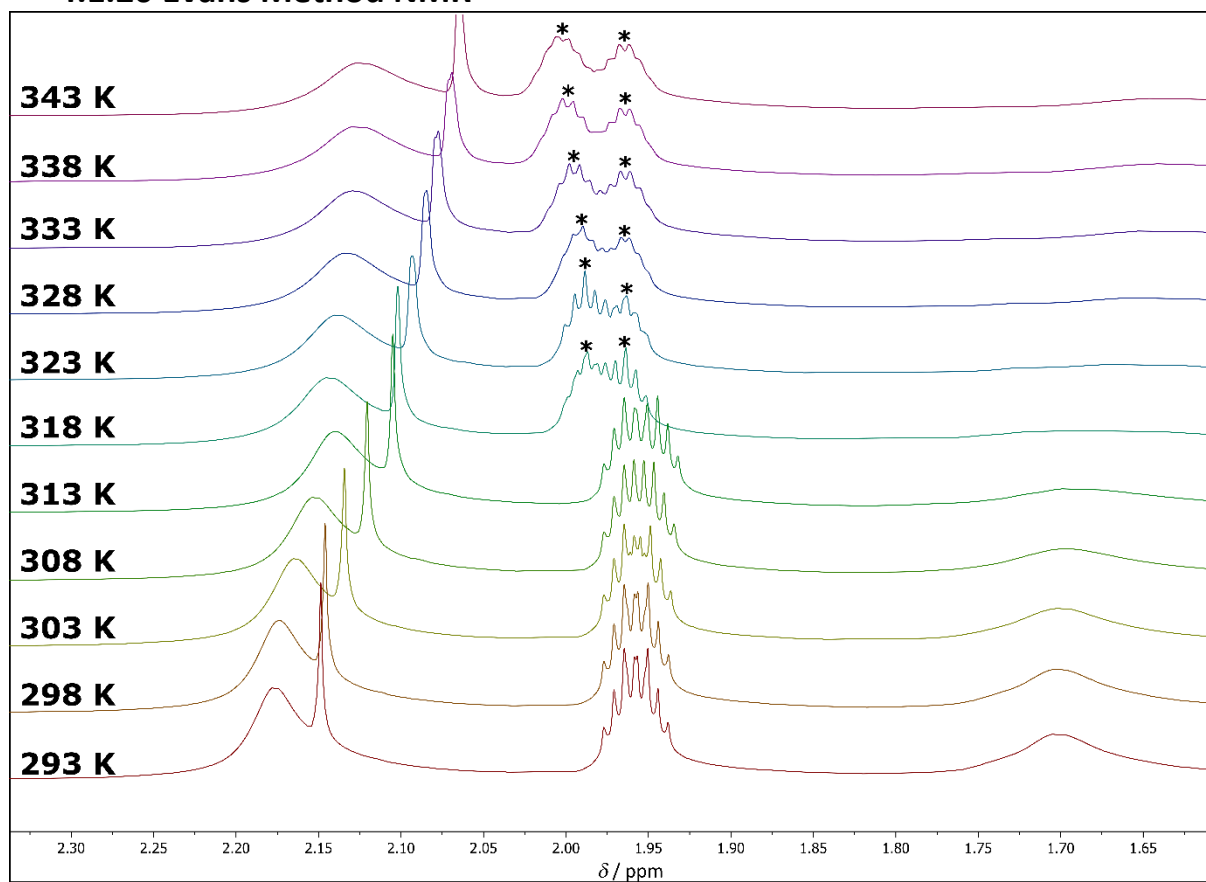


Figure S100: Evans method ^1H NMR (6 mM) at variable temperatures of previously reported $[\text{Co}_2(\text{L})(\text{dbucat})_2] (\text{ClO}_4)_2 \cdot 1.5 \text{H}_2\text{O}[1]$ over a temperature range of 293K to 343K in acetonitrile [400 MHz] in 5K steps.

Table S32: Evans method ^1H NMR Data for of previously reported $[\text{Co}_2(\text{L})(\text{dbucat})_2] (\text{ClO}_4)_2 \cdot 1.5 \text{H}_2\text{O}[1]$ over a temperature range of 293K to 343K in acetonitrile [400MHz] in 5K steps.

T / K	$\chi_M T / \text{cm}^3 \text{Kmol}^{-1}$	$\Delta f / \text{Hz}$
293	0.194	0.00
298	0.207	0.75
303	0.221	1.50
308	0.236	2.30
313	0.254	3.25
318	0.345	9.07
323	0.366	10.1
328	0.393	11.3
333	0.416	12.4
338	0.445	13.9
343	0.478	15.2

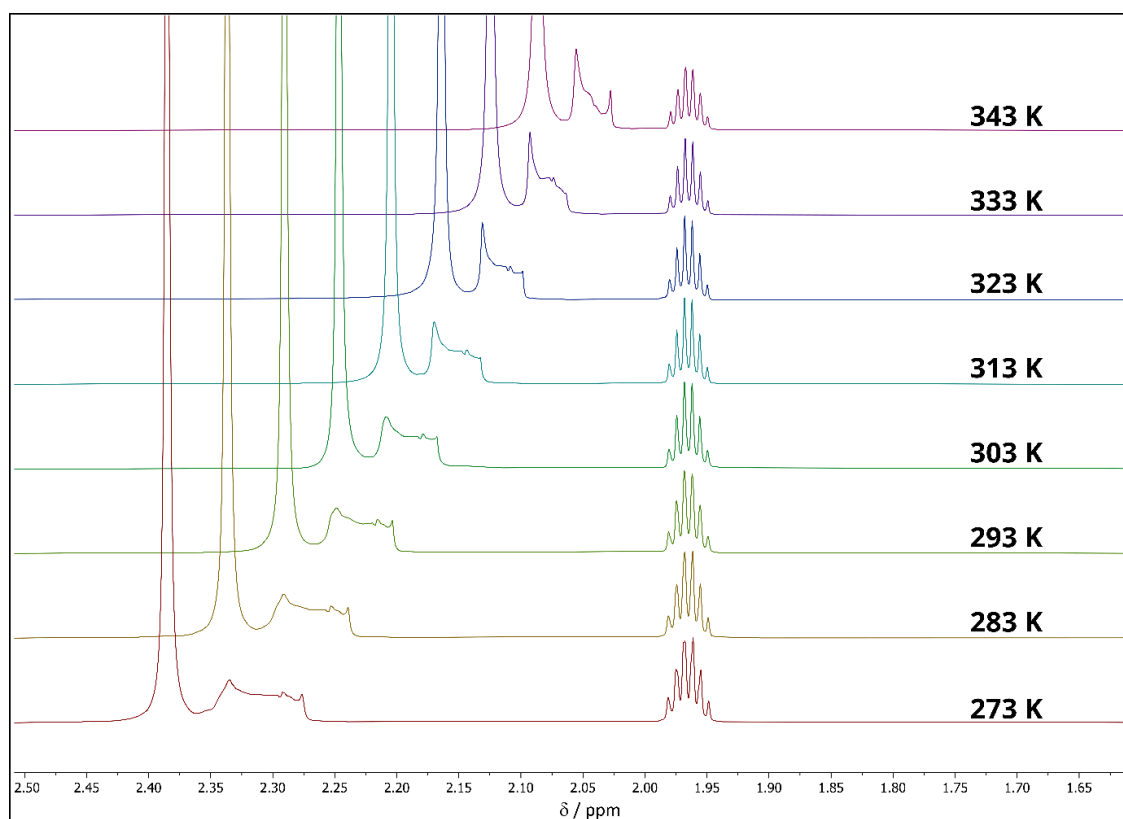


Figure S101: Evans method ^1H NMR (6 mM) at variable temperatures of **C3** over a temperature range of 273K to 343K in acetonitrile [400 MHz] in 10K steps staying diamagnetic, showing no VT transition over the observed temperature range.

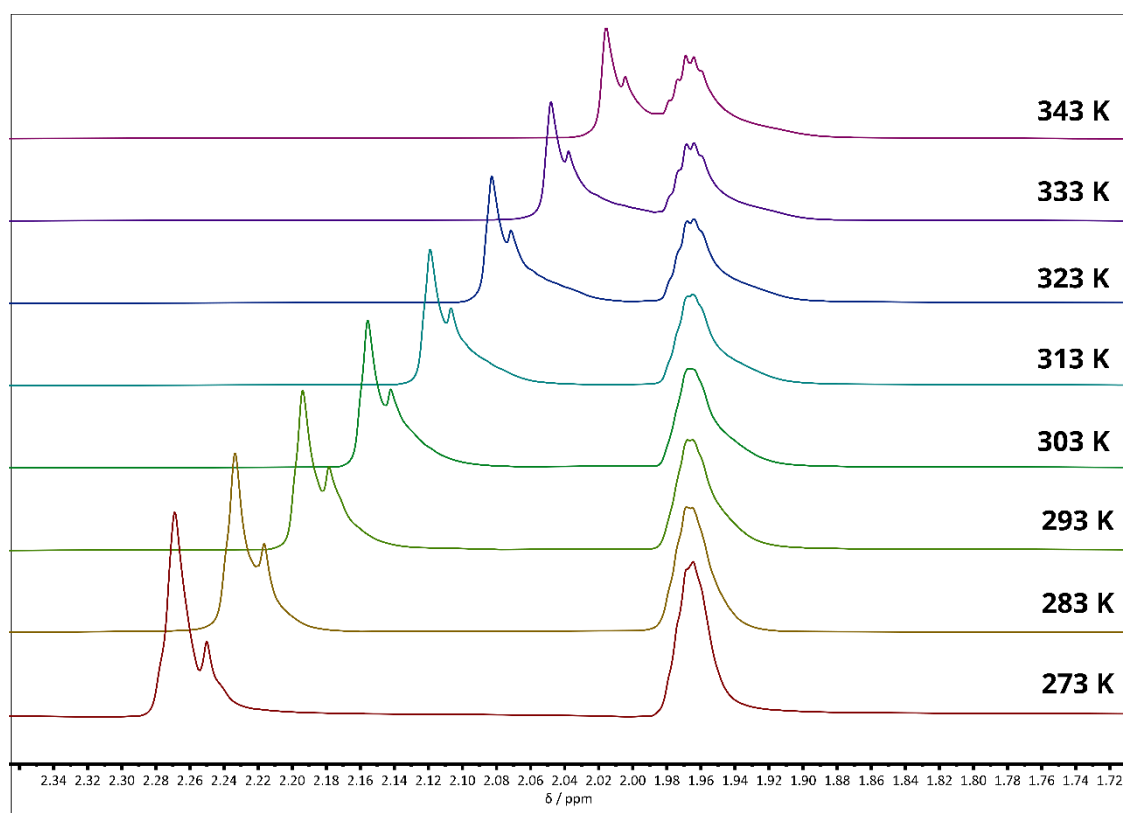


Figure S102: Evans method ^1H NMR (6 mM) at variable temperatures of **C7** over a temperature range of 273K to 343K in acetonitrile [400 MHz] in 10K steps staying diamagnetic, showing no VT transition over the observed temperature range.

- [1] S. Sundaresan, M. Diehl, L. M. Carrella, and E. Rentschler, 'Triggering of Valence Tautomeric Transitions in Dioxolene-Based Cobalt Complexes Influenced by Ligand Substituents, Co-ligands, and Anions', *Magnetochemistry*, **2022**, 8(9), pp. 1–12, DOI: 10.3390/magnetochemistry8090109.

5. Chapter 2: Electronic Tuning of Dinuclear Cobalt VT by modifying an Innocent Bridging Ligand

This chapter investigates the influence of electronic substitution at the *meta* position of the pyridyl units of the redox-innocent bridging ligand on the VT behaviour of dinuclear cobalt-dioxolene complexes. Electron-withdrawing substituents (fluoro, bromo) and an electron-donating group (methyl) were introduced, and a series of complexes bearing either sulfate or hexafluorophosphate counteranions was synthesised and characterised. The hexafluorophosphate salts were included to improve solubility and facilitate solution-state studies. Structural and magnetic characterisation confirms that all complexes adopt the LS Co(III)cat configuration in the solid state at low temperatures. Solution UV-Vis spectroscopy at room temperature reveals a bathochromic shift of the LMCT band upon introduction of electron-withdrawing substituents and a hypsochromic shift for the electron-donating methyl group, relative to the unsubstituted reference complex. Cyclic voltammetry demonstrates that the electrochemical gap between Co(III)/Co(II) and $\text{cat}^{2-}/\text{sq}^{\bullet-}$ redox processes decrease systematically from the methyl-substituted through the unsubstituted to the fluoro-substituted complex. The bromo-substituted complex could not be investigated in solution due to insolubility and limited solution stability. Evans NMR measurements confirm an incomplete VT transition in solution for all three complexes, with the fluoro-substituted complex showing the earliest onset and largest increase in magnetic moment, and the methyl-substituted complex exhibiting only marginal switching. In the solid state, the sulfate-bearing complexes display a clear trend, where electron-withdrawing substituents promote VT, with the fluoro-substituted complex switching at the lowest temperature and gains the highest magnetic moment, while the methyl-substituted analogue switches least effectively. The hexafluorophosphate series does not follow the same trend.

The results are presented as a scientific article in preparation for submission.

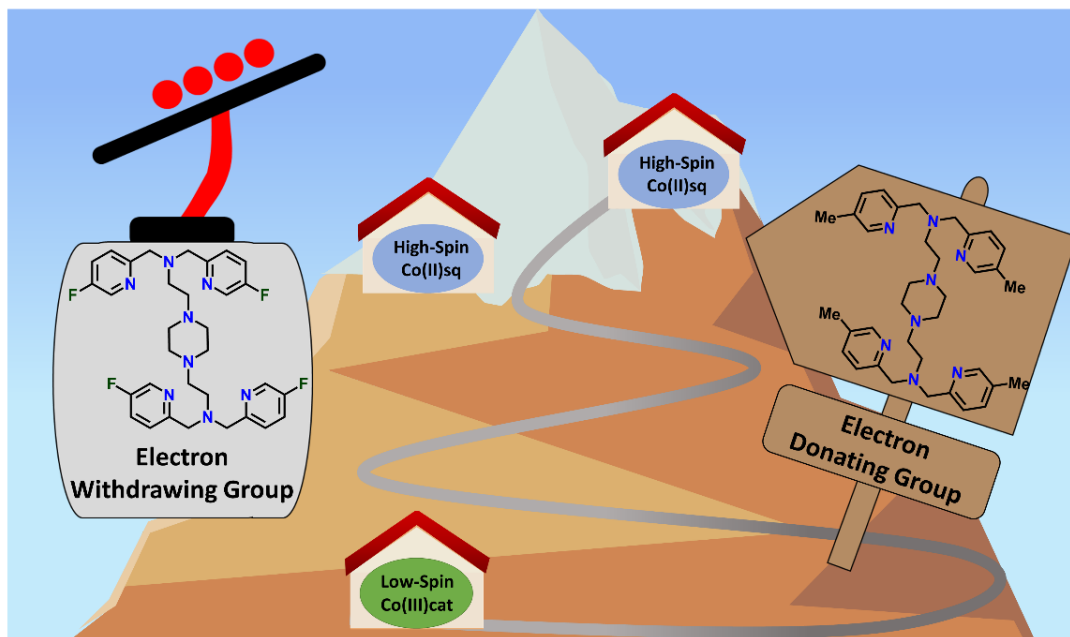
Author Contribution

Synthesis of the brominated ligand and the corresponding sulfate complex, as well as their initial investigation, were carried out by [REDACTED] as part of her bachelor's thesis which was supervised by Tim Hieke. The other ligands and complexes were synthesised and characterised by Tim Hieke, including magnetic measurements and elemental analysis. Single-crystal X-ray diffraction measurements, structure solution, and refinement were performed by [REDACTED]. The manuscript was written by Tim Hieke and revised with input from [REDACTED] and [REDACTED]. [REDACTED] provided overall supervision of the experimental work and the manuscript preparation. All authors have read and approved the final version of the manuscript.

Manuscript: From Push to Pull: Electronic Tuning of Dinuclear Cobalt Valence Tautomerism by modifying an Innocent Bridging Ligand

Department Chemie, Johannes Gutenberg-Universität Mainz, 55128 Mainz, Germany

Graphical Abstract



Abstract

In the class of switchable molecules, the transition temperature of valence tautomerism in cobalt complexes is often tuned by modifying the redox-active, non-innocent bridging ligand, particularly in dinuclear systems. Here, we demonstrate that the transition temperature of the valence-tautomeric process can also be effectively modulated by electronic variation of the innocent bridging ligand *N,N,N',N'*-tetra-2-picoyl-1,4-bis(2-aminoethyl)piperazine (L-H) with electron withdrawing and donating groups on the picoyl unit in meta position (L-Me, L-F, L-Br). A series of seven complexes of the general formula $[\text{Co}_2(\text{L-R})(\text{dtbcate})_2]^{2+} (\text{X})_{1-2}$ (where R = H, Me, Br F; X = SO_4^{2-} or PF_6^- ; dtbcate = 3,5-di-*tert*-butylcatecholate) were synthesised and characterised. Single-crystal X-ray structure determination at 120 K confirm a low-spin Co(III) configuration and the catecholate character of the dioxolanes for all complexes. Investigations in solution by UV-Vis spectroscopy, Evans NMR method and cyclic voltammetry demonstrated that electron-withdrawing substituents promote the valence tautomeric transition by lowering the LUMO energy. Magnetic measurements in the solid state revealed a pronounced increase in magnetic moment at elevated temperatures, confirming that electronic modulation of the innocent ligand backbone influences the transition temperature, with electron-withdrawing groups shifting the transition temperature to lower temperatures. These findings provide a clear design strategy for tuning valence tautomerism through targeted electronic ligand modification of the innocent ligand.

Introduction

Pierpont and Buchanan pioneered the field of valence tautomerism (VT) in metal-complexes in 1980, extending a phenomenon that had previously been confined to purely organic compounds.^{1–5} Since then, a considerable increase in research activity can be observed enlarging the class of compounds from Co-based systems^{6–10} to various transition metals such as iron^{11–13}, manganese^{14–17}, copper¹⁸ and nickel¹⁹, and even more recently in some selected lanthanides like Samarium.^{20,21} Furthermore, the scope has evolved from mononuclear^{22–26} to dinuclear structures^{27–31}, and the tautomeric switching can now be triggered not only thermally, but also by external stimuli such as light^{32–35} or pressure^{36–38}.

The potential of switchable molecules, which exhibit a high degree of sensitivity and reversibility to external stimuli, while displaying a traceable response behaviour, holds significant potential in the field of electronic miniaturisation. Due to the increasing demand for miniaturized functional elements, molecular systems are emerging as an essential component for a range of applications, including adaptive sensors, molecular actuators, displays and spintronics.^{39–44}

The ability for these systems to undergo trackable changes in their physical or chemical characteristics in response to external stimuli, such as temperature, light, or pressure, renders them promising candidates as fundamental components in the development of responsive materials. VT is defined as an intramolecular electron transfer between a metal centre and an organic ligand, and vice versa. This process typically results in a change in both the oxidation state of the metal and the redox state of the ligand, which can be accompanied by a change in the spin state as seen in most cobalt VT complexes.⁴⁵

In order for such an electronic transition to occur, it is necessary for the bound organic ligand to have the ability to undergo a change in its oxidation state. Ligands of this nature are classified as members of a class of redox active ligands known as non-innocent ligands.⁴⁶ In contrast, many transition metal ions are recognised to exist in varying oxidation states in nature. In principle, two building blocks are required for VT to occur: an electron acceptor and an electron donor fragment.⁴⁷ However, combining a metal centre with variable oxidation states and a redox-active ligand does not necessarily lead to a VT system. The occurrence of VT behaviour critically depends on the delicate energetic balance between the metal- and ligand-centred redox states, deviations often result in complexes that remain trapped in one of the energetic states.⁴⁸

Valence tautomerism occurs only when the metal- and ligand-centred frontier orbitals are close in energy and effectively interact through sufficient electronic coupling. It is essential that this coupling exhibits a certain strength that the activation barrier can be overcome by external stimuli. Simultaneously, it is essential that the coupling remains sufficiently weak to ensure the existence of discrete electronic states. It has been demonstrated that even minimal changes in orbital energies can have a significant influence on valence tautomerism behaviour. The valence tautomeric cobalt complexes most often show a spin-switch phenomenon that is occurring simultaneously to the redox reaction. Consequently, a transition from the low-spin Co(III)catecholate (Co(III)cat) state to the high-spin Co(II)semiquinonate (Co(II)sq) state is observed. This spin state change is accompanied by a pronounced alteration of structural, optic and magnetic properties.⁴⁵ Although VT in cobalt-dioxolene systems typically involves a coupled spin change and electron transfer, there are also reports of complexes where no spin-state change occurs during the VT process.^{49,50} In contrast, VT transitions are only rarely observed in manganese or iron systems. In these cases, either the total spin remains unchanged, which renders the transition magnetically silent, or the spin transition occurs independently and sequentially from the electron-transfer event.^{11–13,16,51,52}

Within the field of valence tautomerism, dinuclear cobalt complexes represent an emerging and particularly promising class of compounds, as they provide access to a greater number of addressable redox configurations than their mononuclear counterparts. Unlike mononuclear systems, which are limited to two accessible states^{54,55}, dinuclear complexes can exist not only in the fully Co(III)cat / Co(III)cat and Co(II)sq / Co(II)sq forms, but also in a mixed-valent Co(III)cat / Co(II)sq state⁵³,

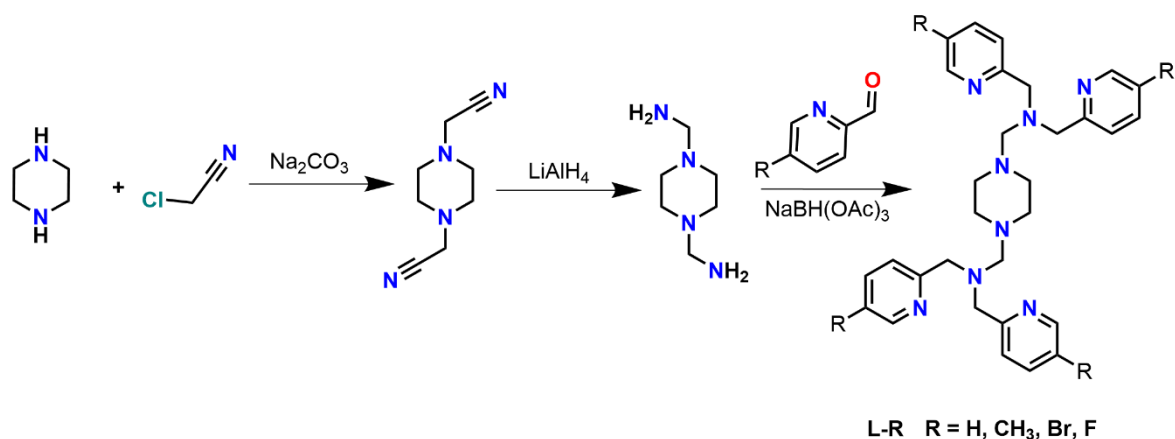
rendering them attractive candidates for future applications in molecular switching. While recent advances in the field have primarily focused on systems featuring redox-active bridging dioxolene ligands such as tetraoxolenes or azide-bridged dioxolenes^{53,56,57}, the influence of redox-innocent bridging ligands on VT behaviour has received considerably less attention^{28,58,59}, despite the fact that such ligands exert a notable influence on the electronic structure of the metal centres and thus on the VT properties of the complexes. Given the frequently incomplete transition profiles observed for VT complexes and the absence of systematic substitution studies on redox-innocent bridging ligands, targeted electronic fine-tuning of such ligands represents a compelling and largely unexplored strategy for modulating VT behaviour.^{8,30,58}

In the present study, a bis-tetradentate bridging ligand was employed, which coordinates cobalt ions efficiently and is known to exhibit VT transitions in combination with catecholate ligands.^{59,60} This design enables modification of the innocent ligand backbone within the same synthetic framework, allowing systematic exploration of substitution effects. Accordingly, three new ligands bearing electron-withdrawing and electron-donating groups were synthesised. The objective of this work is to gain deeper insight into how electronic substitution at the innocent bridging ligand influences the VT behaviour of dinuclear cobalt complexes, an aspect largely overlooked in previous studies.

Results and Discussion

Ligand Synthesis

The unsubstituted bridging ligand (**L-H**) was synthesized according to our previously reported procedure.^{59,60} The selected synthetic route allows late-stage modification of the ligand. In the final step, aldehydes bearing different substituents are introduced in a reductive amination reaction, yielding an electron-donating methyl (**L-Me**) and electron-withdrawing bromine (**L-Br**) and fluorine (**L-F**) derivatives (**Scheme 1**). The successful synthesis and high purity of the ligands was confirmed by several characterization methods e.g.; infrared spectroscopy (**Figures S1-S6**), mass spectrometry (**Figures S7-S9**), ¹H (**Figures S10-S15**), ¹³C (**Figures S16-S19**), ¹⁹F (**Figure S20**) and 2D-NMR techniques (**Figures S20-S31**). All ligands were synthesised on a multi gram scale with yields between 42 - 77%



Scheme 1: Multistep Ligand Synthesis of the innocent bridging ligands *N,N,N',N'*Tetra-2-picolyl-1,4-bis(2-aminoethyl)piperazine (**L^H**), *N,N,N',N'*Tetra-5-methyl-2-picolyl-1,4-bis(2-aminoethyl)piperazine (**L^{Me}**), *N,N,N',N'*Tetra-5-bromo-2-picolyl-1,4-bis(2-aminoethyl)piperazine (**L^{Br}**) and *N,N,N',N'*Tetra-5-fluoro-2-picolyl-1,4-bis(2-aminoethyl)piperazine (**L^F**).

Complex Synthesis

Unless otherwise indicated, the syntheses were performed under anhydrous and oxygen-free conditions. Typically, 2 equiv. of the 3,5-di-*tert*-butylcatecholate and 1 equiv. **L-R** were dissolved in 10 mL of dry, degassed methanol. The cobalt(II) salt was then dissolved in methanol and added dropwise to the first solution under stirring, followed by slow addition of 4 equiv. of triethylamine. In general, the sulphate complexes were oxidized by exposure to atmospheric oxygen under ambient conditions, whereas oxidation of the hexafluorophosphate salts was carried out using ferrocenium hexafluorophosphate. The resulting solids were air-dried, and single crystals suitable for X-ray diffraction were obtained under ambient conditions by slow evaporation or by diethyl ether diffusion. Detailed synthetic procedures for all complexes are provided in the experimental section of the supporting information. For sake of clarity, the complexes are denoted here after as $[\text{Co}_2\text{L}^{\text{X}}]\text{A}_{1-2}$ throughout this manuscript, with X representing Me, H, Br or F, and A representing SO_4^{2-} or PF_6^- .

Crystal Structure Description

Single crystal X-ray data collection was carried out at 120 K. The cationic fragment of $[\text{Co}_2\text{L}^{\text{Me}}](\text{PF}_6)_2$ is shown in **Figure 1** as a representative example for the complexes $[\text{Co}_2\text{L}^{\text{H}}](\text{PF}_6)_2$, $[\text{Co}_2\text{L}^{\text{F}}](\text{PF}_6)_2$, $[\text{Co}_2\text{L}^{\text{Me}}]\text{SO}_4$ and $[\text{Co}_2\text{L}^{\text{F}}]\text{SO}_4$; detailed representation for the latter complexes can be found in the SI. (Figures S54-S58)

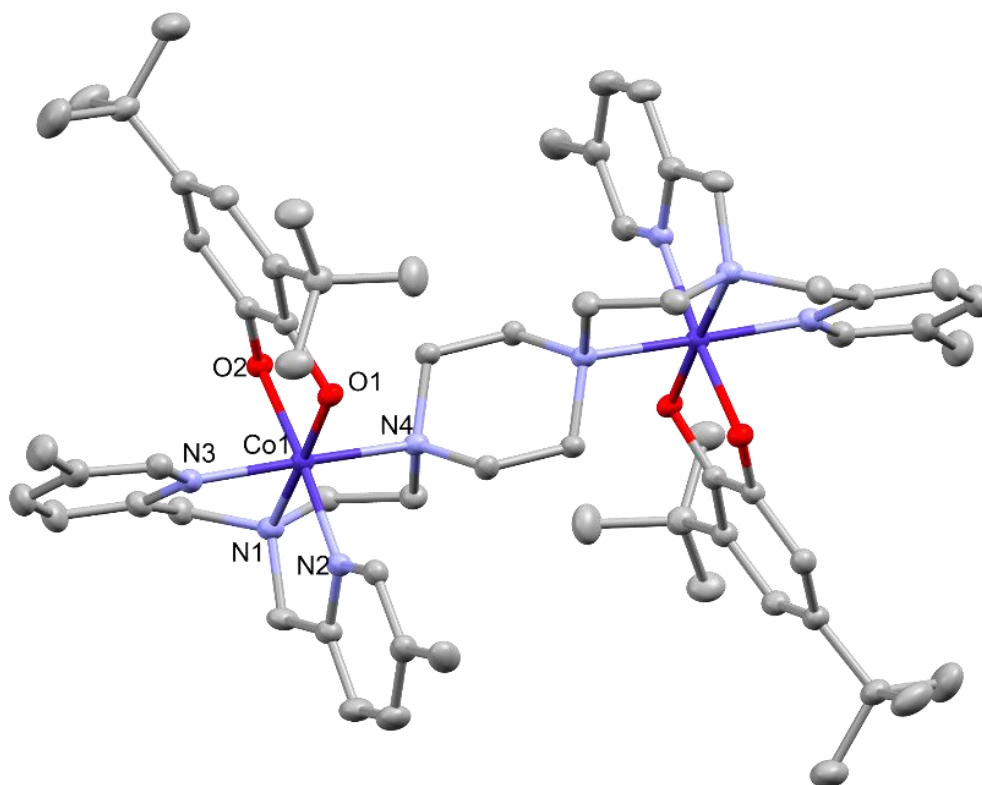


Figure 1: Molecular structure of $[\text{Co}_2(\text{L}^{\text{Me}})(\text{dtbcat})_2]^{2+}$ $[\text{Co}_2\text{L}^{\text{Me}}]^{2+}$ at 120 K. Lattice solvent molecules, anions and hydrogen atoms are omitted for clarity. The probability level for the displacement of the ellipsoid is 50%. Colour Code: carbon (grey), cobalt (dark blue), nitrogen (light blue), oxygen (red).

Analysis of the investigated molecular structures revealed that the complex cations share a common molecular scaffold, while differences in crystal packing led to distinct lattice structures. These variations arise from multiple factors, including substitution at the *meta* position of the ligand (defined by L^{X}), the nature of the counterions (sulfate or hexafluorophosphate), and the solvents used for recrystallisation. Accordingly, complexes $[\text{Co}_2\text{L}^{\text{H}}](\text{PF}_6)_2$ and $[\text{Co}_2\text{L}^{\text{F}}](\text{PF}_6)_2$ are isostructural and crystallise in the monoclinic space group $C2/c$ ($Z = 4$), complexes $[\text{Co}_2\text{L}^{\text{Me}}](\text{PF}_6)_2$ and $[\text{Co}_2\text{L}^{\text{Me}}]\text{SO}_4$ in the triclinic

space group $P-1$, and complex $[\text{Co}_2\text{L}^{\text{F}}]\text{SO}_4$ in the monoclinic space group $P2_1/c$ ($Z = 2$) and all structures belong to centrosymmetric space groups. All complexes are dinuclear, with structurally equivalent cobalt centres bridged by the non-aromatic piperazine unit of the bis-tetradentate bridging ligand. Each cobalt ion adopts an octahedral N_4O_2 coordination environment, comprising four nitrogen donors from the bridging ligand (two pyridine nitrogen atoms, the tertiary amine connecting the pyridine arms to the piperazine, and the piperazine nitrogen) and two oxygen donors from a bidentate, doubly deprotonated dioxolane ligand. Each cobalt centre forms four five-membered chelate rings. The two dioxolene ligands adopt a trans arrangement, providing sufficient space for the sterically demanding tert-butyl groups. The piperazine unit adopts a chair conformation, further relieving steric strain around the dioxolene ligands. No π - π stacking interactions were observed. Instead, the crystal structures feature hydrogen bonds between solvent molecules and sulfate anions, H-F interactions between PF_6 anions and non-acidic protons, as well as halogen-fluorine contacts between PF_6 anions and halogen atoms of the halogenated ligands. Notably, the complexes containing sulfate anions incorporate more solvent molecules into the lattice and display a greater number of intermolecular interactions. This enhanced supramolecular connectivity may contribute to improved switching behaviour in the valence-tautomeric transition, as discussed later and was observed in related systems.⁶⁰ The hexafluorophosphate anions are often disordered, except in the fluorinated complex.

The bond lengths between the metal centre and the donor atoms are in the range of 1.857(1)-1.895(2) Å for Co-O and 1.914(3)-1.959(1) Å for Co-N, consistent with a LS Co(III) configuration. For comparable N_4O_2 -cobalt-dioxolene complexes with a low-spin Co(III) centre, typical Co-N bond lengths range between 1.913(2)-1.954(2) Å⁶¹, whereas analogous high-spin Co(II) complexes exhibit longer Co-N bonds of about 2.105(4)-2.243(5) Å.²⁷ The rigidity of the piperazine unit, combined with its chair conformation, leads to an elongation of the Co-N bond involving the piperazine, with bond lengths of 2.039(6)-2.062(2) Å observed for all complexes.

Continuous shape measurements were performed with the program *SHAPE 2.1* to quantify the coordination geometry.⁶² The low SHAPE values of 0.242-0.333 observed at the cobalt centres reflect only minor deviations from ideal octahedral symmetry when comparing the experimental data with those expected for a perfect octahedron. The slight distortions can be attributed to the elongation of the Co-N bond to the piperazine nitrogen. Typically, low-spin Co(III) exhibit SHAPE values around 0.167 – 0.306, whereas high-spin Co(II) analogues show significantly higher distortions, with values around 1.545, reflecting the greater angular distortions arising from the larger ionic radius of Co(II).⁵⁷ The SHAPE data for all $[\text{CoL}^{\text{x}}]\text{A}$ central metal ions are summarised in **Table 1**. Based on the intraligand C-O and C-C bond lengths, the “metric oxidation state” (MOS) of the dioxolene ligands was determined.⁶³ The calculated MOS values range from -2.048 to -1.83, consistent with a catecholate state. For reference, MOS = 0 corresponds to quinone, -1 to semiquinonate and -2 to catecholate character. A full overview of metal-donor bond lengths, SHAPE values, and MOS data is provided in **Table 1**.

Table 1: Metal-Donor Bond Lengths in Å, SHAPE Values and MOS of the Complexes.

Co-X	$[\text{Co}_2\text{L}^{\text{H}}](\text{PF}_6)_2$	$[\text{Co}_2\text{L}^{\text{Me}}](\text{PF}_6)_2$	$[\text{Co}_2\text{L}^{\text{F}}](\text{PF}_6)_2$	$[\text{Co}_2\text{L}^{\text{Me}}]\text{SO}_4$	$[\text{Co}_2\text{L}^{\text{F}}]\text{SO}_4$
Co1-O1	1.8635(15)	1.8767(10)	1.8721(11)	1.871(2)	1.876(6)
Co1-O2	1.8947(15)	1.8773(10)	1.8570(10)	1.880(3)	1.874(6)
Co1-N1	1.950(2)	1.9515(13)	1.9593(12)	1.937(3)	1.942(7)
Co1-N2	1.9199(18)	1.9404(12)	1.9323(12)	1.914(3)	1.915(7)
Co1-N3	1.9257(18)	1.9208(13))	1.9337(12)	1.927(3)	1.927(6)
Co1-N4	2.0615(17)	2.0498(13)	2.0525(11)	2.050(3)	2.039(6)
SHAPE	0.333	0.276	0.311	0.252	0.242
MOS	-1.955	-1.885	-1.851	-1.831	-2.048

Single crystals suitable for X-ray diffraction analysis could not be obtained for the brominated ligand **L^{Br}**. Attempts to recrystallise the amorphous powders obtained from the synthetic route resulted in decomposition, indicating that complexes bearing the brominated ligand are not stable in solution. Consequently, further solution-state investigations of these compounds were omitted.

The solution stability of all remaining complexes was confirmed by high-resolution ESI⁺ mass spectrometry, with the experimentally observed isotopic patterns of the divalent cationic fragments **[Co₂L^x]²⁺** in excellent agreement with calculated values (**Figures S40-S53**). Infrared spectra (**Figures S33-S39**) display the characteristic bands of the hexafluorophosphate anion at 838-823 cm⁻¹ and 556 cm⁻¹, the sulfate anion at 1085-1048 cm⁻¹, and the C-O stretching vibration of the catecholate ligand at 1440 cm⁻¹. Bulk purity was confirmed by elemental analysis, which also revealed that exposure to air leads to replacement of lattice solvent molecules by water.

Solution State Electronics and Magnetic Characterisation

To gain insights into the solution behaviour of the complexes, UV-Vis spectra were recorded in acetonitrile at room temperature. Due to the limited solubility of the sulfate complexes, measurements were restricted to the corresponding hexafluorophosphate complexes. The resulting spectra, shown in **Figure 2**, display very similar features for all three complexes.

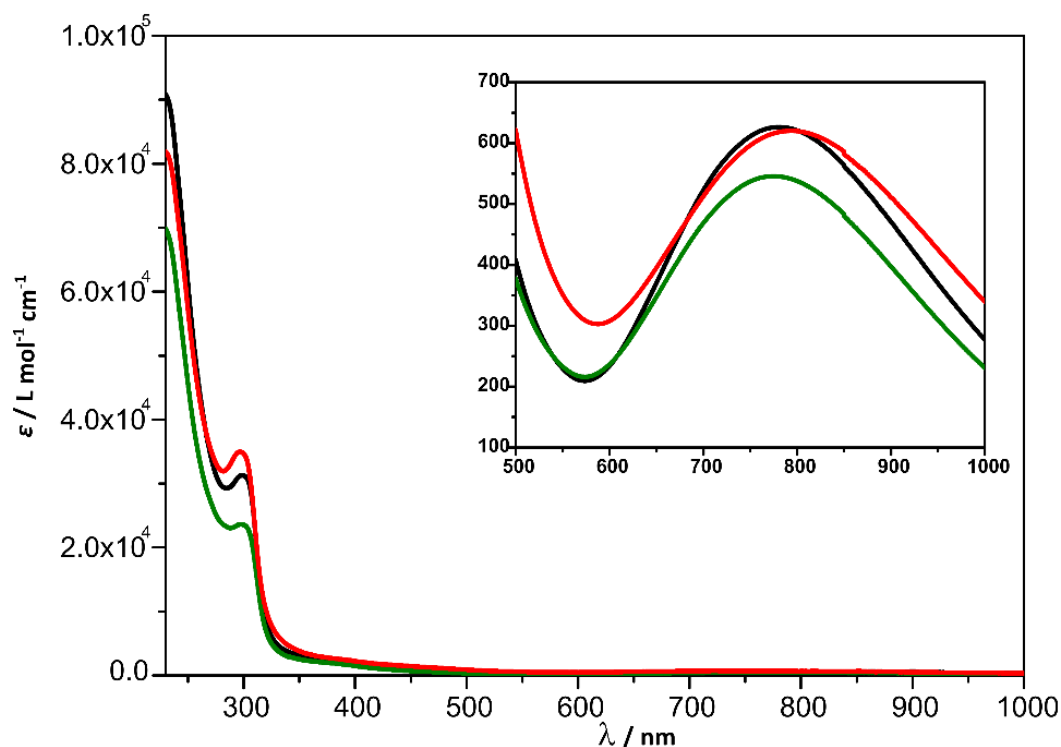


Figure 2: UV-Vis absorption spectra for acetonitrile solutions of **[Co₂L^H](PF₆)₂** (black), **[Co₂L^{Me}](PF₆)₂** (green) and **[Co₂L^F](PF₆)₂** (red) at the concentration of 0.01 mM with a zoomed in region from 500 - 1000 nm at a concentration of 1 mM.

All spectra display an intense absorption band around 299 nm, assignable to ligand-centred π - π^* transitions. In addition, a weak, broad absorption band is observed in the low-energy region, consistent with a symmetry-forbidden ligand-to-metal charge-transfer (LMCT) transition characteristic of low-spin Co(III) catecholate species, in accordance with the literature.^{27,60}

Here, a discernible trend emerges upon comparison of the LMCT band positions: the band maximum undergoes a systematic bathochromic shift with increasing electron-withdrawing strength of the substituents, shifting from 775 nm for **[Co₂L^{Me}](PF₆)₂** to 782 nm for **[Co₂L^H](PF₆)₂** and 795 nm for **[Co₂L^F](PF₆)₂** (**Table S13, Figures S59-S64**). This redshift can be attributed to the reduced electron density at the cobalt centres imposed by the electron-withdrawing substituents, which simultaneously

lower the energy of the metal-centred LUMO and thus reduce the energy gap between the frontier orbitals. Consequently, the activation barrier for the valence tautomeric transition is expected to decrease, facilitating the thermally induced intramolecular electron transfer

The redox properties of complexes $[\text{Co}_2\text{L}^{\text{Me}}](\text{PF}_6)_2$ and $[\text{Co}_2\text{L}^{\text{F}}](\text{PF}_6)_2$ were investigated by cyclic voltammetry (CV) and the data was compared to the previously reported CV data of the perchlorate salt of complex $[\text{Co}_2\text{L}^{\text{H}}]\text{ClO}_4$.⁶⁰ These investigations are of particular interest in the context of valence tautomerism, a phenomenon involving two coupled redox events: oxidation of the catecholate to semiquinonate and the reduction of Co(III) to Co(II). CV measurements allow these processes to be observed individually and their redox potentials to be determined experimentally, thereby providing insights into the relative energetics of the states involved. The potential difference between the two redox events can be considered a measure of the energetic barrier associated with valence tautomerism; a smaller separation indicates a thermodynamically more accessible VT transition.^{8,60,64}

For reversible and quasi-reversible processes, the half-step potentials (E_m) and peak separation (ΔE_p) were determined, whereas for irreversible processes only the peak potentials (E_p) were evaluated vs. ferrocene/ferrocenium (Fc/Fc^+).

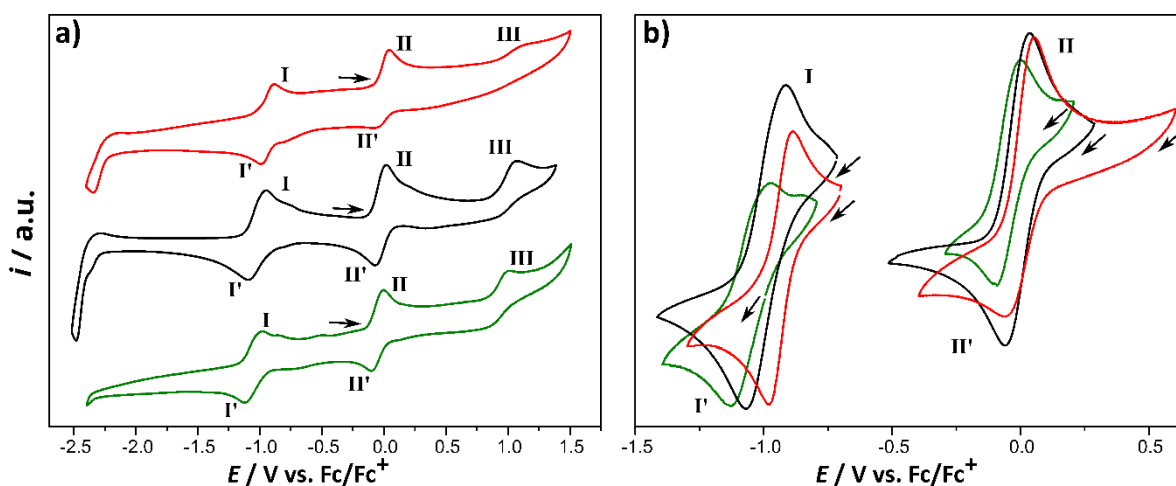


Figure 3: a) cyclic voltammograms, b) overlay of the cyclic voltammograms for redox processes (I/I') and (II/II') for complexes $[\text{Co}_2\text{L}^{\text{Me}}](\text{PF}_6)_2$ (green), $[\text{Co}_2\text{L}^{\text{F}}](\text{PF}_6)_2$ (red) and previously reported $[\text{Co}_2\text{L}^{\text{H}}]\text{ClO}_4$ (black). (Conditions: 1 mM with 0.1 M $n\text{-Bu}_4\text{PF}_6$ in acetonitrile obtained with a scan rate of 0.1 V s^{-1} , with a glassy carbon electrode, a silver / silver nitrate reference electrode, platinum counter electrode, referenced internally against the redox pair ferrocene / ferrocenium.)

Table 2: Cyclic Voltammetry Data for $[\text{Co}_2\text{L}^{\text{H}}]\text{ClO}_4$, $[\text{Co}_2\text{L}^{\text{Me}}](\text{PF}_6)_2$, and $[\text{Co}_2\text{L}^{\text{F}}](\text{PF}_6)_2$, in MeCN, E_m / V ($\Delta E_p / \text{mV}$) or $E_p / \text{V vs. Fc} / \text{Fc}^+$. E_m was experimentally obtained as the average potential between the corresponding anodic and cathodic events of a reversible or quasi-reversible electrochemical event, while E_p is the peak potential of irreversible electrochemical events.

Compound	I/I'	II/II'	III	$\Delta (I/I' - II/II')$
$[\text{Co}_2\text{L}^{\text{Me}}](\text{PF}_6)_2$	-1.056 (141)	-0.051 (102)	1.013	1.005
$[\text{Co}_2\text{L}^{\text{H}}]\text{ClO}_4$ ⁶⁰	-1.022 (147)	-0.027 (91)	1.070	995
$[\text{Co}_2\text{L}^{\text{F}}](\text{PF}_6)_2$	-0.940 (105)	-0.019 (119)	1.128	921

The stability of all three complexes was confirmed across the entire electrochemical window of acetonitrile during the measurement. In each case, three distinct redox processes were observed. The first couple (I/I') is assigned to the Co(II)/Co(III) redox event, while the second couple (II/II') corresponds to the ligand-based catecholate / semiquinonate redox system. Both processes are quasi-reversible. The third process (III) is irreversible and attributed to the oxidation from semiquinonate to quinone. These assignments are consistent with previously reported data for related cobalt-dioxolene systems.^{27,60,64}

Scan rate dependent measurements (Figures **S65-S67**) confirmed the quasi-reversible nature of processes (I/I') and (II/II'). Increasing the scan rate results in a clear divergence of the anodic and cathodic peak potentials and the peak separations exceed the theoretical value of 59 mV expected for a fully reversible one-electron event.⁶⁵ The irreversibility of the third process (III) can be attributed to the poor coordinating ability of the oxidised quinone form, which often induces ligand dissociation and subsequent decomposition of the metal complex.³¹

The cyclic voltammograms of the three complexes are compiled in **Figure 3** to allow direct comparison of their electrochemical behaviour. The corresponding redox couples (I/I') and (II/II') are displayed on the right-hand side of the figure. UV-Vis spectroscopy confirmed that the complexes exist as Co(III) catecholate species in solution at room temperature. The electrochemically relevant parameters extracted from cyclic voltammetry are summarised in **Table 2**.

Notably, process (II/II') exhibits only a marginal potential shift across the series. Compounds $[\text{Co}_2\text{L}^{\text{H}}]\text{ClO}_4$ and $[\text{Co}_2\text{L}^{\text{F}}](\text{PF}_6)_2$ display nearly identical potentials for process (II/II'), whereas the methyl-substituted analogue $[\text{Co}_2\text{L}^{\text{Me}}](\text{PF}_6)_2$ shows a slightly shifted potential, most likely due to the steric influence of the methyl substituent.

As expected, the redox process (I/I'), associated with the cobalt centre, is more strongly affected by the electronic nature of the ligand substituents than the catechol-based process (II/II'). Accordingly, process (I/I') exhibits a more pronounced shift in redox potential. Relative to the unsubstituted ligand of $[\text{Co}_2\text{L}^{\text{H}}]\text{ClO}_4$, the methyl-substituted analogue shows a shift towards more anodic potentials, while the fluorinated derivative displays a cathodic shift.

This trend reflects the electronic effects of the substituents: the electron-donating methyl group increases the electron density at the cobalt centre, facilitating oxidation and hindering reduction. In contrast, the electron-withdrawing fluorine substituent decreases the electron density, thereby favouring reduction and impeding oxidation.

In the context of valence tautomerism, the potential difference between processes (I) and (II), corresponding to the Co(II)/Co(III) and catecholate/semiquinonate redox couples, is of particular relevance, as these processes are closely coupled and reflect the electronic rearrangement mechanism underlying the VT transition.

For VT-active complexes, it is therefore essential that the redox potentials, and consequently the activation barriers for intramolecular electron transfer, converge.

The corresponding potential differences are summarised in **Table 2**. A clear trend is observed that electron-donating substituents increase the potential separation up to 1005 mV, whereas electron-withdrawing substituents decrease it to 921 mV. The values are lower than those previously reported for complexes bearing halogenated catecholates. (1152 mV)⁶⁰ In comparison, other VT complexes display potential separations ranging from 340 mV up to 1110 mV.^{12,19} It has been proposed that complexes with a potential separation below 740 mV may exhibit valence tautomeric behaviour.⁸ Nevertheless, exceptions are known in the literature, including systems such as the present ones, which show larger potential separations but still undergo valence tautomeric transitions.

As both UV-Vis and CV indicated that electron-withdrawing substituents favour VT in solution, the magnetic properties of complexes $[\text{Co}_2\text{L}^{\text{Me}}](\text{PF}_6)_2$ and $[\text{Co}_2\text{L}^{\text{F}}](\text{PF}_6)_2$ in solution were examined to substantiate this trend. Temperature dependent Evans ¹H NMR measurements were performed in the range from 293 to 343 K (in 10 K increments) and compared with our previously reported data for $[\text{Co}_2\text{L}^{\text{H}}]\text{ClO}_4$ ⁶⁰ (**Figure 4**).

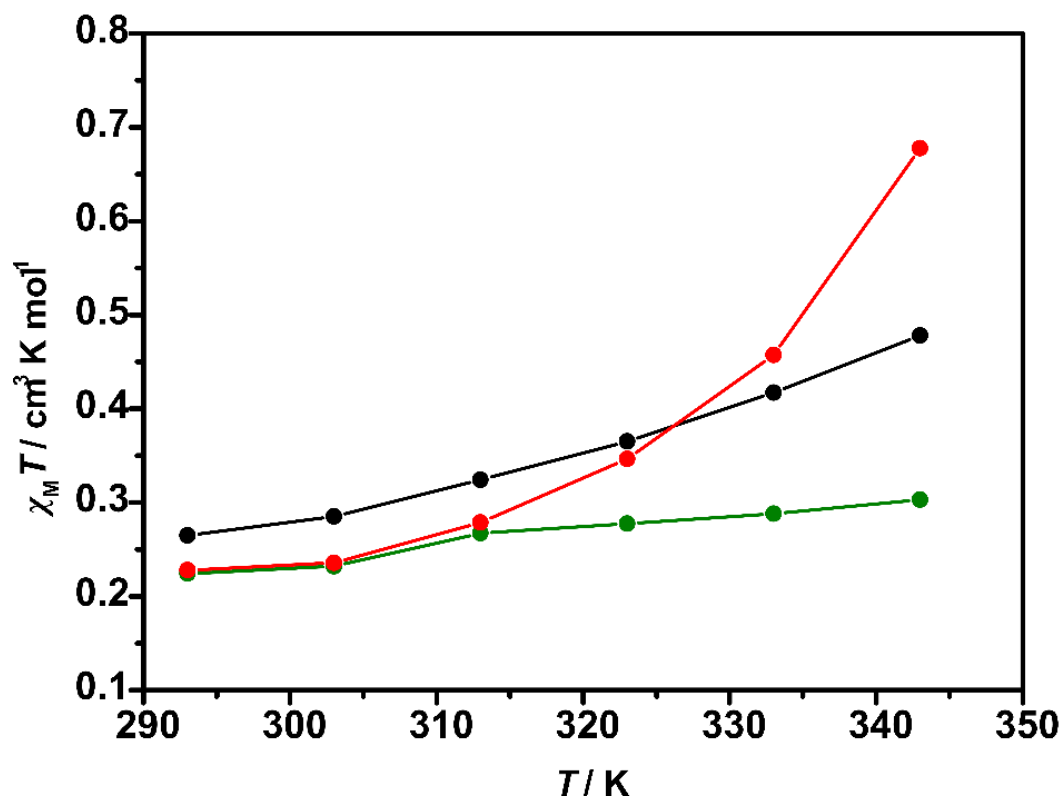


Figure 4: ¹H Evans Method NMR at 6mM in deuterated acetonitrile in a temperature range of 293 K to 343 K, measured in 10 K steps. ([Co₂L^H]ClO₄ (black)⁶⁰, [Co₂L^{Me}](PF₆)₂ (green) and [Co₂L^F](PF₆)₂ (red)) [400 MHz]

The measurements were performed in deuterated acetonitrile at a concentration of 6 mM. For the NMR-based Evans method the typical relative error of the determined magnetic moments is approximately 5-10%.^{65,66}

As shown in **Figure 4**, all three complexes are diamagnetic in solution at room temperature, corresponding to the low-spin Co(III)-catecholate state, in agreement with the results obtained from UV-Vis and electrochemical studies. Upon heating, all complexes exhibit an increase in $\chi_M T$, indicating the onset of a valence tautomeric transition in solution. However, the transitions remain incomplete within the investigated temperature range limited by the solvent.

A distinct trend is observed among the three complexes. The methyl-substituted complex ([Co₂L^{Me}](PF₆)₂) shows only a very modest increase in $\chi_M T$, reaching a value of 0.30 cm³ K mol⁻¹ in $\chi_M T$, indicating that it remains well within the low-spin region. The unsubstituted complex ([Co₂L^H]ClO₄) exhibits a more gradual rise, attaining 0.48 cm³ K mol⁻¹ at 343 K, which suggests the onset of the transition but still below the transition temperature. In contrast, the fluorinated complex ([Co₂L^F](PF₆)₂) displays the strongest magnetic response with $\chi_M T$ increasing to 0.68 cm³ K mol⁻¹, indicating the onset of a transition, however, still below the transition temperature. These observations provide evidence that electron-withdrawing substituents facilitate the valence-tautomeric transitions in solution.

It was determined that the complexes within the investigated temperature range limited by the solvent boiling point did not exceed the respective transition temperature. This conclusion is supported by the absence of an inflection point on the $\chi_M T$ curves. Thus, we refrained from modelling the data with low accuracy.

Within the investigated temperature range, limited by the solvent boiling point, none of the complexes exceeded the respective transition temperature, as evidenced by the absence of an inflection point in the $\chi_M T$ curves. The data were therefore not subjected to quantitative modelling. It is well established that polar solvents stabilise the more polar Co(III)cat state, and non-polar solvents such as

dichloroethane are consequently often employed in the literature to investigate solvato-magnetic effects.^{8,26,67} However, the poor solubility of the present complexes in non-polar media precluded such investigations in this study.

Solid State Magnetic Characterisation

While the solution studies reveal the local electronic influence of the ligand substitution on the valence tautomerism, additional cooperative effects arising from crystal packing and intermolecular interactions become important in the solid state. To evaluate how these factors modulate the electronic trends established in solution, the temperature-dependent magnetic properties of all complexes were examined using a SQUID magnetometer in the temperature range 10-400 K. (Figure 5).

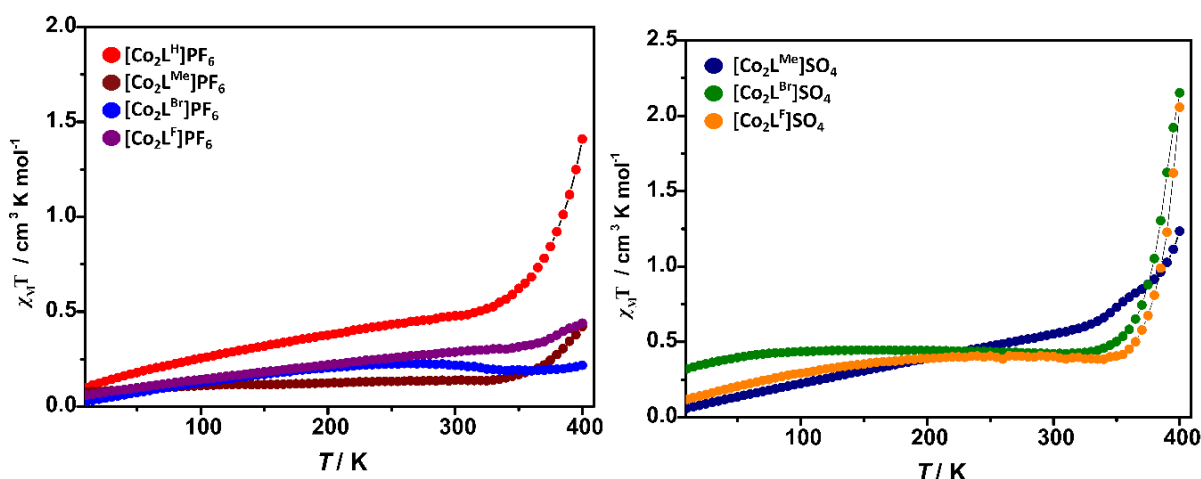


Figure 5: Temperature dependence of the molar magnetic susceptibility $\chi_M T$ as a function of temperature for $[\text{Co}_2\text{L}^{\text{H}}](\text{PF}_6)_2$ (red), $[\text{Co}_2\text{L}^{\text{Me}}](\text{PF}_6)_2$ (maroon), $[\text{Co}_2\text{L}^{\text{Br}}](\text{PF}_6)_2$ (blue), $[\text{Co}_2\text{L}^{\text{F}}](\text{PF}_6)_2$ (purple), $[\text{Co}_2\text{L}^{\text{Me}}]\text{SO}_4$ (navy), $[\text{Co}_2\text{L}^{\text{Br}}]\text{SO}_4$ (green) and $[\text{Co}_2\text{L}^{\text{F}}]\text{SO}_4$ (orange) in the temperature window of 10-400 K. Left: hexafluorophosphate complexes; right: sulfate complexes.

Magnetic data were collected in both heating and cooling modes to probe the reversibility of the valence tautomeric transition. The elevated high temperatures required for the transition, however, promote the loss of lattice solvent molecules, rendering the VT behaviour irreversible in most cases. The heating and cooling cycles are provided in the SI (Figures S71-S77).

Below 300 K, all complexes exhibit diamagnetic behaviour consistent with a low-spin Co(III)-cat ground state, as confirmed by the metal-ligand bond lengths, SHAPE parameters, and MOS values derived from single-crystal X-ray diffraction at 120 K.

With the exception of complex $[\text{Co}_2\text{L}^{\text{Br}}](\text{PF}_6)_2$, all compounds exhibit an increase in magnetic susceptibility at elevated temperatures, indicating the onset of a valence tautomeric transition. In contrast, complex $[\text{Co}_2\text{L}^{\text{Br}}](\text{PF}_6)_2$ remains diamagnetic up to 400 K and therefore does not undergo a VT transition within the investigated temperature range.

The transitions remain incomplete in all VT-active complexes, a behaviour commonly observed in solid-state VT systems.^{69–72} To quantitatively characterise the onset of the transitions, the temperature at which a pronounced increase in the slope of the $\chi_M T(T)$ curve occurs was determined. The following onset temperatures were determined: $[\text{Co}_2\text{L}^{\text{H}}](\text{PF}_6)_2$, 330 K, $[\text{Co}_2\text{L}^{\text{Me}}](\text{PF}_6)_2$, 340 K, $[\text{Co}_2\text{L}^{\text{F}}](\text{PF}_6)_2$, 365 K, $[\text{Co}_2\text{L}^{\text{Me}}]\text{SO}_4$, 325 K, $[\text{Co}_2\text{L}^{\text{Br}}]\text{SO}_4$, 345 K, and $[\text{Co}_2\text{L}^{\text{F}}]\text{SO}_4$, 360 K.

Comparison of the two anion series reveals a pronounced anion influence on the VT behaviour, with the sulphate salts consistently exhibiting lower onset temperatures and more pronounced transitions than their hexafluorophosphate analogues. Valence tautomerism is unambiguously observed across all complexes of both anion series, with the sole exception of $[\text{Co}_2\text{L}^{\text{Br}}](\text{PF}_6)_2$, underscoring the robustness of the VT activity within this compound family. Within the sulfate series, $[\text{Co}_2\text{L}^{\text{Br}}]\text{SO}_4$

reaches the highest $\chi_M T$ value of $1.90 \text{ cm}^3 \text{ K mol}^{-1}$ at 400 K, with $[\text{Co}_2\text{L}^{\text{F}}]\text{SO}_4$ displaying comparably high values. The transitions remain incomplete within the accessible temperature range, as the $\chi_M T$ values have not yet reached those expected for fully converted $\text{Co(II)}_2(\text{sq})_2$ systems (typically $6.0\text{--}7.40 \text{ cm}^3 \text{ K mol}^{-1}$)^{27,57}, and onset temperatures are therefore reported as a meaningful comparative parameter instead of transition temperatures.

The maximum $\chi_M T$ values observed for the present complexes remain slightly below the spin-only value of $2.25 \text{ cm}^3 \text{ K mol}^{-1}$ expected for a high-spin Co(II) centre ($S = 3/2$) coupled to a semiquinonate radical ($S = 1/2$), consistent with an incomplete valence tautomeric transition within the accessible temperature range. In fully converted systems, significantly higher $\chi_M T$ values are typically observed, as the unquenched orbital angular momentum of octahedral Co(II) ions bearing a $^4\text{T}_1$ ground term contributes substantially to the overall magnetic moment, accounting for the elevated values reported for fully switched $\text{Co(II)}_2(\text{sq})_2$ complexes in the literature.^{73–75}

Within the sulfate series, a clear trend emerges. Electron-withdrawing substituents favour the valence-tautomeric (VT) transition, whereas electron-donating substituents tend to suppress it. The halogenated derivatives exhibit the most pronounced transitions, while the methyl-substituted complex undergoes a more gradual and less complete conversion. The previously reported unsubstituted analogue displays intermediate behaviour, falling between the methyl-substituted and halogenated derivatives and thus confirming the observed substituent trend.⁵⁹

Interestingly, the VT transitions of the halogenated complexes $[\text{Co}_2\text{L}^{\text{Br}}]\text{SO}_4$ and $[\text{Co}_2\text{L}^{\text{F}}]\text{SO}_4$ occur at slightly higher onset temperatures compared to the methyl analogue $[\text{Co}_2\text{L}^{\text{Me}}]\text{SO}_4$. While the methyl-substituted complex exhibits a gradual increase in $\chi_M T$ with only a sharper rise at the end of the temperature range, the halogenated derivatives display much more abrupt transitions, reaching higher $\chi_M T$ values overall. This behaviour can be attributed to additional intermolecular interactions introduced by the halogen substituents, particularly halogen-hydrogen contacts, which complement the existing hydrogen-bonding network. These interactions restrict the structural flexibility required for the elongation of Co-donor bonds during the Co(III) to Co(II) conversion. At the same time, they enhance the cooperativity within the crystal lattice, resulting in a steeper transition profile despite the shift of the onset to slightly higher temperatures. The more abrupt increase observed for the methyl compound at elevated temperatures is most likely associated with solvent loss rather than intrinsic cooperativity.

In the case of the hexafluorophosphate salts the trend is less distinct. Electron-donating substituents again prove unfavourable, as indicated by higher onset temperatures and lower maximum $\chi_M T$ values. However, among the halogenated complexes $[\text{Co}_2\text{L}^{\text{Br}}](\text{PF}_6)_2$ and $[\text{Co}_2\text{L}^{\text{F}}](\text{PF}_6)_2$, the trend observed for the sulfates does not persist. The fluorinated derivative $[\text{Co}_2\text{L}^{\text{F}}](\text{PF}_6)_2$ shows a weak transition only at very high temperatures and reaches $\chi_M T$ values comparable to those of the methyl analogue $[\text{Co}_2\text{L}^{\text{Me}}](\text{PF}_6)_2$, whereas the brominated complex $[\text{Co}_2\text{L}^{\text{Br}}](\text{PF}_6)_2$ remains invariant throughout the temperature range.

Structurally, the fluorinated hexafluorophosphate compound $[\text{Co}_2\text{L}^{\text{F}}](\text{PF}_6)_2$ is noteworthy as it is the only complex in this series that crystallises without anion disorder and displays particularly strong intermolecular interactions, including hydrogen bonds and numerous H-F and F-F contacts. This can also be assumed for the brominated complex. It is therefore reasonable to assume that this high density of intermolecular interactions severely restricts the breathing motion required for bond elongation during VT, thereby inhibiting the transition much more strongly than in the analogues sulfate salt.

Conclusion and Outlook

The valence tautomeric behaviour of the dinuclear cobalt complexes bearing a redox-innocent bridging ligand follows a consistent trend. The electronic influence of the innocent bridging ligand plays a decisive role in facilitating the valence tautomeric transition, particularly when electron-withdrawing substituents are introduced. This trend is evident in solution, where the complexes display red-shifted LMCT bands in the UV-Vis spectra, smaller potential differences between the cobalt- and dioxolane-centred redox events in cyclic voltammetry, and higher molar susceptibilities in Evans measurements.

In the solid state, the same tendency is confirmed. Complexes bearing electron-withdrawing substituents exhibit more pronounced VT behaviour, demonstrating that the electronic nature of the bridging ligand directly affects the thermally induced electron transfer between cobalt and the redox-active dioxolane moiety. The results highlight that the innocent ligand, often overlooked in the design of VT-active compounds, has a significant impact on the switching characteristics and should be considered as an effective handle for fine-tuning the transition. This approach is particularly powerful, as systematic variation of the substituents at the redox-innocent bridging ligand offers a synthetically straightforward strategy to effectively modulate the valence tautomeric properties of the complexes.

Material and Methods

All chemicals were purchased from commercial suppliers (TCI, Thermo Scientific, Sigma-Aldrich, BLD Pharm, ABCR Chemicals, VWR and Fisher Chemicals) and used without further purification. Dry, degassed acetonitrile (Thermo Scientific) was used for cyclic voltammetry measurement. Dry Methanol (Thermo Scientific) was used for air-sensitive synthesis steps in a glovebox operated under an argon atmosphere. Dry THF was taken from a MBRAUN MG-SPS-800 solvent purification system. Deuterated solvents for NMR spectroscopy were obtained from Deutero. Unless otherwise stated, all reactions were carried out under ambient conditions using HPLC-grade solvents. Infrared spectra were recorded at room temperature and under air conditions within 4000-400 cm^{-1} range using a Bruker ALPHA II ATR-IR spectrometer. The data were analysed using OPUS software and plotted using Origin V7.5. UV-Vis spectra were recorded using a JASCO V-770 spectrometer in dual-beam mode and quartz glass cuvettes with an optical path length of 1 cm. The background was corrected using a cuvette containing pure solvent. The obtained spectra were plotted with origin V7.5. Single-crystal structure analyses were performed at 120 K using a STOE STADIVARI diffractometer at Johannes Gutenberg University of Mainz. The structures were solved and refined using SHELXT⁷⁶ and SHELXL⁷⁷, employing the Olex2⁷⁸ software. The crystal structure data are planned to be archived at the CCDC database. Crystal structure pictures were made with the software mercury. Cyclovoltammetry measurements were performed using a Metrohm Autolab potentiostat and measured with the software Nova 2.1.4. A three-electrode system consisting of a glassy carbon working electrode, a silver/silver nitrate reference electrode, and a platinum counter electrode. Prior to each series of measurements, the glassy carbon electrode was immersed in nitric acid for 20 minutes. It was then rinsed with distilled water and polished using aluminium oxide polishing paste (Buehler) on a microfiber cloth in a figure-of-eight motion. Finally, it was rinsed thoroughly again. The solutions were degassed with argon prior to the measurement and maintained under a continuous argon atmosphere. 0.1 mol tetrabutylammonium hexafluorophosphate was used as the conducting salt. At the end of each series of measurements, the potentials were referenced to the ferrocene/ferrocenium pair. The voltammograms were plotted using Origin V7.5. High-resolution mass spectra (HRes ESI-MS) were recorded in positive mode (ESI⁺) using an Agilent 6200 TOF/6500 G-TOF spectrometer at Johannes Gutenberg University Mainz. Magnetic measurements were performed using a Quantum Design MPMS3 SQUID magnetometer with an evercool system. The samples were prepared in plastic capsules, without eicosane, and fixed in a brass holder. Temperature-dependent measurements were performed at an applied magnetic field of 0.1 T in heating and cooling mode within the range of 10-400 K. Along a scan length of 4 cm, 24 data points were recorded, with each point being measured three times and the results being averaged. The diamagnetic contributions from the capsule and holder were determined experimentally and

subtracted from the raw data using SquidLab⁷⁹. Within the temperature range up to 300 K, the mean derivative value and corresponding standard deviation were determined to determine the onset temperature of the VT transition. The onset temperature was defined as the point at which the derivative first exceeded the threshold of the mean value plus five times the standard deviation. This temperature was defined as the onset of the valence tautomerism phenomenon. The magnetic data were plotted using origin V7.5. Elemental analyses (C, H, N) were carried out using an Elementar Vario EL Cube at the Johannes Gutenberg University Mainz. NMR-spectra and Evans method measurements were carried out on Bruker Avance III HD 300 (¹H: 400,13 MHz; ¹⁹F: 376 MHz; ¹³C: 100,1 MHz), Avance II 400 (¹H: 400,13 MHz; ¹³C: 100,1 MHz) und DRX 400 (¹H: 400,13 MHz; ¹³C: 100,1 MHz). All chemical shifts are reported in ppm relative to external tetramethylsilane (TMS). Spectral processing and visualization were performed using MestreNova.

Experimental Section

Complete synthetic procedures of the ligands and complexes can be found in the SI.

Ferrocenium hexafluorophosphate

Was prepared as previously reported.⁸⁰

L-H

Was prepared as previously reported.⁵⁹

L-Me

Pale yellow powder (1.98 g, 3.34 mmol, 57%), **IR** $\tilde{\nu}$ [cm⁻¹]: 3002(m), 2937(v CH₃ m), 2926(m), 2888(m), 2871(m), 2808(s), 2787(m), 2719(m), 1600(m), 1566(m), 1489(s), 1450(s), 1380(m), 1365(s), 1341(m), 1312(m), 1300(m), 1276(m), 1248(m), 1219(m), 1169(m), 1139(m), 1116(m), 1106(s), 1044(m), 1033(s), 1007(s), 976(m), 964(s), 930(m), 851(s), 830(ss), 815(s), 783(m), 766(m), 738(m), 724(m), 648(s), 589(m), 528(m), 495(s), 420(m), 404(m), **Elemental Analysis**: Found: C, 73.02%; H, 8.17%; N, 18.62%. Calc. for C₃₆H₄₈N₈: C, 72.94%; H, 8.16%; N, 18.90%, **Mass spectrometry** [*m/z*]: 593.408 [**L-Me + H**]⁺ (calc. = 593.408), **¹H-NMR** (CDCl₃ [400 MHz]) δ [ppm] = 8.33(s, 4H, H¹¹), 7.44 (dd, 4H, *J*³=8.1, 2.2 Hz, H¹³), 7.40 (d, 4H, *J*³=8.0 Hz, H¹⁴), 3.79 (s, 8H, H⁸), 2.69-2.66 (m, 4H, H⁶), 2.52-2.49 (m, 4H, H⁵), 2.37 (s, 8H, H^{2,3}), 2.29 (s, 12H, H¹⁵), **¹³C-NMR** (CDCl₃ [101 MHz]): δ [ppm] = 157(C⁹), 149(C¹¹), 137(C¹³), 131(C¹²), 122(C¹⁴), 60(C⁸), 56(C⁵), 53(C^{2,3}), 51(C⁶), 18(C¹⁵).

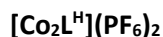
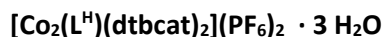
L-Br

Yellow powder (3.52 g, 4.13 mmol, 47%), **IR** $\tilde{\nu}$ [cm⁻¹]: 3039 (m), 3003 (m), 2935 (m), 2817 (m), 1573 (m), 1556 (m), 1459 (s), 1369 (s), 1352 (m), 1325 (m), 1295 (m), 1264 (m), 1236 (m), 1161 (m), 1139 (m), 1119 (s), 1087 (s), 1046 (s), 1007 (ss), 990 (s), 960 (m), 936 (m), 916 (m), 884 (m), 828 (ss), 779 (m), 728 (m), 654 (m), 632 (ss), 496 (s), 458 (s), 408 (s), **Elemental Analysis**: Found: C, 45.05%; H, 4.63%; N, 12.80%. Calc. for C₃₂H₃₆N₈Br₄: C, 45.10%; H, 4.26%; N, 13.15%, **Mass spectrometry** [*m/z*]: 852.9849 [**L-Br + H**]⁺ (calc. = 852.9829). **¹H-NMR** (CDCl₃ [400 MHz]) δ [ppm] = 8.56 (dd, 4H, *J* = 2.4, 0.7 Hz, H¹¹), 7.75 (dd, 4H, *J* = 8.4, 2.4 Hz, H¹³), 7.41 (d, 4H, *J*³ = 8.4 Hz, H¹⁴), 3.79 (s, 8H, H⁸), 2.70-2.67 (m, 4H, H⁵), 2.51-2.48 (m, 4H, H⁶), 2.38 (s, 8H, H^{2,3}), **¹³C-NMR** (CDCl₃ [101 MHz]): δ [ppm] = 158 (C¹²), 150 (C¹¹), 139 (C¹³), 124 (C¹⁴), 119 (C⁹), 60 (C⁸), 56 (C⁶), 54 (C^{2,3}), 51 (C⁵).

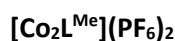
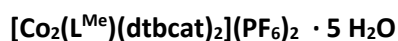
L-F

Yellow powder (1.47 g, 2.42 mmol, 42%), **IR** $\tilde{\nu}$ [cm⁻¹]: 3048 (vw), 3034 (vw), 2990 (vw), 2952 (w), 2929 (w), 2851 (w), 2815 (w), 2779 (vw), 2753 (vw), 2731 (vw), 2691 (vw), 1582 (w), 1479 (vs), 1460 (m), 1441 (m), 1392 (w), 1371 (w), 1358 (w), 1318 (w), 1298 (m), 1266 (w), 1223 (vs), 1158 (m), 1111 (m), 1069 (w), 1039 (m), 1024 (w), 1010 (m), 979 (w), 967 (m), 934 (w), 909 (m), 875 (w), 847 (vs), 794 (w), 775 (w), 735 (m), 716 (w), 659 (w), 636 (m), 586 (m), 557 (m), 509 (m), 472 (w), 443 (m), 418 (vs).

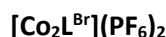
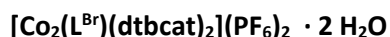
Elemental Analysis: Found: C, 63.14 %; H, 5.99 %; N, 18.40 %. Calc. for $C_{32}H_{36}N_8F_4$: C, 63.14 %; H, 5.96 %; N, 18.41 %, **Mass spectrometry** [m/z]: 609.3070 [$L-F + H$]⁺ (calc. = 609.3072), **1H -NMR** ($CDCl_3$ [400 MHz]) δ [ppm] = 8.39 (d, 4H, $J^3 = 2.9$ Hz, H^{11}), 7.52 (dd, 4H, $J^3 = 8.6$, 4.6 Hz, H^{13}), 7.37 (td, 4H, $J^3 = 8.4$, 2.9 Hz, H^{14}), 3.83 (s, 8H, H^8), 2.72-2.69 (m, 4H, H^5), 2.54-2.50 (m, 4H, H^6), 2.40 (s, 8H, $H^{2,3}$). **^{13}C -NMR** ($CDCl_3$ [101 MHz]): δ [ppm] = 158 (d, C^{12}), 155 (d, C^9), 137 (d, C^{11}), 123.8 (d, C^{14}), 123.2 (d, C^{13}), 60 (C^8), 56 (C^5), 54 (C^2), 51 (C^6), ^{19}F ($CDCl_3$ [376 MHz]) -129.82 (dd, $J = 8.6$ Hz, 4.2 Hz).



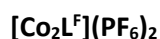
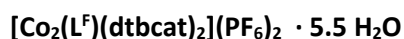
Green plates (30 mg, 0.022 mmol, 22%), **IR** $\tilde{\nu}$ [cm^{-1}]: 2958(w), 2913(w), 2865(w), 1609(w), 1557(w), 1462(m), 1440(m), 1410(m), 1359(w), 1315(w), 1279(m), 1240(m), 1205(w), 1160(w), 1130(w), 1101(w), 1086(w), 1058(w), 1025(w), 974(m), 953(w), 936(w), 914(w), 903(w), 834(s), 769(s), 718(m), 682(w), 652(m), 616(m), 582(w), 556(s), 511(m), 494(m), 476(m), 452(m), 431(m), 405(m), **Mass spectrometry** [m/z]: 547.247 [C]²⁺ (calc. = 547.247), **Elemental Analysis:** Found: C, 49.70%; H, 6.32%; N, 8.02%. Calc. for $C_{60}H_{80}Co_2F_{12}N_8O_4P_2 + 3 H_2O$: C, 50.07%; H, 6.02%; N, 7.79%.



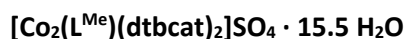
Green plates (78 mg, 0.054 mmol, 54%), **IR** $\tilde{\nu}$ [cm^{-1}]: 3647(w), 2954(m), 2907(m), 2869(w), 1614(m), 1554(m), 1502(m), 1459(m), 1439(m), 1411(m), 1360(m), 1319(m), 1282(m), 1238(m), 1204(m), 1140(m), 1100(w), 1053(m), 1025(m), 981(m), 954(m), 840(ss), 826(ss), 768(m), 752(m), 714(m), 679(m), 654(m), 615(m), 557(s), 522(m), 470(m), 449(m), 431(m), 416(m), **Mass spectrometry** [m/z]: 575.2805 [C]²⁺ (calc. = 575.2791), **Elemental Analysis:** Found: C, 50.01%; H, 6.28%; N, 7.61%. Calc. for $C_{64}H_{88}Co_2F_{12}N_8O_4P_2 + 5 H_2O$: C, 50.20%; H, 6.45%; N, 7.32%.



Brown powder (126 mg, 0.074 mmol, 74%), **IR** $\tilde{\nu}$ [cm^{-1}]: 3101(w), 3043(w), 2951(m), 2904(w), 2865(w), 1629(w), 1595(w), 1555(m), 1460(m), 1438(m), 1412(m), 1391(m), 1356(w), 1327(m), 1283(m), 1237(m), 1203(m), 1137(w), 1100(m), 1049(m), 1022(w), 980(m), 943(w), 925(w), 823(ss), 773(m), 753(m), 714(m), 694(m), 664(m), 652(m), 624(m), 600(m), 557(s), 504(m), 463(m), 447(m), 411(m), **Mass spectrometry** [m/z]: 705.068 [C]²⁺ (calc. = 705.067), **Elemental Analysis:** Found: C, 41.27%; H, 4.82%; N, 6.76%. Calc. for $C_{60}H_{76}Co_2Br_4F_{12}N_8O_4P_2 + 2 H_2O$: C, 41.49%; H, 4.64%; N, 6.45%.



Green plates (102 mg, 0.070 mmol, 70%), **IR** $\tilde{\nu}$ [cm^{-1}]: 3649 (vw), 3070 (vw), 3044 (vw), 2949 (w), 2903 (vw), 2865 (vw), 1620 (vw), 1586 (w), 1557 (vw), 1501 (m), 1441 (w), 1414 (m), 1361 (vw), 1319 (w), 1278 (w), 1238 (m), 1205 (w), 1129 (vw), 1105 (vw), 1041 (w), 1023 (w), 999 (w), 985 (w), 952 (w), 931 (vw), 906 (vw), 838 (vs), 821 (vs), 768 (w), 756 (w), 739 (w), 712 (w), 666 (w), 655 (w), 630 (w), 611 (w), 556 (vs), 513 (vw), 472 (w), 454 (w), 435 (w), **Mass spectrometry** [m/z]: 583.2311 [C]²⁺ (calc. = 583.2290), **Elemental Analysis:** Found: C, 45.96%; H, 5.75%; N, 7.40%. Calc. for $C_{60}H_{76}Co_2F_{16}N_8O_4P_2 + 5.5 H_2O$: C, 46.31%; H, 5.63%; N, 7.20%.



Green plates (46 mg, 0.037 mmol, 37%), **IR** $\tilde{\nu}$ [cm^{-1}]: 3273(w), 2948(m), 2909(w), 2867(w), 1635(w), 1575(w), 1555(w), 1504(w), 1495(w), 1461(m), 1440(m), 1412(m), 1360(w), 1323(w), 1278(m), 1240(m), 1202(w), 1062(s), 1022(m), 977(m), 945(w), 876(m), 852(m), 829(m), 809(w), 767(m), 752(m), 712(m), 671(m), 653(m), 613(s), 565(m), 548(m), 515(m), 471(m), 449(s), 428(s), **Mass spectrometry** [m/z]: 575.2787 [C]²⁺ (calc. = 575.2790), **Elemental Analysis:** Found: C, 50.35%; H, 7.86%; N, 7.34%. Calc. for $C_{64}H_{88}Co_2N_8O_8S + 15.5 H_2O$: C, 50.19%; H, 7.90%; N, 7.47%.

[Co₂(L^{Br})(dtbcat)₂]₂SO₄ · 11 H₂O [Co₂L^{Br}]₂SO₄

Brown powder (75 mg, 0.049 mmol, 49%), **IR** $\tilde{\nu}$ [cm⁻¹]: 3300 (w), 3099 (w), 2951 (w), 2904 (w), 1635 (w), 1594 (w), 1555 (w), 1463 (m), 1440 (m), 1413 (m), 1390 (w), 1359 (w), 1318 (w), 1284 (w), 1240 (w), 1204 (w), 1097 (s), 1049 (s), 1028 (s), 978 (m), 947 (m), 873 (m), 840 (m), 826 (m), 810 (m), 767 (m), 754 (m), 700 (m), 665 (m), 653 (m), 606 (m), 550 (m), 534 (m), 491 (m), 463 (m), 444 (m), 431 (m), **Mass spectrometry** [*m/z*]: 705.067 [C]²⁺ (calc. = 705.067), **Elemental Analysis**: Found: C, 42.09 %; H, 5.46 %; N, 6.59%, S, 2.03%. Calc. for C₆₀H₇₆Co₂Br₄N₈O₈S + 11 H₂O: C, 42.27 %; H, 5.79 %; N, 6.57 %, S, 1.88 %.

[Co₂(L^F)(dtbcat)₂]₂SO₄ · 17 H₂O [Co₂L^F]₂SO₄

Green plates (46 mg, 0.037 mmol, 37%), **IR** $\tilde{\nu}$ [cm⁻¹]: 3381(m), 3071(m), 2953(m), 2867(w), 1634(w), 1584(w), 1555(w), 1495(m), 1461(m), 1440(m), 1412(m), 1359(w), 1321(w), 1276(m), 1239(s), 1203(w), 1083(s), 1024(m), 1002(w), 978(m), 945(w), 878(m), 848(m), 827(w), 810(w), 795(w), 768(w), 753(m), 713(m), 684(w), 666(m), 655(m), 610(m), 566(m), 471(w), 453(w), 431(w), 410(s), **Mass spectrometry** [*m/z*]: 583.2282 [C]²⁺ (calc. = 583.2290), **Elemental Analysis**: Found: C, 46.26%; H, 7.02%; N, 7.26%, S, 1.76%. Calc. for C₆₀H₇₆Co₂F₄N₈O₈S + 17 H₂O: C, 45.92%; H, 7.06%; N, 7.26%, S, 2.04%.

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Notes

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5.1 ESI: Electronic Tuning of Dinuclear Cobalt VT by modifying an Innocent Bridging Ligand

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5.1.1 Experimental Synthesis

L-H (Synthesized as previously reported)¹²

L-Me

N,N'-Bis(2-aminoethyl)piperazine (1.00 g, 5.80 mmol, 1.0 equiv.) was dissolved in 100 mL dichloromethane. Sodium triacetoxyborohydride (6.15 g, 29 mmol, 5.0 equiv.) was added in small portions while stirring. A solution of 5-methyl-2-picolinaldehyde (2.95 g, 24.4 mmol, 4.2 equiv.) in dichloromethane (10 mL) was added dropwise over 30 minutes. The reaction mixture was stirred at room temperature overnight. Saturated aqueous NaHCO₃ (50 mL) was then added and the mixture was stirred for a further 30 minutes. The phases were separated and the aqueous phase was extracted with dichloromethane (50 mL). The combined organic phases were dried over sodium sulfate and the solvent was removed under pressure. The remaining yellow oil was recrystallized twice from 15 mL of acetonitrile giving a yellow powder

Pale yellow powder (1.98 g, 3.34 mmol, 57%), **IR** $\tilde{\nu}$ [cm⁻¹]: 3002(m), 2937(v CH₃ m), 2926(m), 2888(m), 2871(m), 2808(s), 2787(m), 2719(m), 1600(m), 1566(m), 1489(s), 1450(s), 1380(m), 1365(s), 1341(m), 1312(m), 1300(m), 1276(m), 1248(m), 1219(m), 1169(m), 1139(m), 1116(m), 1106(s), 1044(m), 1033(s), 1007(s), 976(m), 964(s), 930(m), 851(s), 830(ss), 815(s), 783(m), 766(m), 738(m), 724(m), 648(s), 589(m), 528(m), 495(s), 420(m), 404(m), **Elemental Analysis**: Found: C, 73.02%; H, 8.17%; N, 18.62%. Calc. for C₃₆H₄₈N₈: C, 72.94%; H, 8.16%; N, 18.90%, **Mass spectrometry** [*m/z*]: 593.408 [**L-Me + H**]⁺ (calc. = 593.408), **¹H-NMR** (CDCl₃ [400 MHz]) δ [ppm] = 8.33(s, 4H, H¹¹), 7.44 (dd, 4H, *J*³=8.1, 2.2 Hz, H¹³), 7.40 (d, 4H, *J*³=8.0 Hz, H¹⁴), 3.79 (s, 8H, H⁸), 2.69-2.66 (m, 4H, H⁶), 2.52-2.49 (m, 4H, H⁵), 2.37 (s, 8H, H^{2,3}), 2.29 (s, 12H, H¹⁵), **¹³C-NMR** (CDCl₃ [101 MHz]): δ [ppm] = 157(C⁹), 149(C¹¹), 137(C¹³), 131(C¹²), 122(C¹⁴), 60(C⁸), 56(C⁵), 53(C^{2,3}), 51(C⁶), 18(C¹⁵).

L-Br

N,N'-Bis(2-aminoethyl)piperazine (1.50 g, 8.71 mmol, 1.0 equiv.) was dissolved in 200 mL dichloromethane. Sodium triacetoxyborohydride (9.23 g, 43.5 mmol, 5.0 equiv.) was added in small portions while stirring. A solution of 5-bromo-2-picolinaldehyde (6.62 g, 24.4 mmol, 4.2 equiv.) in dichloromethane (100 mL) was added dropwise over 30 minutes. The reaction mixture was stirred at room temperature overnight. Saturated aqueous NaHCO₃ (50 mL) was then added and the mixture was stirred for a further 30 minutes. The phases were separated and the aqueous phase was extracted with dichloromethane (50 mL). The combined organic phases were dried over sodium sulfate and the solvent was removed under pressure. The remaining yellow oil was recrystallized twice from 15 mL of ethanol giving a yellow powder

Yellow powder (3.52 g, 4.13 mmol, 47%), **IR** $\tilde{\nu}$ [cm⁻¹]: 3039 (m), 3003 (m), 2935 (m), 2817 (m), 1573 (m), 1556 (m), 1459 (s), 1369 (s), 1352 (m), 1325 (m), 1295 (m), 1264 (m), 1236 (m), 1161 (m), 1139 (m), 1119 (s), 1087 (s), 1046 (s), 1007 (ss), 990 (s), 960 (m), 936 (m), 916 (m), 884 (m), 828 (ss), 779 (m), 728 (m), 654 (m), 632 (ss), 496 (s), 458 (s), 408 (s), **Elemental Analysis**: Found: C, 45.05%; H, 4.63%; N, 12.80%. Calc. for C₃₂H₃₆N₈Br₄: C, 45.10%; H, 4.26%; N, 13.15%, **Mass spectrometry** [*m/z*]: 852.9849 [**L-Br + H**]⁺ (calc. = 852.9829), **¹H-NMR** (CDCl₃ [400 MHz]) δ [ppm] = 8.56 (dd, 4H, *J* = 2.4, 0.7 Hz, H¹¹), 7.75 (dd, 4H, *J* = 8.4, 2.4 Hz, H¹³), 7.41 (d, 4H, *J*³ = 8.4 Hz, H¹⁴), 3.79 (s, 8H, H⁸), 2.70-2.67 (m, 4H, H⁵), 2.51-2.48 (m, 4H, H⁶), 2.38 (s, 8H, H^{2,3}), **¹³C-NMR** (CDCl₃ [101 MHz]): δ [ppm] = 158 (C¹²), 150 (C¹¹), 139 (C¹³), 124 (C¹⁴), 119 (C⁹), 60 (C⁸), 56 (C⁶), 54 (C^{2,3}), 51 (C⁵).

L-F

N,N'-Bis(2-aminoethyl)piperazine (0.9 g, 5.22 mmol, 1.0 equiv.) was dissolved in 100 mL dichloromethane. Sodium triacetoxyborohydride (6.15 g, 29.5 mmol, 5.0 equiv.) was added in small portions while stirring. A solution of 5-bromo-2-picolinaldehyde (2.91 g, 23.2 mmol, 4.0 equiv.) in dichloromethane (100 mL) was added dropwise over 30 minutes. The reaction mixture was stirred at room temperature overnight. Saturated aqueous NaHCO₃ (50 mL) was then added and the mixture was stirred for a further 30 minutes. The phases were separated and the aqueous phase was extracted with dichloromethane (50 mL). The combined organic phases were dried over sodium sulfate and the solvent was removed under pressure. The remaining yellow oil was recrystallized twice from 5 mL of acetonitrile giving a yellow powder.

Yellow powder (1.47 g, 2.42 mmol, 42%), **IR** $\tilde{\nu}$ [cm⁻¹]: 3048 (vw), 3034 (vw), 2990 (vw), 2952 (w), 2929 (w), 2851 (w), 2815 (w), 2779 (vw), 2753 (vw), 2731 (vw), 2691 (vw), 1582 (w), 1479 (vs), 1460 (m), 1441 (m), 1392 (w), 1371 (w), 1358 (w), 1318 (w), 1298 (m), 1266 (w), 1223 (vs), 1158 (m), 1111 (m), 1069 (w), 1039 (m), 1024 (w), 1010 (m), 979 (w), 967 (m), 934 (w), 909 (m), 875 (w), 847 (vs), 794 (w), 775 (w), 735 (m), 716 (w), 659 (w), 636 (m), 586 (m), 557 (m), 509 (m), 472 (w), 443 (m), 418 (vs). **Elemental Analysis**: Found: C, 63.14 %; H, 5.99 %; N, 18.40 %. Calc. for C₃₂H₃₆N₈F₄: C, 63.14 %; H, 5.96 %; N, 18.41 %, **Mass spectrometry** [*m/z*]: 609.3070 [**L-F** + H]⁺ (calc. = 609.3072), **¹H-NMR** (CDCl₃ [400 MHz]) δ [ppm] = 8.39 (d, 4H, *J*³ = 2.9 Hz, H¹¹), 7.52 (dd, 4H, *J*³ = 8.6, 4.6 Hz, H¹³), 7.37 (td, 4H, *J*³ = 8.4, 2.9 Hz, H¹⁴), 3.83 (s, 8H, H⁸), 2.72-2.69 (m, 4H, H⁵), 2.54-2.50 (m, 4H, H⁶), 2.40 (s, 8H, H^{2,3}). **¹³C-NMR** (CDCl₃ [101 MHz]): δ [ppm] = 158 (d, C¹²), 155 (d, C⁹), 137 (d, C¹¹), 123.8 (d, C¹⁴), 123.2 (d, C¹³), 60 (C⁸), 56 (C⁵), 54 (C²), 51 (C⁶), **¹⁹F** (CDCl₃ [376 MHz]) -129.82 (dd, *J* = 8.6 Hz, 4.2 Hz).

[Co₂L^H](PF₆)₂

In a glovebox, **L-H** (54 mg, 0.10 mmol, 1.0 equiv.) was dissolved in dry methanol (5 mL). A solution of dtbcat (45 mg, 0.20 mmol, 2.0 equiv.) and CoCl₂ (28 mg, 0.20 mmol, 2.0 equiv.) in dry methanol (10 mL) was added dropwise to the ligand solution under stirring. Triethylamine (41 mg, 0.40 mmol, 4.0 equiv.) was added dropwise, resulting in a colour change to red. FcPF₆ (66 mg, 0.20 mmol, 2.0 equiv.) was then added as a solid. The suspension was stirred overnight, during which the colour changed to green. The mixture was heated to reflux to redissolve the solids, and after filtration, single crystals suitable for X-ray diffraction were obtained from the mother liquor by slow diethyl ether diffusion. Suitable crystals were isolated after one week.

Green plates (30 mg, 0.022 mmol, 22%), **IR** $\tilde{\nu}$ [cm⁻¹]: 2958(w), 2913(w), 2865(w), 1609(w), 1557(w), 1462(m), 1440(m), 1410(m), 1359(w), 1315(w), 1279(m), 1240(m), 1205(w), 1160(w), 1130(w), 1101(w), 1086(w), 1058(w), 1025(w), 974(m), 953(w), 936(w), 914(w), 903(w), 834(s), 769(s), 718(m), 682(w), 652(m), 616(m), 582(w), 556(s), 511(m), 494(m), 476(m), 452(m), 431(m), 405(m), **Mass spectrometry** [*m/z*]: 547.247 [**C**]²⁺ (calc. = 547.247), **Elemental Analysis**: Found: C, 49.70%; H, 6.32%; N, 8.02%. Calc. for C₆₀H₈₀Co₂F₁₂N₈O₄P₂ + 3 H₂O: C, 50.07%; H, 6.02%; N, 7.79%.

[Co₂L^{Me}](PF₆)₂

In a glovebox, **L-Me** (59 mg, 0.10 mmol, 1.0 equiv.) was dissolved in dry methanol (5 mL). A solution of dtbcat (45 mg, 0.20 mmol, 2.0 equiv.) and CoCl₂ (28 mg, 0.20 mmol, 2.0 equiv.) in dry methanol (10 mL) was added dropwise to the ligand solution under stirring. Triethylamine (41 mg, 0.40 mmol, 4.0 equiv.) was added dropwise, resulting in a colour change to red. FcPF₆ (66 mg, 0.20 mmol, 2.0 equiv.) was then added as a solid. The suspension was stirred overnight, during which the colour changed to green. The green precipitate was collected by centrifugation, filtered and dried in air. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a tetrahydrofuran solution after recrystallization, which yielded single crystals after 3 months.

Green plates (78 mg, 0.054 mmol, 54%), **IR** $\tilde{\nu}$ [cm⁻¹]: 3647(w), 2954(m), 2907(m), 2869(w), 1614(m), 1554(m), 1502(m), 1459(m), 1439(m), 1411(m), 1360(m), 1319(m), 1282(m), 1238(m), 1204(m), 1140(m), 1100(w), 1053(m), 1025(m), 981(m), 954(m), 840(ss), 826(ss), 768(m), 752(m), 714(m), 679(m), 654(m), 615(m), 557(s), 522(m), 470(m), 449(m), 431(m), 416(m), **Mass spectrometry** [*m/z*]: 575.2805 [C]²⁺ (calc. = 575.2791), **Elemental Analysis**: Found: C, 50.01%; H, 6.28%; N, 7.61%. Calc. for C₆₄H₈₈Co₂F₁₂N₈O₄P₂ + 5 H₂O: C, 50.20%; H, 6.45%; N, 7.32%.

[Co₂L^{Br}](PF₆)₂

In a glovebox, **L-Br** (85 mg, 0.10 mmol, 1.0 equiv.) was dissolved in dry methanol (5 mL). A solution of dtbcat (45 mg, 0.20 mmol, 2.0 equiv.) and CoCl₂ (28 mg, 0.20 mmol, 2.0 equiv.) in dry methanol (10 mL) was added dropwise to the ligand solution under stirring. Triethylamine (41 mg, 0.40 mmol, 4.0 equiv.) was added dropwise, resulting in a colour change to red. FcPF₆ (66 mg, 0.20 mmol, 2.0 equiv.) was then added as a solid. The suspension was stirred overnight, during which the colour changed to green. The green precipitate was collected by centrifugation, filtered and dried in air. While drying in air, the green powder turned brownish.

Brown powder (126 mg, 0.074 mmol, 74%), **IR** $\tilde{\nu}$ [cm⁻¹]: 3101(w), 3043(w), 2951(m), 2904(w), 2865(w), 1629(w), 1595(w), 1555(m), 1460(m), 1438(m), 1412(m), 1391(m), 1356(w), 1327(m), 1283(m), 1237(m), 1203(m), 1137(w), 1100(m), 1049(m), 1022(w), 980(m), 943(w), 925(w), 823(ss), 773(m), 753(m), 714(m), 694(m), 664(m), 652(m), 624(m), 600(m), 557(s), 504(m), 463(m), 447(m), 411(m), **Mass spectrometry** [*m/z*]: 705.068 [C]²⁺ (calc. = 705.067), **Elemental Analysis**: Found: C, 41.27%; H, 4.82%; N, 6.76%. Calc. for C₆₀H₇₆Co₂Br₄F₁₂N₈O₄P₂ + 2 H₂O: C, 41.49%; H, 4.64%; N, 6.45%.

[Co₂L^F](PF₆)₂

In a glovebox, **L-F** (61 mg, 0.10 mmol, 1.0 equiv.) was dissolved in dry methanol (5 mL). A solution of dtbcat (45 mg, 0.20 mmol, 2.0 equiv.) and CoCl₂ (28 mg, 0.20 mmol, 2.0 equiv.) in dry methanol (10 mL) was added dropwise to the ligand solution under stirring. Triethylamine (41 mg, 0.40 mmol, 4.0 equiv.) was added dropwise, resulting in a colour change to red. FcPF₆ (66 mg, 0.20 mmol, 2.0 equiv.) was then added as a solid. The suspension was stirred overnight, during which the colour changed to green. The green precipitate was collected by centrifugation, filtered and dried in air. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a tetrahydrofuran solution after recrystallization, which yielded single crystals after 1 week.

Green plates (102 mg, 0.070 mmol, 70%), **IR** $\tilde{\nu}$ [cm⁻¹]: 3649 (vw), 3070 (vw), 3044 (vw), 2949 (w), 2903 (vw), 2865 (vw), 1620 (vw), 1586 (w), 1557 (vw), 1501 (m), 1441 (w), 1414 (m), 1361 (vw), 1319 (w), 1278 (w), 1238 (m), 1205 (w), 1129 (vw), 1105 (vw), 1041 (w), 1023 (w), 999 (w), 985 (w), 952 (w), 931 (vw), 906 (vw), 838 (vs), 821 (vs), 768 (w), 756 (w), 739 (w), 712 (w), 666 (w), 655 (w), 630 (w), 611 (w), 556 (vs), 513 (vw), 472 (w), 454 (w), 435 (w), **Mass spectrometry** [*m/z*]: 583.2311 [C]²⁺ (calc. = 583.2290), **Elemental Analysis**: Found: C, 45.96%; H, 5.75%; N, 7.40%. Calc. for C₆₀H₇₆Co₂F₁₆N₈O₄P₂ + 5.5 H₂O: C, 46.31%; H, 5.63%; N, 7.20%.

[Co₂L^{Me}]⁺SO₄⁻

L-Me (59 mg, 0.10 mmol, 1.0 equiv.) was dissolved in methanol (5 mL). A solution of dtbcat (45 mg, 0.20 mmol, 2.0 equiv.) and CoSO₄ 7 H₂O (56 mg, 0.20 mmol, 2.0 equiv.) in methanol (10 mL) was added dropwise to the ligand solution under stirring. Triethylamine (41 mg, 0.40 mmol, 4.0 equiv.) was added dropwise, resulting in a colour change to green. The solution was heated under reflux for 1 hour. After cooling to room temperature, it was filtered. Suitable single crystals for X-Ray diffraction were obtained after 1 day of a diethyl ether diffusion.

Green plates (46 mg, 0.037 mmol, 37%), **IR** $\tilde{\nu}$ [cm⁻¹]: 3273(w), 2948(m), 2909(w), 2867(w), 1635(w), 1575(w), 1555(w), 1504(w), 1495(w), 1461(m), 1440(m), 1412(m), 1360(w), 1323(w), 1278(m), 1240(m), 1202(w), 1062(s), 1022(m), 977(m), 945(w), 876(m), 852(m), 829(m), 809(w), 767(m), 752(m), 712(m), 671(m), 653(m), 613(s), 565(m), 548(m), 515(m), 471(m), 449(s), 428(s), **Mass spectrometry** [*m/z*]: 575.2787 [**C**]²⁺ (calc. = 575.2790), **Elemental Analysis**: Found: C, 50.35%; H, 7.86%; N, 7.34%. Calc. for C₆₄H₈₈Co₂N₈O₈S + 15.5 H₂O: C, 50.19%; H, 7.90%; N, 7.47%.

[Co₂L^{Br}]⁺SO₄⁻

L-Br (85 mg, 0.10 mmol, 1.0 equiv.) was dissolved in methanol (5 mL). A solution of dtbcat (45 mg, 0.20 mmol, 2.0 equiv.) and CoSO₄ 7 H₂O (56 mg, 0.20 mmol, 2.0 equiv.) in methanol (10 mL) was added dropwise to the ligand solution under stirring. Triethylamine (41 mg, 0.40 mmol, 4.0 equiv.) was added dropwise, resulting in a colour change to green. The suspension was heated under reflux for 1 hour. After cooling to room temperature, it was filtered.

Brown powder (75 mg, 0.049 mmol, 49%), **IR** $\tilde{\nu}$ [cm⁻¹]: 3300 (w), 3099 (w), 2951 (w), 2904 (w), 1635 (w), 1594 (w), 1555 (w), 1463 (m), 1440 (m), 1413 (m), 1390 (w), 1359 (w), 1318 (w), 1284 (w), 1240 (w), 1204 (w), 1097 (s), 1049 (s), 1028 (s), 978 (m), 947 (m), 873 (m), 840 (m), 826 (m), 810 (m), 767 (m), 754 (m), 700 (m), 665 (m), 653 (m), 606 (m), 550 (m), 534 (m), 491 (m), 463 (m), 444 (m), 431 (m), **Mass spectrometry** [*m/z*]: 705.067 [**C**]²⁺ (calc. = 705.067), **Elemental Analysis**: Found: C, 42.09 %; H, 5.46 %; N, 6.59%, S, 2.03%. Calc. for C₆₀H₇₆Co₂Br₄N₈O₈S + 11 H₂O: C, 42.27 %; H, 5.79 %; N, 6.57 %, S, 1.88 %.

[Co₂L^F]⁺SO₄⁻

In a glovebox, **L-F** (61 mg, 0.10 mmol, 1.0 equiv.) and dtbcat (45 mg, 0.20 mmol, 2.0 equiv.) were dissolved in dry acetonitrile (10 mL). A solution of and CoCl₂ (28 mg, 0.20 mmol, 2.0 equiv.) in dry acetonitrile (5 mL) was added dropwise to the ligand solution under stirring. Triethylamine (41 mg, 0.40 mmol, 4.0 equiv.) was added dropwise, resulting in a colour change to red. After stirring for 1 hour the red solution was oxidized on air and the solution turned green. Tetrabutylammonium sulfate 50% in water (120 mg, 0.1 mmol, 1 equiv.) was added, directly a green precipitate formed. The green powder was isolated by centrifugation, filtration and was air dried overnight. The green powder was recrystallized by refluxing in methanol. Suitable crystals for X-ray diffraction were obtained by slow evaporation from the filtered mother liquor at 5°C over 3 weeks.

Green plates (46 mg, 0.037 mmol, 37%), **IR** $\tilde{\nu}$ [cm⁻¹]: 3381(m), 3071(m), 2953(m), 2867(w), 1634(w), 1584(w), 1555(w), 1495(m), 1461(m), 1440(m), 1412(m), 1359(w), 1321(w), 1276(m), 1239(s), 1203(w), 1083(s), 1024(m), 1002(w), 978(m), 945(w), 878(m), 848(m), 827(w), 810(w), 795(w), 768(w), 753(m), 713(m), 684(w), 666(m), 655(m), 610(m), 566(m), 471(w), 453(w), 431(w), 410(s), **Mass spectrometry** [*m/z*]: 583.2282 [**C**]²⁺ (calc. = 583.2290), **Elemental Analysis**: Found: C, 46.26%; H, 7.02%; N, 7.26%, S, 1.76%. Calc. for C₆₀H₇₆Co₂F₄N₈O₈S + 17 H₂O: C, 45.92%; H, 7.06%; N, 7.26%, S, 2.04%.

5.1.2 IR-Spectra Ligand

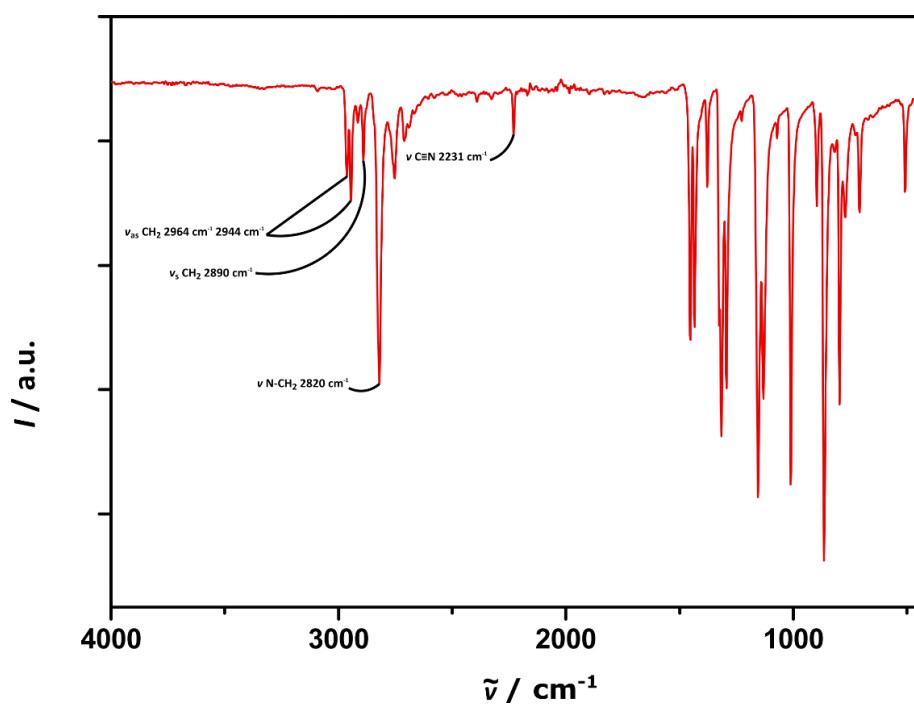


Figure S1: ATR-IR-spectrum of *N, N'*-Bis(cyanomethyl)piperazine.

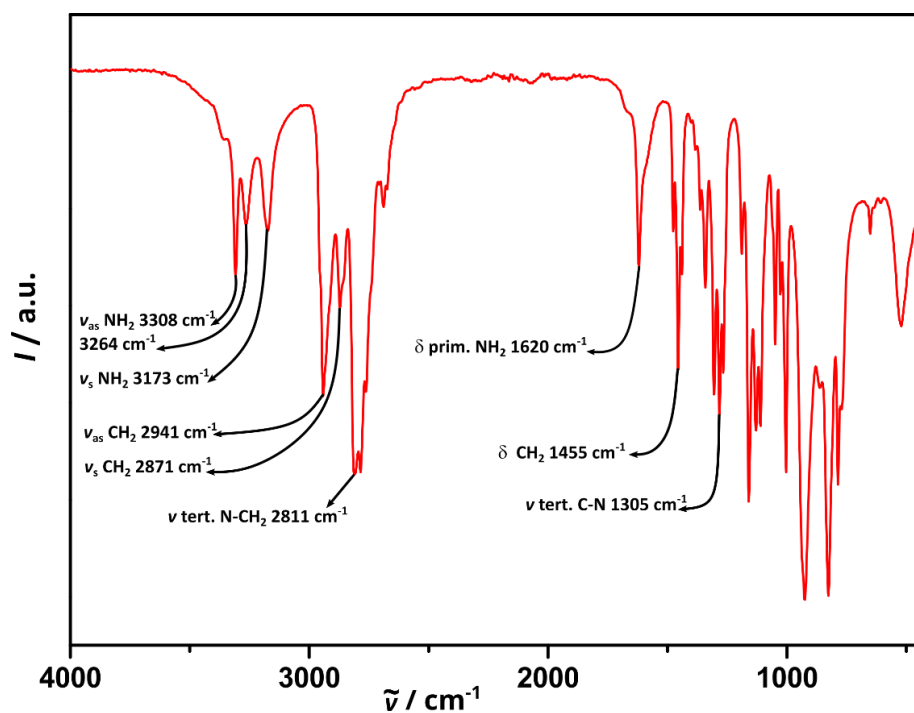


Figure S2: ATR-IR-spectrum of *N, N'*-bis(aminoethyl)piperazine.

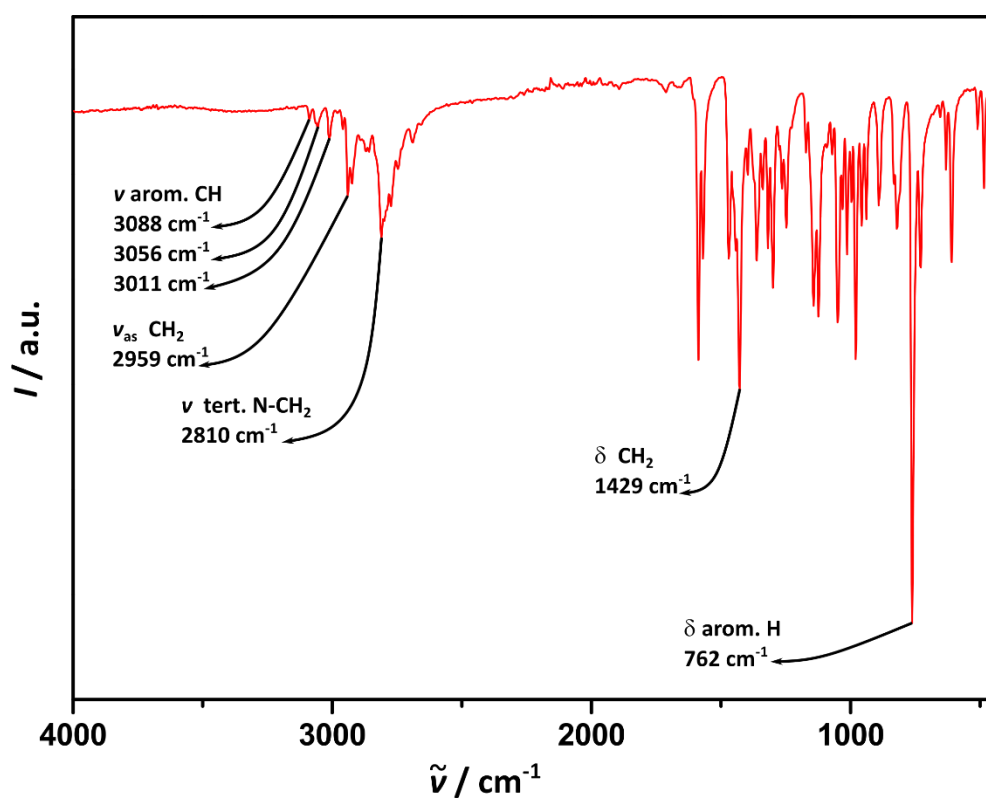


Figure S3: ATR-IR of *N, N', N'*-Tetra-2-picoly-1,4-bis(2-aminoethyl)piperazine (**L-H**).

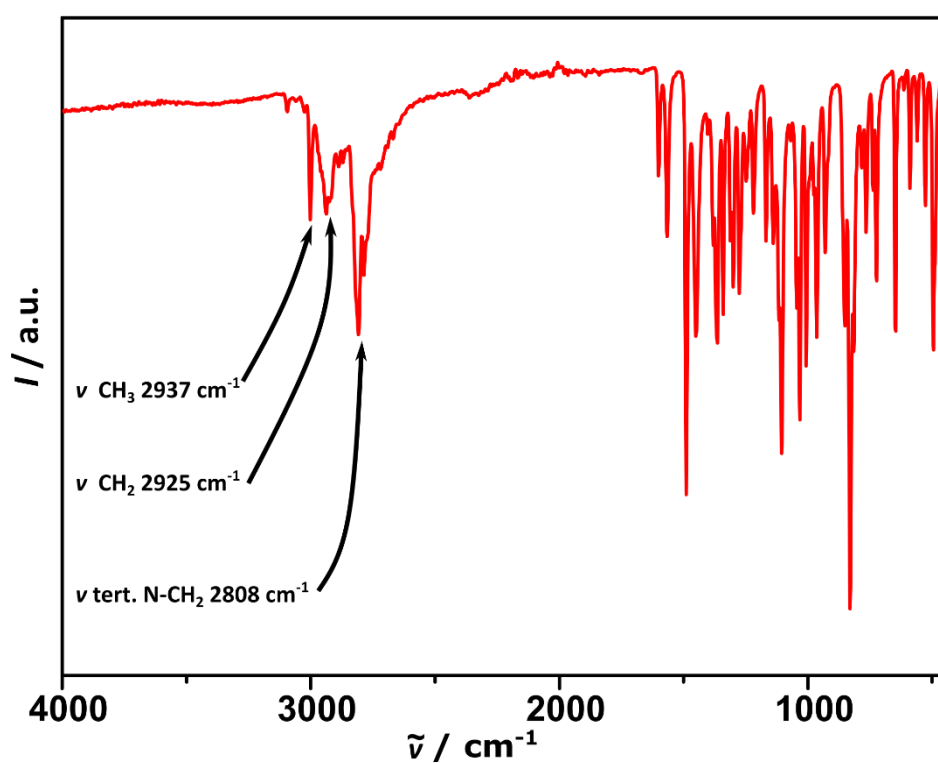


Figure S4: ATR-IR of *N, N', N'*-Tetra-5-methyl-2-picoly-1,4-bis(2-aminoethyl)piperazine (**L-Me**).

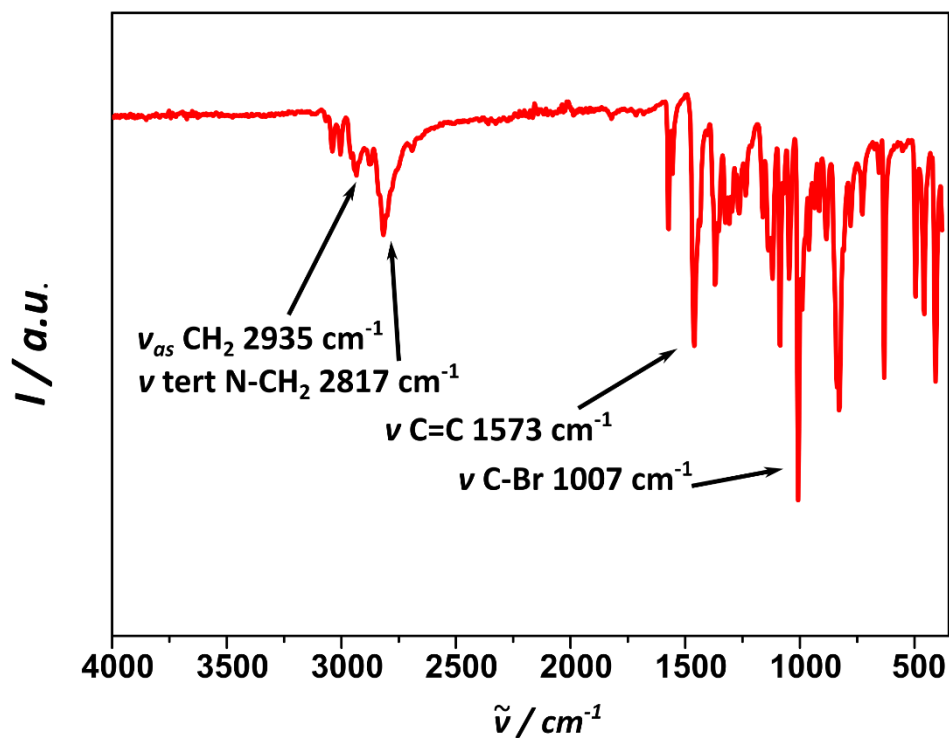


Figure S5: ATR-IR of *N, N, N', N'*-Tetra-5-bromo-2-picoly-1,4-bis(2-aminoethyl)piperazine (**L-Br**).

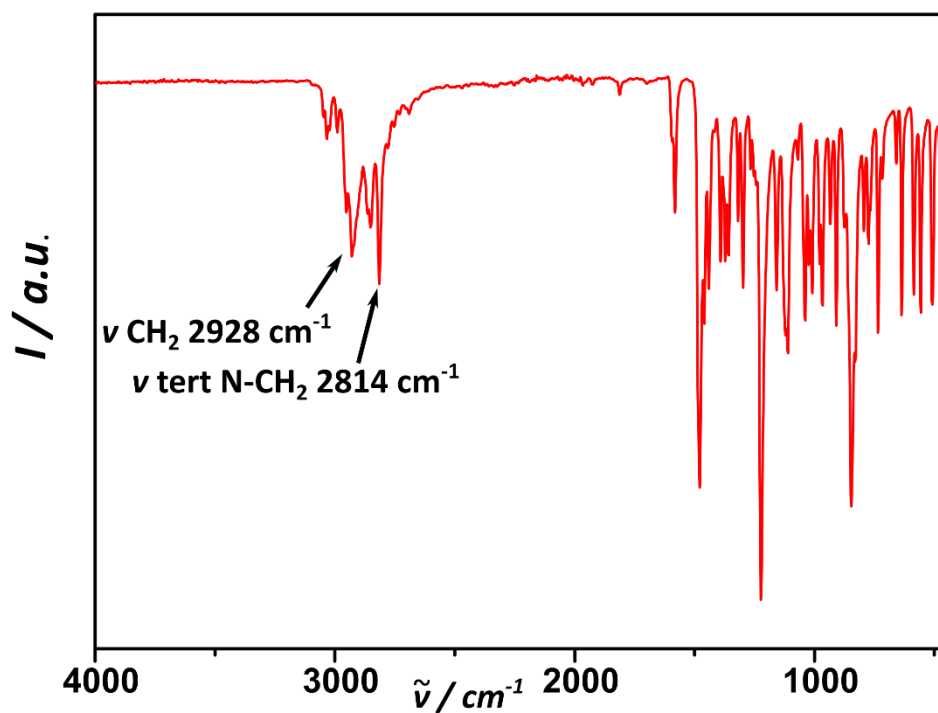


Figure S6: ATR-IR of *N, N, N', N'*-Tetra-5-fluoro-2-picoly-1,4-bis(2-aminoethyl)piperazine (**L-F**).

5.1.3 Mass Spectrometry Ligand

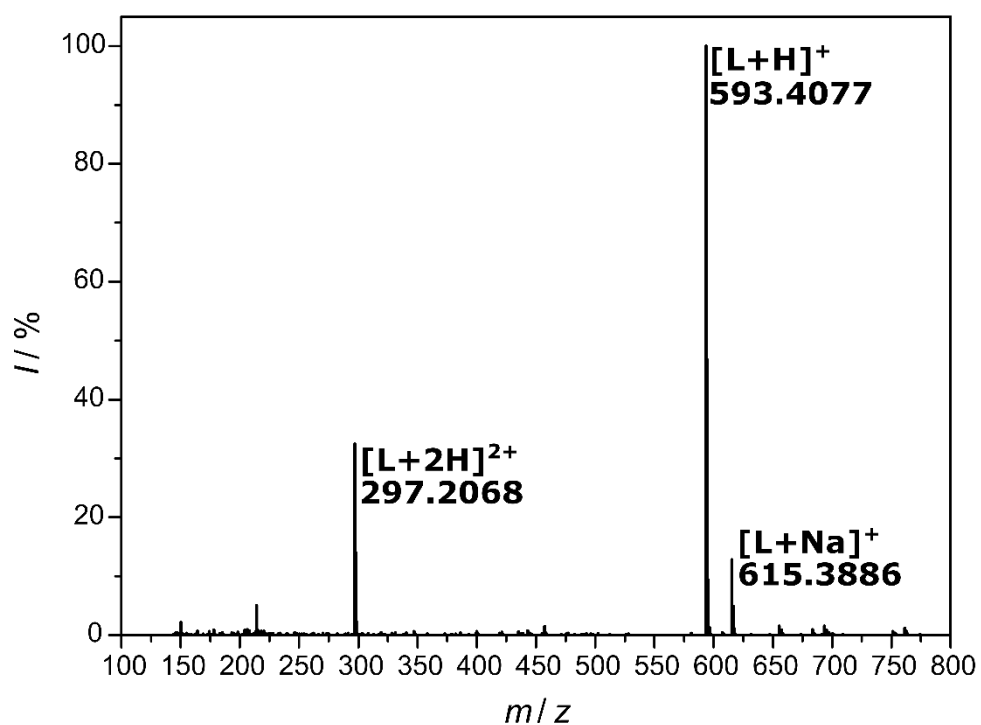


Figure S7: ESI⁺- MS of L-Me showing the double protonated adduct $[L-Me+2H]^{2+}$ at 297.2068 m/z, the protonated adduct $[L-Me+H]^+$ at 593.4077 m/z and the sodium adduct $[L-Me+Na]^+$ at 615.3886 m/z.

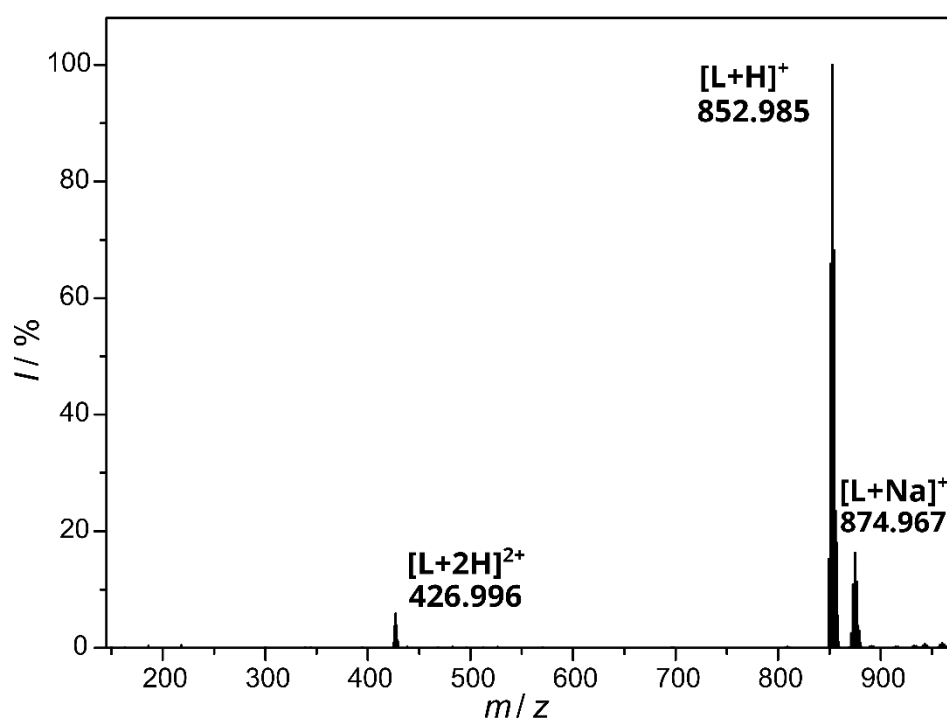


Figure S8: ESI⁺- MS of L-Br showing the double protonated adduct $[L-Br+2H]^{2+}$ at 426.996 m/z, the protonated adduct $[L-Br+H]^+$ at 852.985 m/z and the sodium adduct $[L-Br+Na]^+$ at 874.967 m/z.

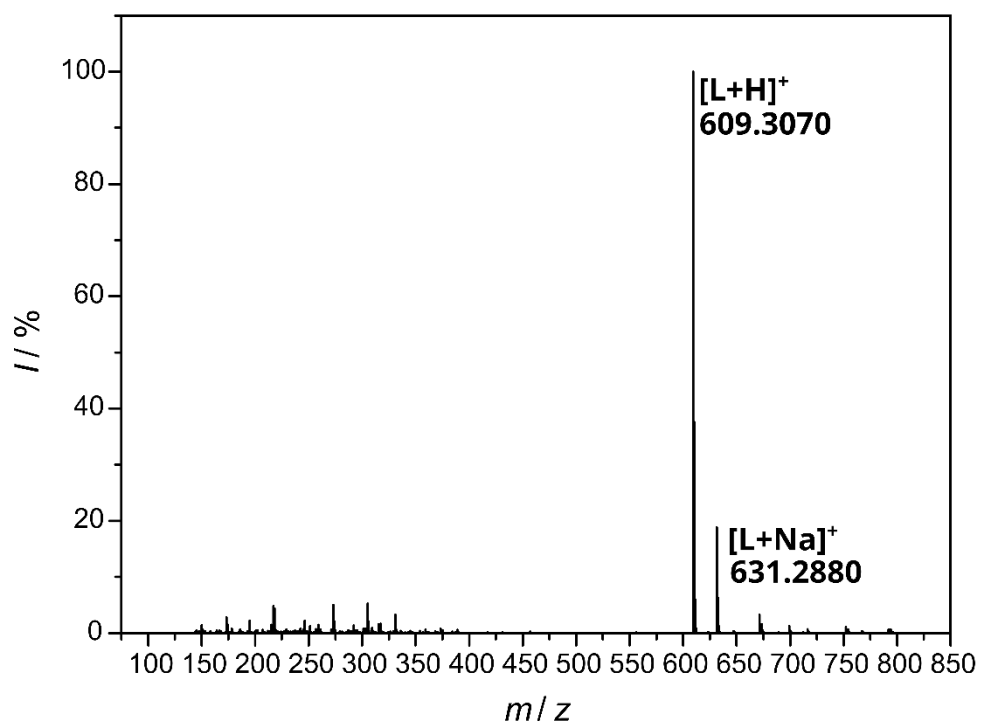


Figure S9: ESI⁺- MS of L-F showing the protonated adduct $[L-F+H]^+$ at 609.3070 m/z and the sodium adduct $[L-F+Na]^+$ at 631.2880 m/z .

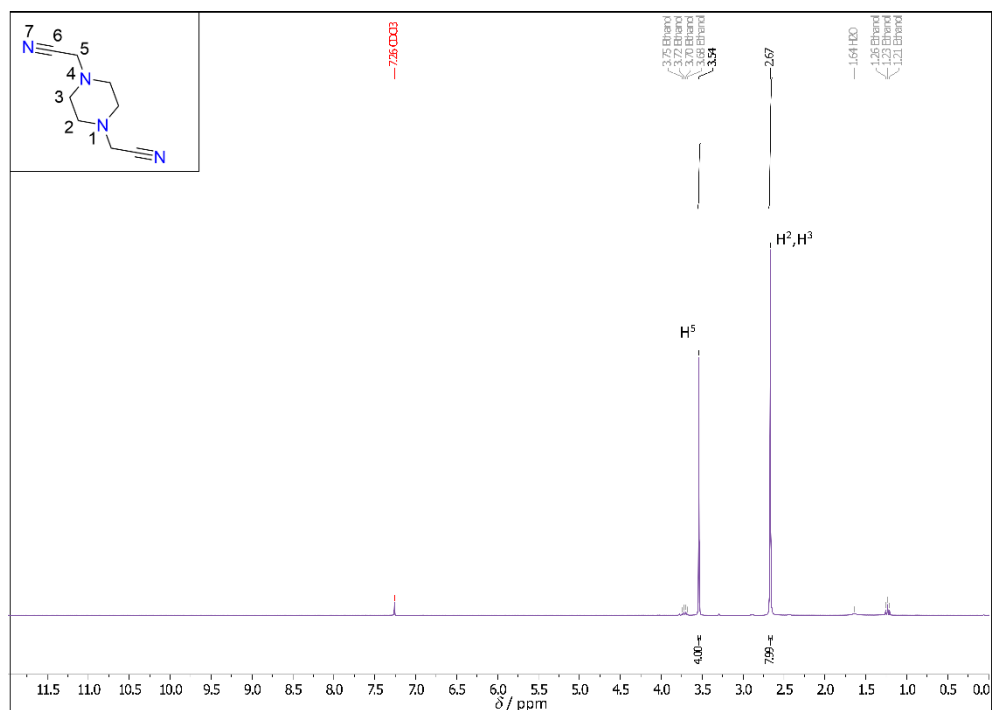
5.1.4 ^1H -NMR Ligand

Figure S10: ^1H -NMR-Spectrum of *N,N'*-bis(cyanomethyl)piperazine in CDCl_3 [400 MHz].

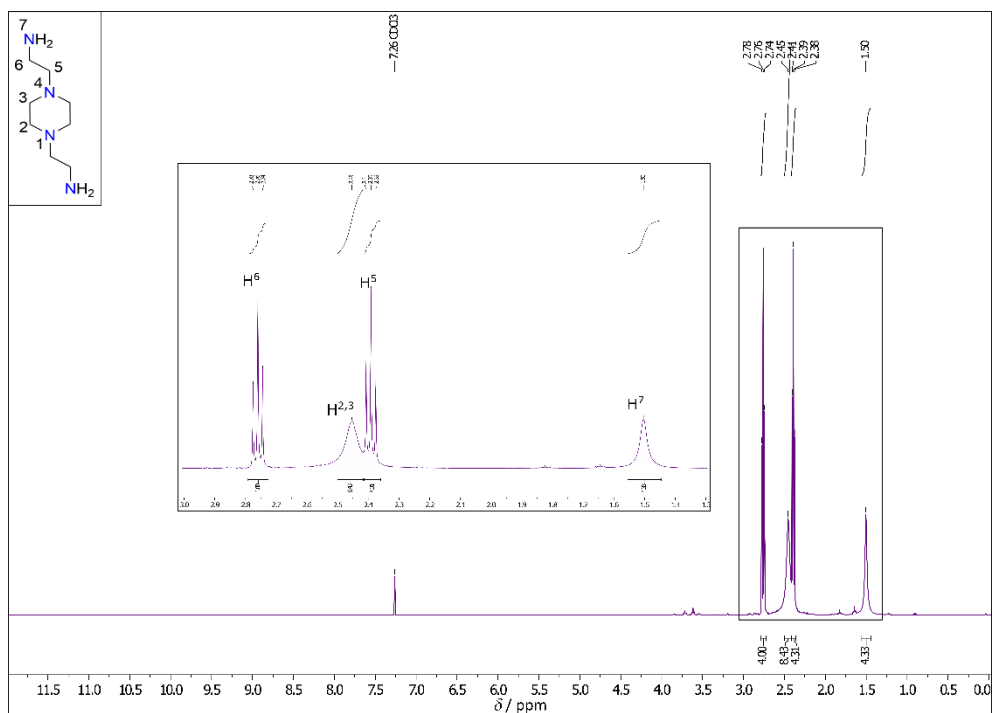


Figure S11: ^1H -NMR-Spectrum of *N,N'*-bis(aminoethyl)piperazine in CDCl_3 [400 MHz].

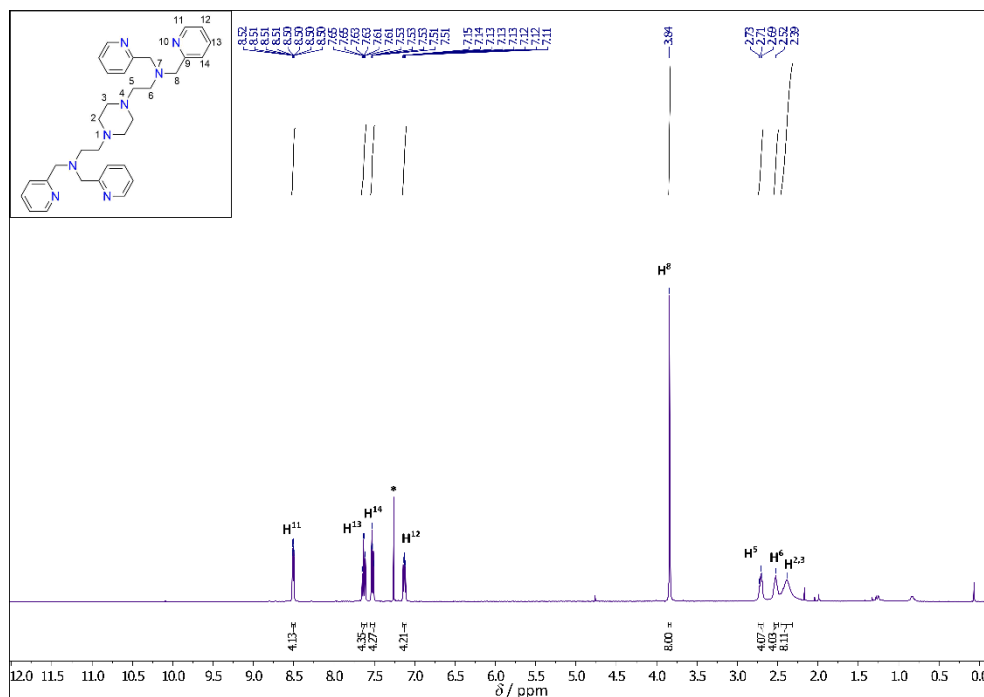


Figure S12: ^1H -NMR-Spectrum of **L-H** in CDCl_3 [400 MHz].

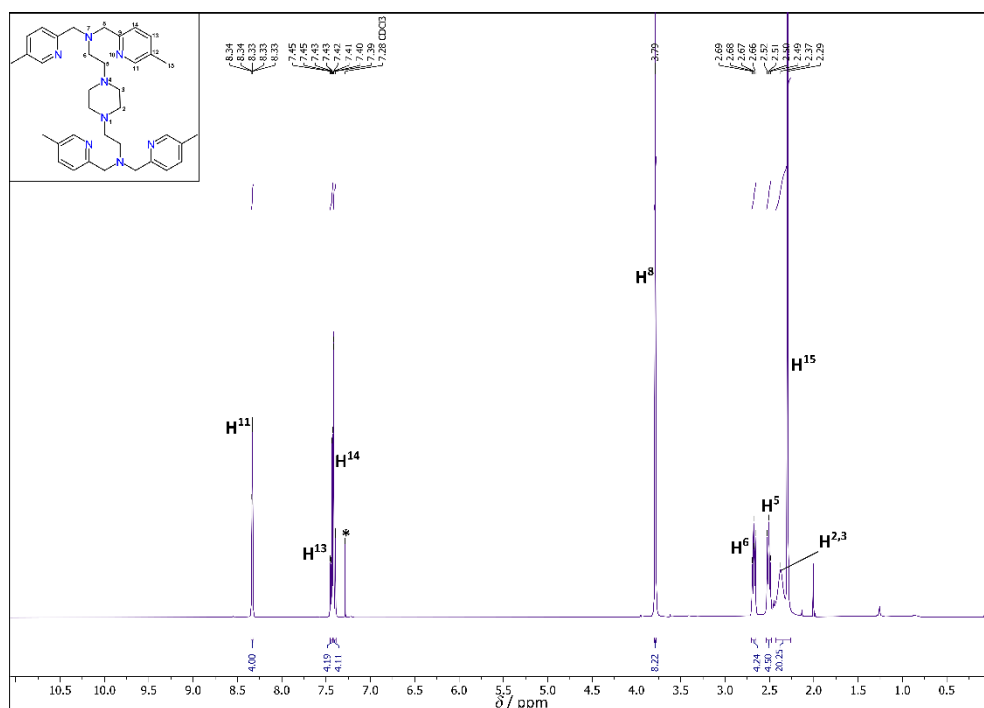


Figure S13: ^1H -NMR-Spectrum of **L-Me** in CDCl_3 [400 MHz].

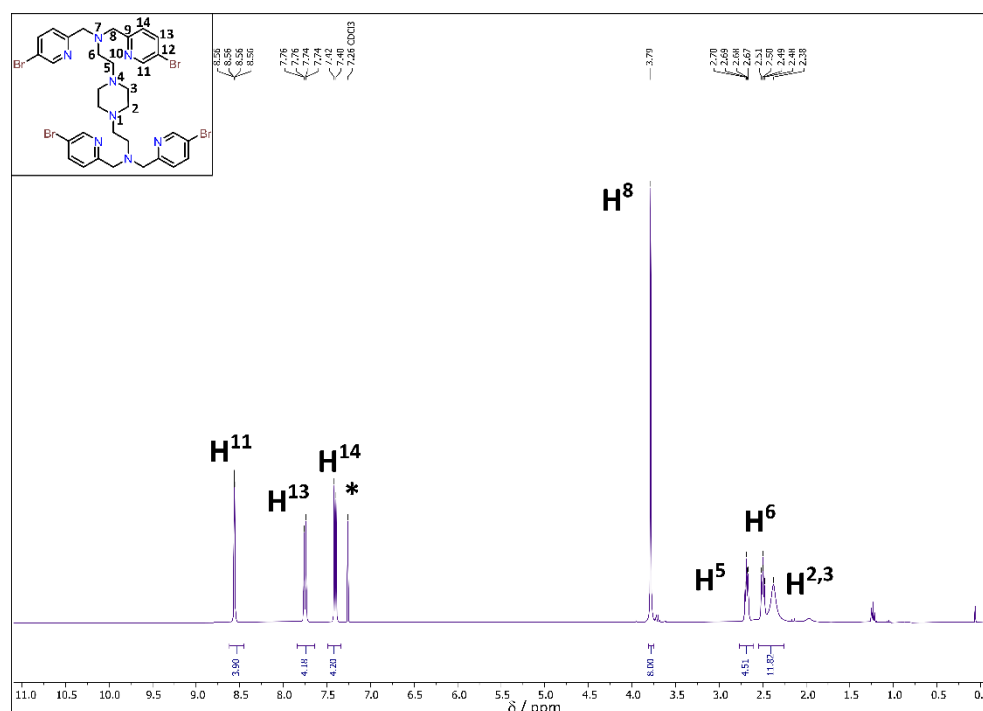


Figure S14: ^1H -NMR-Spectrum of **L-Br** in CDCl_3 [400 MHz].

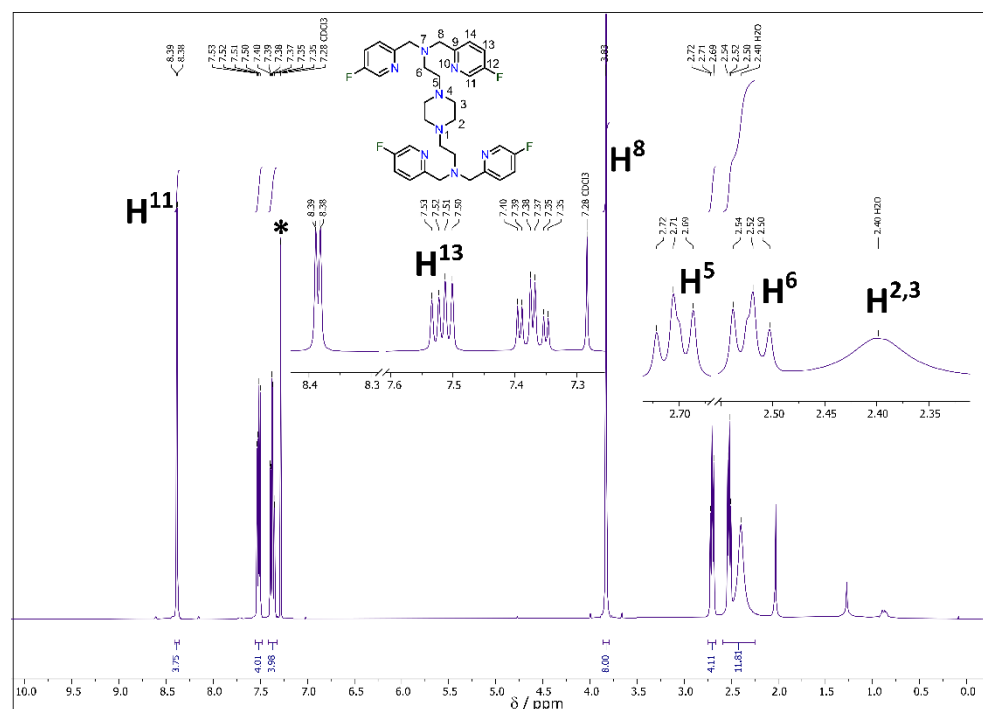
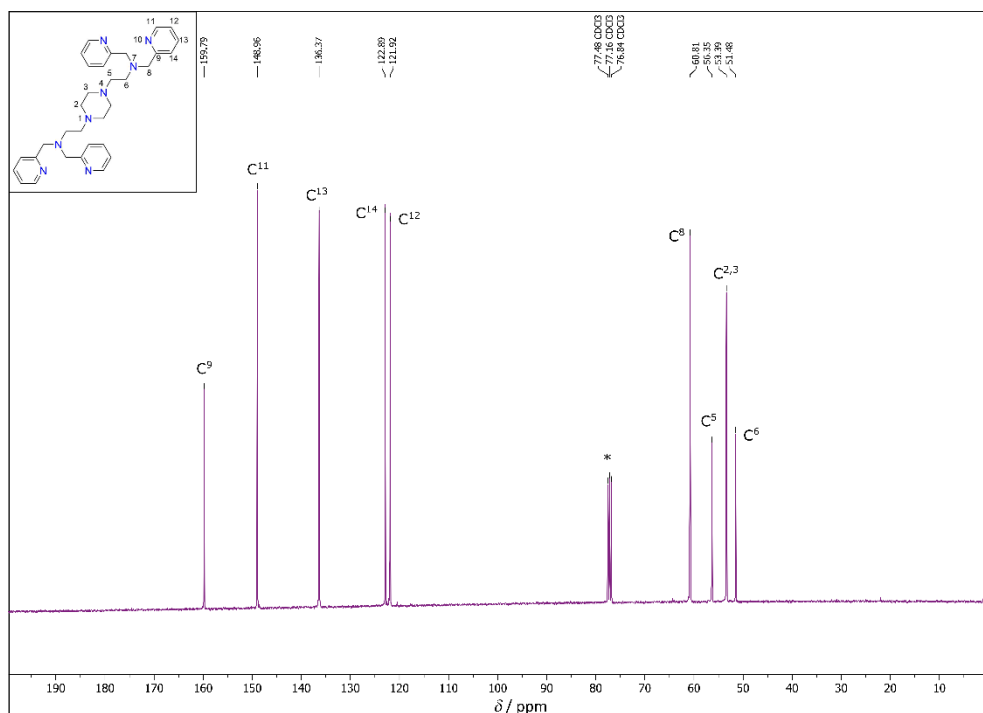
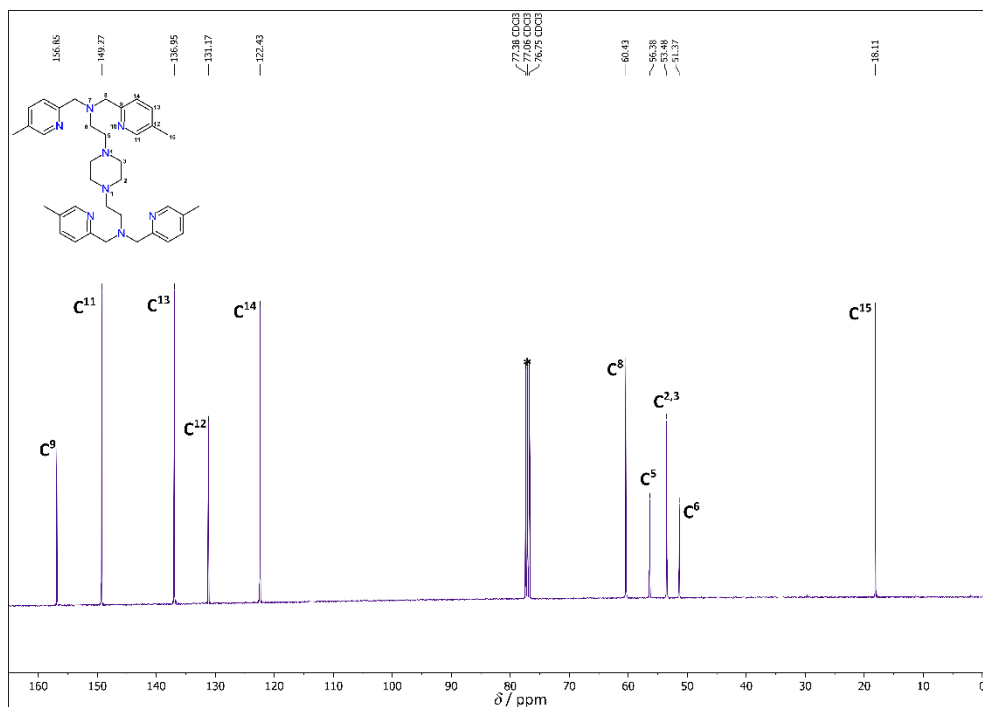


Figure S15: ^1H -NMR-Spectrum of **L-F** in CDCl_3 [400 MHz].

5.1.5 ^{13}C -NMR-Spectra LigandFigure S16: ^{13}C -NMR-Spectrum of **L-H** in CDCl_3 [101 MHz].Figure S17: ^{13}C -NMR-Spectrum of **L-Me** in CDCl_3 [101 MHz].

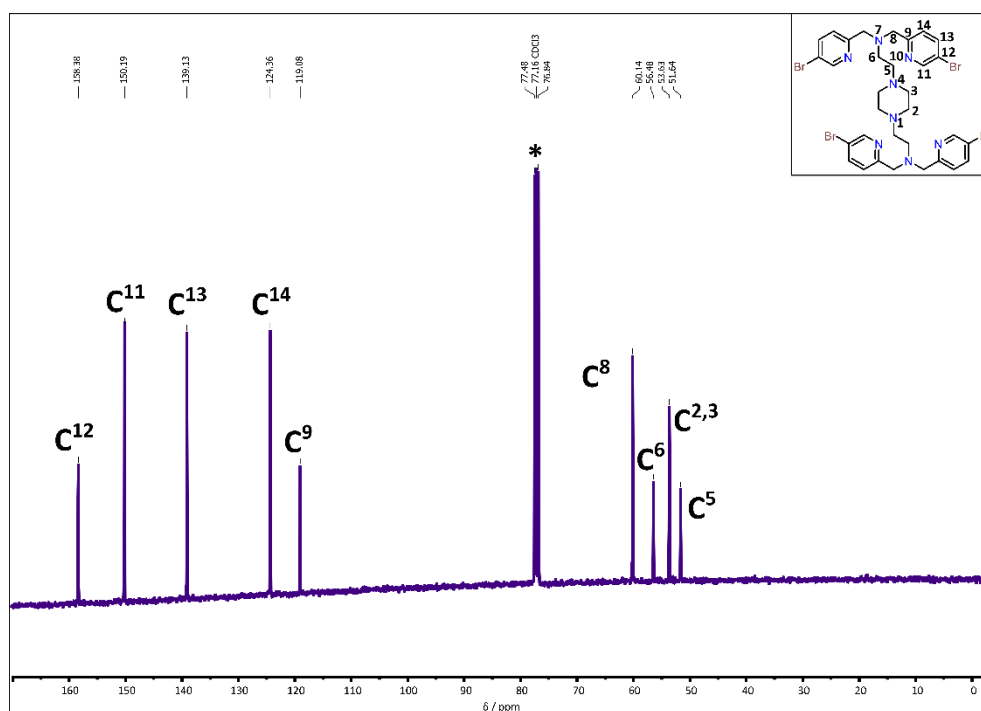


Figure S18: ^{13}C -NMR-Spectrum of **L-Br** in CDCl_3 [101 MHz].

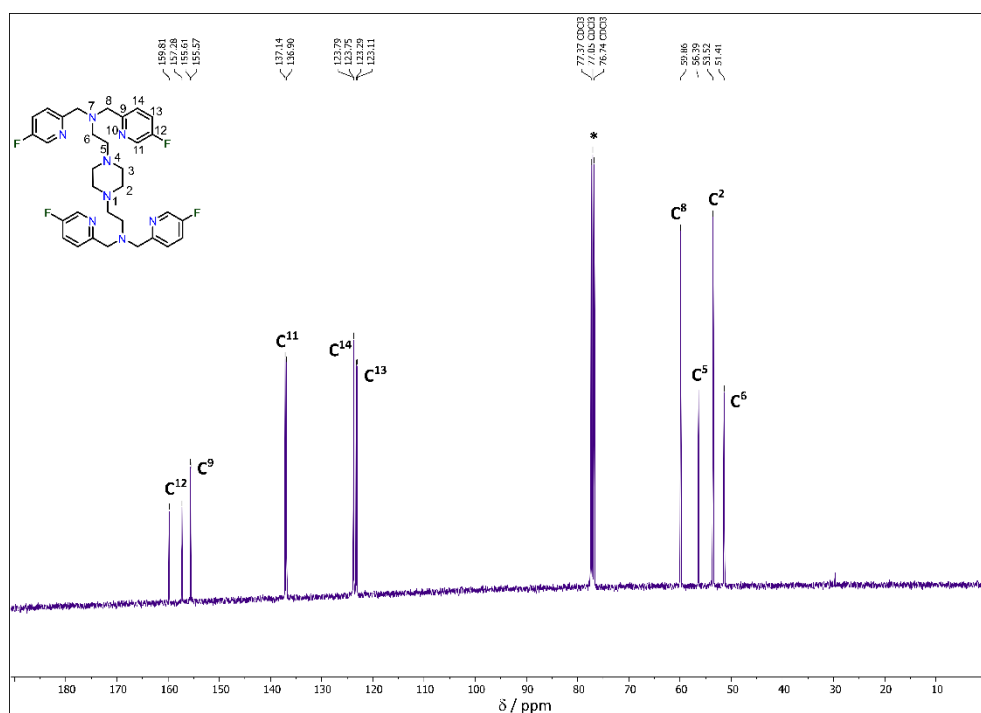


Figure S19: ^{13}C -NMR-Spectrum of **L-F** in CDCl_3 [101 MHz].

5.1.6 ^{19}F -NMR-Spectrum

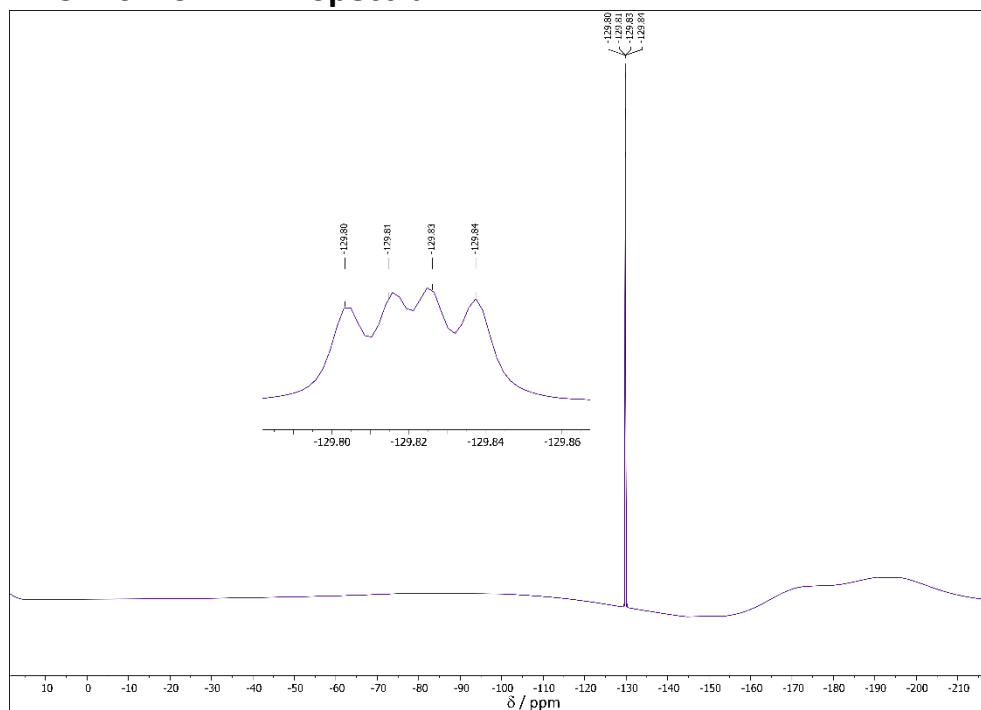
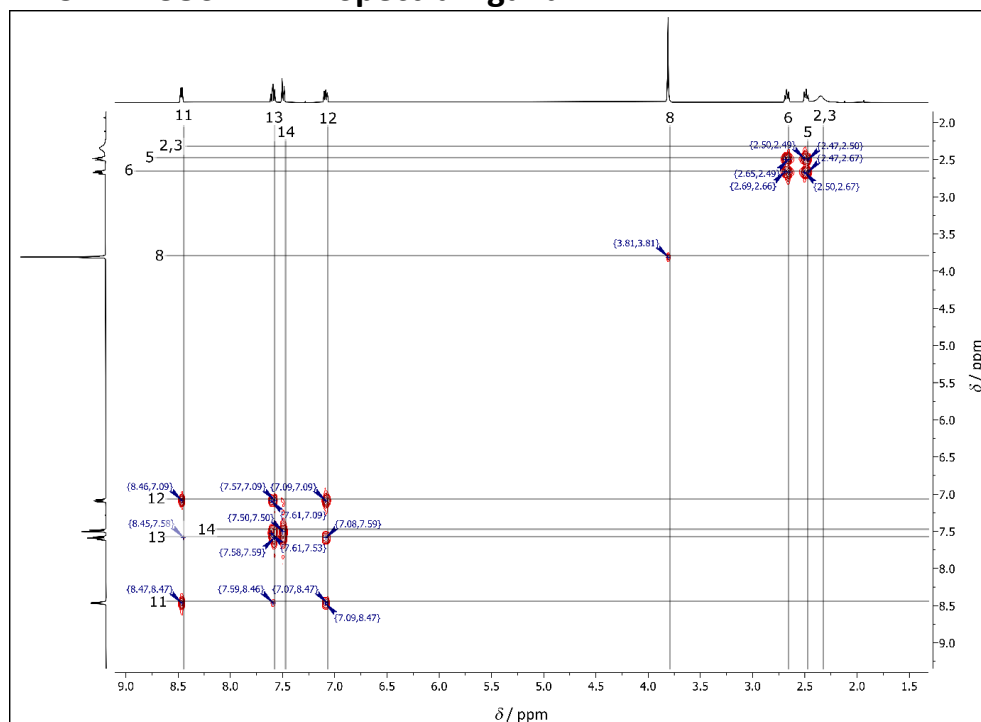
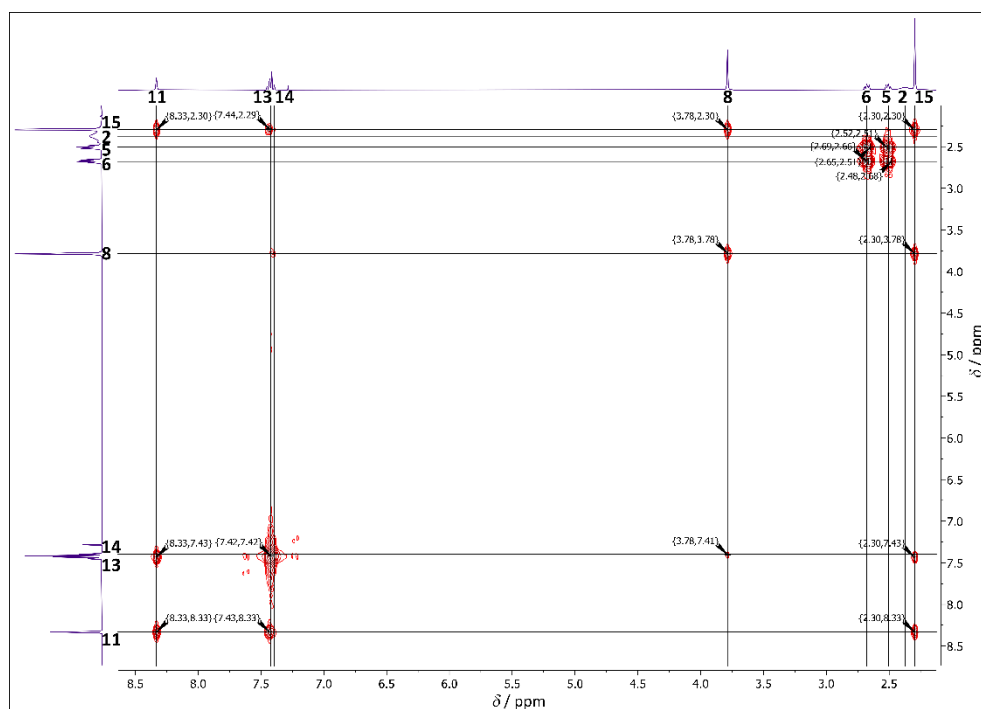


Figure S20: ^{19}F -NMR-Spectrum of **L-F** in CDCl_3 [376 MHz].

5.1.7 COSY-NMR-Spectra Ligand

Figure S21: COSY-NMR-Spectrum of *L-H* in CDCl_3 .Figure S22: COSY-NMR-Spectrum of *L-Me* in CDCl_3 .

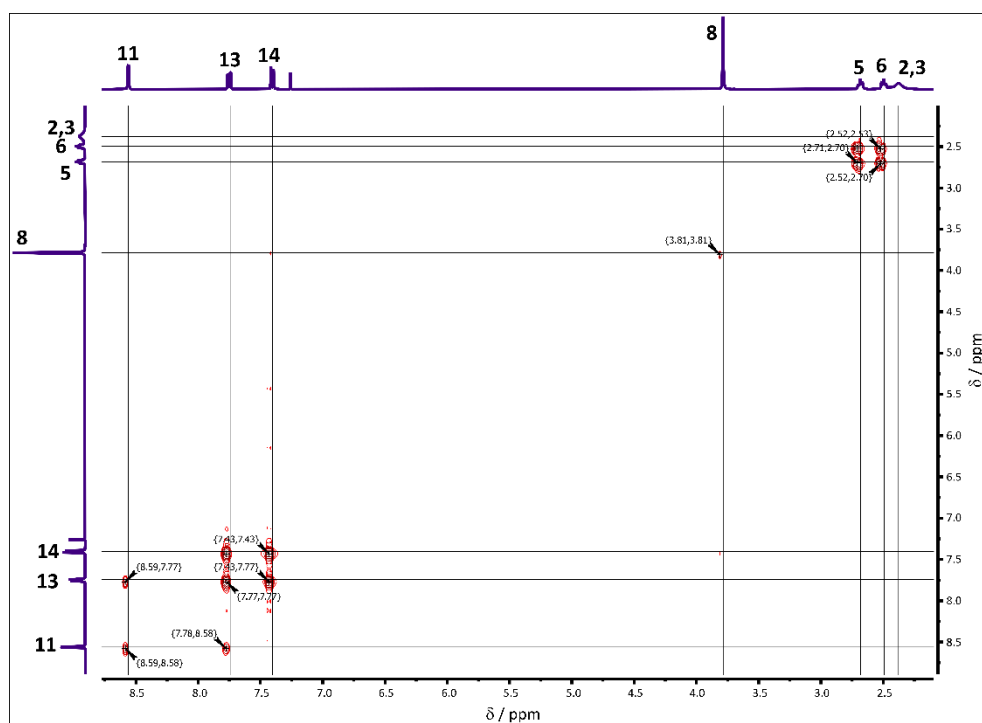


Figure S23: COSY-NMR-Spectrum of **L-Br** in CDCl_3 .

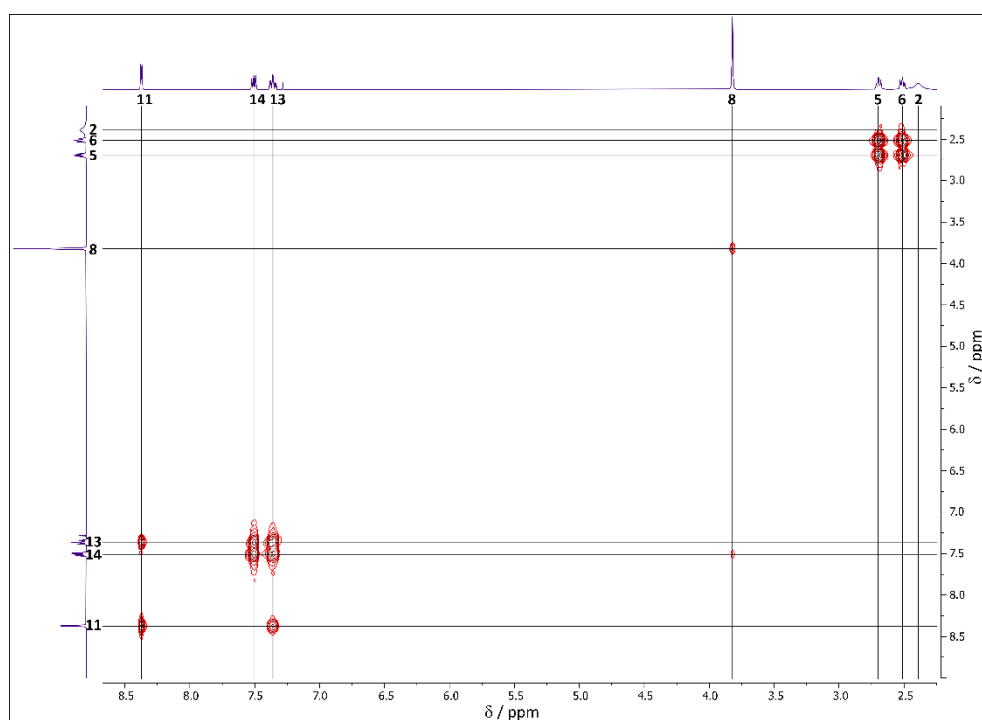
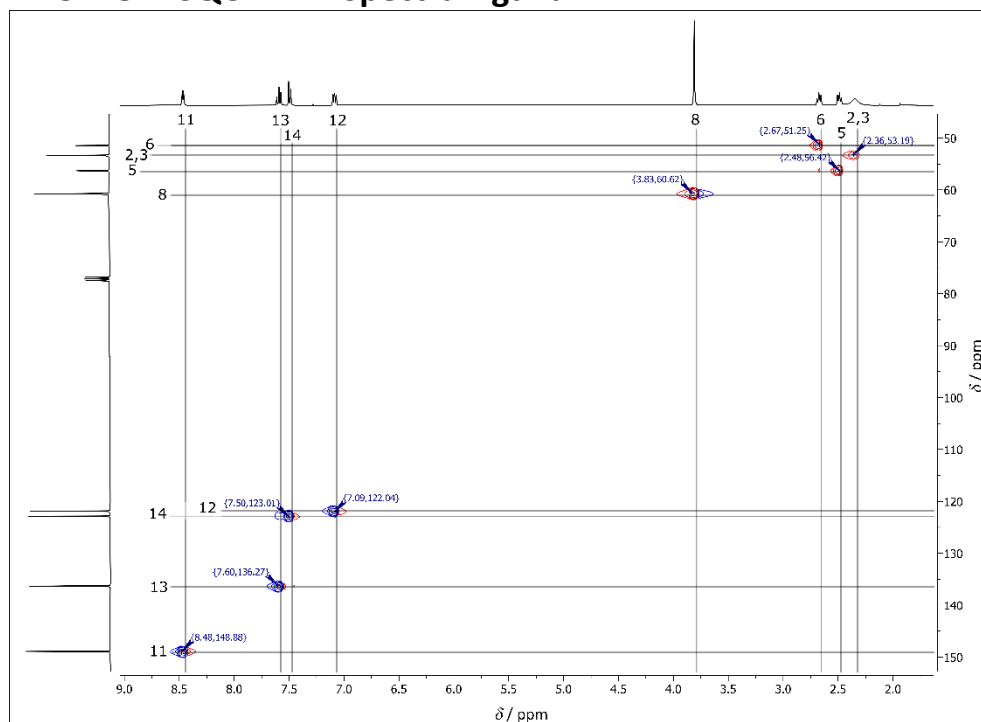
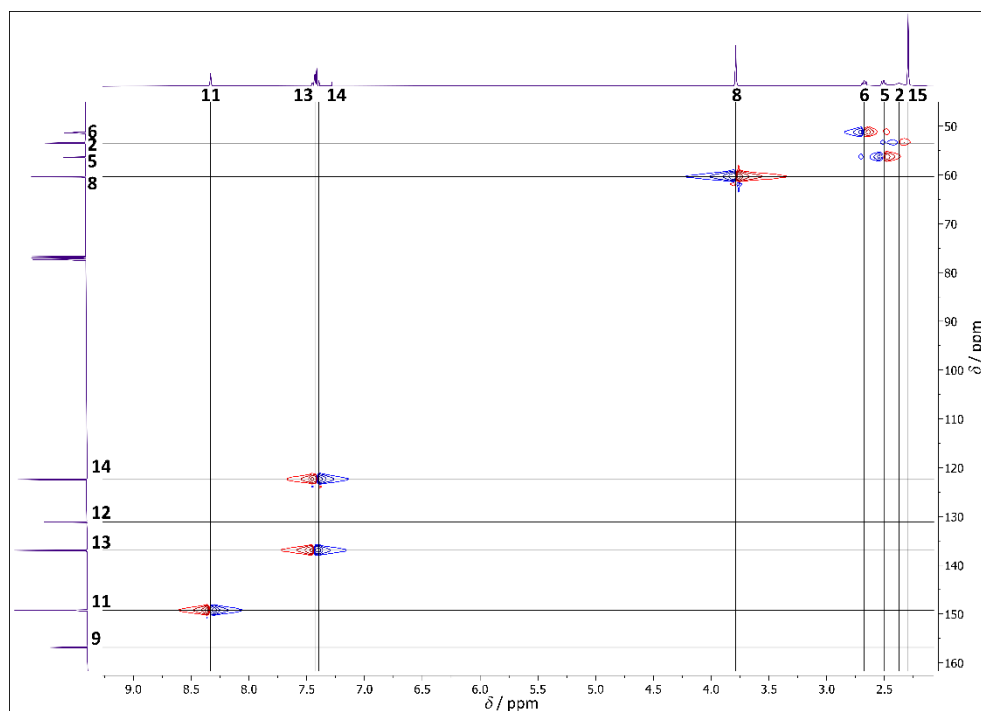


Figure S24: COSY-NMR-Spectrum of **L-F** in CDCl_3 .

5.1.8 HSQC-NMR-Spectra Ligand

Figure S25: HSQC-NMR-Spectrum of **L-H** in CDCl_3 .Figure S26: HSQC-NMR-Spectrum of **L-Me** in CDCl_3 .

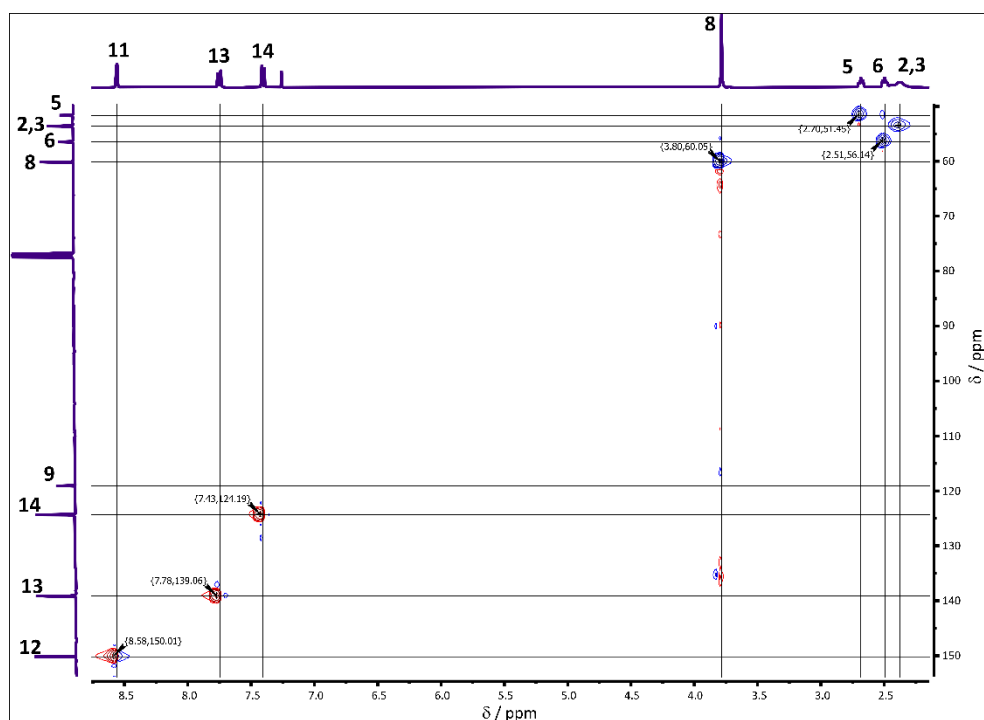


Figure S27: HSQC-NMR-Spectrum of **L-Br** in CDCl_3 .

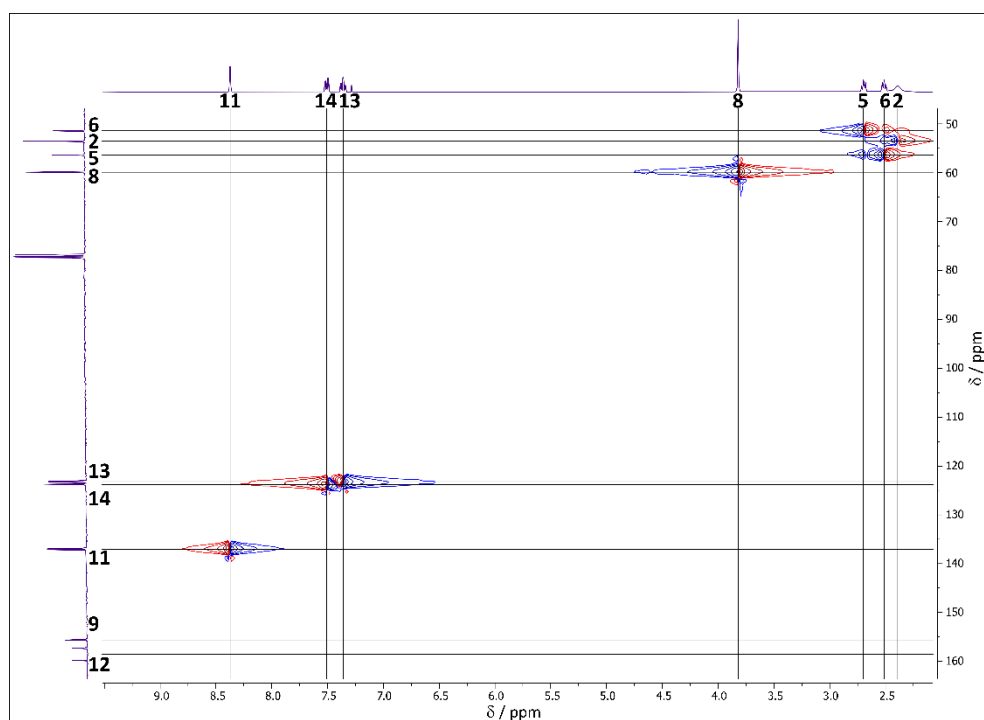
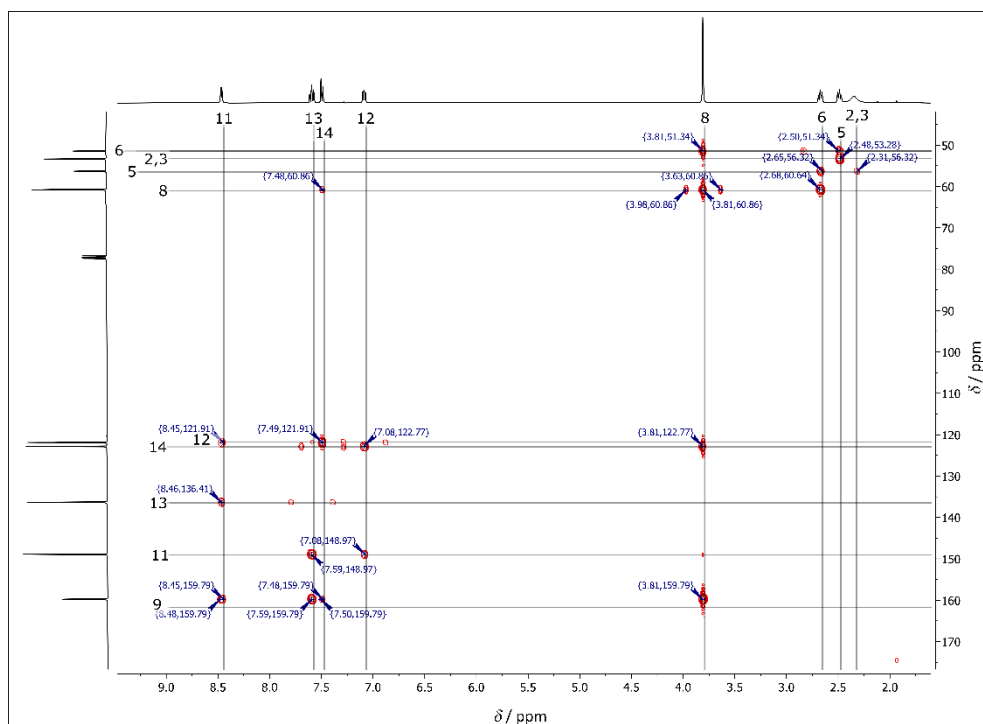
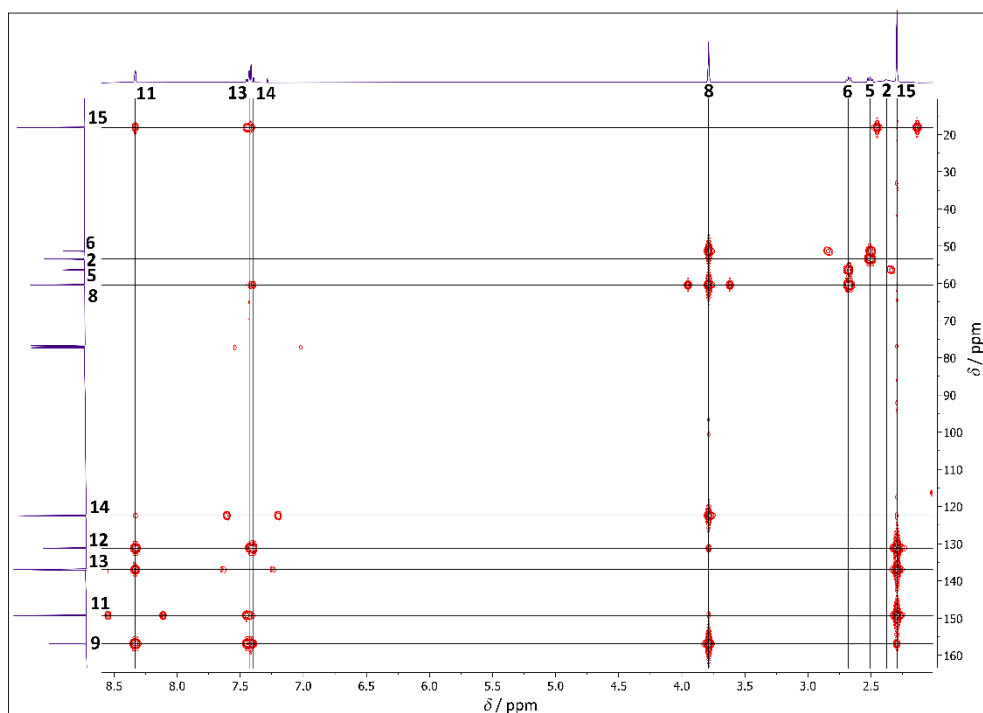


Figure S28: HSQC-NMR-Spectrum of **L-F** in CDCl_3 .

5.1.9 HMBC-NMR-Spectra Ligand

Figure S29: HMBC-NMR-Spectrum of *L-H* in CDCl_3 .Figure S30: HMBC-NMR-Spectrum of *L-Me* in CDCl_3 .

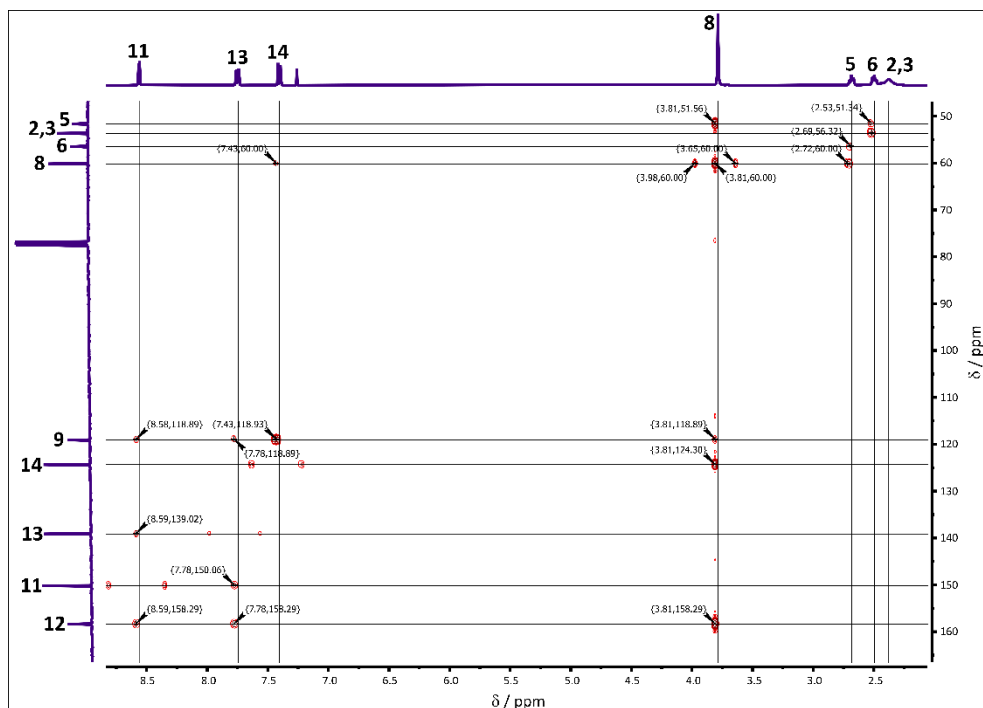


Figure S31: HMBC-NMR-Spectrum of *L-Br* in CDCl_3 .

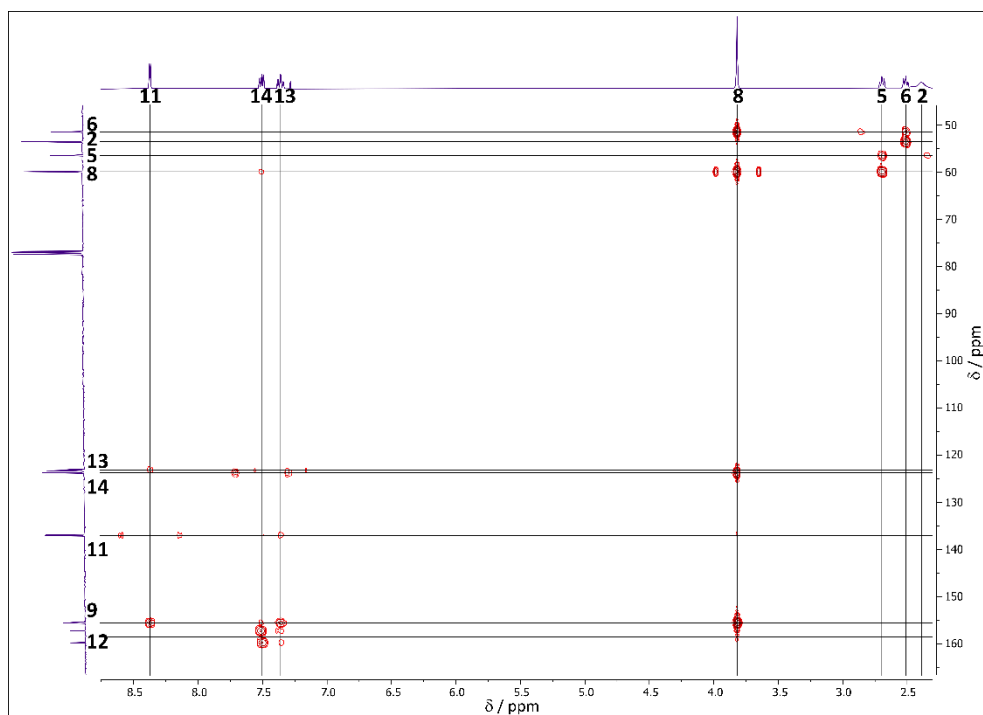
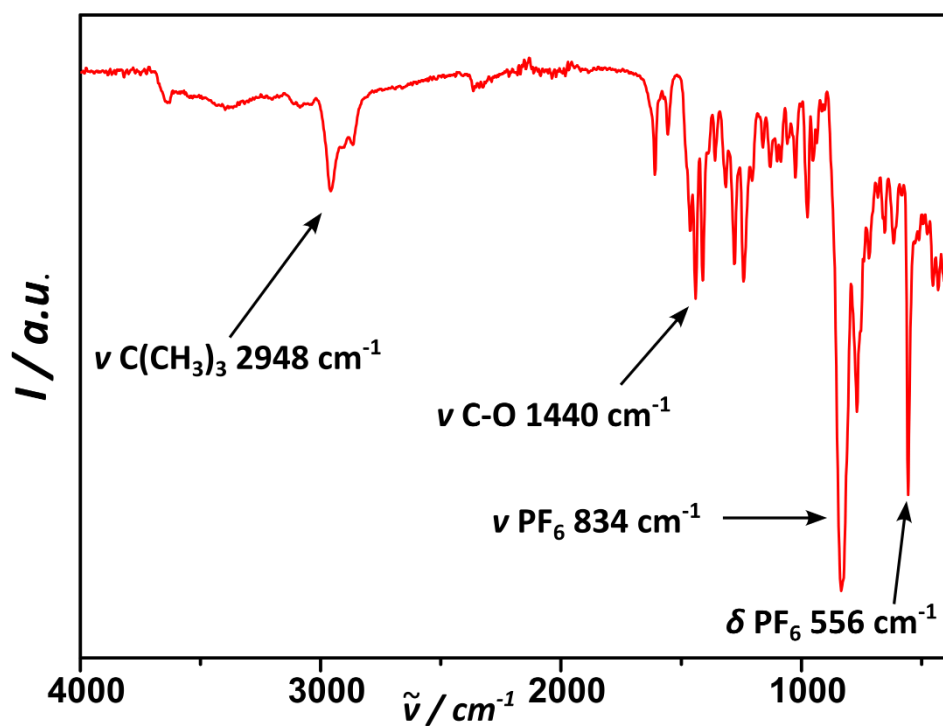
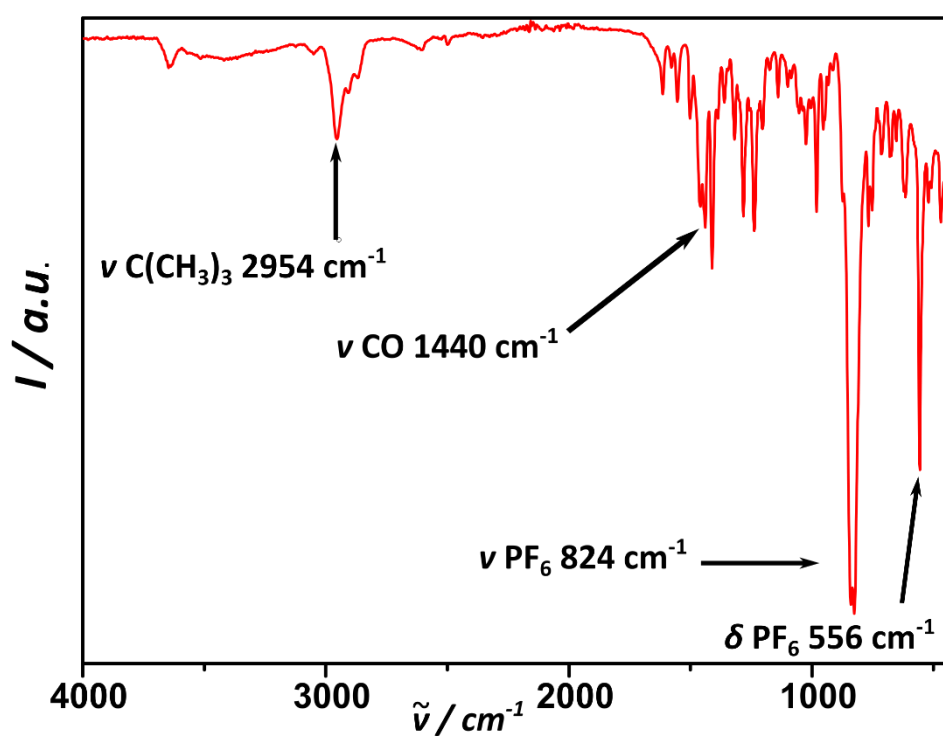
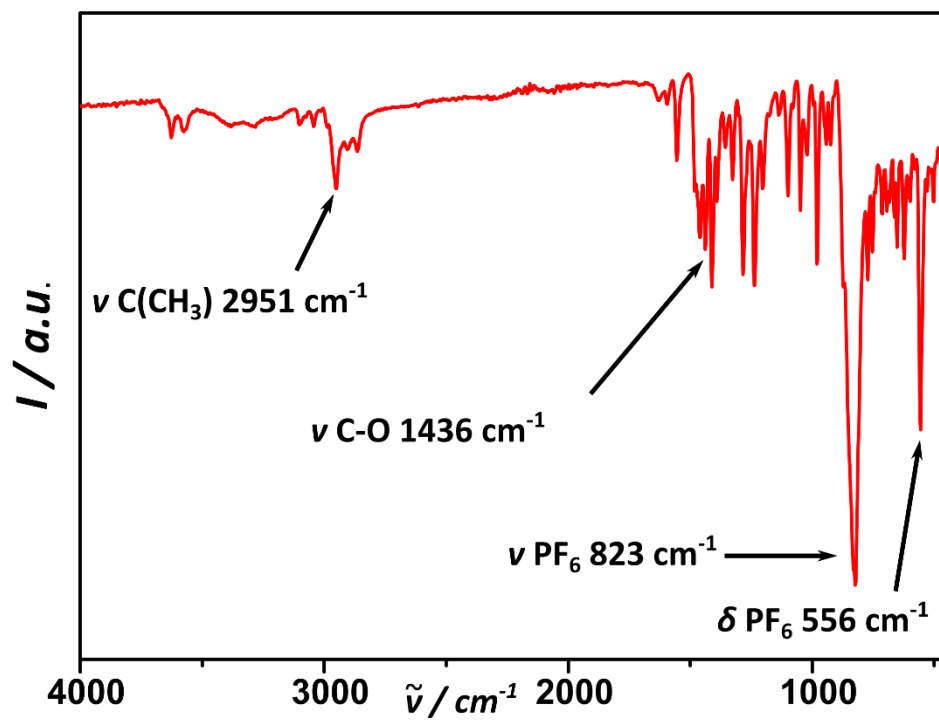
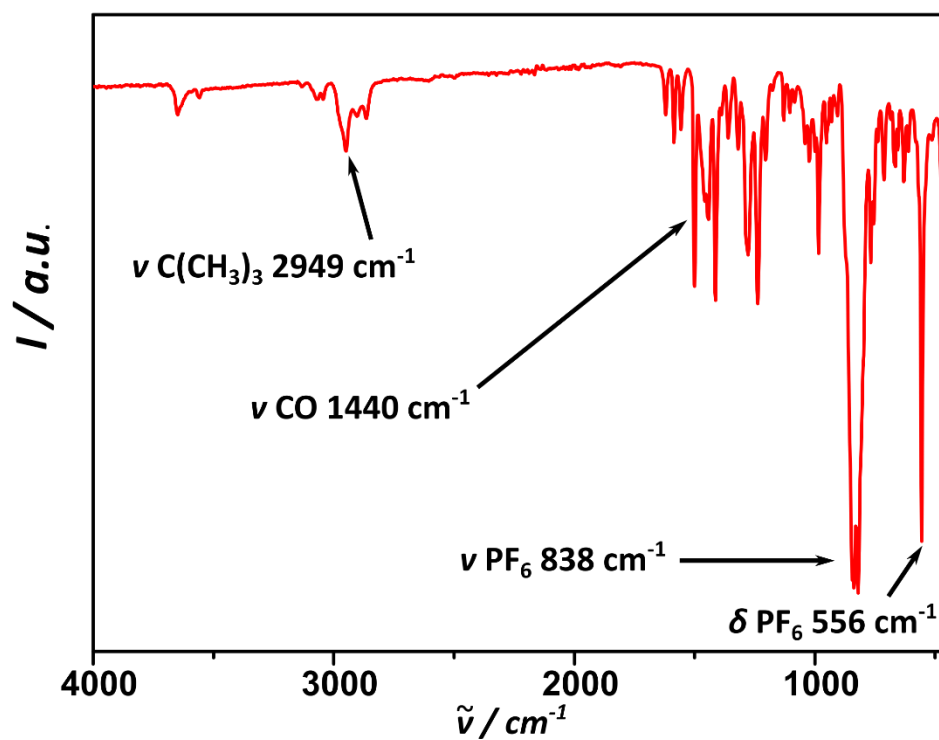


Figure S32: HMBC-NMR-Spectrum of *L-F* in CDCl_3 .

5.1.10 Infrared Spectroscopy Complexes

Figure S33: ATR-IR of $[\text{Co}_2\text{L}^{\text{H}}](\text{PF}_6)_2$.Figure S34: ATR-IR of $[\text{Co}_2\text{L}^{\text{Me}}](\text{PF}_6)_2$.

Figure S35: ATR-IR of $[\text{Co}_2\text{L}^{\text{Br}}](\text{PF}_6)_2$.Figure S36: ATR-IR of $[\text{Co}_2\text{L}^{\text{F}}](\text{PF}_6)_2$.

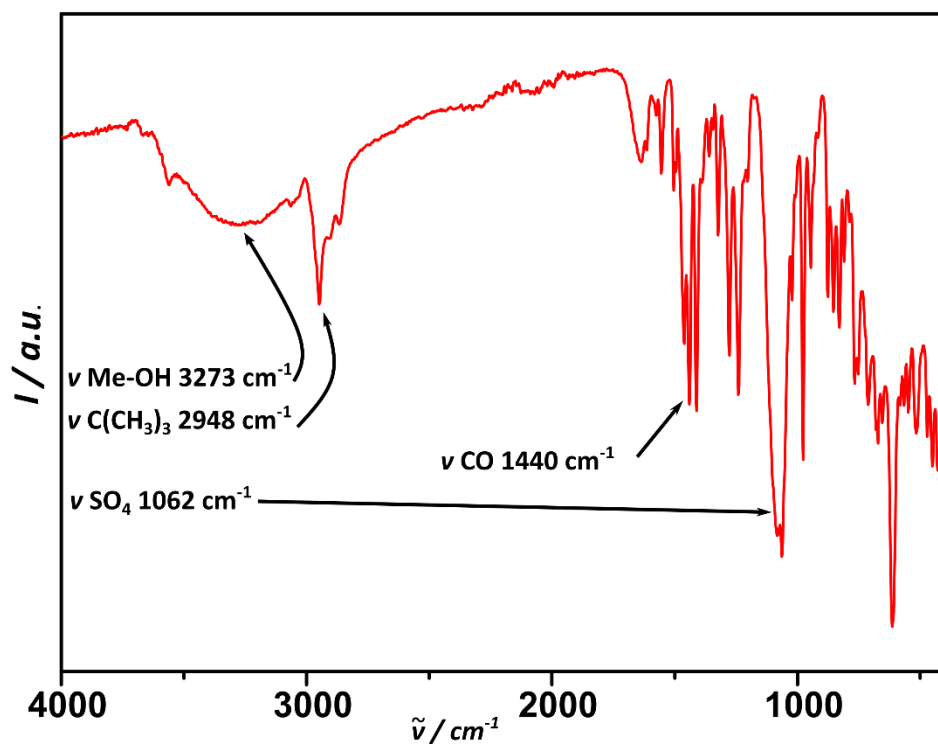


Figure S37: ATR-IR of $[\text{Co}_2\text{L}^{\text{Me}}]\text{SO}_4$.

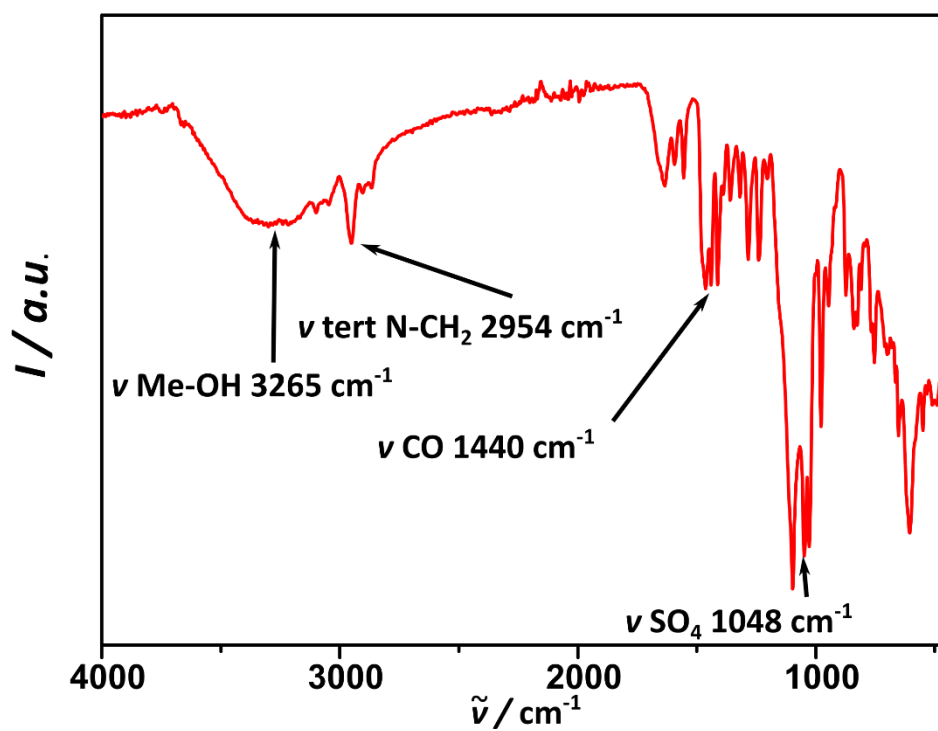


Figure S38: ATR-IR of $[\text{Co}_2\text{L}^{\text{Br}}]\text{SO}_4$.

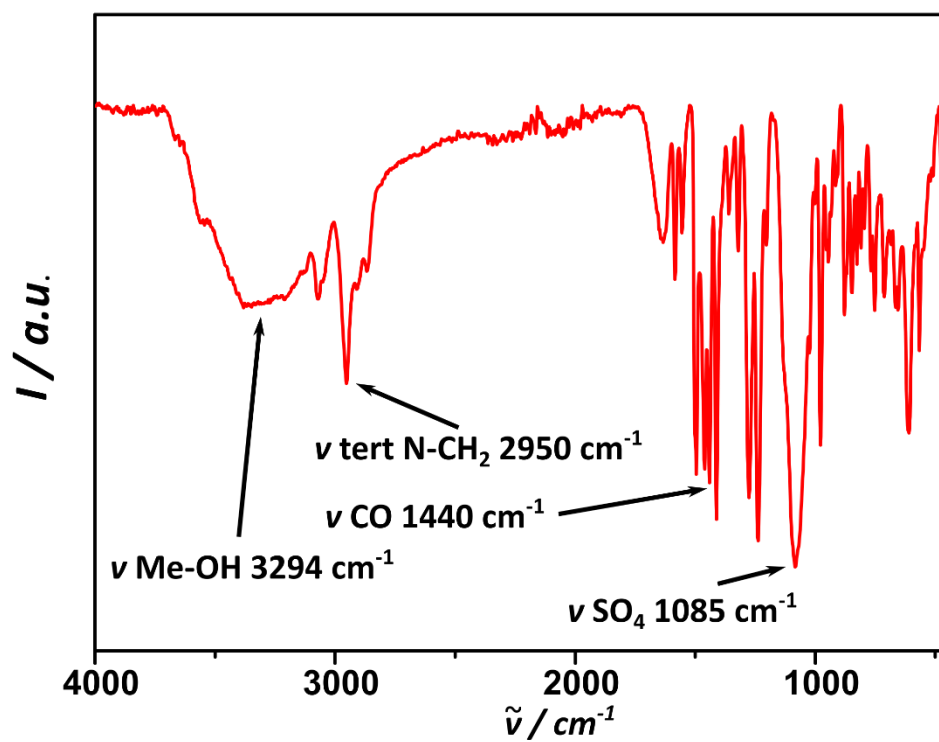


Figure S39: ATR-IR of $[\text{Co}_2\text{L}^{\text{F}}]\text{SO}_4$.

5.1.11 MS Spectra Complexes

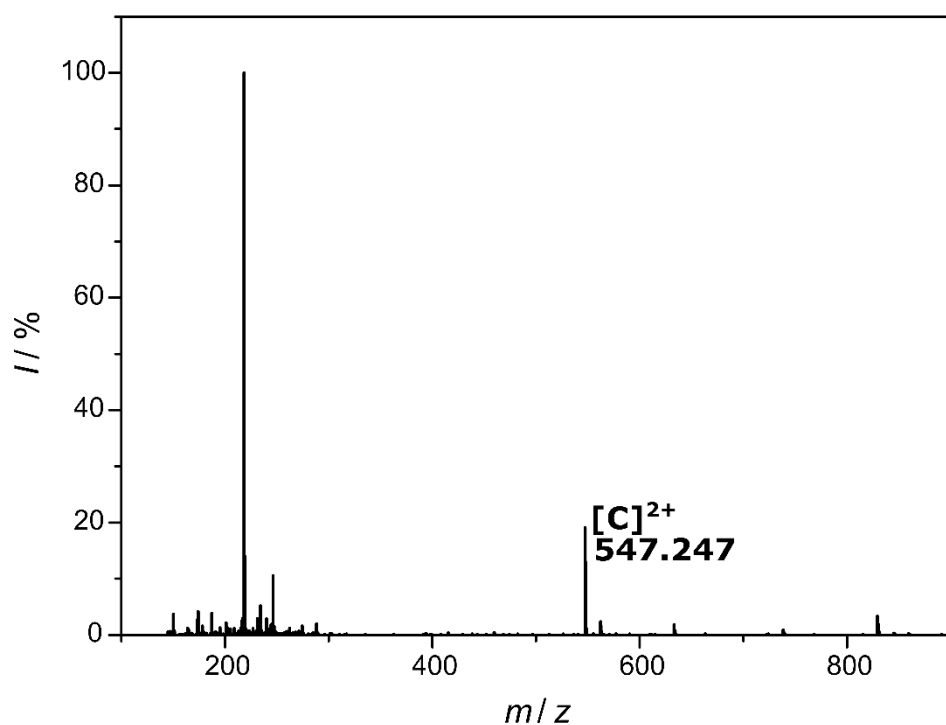


Figure S40: ESI⁺-mass spectrum of $[Co_2L^H](PF_6)_2$ with the dicationic fragment $[C]^{2+}$.

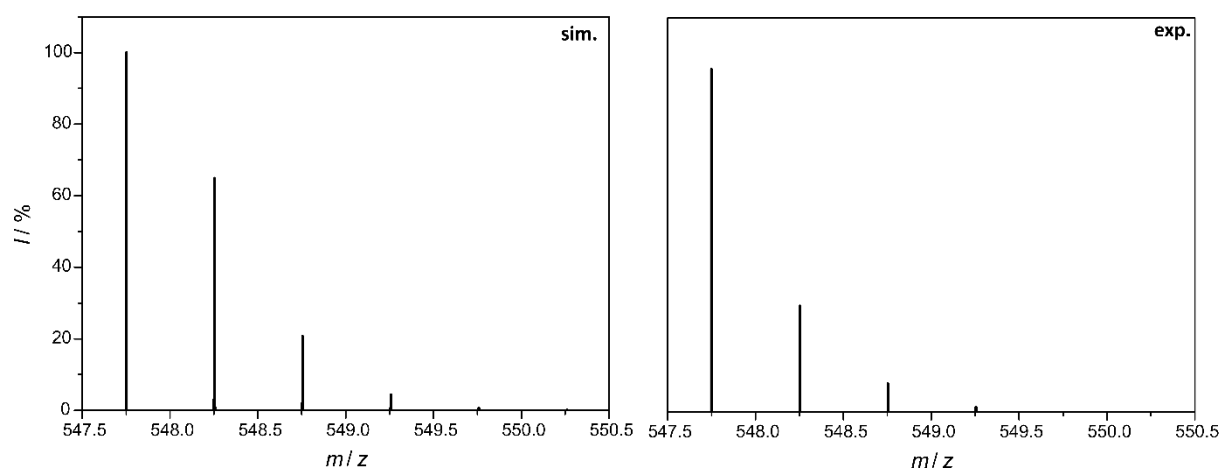


Figure S41: Comparison of the isotopic peak pattern of $[Co_2L^H](PF_6)_2$.

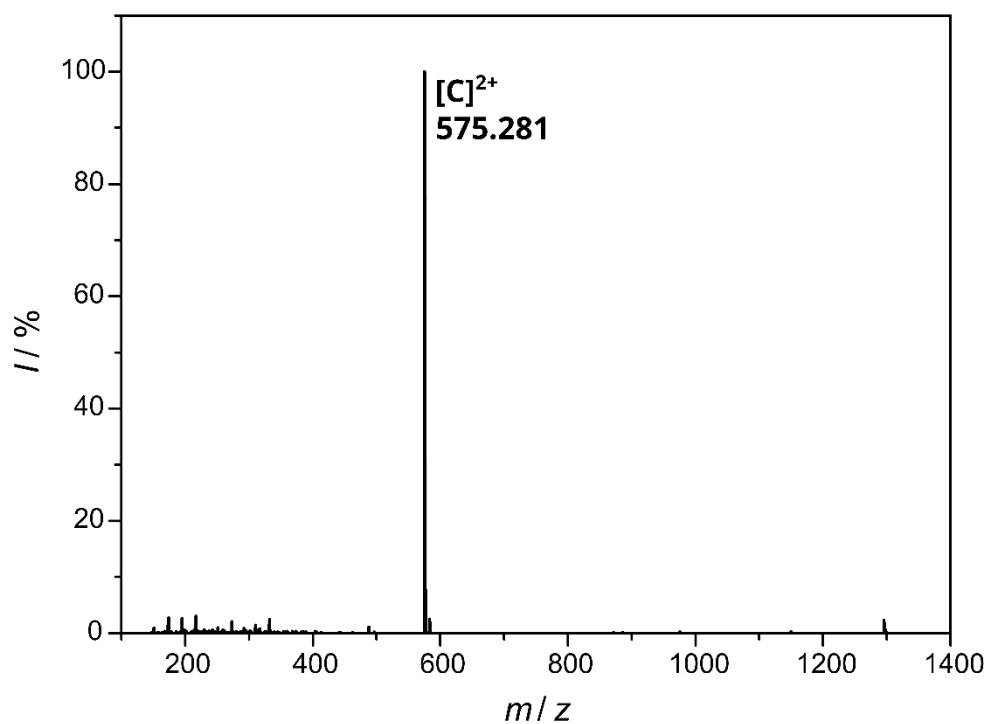


Figure S42: Esi⁺-mass spectrum of $[\text{Co}_2\text{L}^{\text{Me}}](\text{PF}_6)_2$ with the dicationic fragment $[\text{C}]^{2+}$.

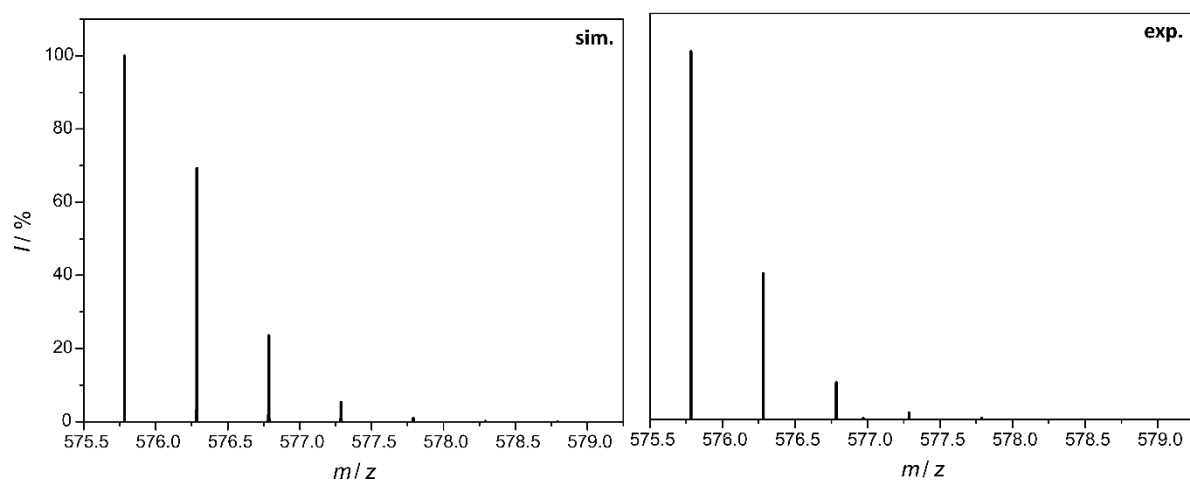


Figure S43: Comparison of the isotopic peak pattern of $[\text{Co}_2\text{L}^{\text{Me}}](\text{PF}_6)_2$.

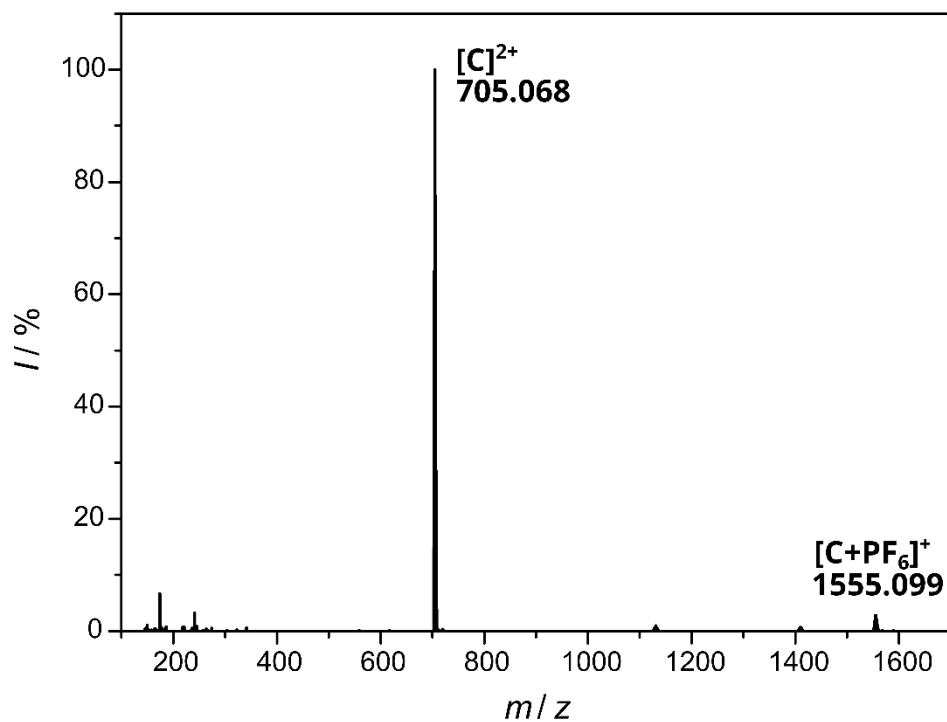


Figure S44: ESI+-mass spectrum of $[\text{Co}_2\text{L}^{\text{Br}}](\text{PF}_6)_2$ with the dicationic fragment $[\text{C}]^{2+}$ and the monocationic PF_6^- adduct.

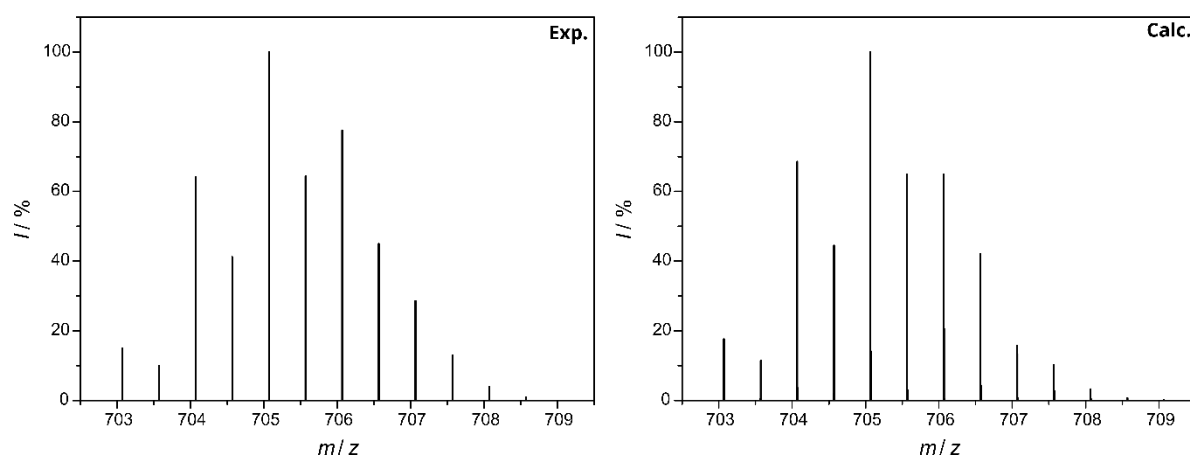


Figure S45: Comparison of the isotopic peak pattern of $[\text{Co}_2\text{L}^{\text{Br}}](\text{PF}_6)_2$.

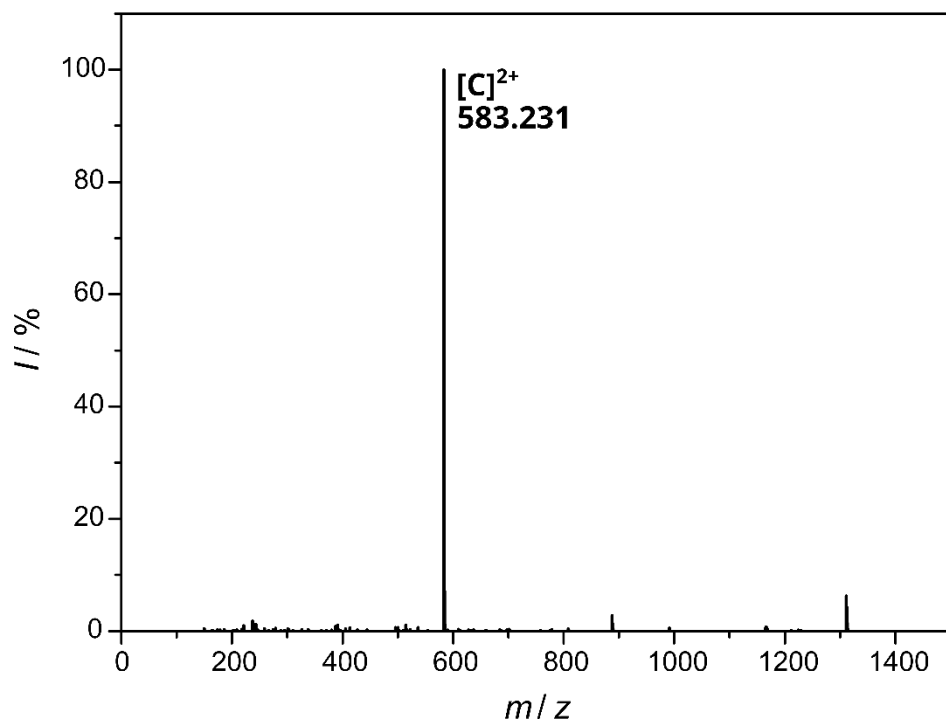


Figure S46: Esi⁺-mass spectrum of $[\text{Co}_2\text{L}^{\text{F}}](\text{PF}_6)_2$ with the dicationic fragment $[\text{C}]^{2+}$.

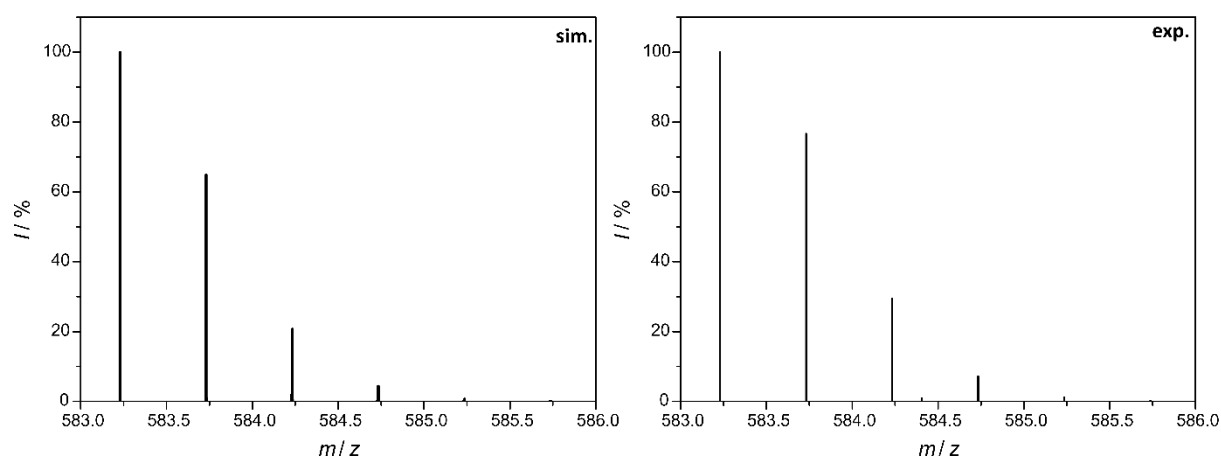


Figure S47: Comparison of the isotopic peak pattern of $[\text{Co}_2\text{L}^{\text{F}}](\text{PF}_6)_2$.

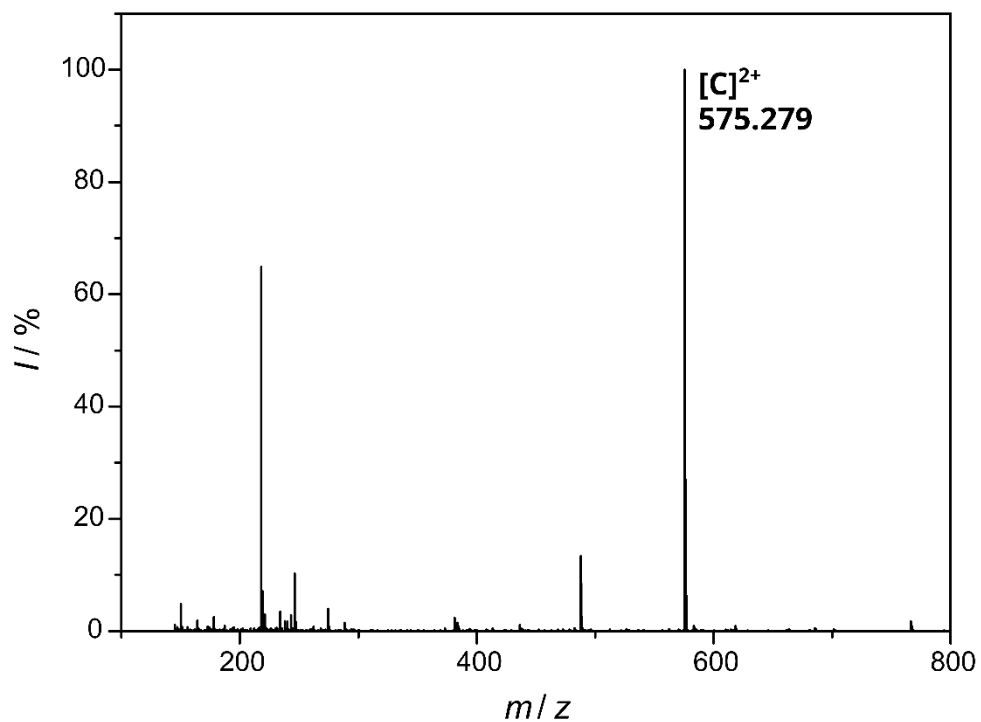


Figure S48: ESI⁺-mass spectrum of $[Co_2L^{Me}]SO_4$ with the dicationic fragment $[C]^{2+}$.

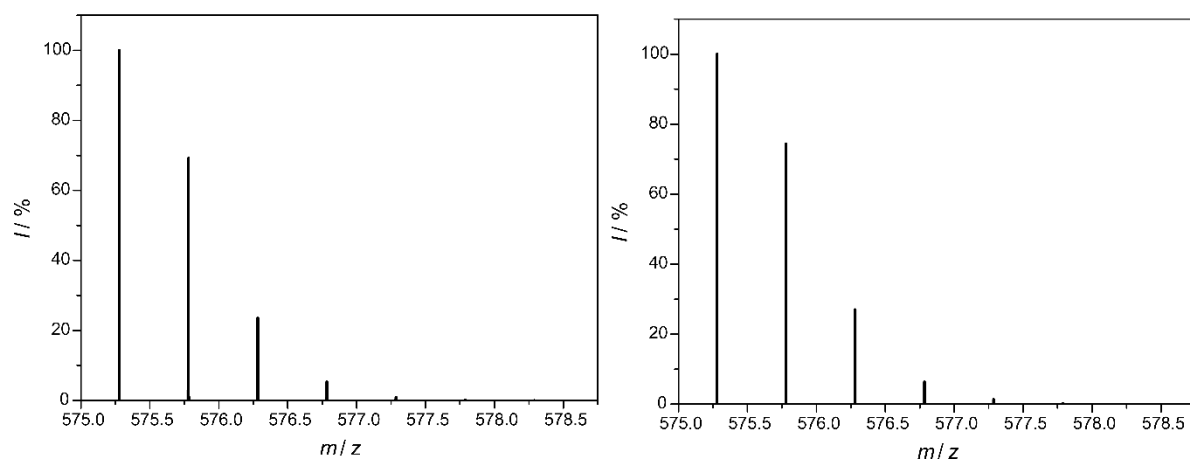


Figure S49: Comparison of the isotopic peak pattern of $[Co_2L^{Me}]SO_4$.

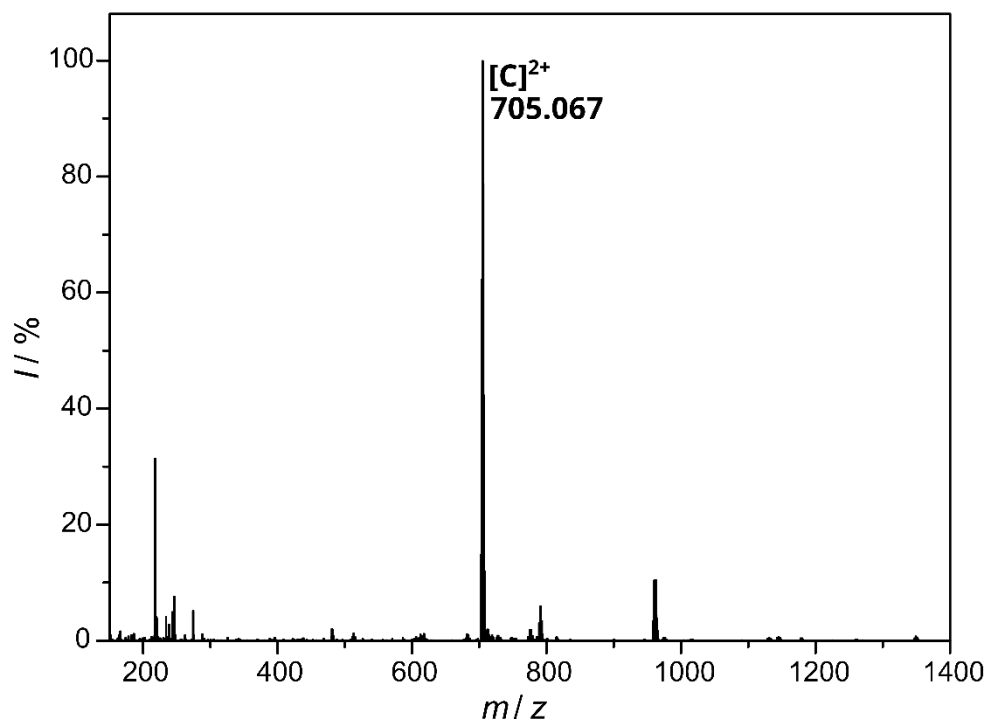


Figure S50: ESI⁺-mass spectrum of $[Co_2L^{Br}]SO_4$ with the dicationic fragment $[C]^{2+}$.

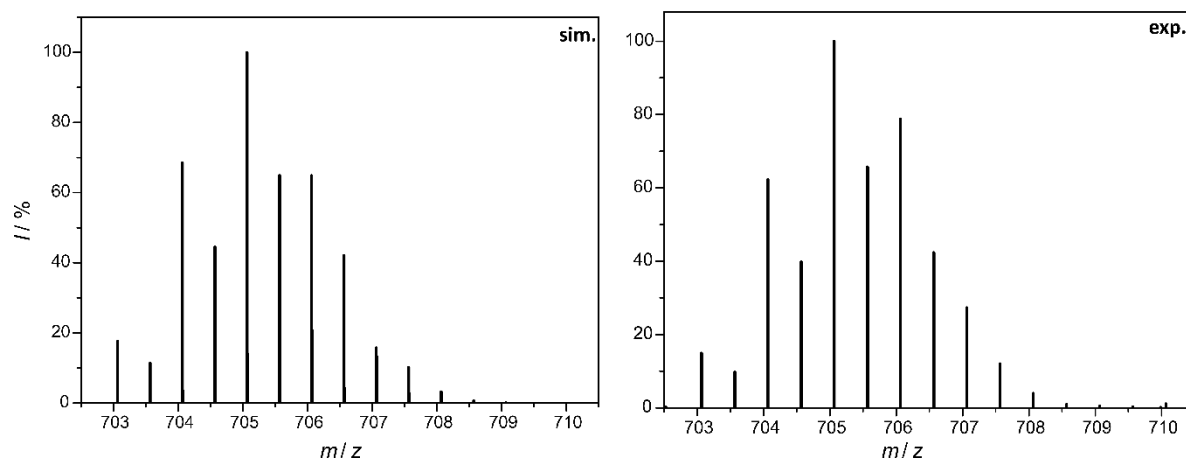


Figure S51: Comparison of the isotopic peak pattern of $[Co_2L^{Br}]SO_4$.

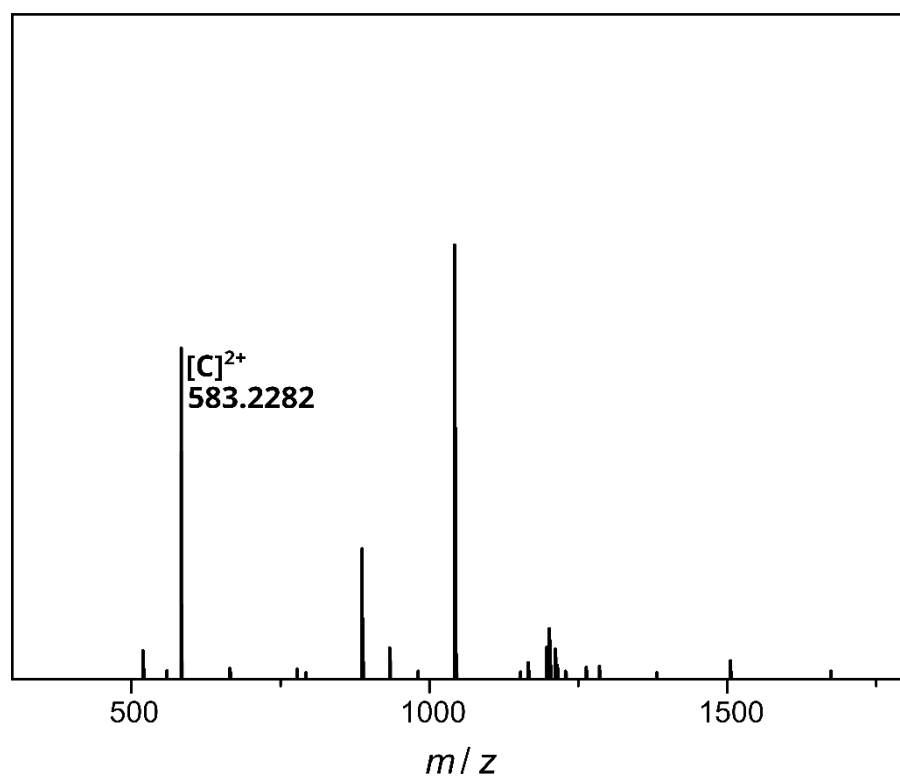


Figure S52: ESI⁺-mass spectrum of $[\text{Co}_2\text{L}^{\text{F}}]\text{SO}_4$ with the dicationic fragment $[\text{C}]^{2+}$.

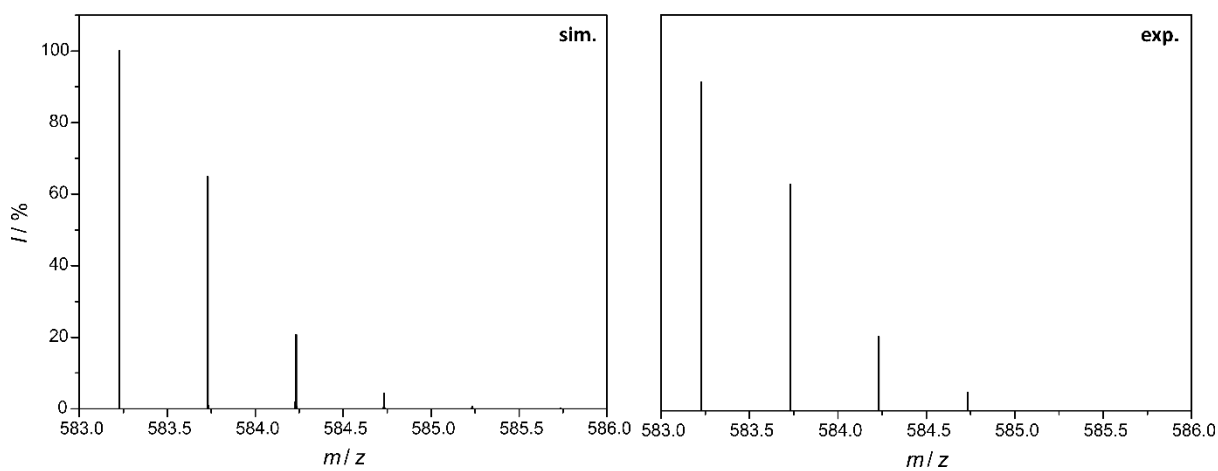


Figure S53: Comparison of the isotopic peak pattern of $[\text{Co}_2\text{L}^{\text{F}}]\text{SO}_4$.

5.1.12 Crystal Structures

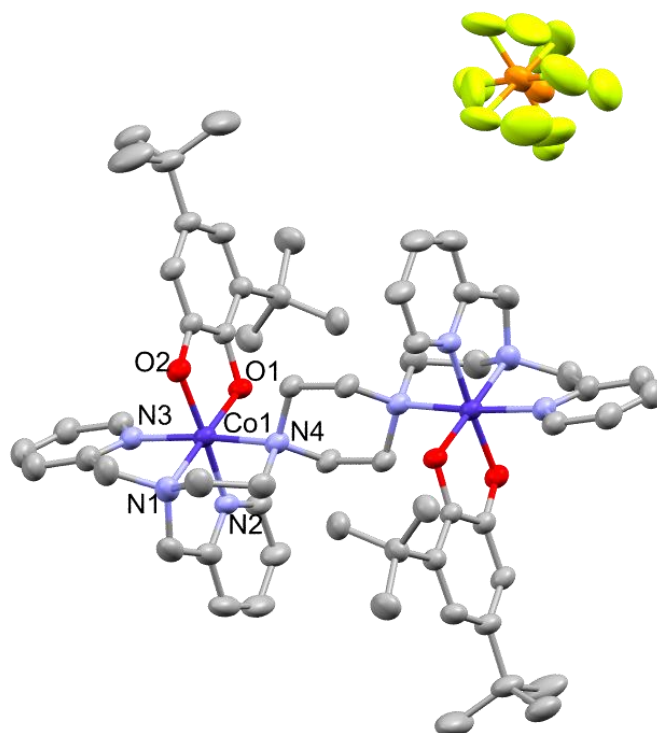


Figure S54: Complex structure of $[\text{Co}_2(\text{L}^{\text{H}})(\text{dtbcat})_2](\text{PF}_6)_2 \cdot 4 \text{ MeOH} \cdot 1.5 \text{ H}_2\text{O}$ at 120K. Lattice solvent molecules and hydrogen atoms are omitted for clarity. The probability level for the displacement of the ellipsoid is 50%. Colour Code: carbon (grey), cobalt (dark blue), nitrogen (light blue), oxygen (red), phosphorous (orange) and fluorine (light green).

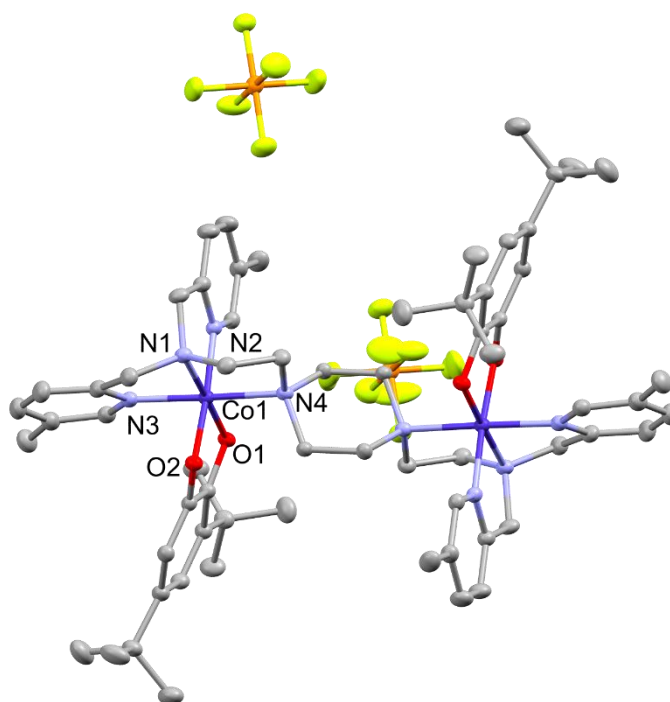


Figure S55: Complex structure of $[\text{Co}_2(\text{L}^{\text{Me}})(\text{dtbcat})_2](\text{PF}_6)_2 \cdot 5 \text{ THF}$ at 120K. Lattice solvent molecules and hydrogen atoms are omitted for clarity. The probability level for the displacement of the ellipsoid is 50%. Colour Code: carbon (grey), cobalt (dark blue), nitrogen (light blue), oxygen (red), phosphorous (orange) and fluorine (light green).

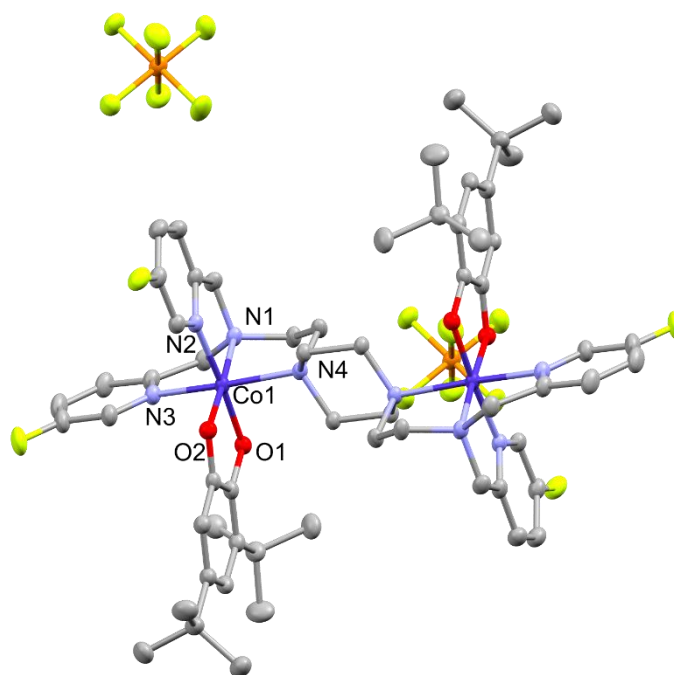


Figure S56: Complex structure of $[\text{Co}_2(\text{L}^{\text{F}})(\text{dtbcat})_2](\text{PF}_6)_2 \cdot 4 \text{ THF} \cdot 0.3 \text{ H}_2\text{O}$ at 120K. Lattice solvent molecules and hydrogen atoms are omitted for clarity. The probability level for the displacement of the ellipsoid is 50%. Colour Code: carbon (grey), cobalt (dark blue), nitrogen (light blue), oxygen (red), phosphorous (orange) and fluorine (light green).

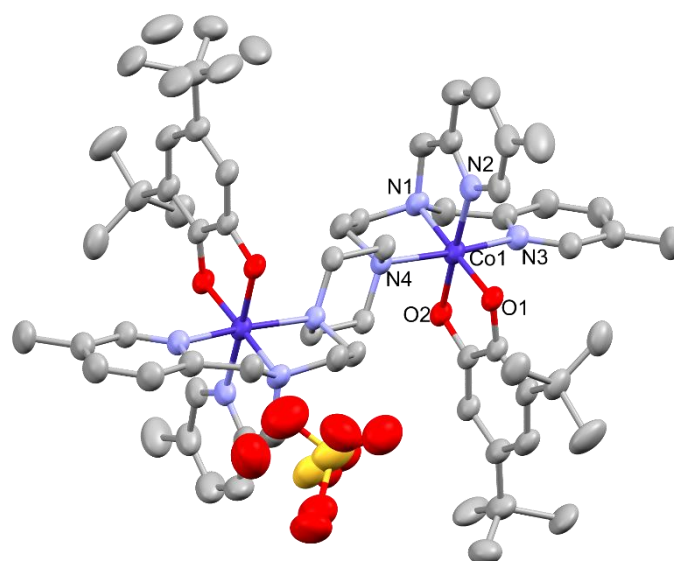


Figure S57: Complex structure of $[\text{Co}_2(\text{L}^{\text{Me}})(\text{dtbcat})_2]\text{SO}_4 \cdot 4 \text{ MeCN} \cdot 7 \text{ H}_2\text{O}$ at 120K. Lattice solvent molecules and hydrogen atoms are omitted for clarity. The probability level for the displacement of the ellipsoid is 50%. Colour Code: carbon (grey), cobalt (dark blue), nitrogen (light blue), oxygen (red), sulphur (yellow).

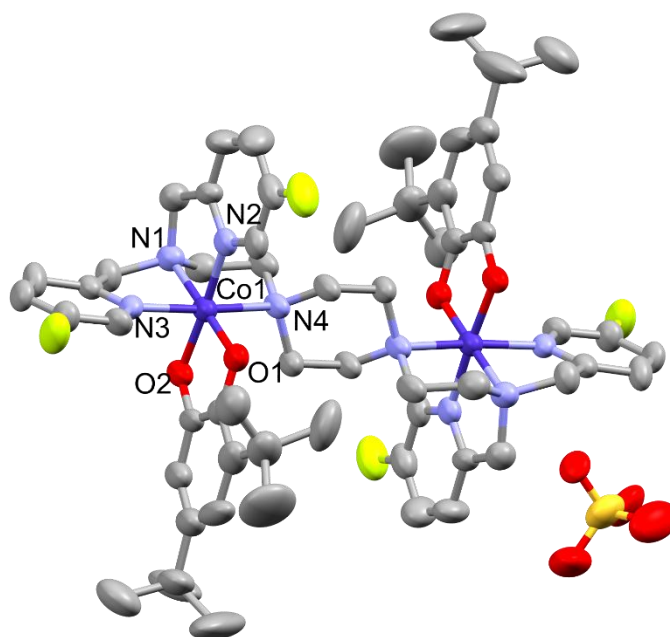


Figure S58: Complex structure of $[\text{Co}_2(\text{L}^{\text{F}})(\text{dtbcac})_2]\text{SO}_4 \cdot 11 \text{H}_2\text{O}$ at 120K. Lattice solvent molecules and hydrogen atoms are omitted for clarity. The probability level for the displacement of the ellipsoid is 50%. Colour Code: carbon (grey), cobalt (dark blue), nitrogen (light blue), oxygen (red), sulphur (yellow), fluorine (light green).

5.1.13 SHAPE Measurements

Table S1: Continuous SHAPE calculation of $[\text{Co}_2\text{L}^{\text{H}}](\text{PF}_6)_2$.

ML6	Symmetry	Name	CSHM
HP-6	D6h	Hexagon	31.19651
PPY-6	C5v	Pentagonal pyramid	26.84457
OC-6	Oh	Octahedron	0.33253
TPR-6	D3h	Trigonal prism	14.47456
JPPY-6	C5v	Johnson pentagonal pyramid	30.27615

Table S2: Continuous SHAPE calculation of $[\text{Co}_2\text{L}^{\text{Me}}](\text{PF}_6)_2$.

ML6	Symmetry	Name	CSHM
HP-6	D6h	Hexagon	31.05235
PPY-6	C5v	Pentagonal pyramid	27.51635
OC-6	Oh	Octahedron	0.27596
TPR-6	D3h	Trigonal prism	15.24891
JPPY-6	C5v	Johnson pentagonal pyramid	31.15992

Table S3: Continuous SHAPE calculation of $[\text{Co}_2\text{L}^{\text{F}}](\text{PF}_6)_2$.

ML6	Symmetry	Name	CSHM
HP-6	D6h	Hexagon	31.69493
PPY-6	C5v	Pentagonal pyramid	27.29054
OC-6	Oh	Octahedron	0.31131
TPR-6	D3h	Trigonal prism	14.54528
JPPY-6	C5v	Johnson pentagonal pyramid	30.89791

Table S4: Continuous SHAPE calculation of $[\text{Co}_2\text{L}^{\text{Me}}]\text{SO}_4$.

ML6	Symmetry	Name	CSHM
HP-6	D6h	Hexagon	31.79977
PPY-6	C5v	Pentagonal pyramid	27.79359
OC-6	Oh	Octahedron	0.25175
TPR-6	D3h	Trigonal prism	15.07697
JPPY-6	C5v	Johnson pentagonal pyramid	31.30697

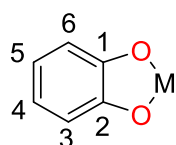
Table S5: Continuous SHAPE calculation of $[\text{Co}_2\text{L}^{\text{F}}]\text{SO}_4$.

ML6	Symmetry	Name	CSHM
HP-6	D6h	Hexagon	31.96477
PPY-6	C5v	Pentagonal pyramid	28.01565
OC-6	Oh	Octahedron	0.24194
TPR-6	D3h	Trigonal prism	15.09026
JPPY-6	C5v	Johnson pentagonal pyramid	31.50528

5.1.14 Metric Oxidation State (MOS)

Table S6: The MOS of the catecholate ligands of C1-C7.

Compound	C-O avg.	C1-C2	C2-C3 avg.	C3-C4 avg.	C4-C5	Calc. MOS
$[\text{Co}_2\text{L}^{\text{H}}](\text{PF}_6)_2$	1.3585	1.397	1.4035	1.3925	1.396	-1.955
$[\text{Co}_2\text{L}^{\text{Me}}](\text{PF}_6)_2$	1.356	1.413	1.401	1.398	1.399	-1.885
$[\text{Co}_2\text{L}^{\text{F}}](\text{PF}_6)_2$	1.3515	1.414	1.4015	1.403	1.401	-1.851
$[\text{Co}_2\text{L}^{\text{Me}}]\text{SO}_4$	1.3465	1.420	1.389	1.401	1.401	-1.831
$[\text{Co}_2\text{L}^{\text{F}}]\text{SO}_4$	1.359	1.384	1.406	1.4045	1.390	-2.048



5.1.15 Catecholate Bond Lengths

Table S7: Catecholate Bond Lengths of Complexes $[\text{Co}_2\text{L}^{\text{H}}](\text{PF}_6)_2$, $[\text{Co}_2\text{L}^{\text{Me}}](\text{PF}_6)_2$ and $[\text{Co}_2\text{L}^{\text{F}}](\text{PF}_6)_2$.

$[\text{Co}_2\text{L}^{\text{H}}](\text{PF}_6)_2$	Bond Length / Å	$[\text{Co}_2\text{L}^{\text{Me}}](\text{PF}_6)_2$	Bond Length / Å	$[\text{Co}_2\text{L}^{\text{F}}](\text{PF}_6)_2$	Bond Length / Å
C17-C18	1.406(3)	C19-C20	1.408(2)	C17-C18	1.405(2)
C18-C19	1.398(3)	C20-C21	1.404(2)	C18-C19	1.409(2)
C19-C20	1.396(3)	C21-C22	1.399(2)	C19-C20	1.401(2)
C20-C21	1.387(3)	C22-C23	1.392(2)	C20-C21	1.397(2)
C21-C22	1.401(3)	C23-C24	1.394(2)	C21-C22	1.398(2)
C22-C17	1.397(3)	C24-C19	1.4125(19)	C22-C17	1.414(2)

Table S8: Catecholate Bond Lengths of Complexes $[\text{Co}_2\text{L}^{\text{Me}}]\text{SO}_4$ and $[\text{Co}_2\text{L}^{\text{F}}]\text{SO}_4$.

$[\text{Co}_2\text{L}^{\text{Me}}]\text{SO}_4$	Bond Length / Å	$[\text{Co}_2\text{L}^{\text{F}}]\text{SO}_4$	Bond Length / Å
C19-C20	1.399(5)	C17-C18	1.406(13)
C20-C21	1.403(6)	C17-C22	1.383(14)
C21-C22	1.401(6)	C18-C19	1.458(17)
C22-C23	1.398(5)	C19-C20	1.389(19)
C23-C24	1.379(5)	C20-C21	1.351(16)
C24-C19	1.419(5)	C21-C22	1.406(13)

5.1.16 Metal Donor Bond Angles

Table S9: Metal Donor Bond Angles of Complexes $[\text{Co}_2\text{L}^{\text{H}}](\text{PF}_6)_2$, $[\text{Co}_2\text{L}^{\text{Me}}](\text{PF}_6)_2$, $[\text{Co}_2\text{L}^{\text{F}}](\text{PF}_6)_2$, $[\text{Co}_2\text{L}^{\text{Me}}]\text{SO}_4$ and C7.

	$[\text{Co}_2\text{L}^{\text{H}}](\text{PF}_6)_2 / ^\circ$	$[\text{Co}_2\text{L}^{\text{Me}}](\text{PF}_6)_2 / ^\circ$	$[\text{Co}_2\text{L}^{\text{F}}](\text{PF}_6)_2 / ^\circ$	$[\text{Co}_2\text{L}^{\text{Me}}]\text{SO}_4 / ^\circ$	$[\text{Co}_2\text{L}^{\text{F}}]\text{SO}_4 / ^\circ$
O1 Co1 O2	87.58(6)	87.87(4)	92.45(5)	88.06(10)	88.4(3)
O1 Co1 N1	178.17(8)	178.47(5)	175.48(5)	178.58(11)	178.0(3)
O1 Co1 N2	92.23(7)	94.86(5)	85.48(5)	93.54(13)	93.4(3)
O1 Co1 N3	96.05(7)	95.29(5)	91.66(5)	94.56(12)	94.0(3)
O1 Co1 N4	93.04(7)	92.66(5)	88.86(5)	93.57(11)	94.3(3)
O2 Co1 N1	94.08(8)	90.89(5)	177.67(5)	92.05(12)	92.5(3)
O2 Co1 N2	176.42(7)	175.94(5)	92.29(5)	176.54(11)	176.7(3)
O2 Co1 N3	86.96(7)	85.13(5)	94.96(5)	87.28(12)	87.6(2)
O2 Co1 N4	92.70(7)	91.64(5)	93.79(5)	91.23(11)	91.0(2)
N1 Co1 N4	87.66(8)	88.27(5)	88.10(5)	87.85(12)	87.5(3)
N2 Co1 N1	86.06(9)	86.33(5)	86.26(5)	86.27(14)	85.6(3)
N2 Co1 N3	89.50(8)	91.24(5)	90.07(5)	89.54(13)	89.5(3)
N2 Co1 N4	90.88(7)	83.71(5)	92.62(5)	91.72(12)	91.7(3)
N3 Co1 N1	83.27(8)	91.62(5)	83.22(5)	84.03(13)	84.3(3)
N3 Co1 N4	170.88(8)	171.30(5)	170.73(5)	171.69(12)	171.5(3)

5.1.17 Crystallographic Parameters

Table S10: Crystallographic Data of Complexes $[\text{Co}_2\text{L}^{\text{H}}](\text{PF}_6)_2$ and $[\text{Co}_2\text{L}^{\text{Me}}](\text{PF}_6)_2$.

	$[\text{Co}_2\text{L}^{\text{H}}](\text{PF}_6)_2$	$[\text{Co}_2\text{L}^{\text{Me}}](\text{PF}_6)_2$
Empirical formula	$\text{C}_{64}\text{H}_{99}\text{Co}_2\text{F}_{12}\text{N}_8\text{O}_{9.5}\text{P}_2$	$\text{C}_{84}\text{H}_{128}\text{Co}_2\text{F}_{12}\text{N}_8\text{O}_9\text{P}_2$
Formula weight	1540.31	1801.74
Temperature/K	120.00	120.00
Crystal system	monoclinic	triclinic
Space group	C2/c	P-1
a/Å	25.1591(5)	10.0660(5)
b/Å	17.3702(4)	12.4519(6)
c/Å	17.2127(4)	17.4275(9)
$\alpha/^\circ$	90	92.848(4)
$\beta/^\circ$	107.062(2)	95.607(4)
$\gamma/^\circ$	90	90.133(4)
Volume/Å³	7191.2(3)	2171.18(19)
Z	4	1
$\rho_{\text{calc}}/\text{cm}^3$	1.423	1.378
μ/mm^{-1}	0.596	0.504
F(000)	3228.0	952.0
Crystal size/mm³	0.27 × 0.223 × 0.14	0.15 × 0.102 × 0.055
Radiation	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
2θ range for data collection/$^\circ$	4.118 to 67.642	4.066 to 65.426
Index ranges	-36 ≤ h ≤ 39, -24 ≤ k ≤ 24, -24 ≤ l ≤ 24	-15 ≤ h ≤ 13, -17 ≤ k ≤ 18, -25 ≤ l ≤ 23
Reflections collected	59645	41807
Independent reflections	12647 [R_{int} = 0.0441, R_{sigma} = 0.0217]	13622 [R_{int} = 0.0214, R_{sigma} = 0.0231]
Data/restraints/parameters	12647/324/520	13622/79/589
Goodness-of-fit on F^2	1.015	1.051
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0716, wR_2 = 0.2091	R_1 = 0.0493, wR_2 = 0.1253
Final R indexes [all data]	R_1 = 0.0832, wR_2 = 0.2225	R_1 = 0.0580, wR_2 = 0.1321
Largest diff. peak/hole / e Å⁻³	1.57/-0.69	1.19/-0.43

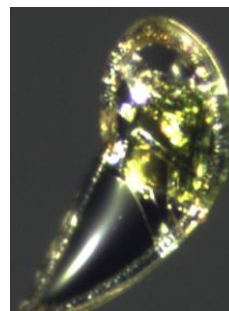
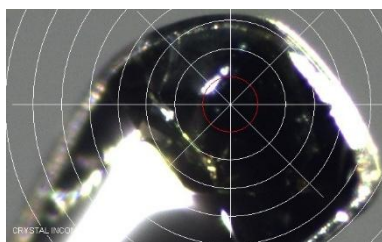


Table S11: Crystallographic Data of Complexes $[\text{Co}_2\text{L}^{\text{F}}](\text{PF}_6)_2$ and $[\text{Co}_2\text{L}^{\text{Me}}]\text{SO}_4$.

	$[\text{Co}_2\text{L}^{\text{F}}](\text{PF}_6)_2$	$[\text{Co}_2\text{L}^{\text{Me}}]\text{SO}_4$
Empirical formula	$\text{C}_{76}\text{H}_{108.6}\text{Co}_2\text{F}_{16}\text{N}_8\text{O}_{8.3}\text{P}_2$	$\text{C}_{72}\text{H}_{114}\text{Co}_2\text{N}_{12}\text{O}_{15}\text{S}$
Formula weight	1750.90	1537.67
Temperature/K	120.00	120.00
Crystal system	monoclinic	triclinic
Space group	C2/c	P-1
a/Å	15.7143(4)	10.7258(5)
b/Å	16.7227(4)	14.3014(7)
c/Å	31.6147(8)	15.6018(7)
$\alpha/^\circ$	90	68.092(3)
$\beta/^\circ$	102.219(2)	77.140(4)
$\gamma/^\circ$	90	75.853(4)
Volume/Å³	8119.7(4)	2129.97(18)
Z	4	1
$\rho_{\text{calc}}/\text{cm}^3$	1.432	1.199
μ/mm^{-1}	0.543	0.478
F(000)	3660.0	820.0
Crystal size/mm³	$0.16 \times 0.123 \times 0.06$	$0.163 \times 0.107 \times 0.07$
Radiation	MoK α ($\lambda = 0.71073$)	MoK α ($\lambda = 0.71073$)
2θ range for data collection/$^\circ$	4.784 to 64.182	4.452 to 56
Index ranges	$-21 \leq h \leq 22, -24 \leq k \leq 22, -47 \leq l \leq 45$	$-14 \leq h \leq 13, -18 \leq k \leq 18, -20 \leq l \leq 20$
Reflections collected	47943	31472
Independent reflections	13102 [$R_{\text{int}} = 0.0180, R_{\text{sigma}} = 0.0188$]	10268 [$R_{\text{int}} = 0.0525, R_{\text{sigma}} = 0.0440$]
Data/restraints/parameters	13102/0/533	10268/198/610
Goodness-of-fit on F^2	1.042	1.056
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0434, wR_2 = 0.1087$	$R_1 = 0.1082, wR_2 = 0.2924$
Final R indexes [all data]	$R_1 = 0.0515, wR_2 = 0.1145$	$R_1 = 0.1256, wR_2 = 0.3192$
Largest diff. peak/hole / e Å⁻³	1.02/-0.67	2.25/-0.97

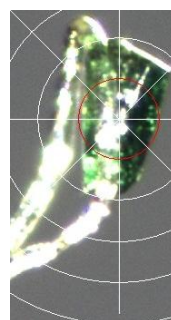
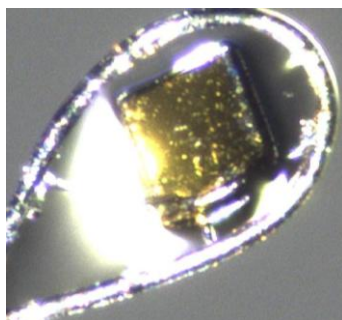
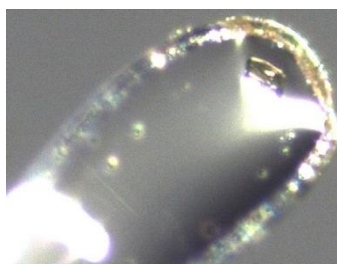


Table S12: Crystallographic Data of Complexes $[\text{Co}_2\text{L}^{\text{F}}]\text{SO}_4$.

	$[\text{Co}_2\text{L}^{\text{F}}]\text{SO}_4$
Empirical formula	$\text{C}_{60}\text{H}_{98}\text{Co}_2\text{F}_4\text{N}_8\text{O}_{19}\text{S}$
Formula weight	1461.38
Temperature/K	120.00
Crystal system	monoclinic
Space group	$\text{P}2_1/\text{c}$
a/Å	13.7666(5)
b/Å	27.7611(7)
c/Å	9.8976(3)
$\alpha/^\circ$	90
$\beta/^\circ$	100.569(3)
$\gamma/^\circ$	90
Volume/Å³	3718.5(2)
Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.305
μ/mm^{-1}	0.553
F(000)	1544.0
Crystal size/mm³	$0.048 \times 0.029 \times 0.012$
Radiation	$\text{MoK}\alpha$ ($\lambda = 0.71073$)
2θ range for data collection/$^\circ$	4.91 to 51.998
Index ranges	$-16 \leq h \leq 16, -34 \leq k \leq 34, -12 \leq l \leq 12$
Reflections collected	27791
Independent reflections	7285 [$R_{\text{int}} = 0.0607, R_{\text{sigma}} = 0.0686$]
Data/restraints/parameters	7285/51/484
Goodness-of-fit on F^2	1.065
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.1219, wR_2 = 0.3292$
Final R indexes [all data]	$R_1 = 0.1775, wR_2 = 0.3665$
Largest diff. peak/hole / $\text{e} \text{ \AA}^{-3}$	1.15/-0.55



5.1.18 UV-Vis Spectroscopy

Table S13: Tabulated molar extinction coefficients in ($\text{L mol}^{-1} \text{cm}^{-1}$) at their respective wavelength in nm for complexes $[\text{Co}_2\text{L}^{\text{H}}](\text{PF}_6)_2$, $[\text{Co}_2\text{L}^{\text{Me}}](\text{PF}_6)_2$ and $[\text{Co}_2\text{L}^{\text{F}}](\text{PF}_6)_2$.

$[\text{Co}_2\text{L}^{\text{H}}](\text{PF}_6)_2$	$[\text{Co}_2\text{L}^{\text{Me}}](\text{PF}_6)_2$	$[\text{Co}_2\text{L}^{\text{F}}](\text{PF}_6)_2$
31296 (299)	23614 (298)	34979 (297)
2569 (378)	1973 (377)	2445 (378)
626 (782)	546 (775)	620 (795)

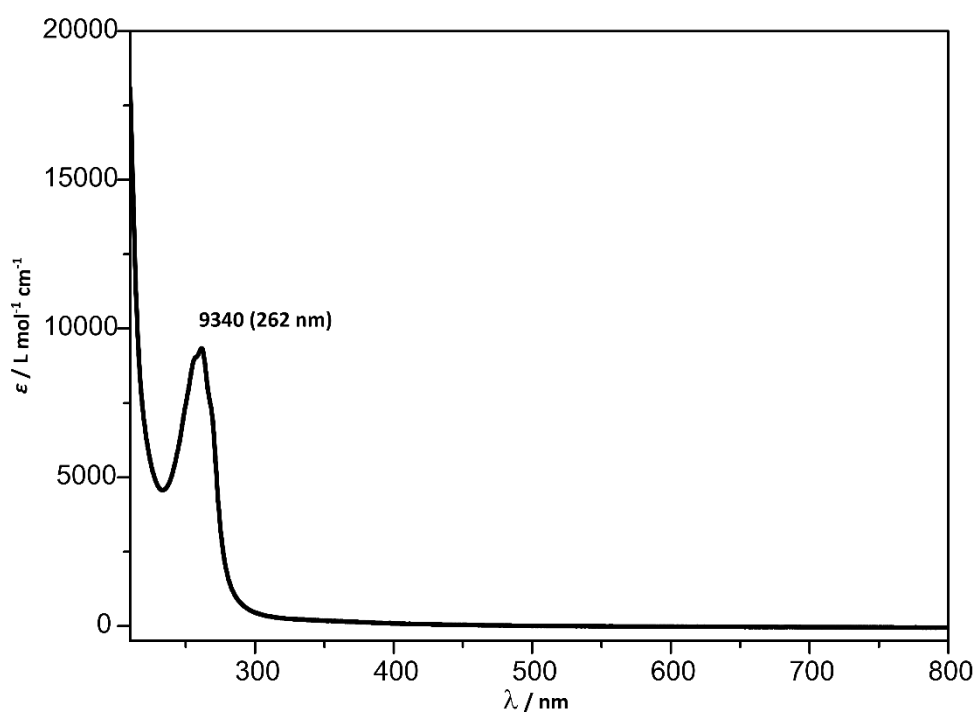


Figure S59: UV-Vis spectrum of **L-H** at RT in MeCN at 0.02 mM.

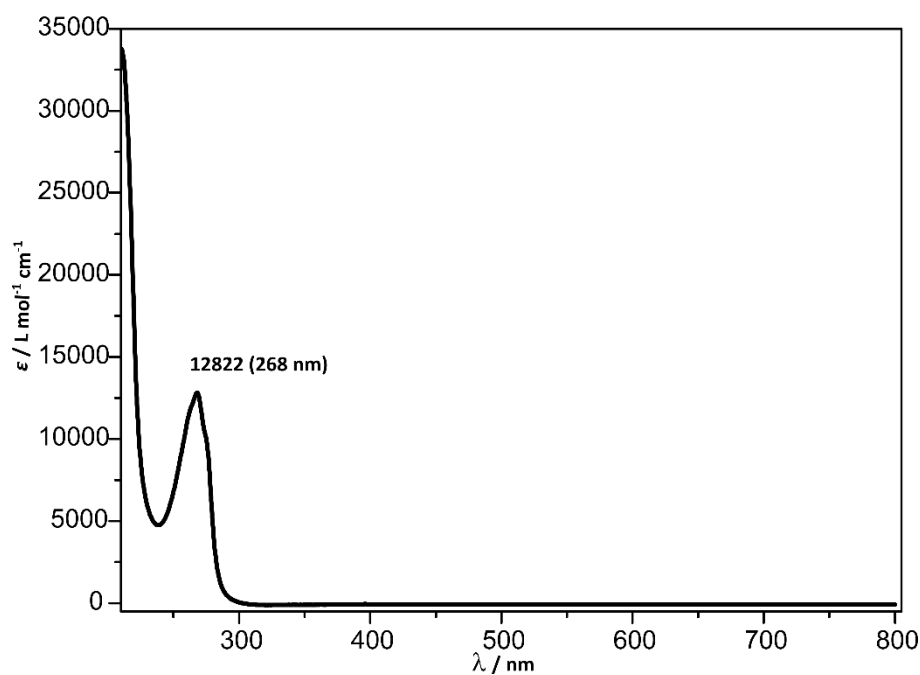


Figure S60: UV-Vis spectrum of **L-Me** at RT in MeCN at 0.02 mM.

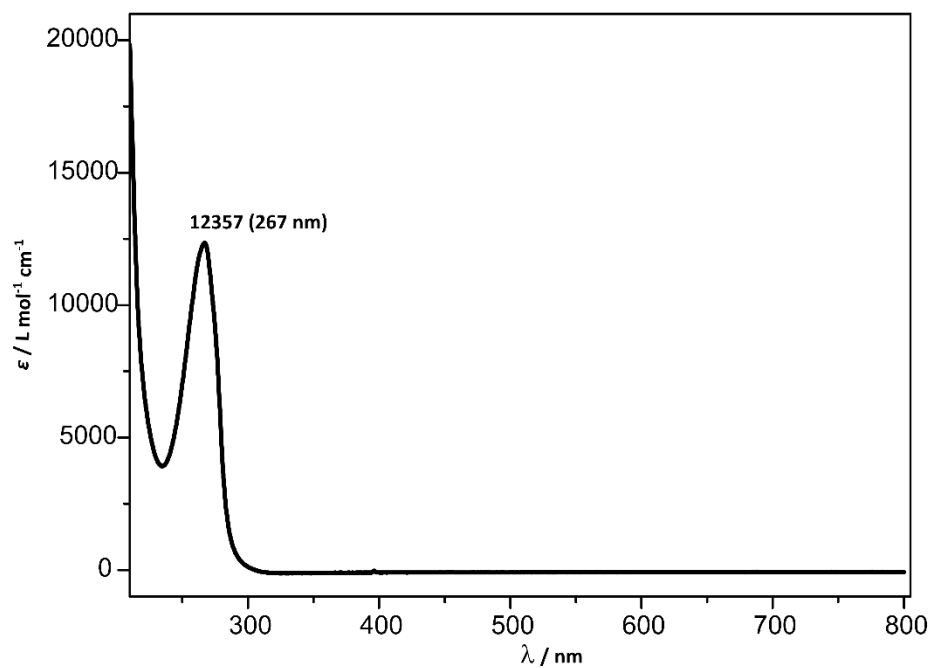


Figure S61: UV-Vis spectrum of L-F at RT in MeCN at 0.02 mM.

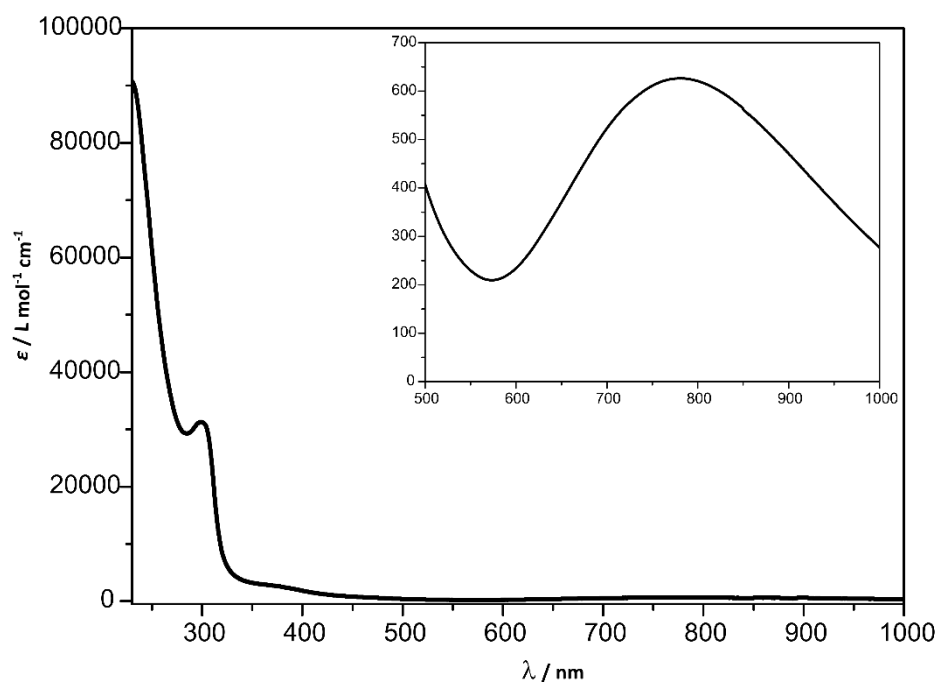


Figure S62: UV-Vis spectrum of $[\text{Co}_2\text{L}^{\text{H}}](\text{PF}_6)_2$ at RT in MeCN at 0.01mM with a zoomed in region at 1mM in MeCN.

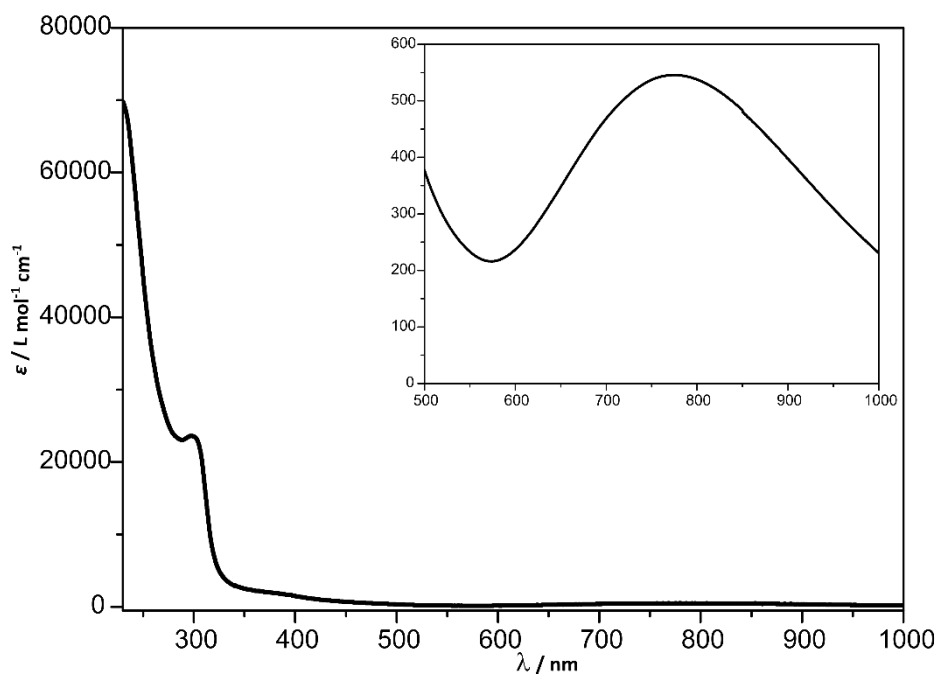


Figure S63: UV-Vis spectrum of $[\text{Co}_2\text{L}^{\text{Me}}](\text{PF}_6)_2$ at RT in MeCN at 0.01mM with a zoomed in region at 1mM in MeCN.

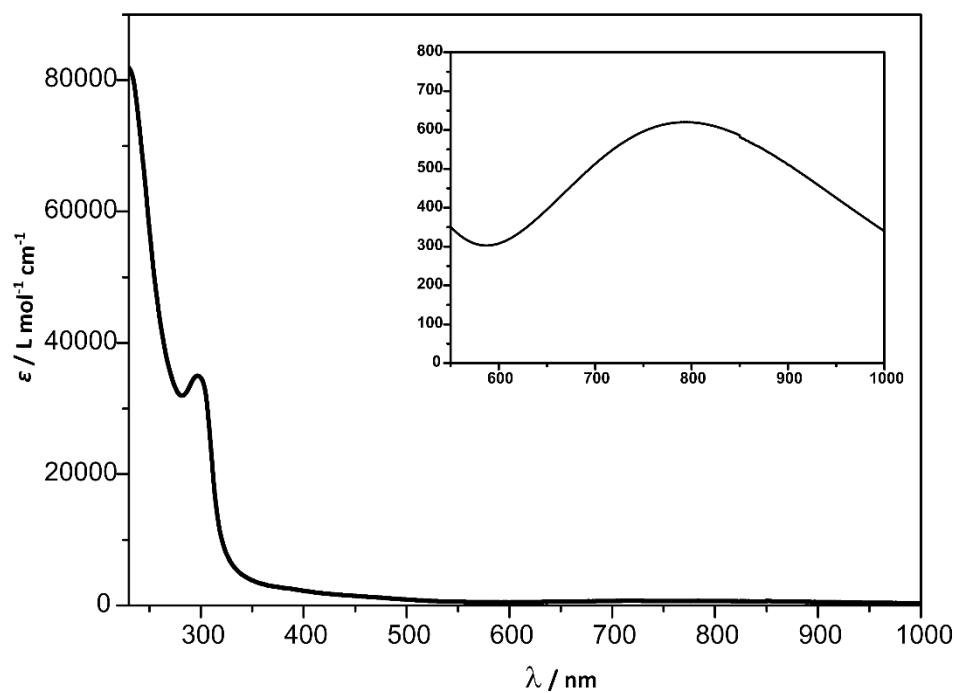


Figure S64: UV-Vis spectrum of $[\text{Co}_2\text{L}^{\text{F}}](\text{PF}_6)_2$ at RT in MeCN at 0.01mM with a zoomed in region at 1mM in MeCN.

5.1.19 Cyclic Voltammetry

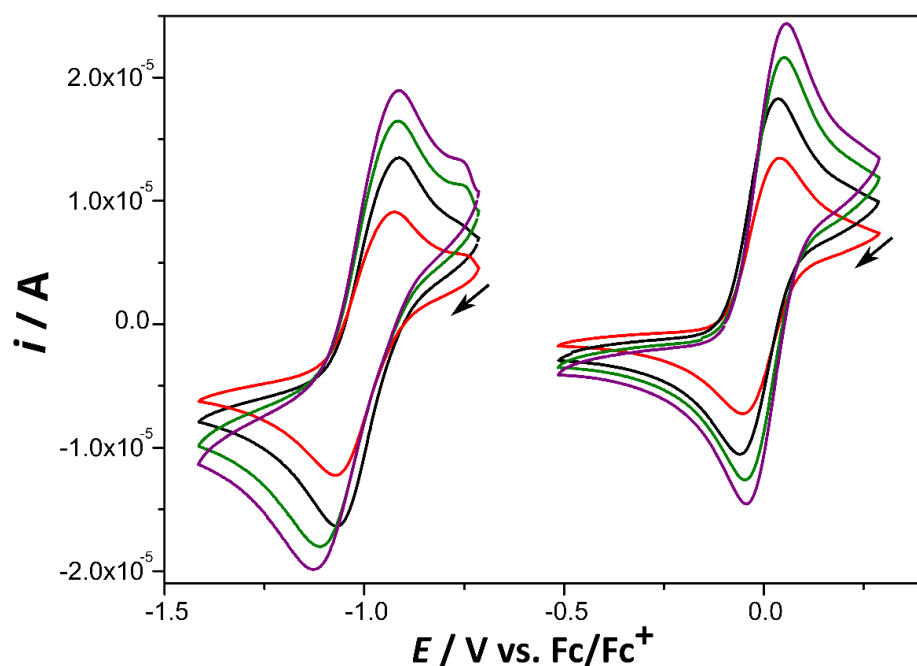


Figure S65: Cyclic voltammogram of previously reported $[\text{Co}_2\text{L}^{\text{H}}](\text{ClO}_4)_2$ in acetonitrile (1 mM, 0.1 M $n\text{-Bu}_4\text{PF}_6$) obtained with different scan rates (50 mV s^{-1} (red), 100 mV s^{-1} (black), 150 mV s^{-1} (green), 200 mV s^{-1} (purple)) of redox processes (I/I') left and (II/II') right, measured with a glassy carbon working electrode and a silver wire pseudo reference electrode, referenced internally against the redox pair of Fc/Fc^+ .

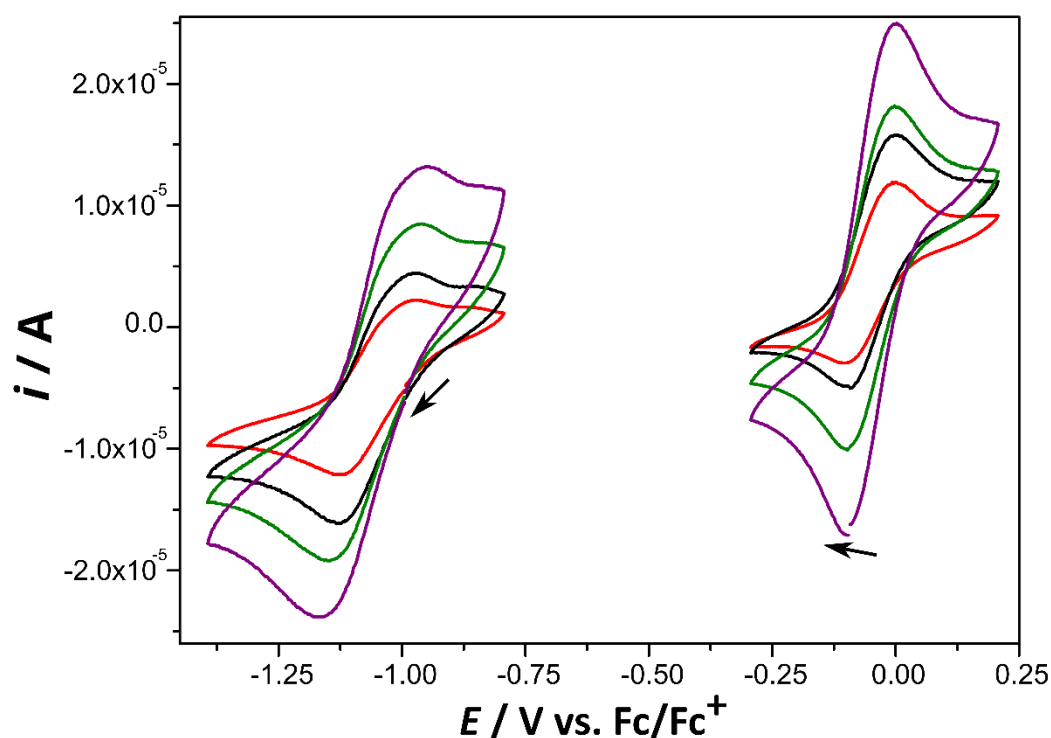


Figure S66: Cyclic voltammogram of $[\text{Co}_2\text{L}^{\text{Me}}](\text{PF}_6)_2$ in acetonitrile (1 mM, 0.1 M $n\text{-Bu}_4\text{PF}_6$) obtained with different scan rates (50 mV s^{-1} (red), 100 mV s^{-1} (black), 150 mV s^{-1} (green), 200 mV s^{-1} (purple)) of redox processes (I/I') left and (II/II') right, measured with a glassy carbon working electrode and a silver / silver nitrate reference electrode, referenced internally against the redox pair of Fc/Fc^+ .

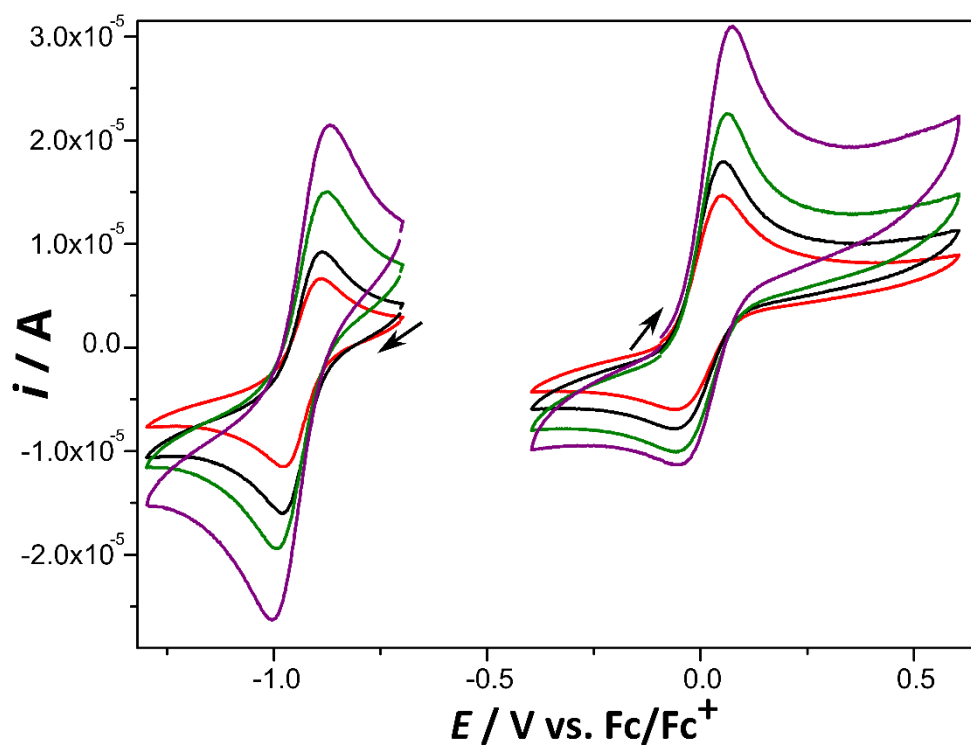


Figure S67: Cyclic voltammogram of $[\text{Co}_2\text{L}^{\text{F}}](\text{PF}_6)_2$ in acetonitrile (1 mM, 0.1 M $n\text{-Bu}_4\text{PF}_6$) obtained with different scan rates (50 mV s^{-1} (red), 100 mV s^{-1} (black), 200 mV s^{-1} (green), 400 mV s^{-1} (purple)) of redox processes (I/I') left and (II/II') right, measured with a glassy carbon working electrode and a silver / silver nitrate reference electrode, referenced internally against the redox pair of Fc/Fc^+ .

5.1.20 Evans Method

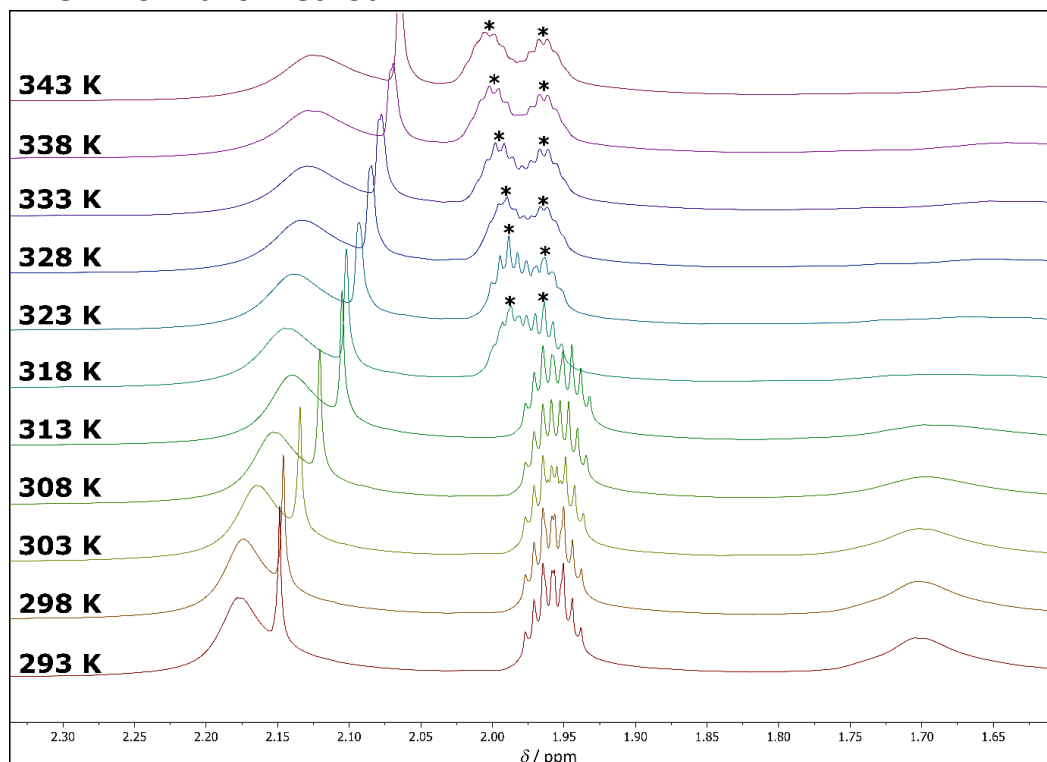


Figure S68: Evans method ^1H NMR (6 mM in MeCN) in a temperature range from 293K to 343K [400 MHz] in 5K steps of previously reported $[\text{Co}_2\text{L}^{\text{H}}](\text{ClO}_4)_2$

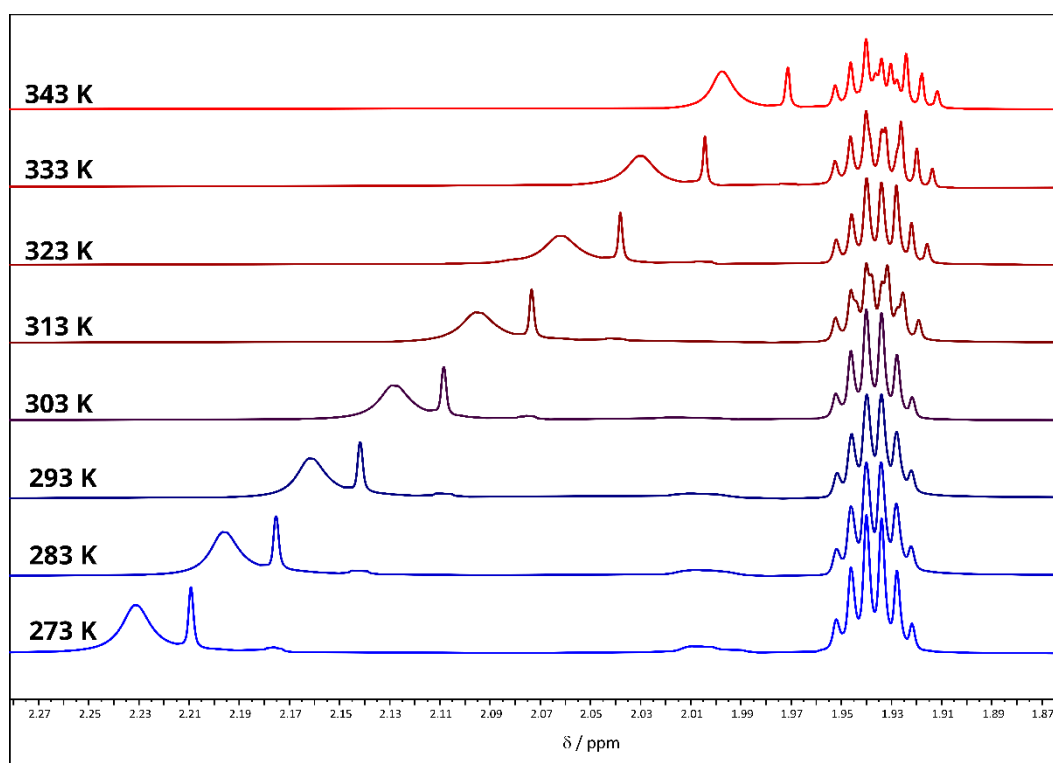


Figure S69: Evans method ^1H NMR (6 mM in MeCN) in a temperature range from 273 K to 343 K [400 MHz] in 10 K steps of $[\text{Co}_2\text{L}^{\text{Me}}](\text{PF}_6)_2$.

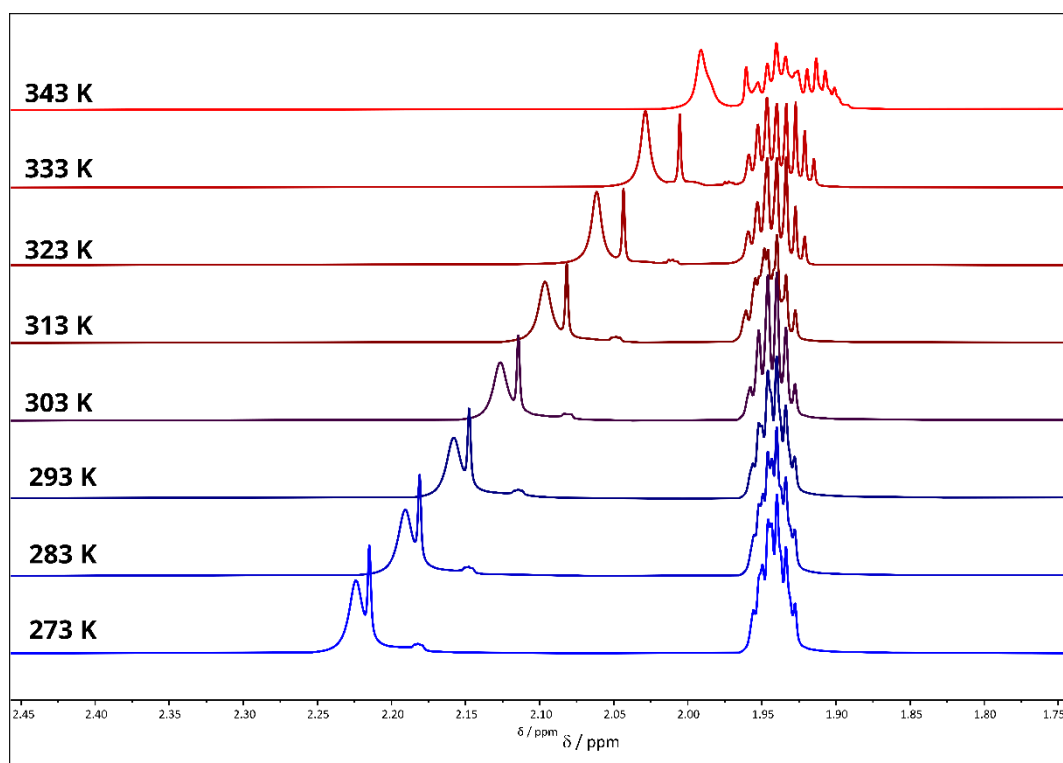


Figure S70: Evans method ^1H NMR (6 mM in MeCN) in a temperature range from 273 K to 343 K [400 MHz] in 10K steps of $[\text{Co}_2\text{L}^{\text{F}}](\text{PF}_6)_2$

5.1.21 SQUID Magnetometry

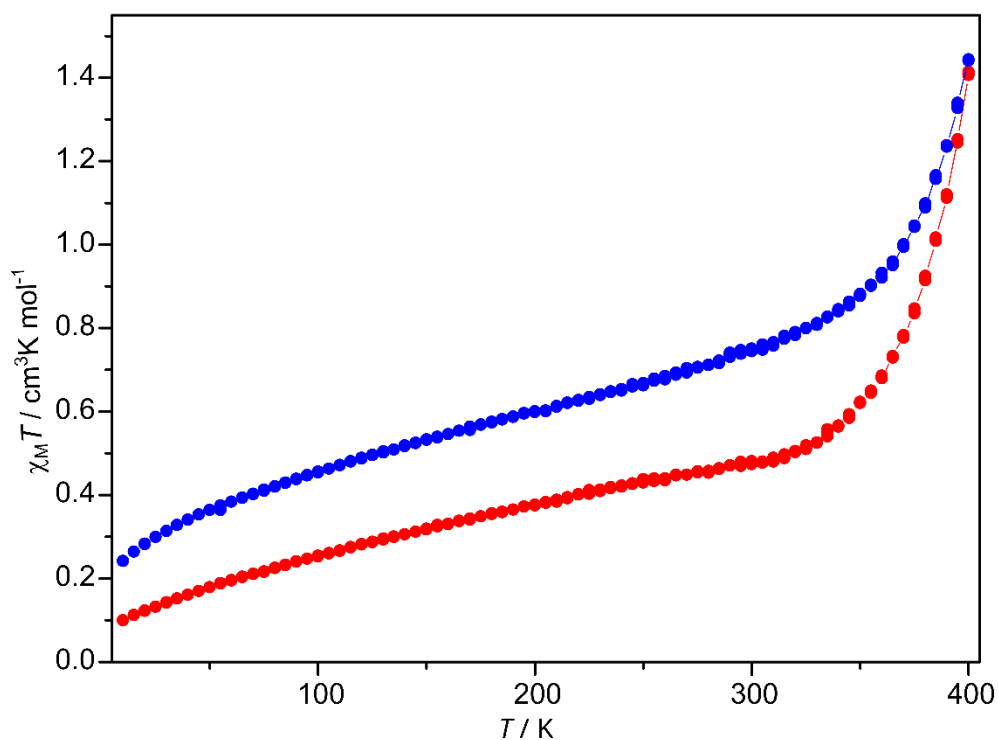


Figure S71: Temperature dependent $\chi_M T (T)$ of $[\text{Co}_2\text{L}^{\text{H}}](\text{PF}_6)_2$ in heating (red) and cooling (blue) mode over the temperature range of 10-400 K, waiting 5 minutes at 400 K.

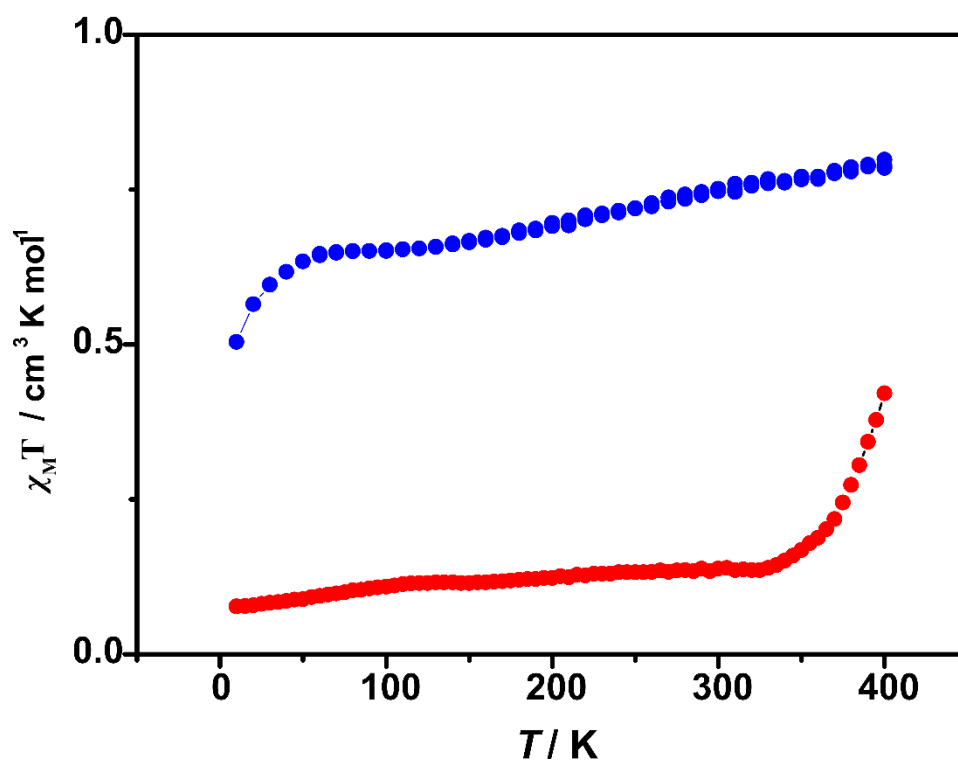


Figure S72: Temperature dependent $\chi_M T (T)$ of $[\text{Co}_2\text{L}^{\text{Me}}](\text{PF}_6)_2$ in heating (red) and cooling (blue) mode over the temperature range of 10-400 K, waiting 5 minutes at 400 K.

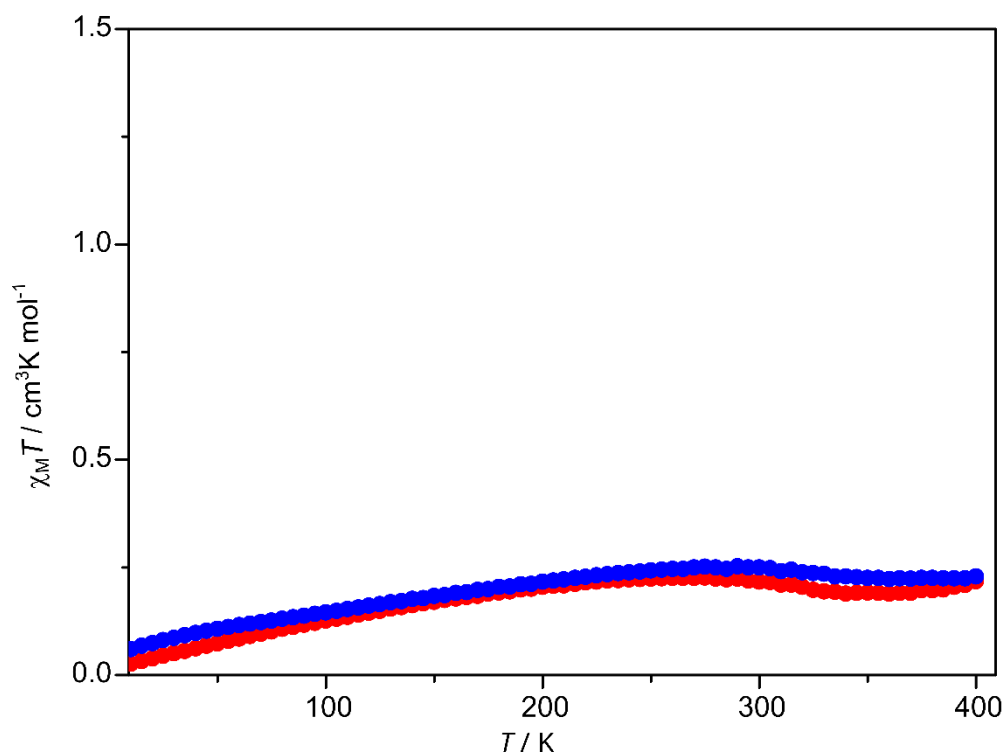


Figure S73: Temperature dependent $\chi_M T(T)$ of $[\text{Co}_2\text{L}^{\text{Br}}](\text{PF}_6)_2$. In heating (red) and cooling (blue) mode over the temperature range of 10-400 K, waiting 5 minutes at 400 K.

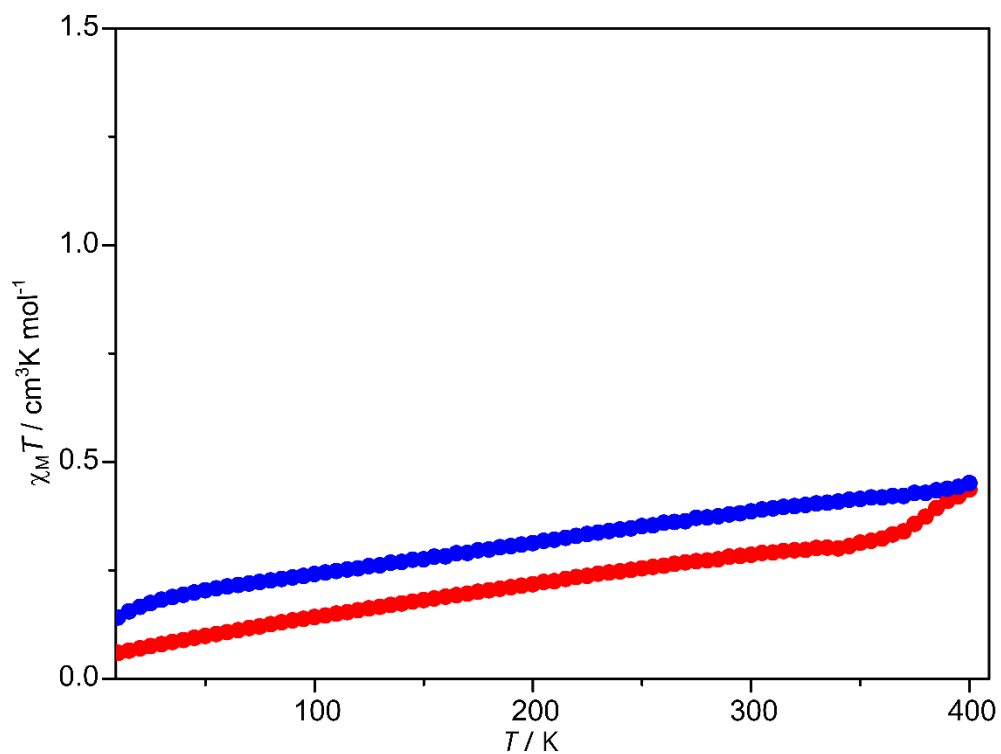


Figure S74: Temperature dependent $\chi_M T(T)$ of $[\text{Co}_2\text{L}^{\text{F}}](\text{PF}_6)_2$. In heating (red) and cooling (blue) mode over the temperature range of 10-400 K, waiting 5 minutes at 400 K.

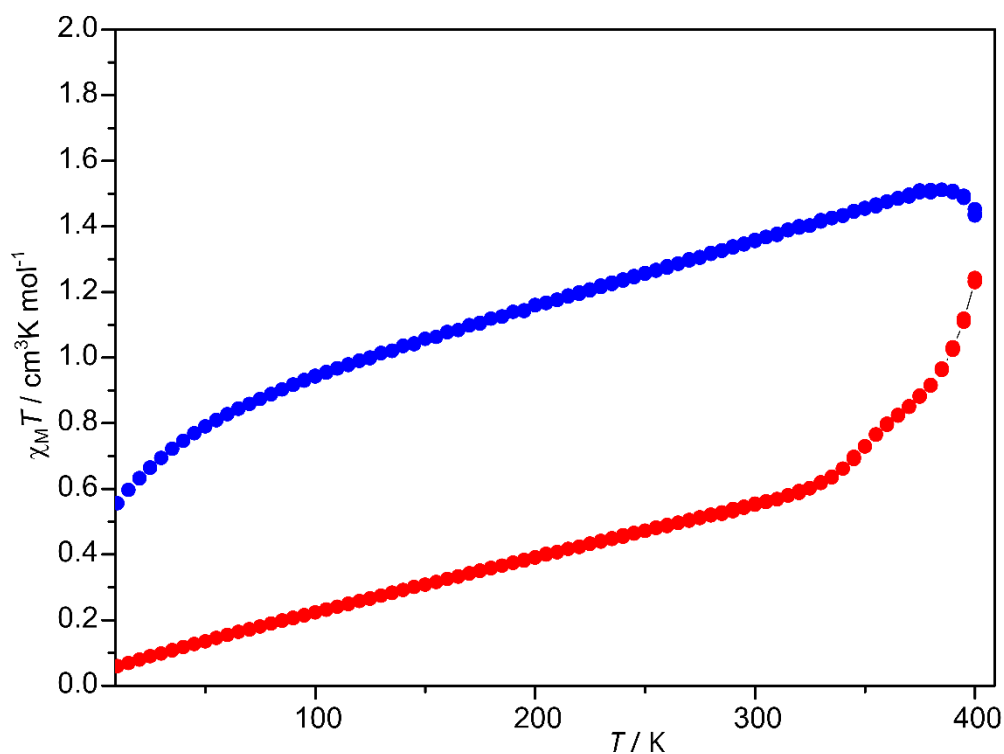


Figure S75: Temperature dependent $\chi_M T$ (T) of $[\text{Co}_2\text{L}^{\text{Me}}]\text{SO}_4$ in heating (red) and cooling (blue) mode over the temperature range of 10-400 K, waiting 5 minutes at 400 K.

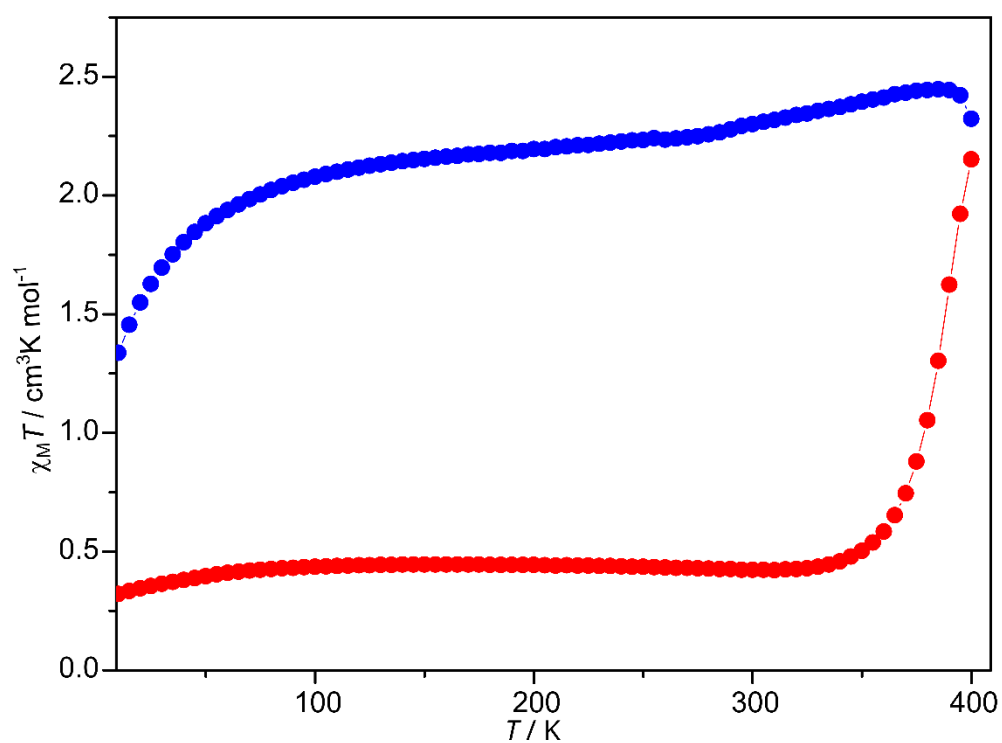


Figure S76: Temperature dependent $\chi_M T$ (T) of $[\text{Co}_2\text{L}^{\text{Br}}]\text{SO}_4$ in heating (red) and cooling (blue) mode over the temperature range of 10-400 K, waiting 5 minutes at 400 K.

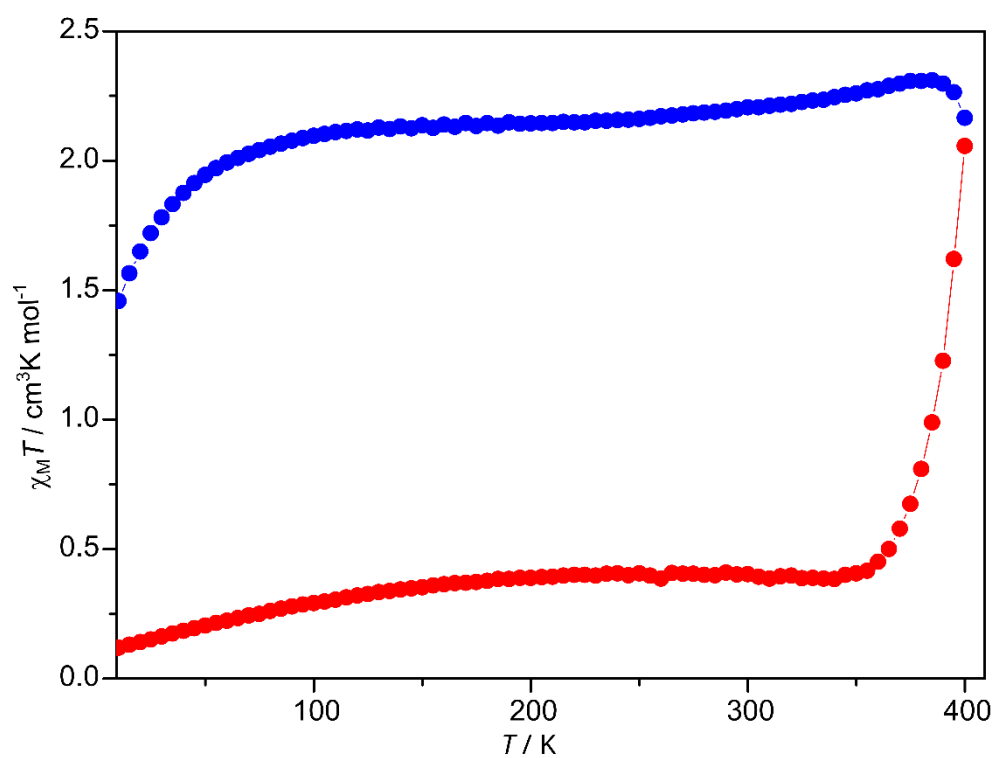


Figure S77: Temperature dependent $\chi_M T$ (T) of $[\text{Co}_2\text{L}^{\text{Me}}]\text{SO}_4$. In heating (red) and cooling (blue) mode over the temperature range of 10-400 K, waiting 5 minutes at 400 K.

6. Chapter 3: Complete and Reversible VT through the Interplay of Sterics and Electronic Design

This chapter introduces a new modification of the redox-innocent bridging ligand through the introduction of a sterically demanding methyl group at the ortho position of the pyridyl units. Four novel dinuclear complexes bearing different catecholate ligands 3,5-di-*tert*-butyl-, tetrachloro-, tetrabromo-, and 4,5-dichlorocatecholate were synthesised with the teraphenylborate counteranion and comprehensively characterised. Single-crystal X-ray diffraction at 120 K confirms that all halogenated catecholate complexes adopt the LS Co(III)cat configuration, while the di-*tert*-butylcatecholate complex is in the HS Co(II)sq state. Assignment of the electronic configuration was supported by Co-N bond lengths, C-O and C-C bond lengths of the dioxolene ring, SHAPE analysis, and metric oxidation state calculations. SQUID magnetometry reveals that the di-*tert*-butylcatecholate complex is temperature-invariant in the HS Co(II)sq state across the entire measured temperature range. The tetrahalogenated complexes exhibit only incomplete VT transitions up to 400 K, with the tetrachloro derivative approaching near-complete conversion. The 4,5-dichlorocatecholate complex undergoes a fully reversible and complete VT transition in an abrupt, concerted one-step transition profile, with a transition temperature of 322 K in the first thermal cycle and 327 K in subsequent cycles. The VT transition was additionally monitored by variable-temperature solid-state ^{13}C MAS NMR spectroscopy and solid-state UV-Vis diffuse reflectance spectroscopy.

The results are presented as a scientific article in preparation for submission.

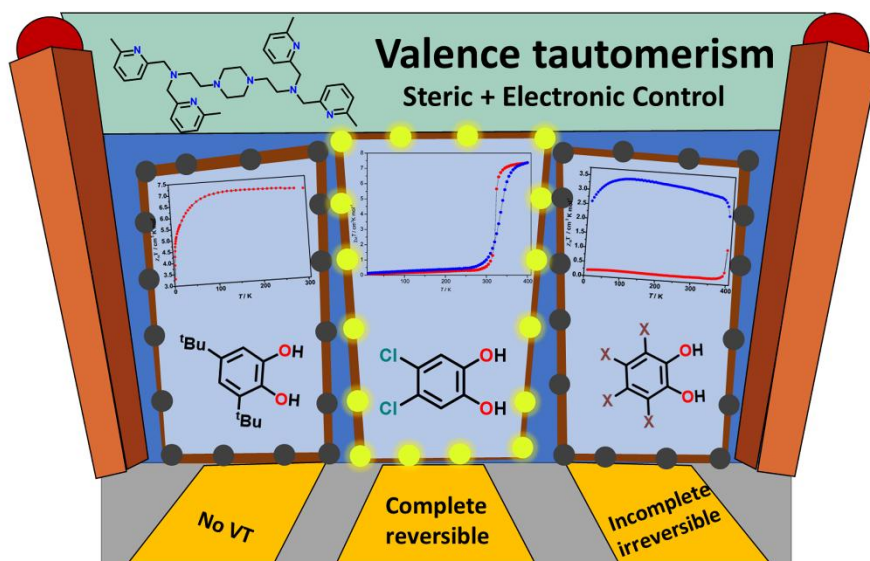
Author Contribution

Synthesis of all ligands and complexes, and their characterisation were carried out by Tim Hieke, with the exception of the synthesis of the tetrabrominated catecholate complexes, which were performed by [REDACTED] supervised by Tim Hieke. Single-crystal X-ray diffraction measurements, structure solution, and refinement were performed by [REDACTED]. The manuscript was written by Tim Hieke and revised with input from [REDACTED] and [REDACTED]. [REDACTED] provided overall supervision of the experimental work and the manuscript preparation. All authors have read and approved the final version of the manuscript.

Manuscript: Unlocking Valence Tautomerism in Dinuclear Cobalt Complexes Through Steric and Electronic Design

Department Chemistry, Johannes Gutenberg University of Mainz, Duesbergweg 10-14, 55128, Mainz, Germany.

Graphical Abstract



Abstract

Valence tautomeric (VT) transitions in cobalt-catecholate complexes are often incomplete, which limits their use as molecular switches. Although steric stabilization of the high-spin (HS) Co(II) state has become an established strategy for favouring the HS tautomer, it often pushes the system too far, resulting in systems that are no longer switchable. Here, we present a molecular design strategy that overcomes this trade-off by combining steric control of the non-redox-active (innocent) bridging ligand with systematic electronic tuning of the redox-active catecholate ligand. A sterically demanding *ortho*-methylated pyridine-based ligand, *N,N,N',N'*-tetra-6-methyl-2-picoyl-1,4-bis(2-aminoethyl)piperazine (**L^{o-Me}**), was employed to stabilize a HS Co(II) framework, which was subsequently rendered switchable through electronic substitution of the catecholate. Four new dinuclear cobalt complexes of the general formula $[\text{Co}_2\text{L}^{\text{o-Me}}(\text{X-cat})_2]^{2+} (\text{BPh}_4)_2^-$ ($\text{X} = \text{Cl}_4, \text{Br}_4, \text{Cl}_2$ or 3,5-di-*tert*-butyl) were synthesized and characterized by single-crystal XRD, UV-Vis spectroscopy, variable-temperature solid-state ^{13}C MAS NMR spectroscopy, and SQUID magnetometry. X-ray diffraction at 120 K reveals a HS Co(II)-semiquinonate state for the di-*tert*-butyl derivative, while all other complexes adopt a low-spin Co(III)-catecholate structure. SQUID magnetometry identifies a temperature-invariant HS state for the di-*tert*-butyl complex, abrupt but incomplete VT transitions that are irreversible for the tetrahalogenated derivatives ($\chi T = 1.21$ and $6.10 \text{ cm}^3 \text{ K mol}^{-1}$ at 400 K for **Co-Br₄cat** and **Co-Cl₄cat**), and a fully reversible abrupt transition at $T_{1/2} = 360 \text{ K}$ for the dichlorinated complex, with a χT value of $7.63 \text{ cm}^3 \text{ K mol}^{-1}$ at 400 K consistent with complete HS conversion. These results demonstrate that combining steric encumbrance of the bridging ligand with electron-withdrawing catecholate substitution enables the rational implementation of a reversible VT switch.

Introduction

Over recent decades, continuous electronic miniaturization has driven technological development from consumer electronics to advanced applications in transportation and space exploration. As electronic components approach their physical limits, alternative concepts beyond conventional semiconductor-based technologies are increasingly explored. In this context, molecular switches and bistable molecules with addressable electronic states represent promising functional units for next-generation molecular electronic devices.^{1–8}

Valence tautomerism (VT) in coordination compounds involves an intramolecular electron transfer between a metal centre and a redox-active ligand, resulting in two electronically distinct but interconvertible states. Among the various systems investigated, cobalt-catecholate complexes have been studied most extensively, as the electron transfer in these systems is frequently coupled to a change in spin state. The interconversion between a diamagnetic low-spin (LS) Co(III)catecholate (cat) state and a paramagnetic high-spin (HS) Co(II)semiquinonate (sq) state enables straightforward detection of VT, for example by SQUID magnetometry.^{9,10}

This spin-state coupled electron transfer leads to pronounced changes in magnetic, optical, and structural properties, including significant variations in metal-ligand bond lengths. Cobalt-catecholate complexes therefore represent particularly well-suited model systems for investigating VT.^{11–15} Importantly, however, a spin-state change is not an intrinsic requirement of the phenomenon, and VT in cobalt systems can also occur without any accompanying change in spin-state¹⁶. Beyond cobalt^{17–20}, valence tautomerism has further been reported for a range of other transition metals and lanthanides.^{10,21–24}

Valence tautomeric transitions can be induced by a variety of external stimuli, including temperature^{25–28}, light^{29–32}, pressure^{33–36}, and by changes in coordination environment³⁷. In recent years, research efforts have increasingly shifted from mononuclear cobalt complexes, typically featuring Co:catecholate ratios of 1:1^{38,39} or 1:2^{40–43}, toward dinuclear architectures. Dinuclear systems offer the advantage of an increased number of electronically distinguishable states and, consequently, a higher density of accessible states within a single molecular entity. In addition to the low-spin Co(III)cat and high-spin Co(II)sq states, mixed states such as LS Co(III)cat-HS Co(II)sq may become accessible and potentially addressable.^{44–49}

To date, most dinuclear valence tautomeric systems rely on redox-active ligands as bridging units between the metal centres. In contrast, the role of innocent bridging ligands has received considerably less attention, despite several inherent advantages, including synthetic accessibility, modular functionalization, and the possibility to create well-defined metal-binding pockets.^{11,50–52} A commonly employed strategy to stabilize the HS Co(II) state involves steric modulation of such innocent ligands, frequently achieved through the introduction of *ortho*-methyl substituents adjacent to coordinating pyridine units. While this approach effectively favours the HS configuration²⁶, it often leads to temperature-invariant HS Co(II)sq compounds that no longer exhibit VT switching, and are thus no longer addressable as molecular switches.^{47,53,54}

Complementary to steric effects, electronic modulation of both the redox-active and the innocent ligand represents a powerful and versatile approach for tuning the VT equilibrium. Previous work has demonstrated that electron-withdrawing catecholates, such as tetrahalogenated derivatives, stabilize the Co(III)cat state, whereas electron-donating substituents on the innocent bridging ligand shift the equilibrium towards Co(III), and electron-withdrawing substituents on the innocent ligand favour the Co(II) tautomer by modulating the electron density at the metal centre.⁵²

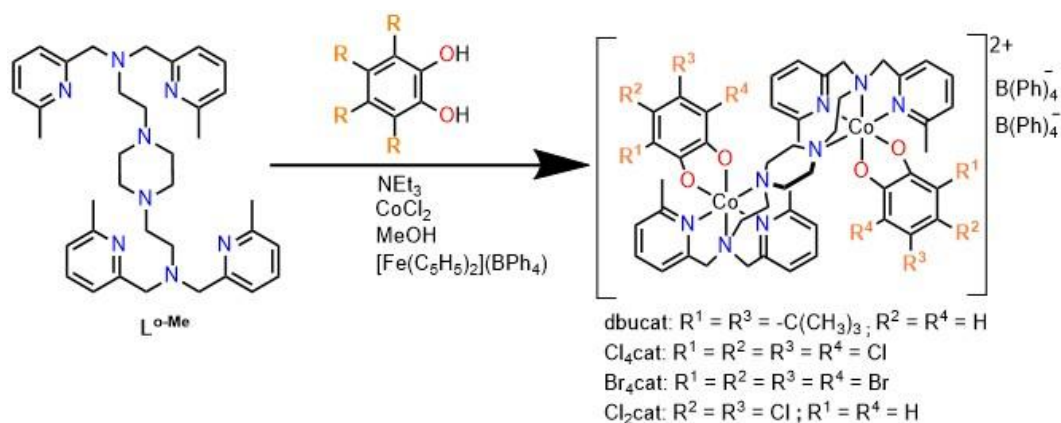
Here, we present a series of four dinuclear cobalt complexes bearing a sterically encumbered innocent bridging ligand, in which the electronic properties of the catecholate are systematically varied with the aim of identifying the conditions required to overcome temperature invariance and achieve full, reversible VT switching.

Ligand Synthesis

Electronic modification of the innocent bridging ligand has previously been shown to promote VT transitions, yet without achieving complete conversion.⁵² To address this limitation, a complementary steric approach was pursued. The synthetic route followed that reported for the parent ligand⁵¹, with modification of the final reductive amination step by substituting pyridine-2-carbaldehyde with 6-methyl-2-pyridinecarboxaldehyde, introducing four *ortho*-methyl substituents in close proximity to the metal centre to enforce elongated metal-donor bond lengths and a more distorted coordination geometry, both of which are known to favour the HS Co(II) configuration.^{47,52,53}

The resulting ligand (**L^{oMe}**) was obtained in good yield and fully characterized by standard spectroscopic methods and elemental analysis (see Experimental Section).

Complex Synthesis



Scheme 1: Synthesis of the dinuclear cobalt complexes with varying catechol ligands.

The complexes are labelled according to the general naming scheme **Co-X**, where X represents the dioxolene coligand: dbucat (3,5-di-*tert*-butyl-catecholate), dbusq (3,5-di-*tert*-butyl-semiquinonate), Br_4cat (tetrabromocatecholate), Cl_4cat (tetrachlorocatecholate), and Cl_2cat (4,5-dichlorocatecholate). The complexes were synthesized by reaction of **L^{oMe}** with the respective catechol and anhydrous cobalt(II) chloride in degassed methanol under inert atmosphere, followed by oxidation with ferrocenium tetraphenylborate (see Experimental Section for details).

In the case of **Cl₂cat**, the standard synthetic route proved unsuccessful. The target complex precipitated as an impure amorphous powder, which resisted recrystallization from acetonitrile due to insolubility. Attempts to dissolve the crude material under harsher conditions using butyronitrile as a high-boiling solvent were accompanied by a colour change, indicative of decomposition rather than clean dissolution, ultimately yielding only the penta-coordinated complex **[Co₂L^{oMe}Cl₂]** (**Figure S26**), in which the catecholate is absent from the coordination sphere.

To circumvent this limitation, a modified route was developed in which the corresponding hexafluorophosphate (PF_6) salt was prepared first. Owing to its significantly improved solubility, this intermediate could be converted to the target tetraphenylborate derivative via anion exchange.

The progress and completion of the complexation reactions were monitored by IR spectroscopy. The characteristic tetraphenylborate bands at $706\text{--}704\text{ cm}^{-1}$ and $611\text{--}609\text{ cm}^{-1}$ are present in all complexes, confirming successful anion incorporation. Importantly, the absence of PF_6^- bands in the spectrum of **Co-Cl₂cat** confirms the completeness of the anion exchange and the purity of the isolated product.

The oxidation state of the coordinated dioxolene ligand can be assessed through the C-O stretching vibrations, which are sensitive to the effective bond order. Catecholates, bearing a formal C-O single bond, exhibit lower stretching frequencies, whereas semiquinonates, with partial double-bond

character (formal bond order of 1.5), display higher vibrational frequencies. Accordingly, **Co-dbusq** shows a C-O stretching band at 1454 cm^{-1} consistent with semiquinonate character, while the tetrahalogenated derivatives **Co-Cl₄cat** and **Co-Br₄cat** exhibit lower frequencies at 1431 cm^{-1} and 1433 cm^{-1} , respectively, indicative of a catecholate oxidation state at room temperature. Notably, **-Cl₂cat** displays the highest C-O stretching frequency of the series at 1468 cm^{-1} , accompanied by pronounced band broadening and the presence of a shoulder.

High-resolution mass spectrometry confirmed the dicationic fragment $[M]^{2+}$ for **Co-dbusq**, **Co-Cl₄cat** and **Co-Br₄cat**, with calculated isotopic peak patterns in excellent agreement with the experimental spectra. Due to the insolubility of **Co-Cl₂cat**, mass spectrometry could not be measured for this complex. Bulk purity was further established by elemental analysis of air-dried samples. Partial loss of lattice solvent and incorporation of water upon air-drying were evident from elemental analysis, and the calculated compositions were adjusted accordingly. All physical measurements were therefore performed on air-dried material.

Crystal Structure Description

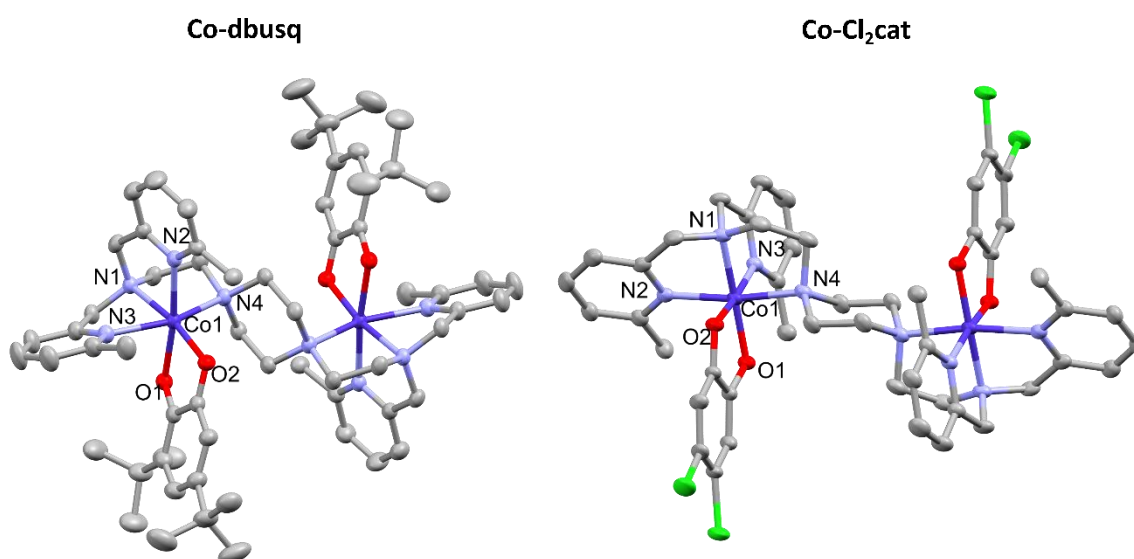


Figure 1: Complex structures of $[Co_2(L^{o-Me})(dbusq)_2] (B(Ph_4)_2)$ left and $[Co_2(L^{o-Me})(Cl_2cat)_2] (B(Ph_4)_2)$ right at 120 K. Lattice solvent molecules, anions, and hydrogen atoms were omitted for clarity. The probability level for the displacement of the ellipsoid is 50%. Colour code: carbon (grey), cobalt (dark blue), nitrogen (light blue), oxygen (red), chloride (green).

Single-crystal X-ray diffraction data were collected at 120 K for all complexes. Molecular structures of **Co-dbusq** and **Co-Br₄cat** are shown in **Figure 1**, representatively. Counter-ions, lattice solvent molecules, and hydrogen atoms are omitted for clarity; the remaining structures are provided in the ESI.

Crystals of **Co-dbusq** were dark blue, whereas the tetrahalogenated derivatives were yellow to brown. **Co-dbusq** · 3 Et₂O crystallized in the monoclinic space group $P2_1/c$, while **Co-Cl₄cat** · MeCN and **Co-Br₄cat** · 4 MeCN crystallized in the orthorhombic space group $Pbca$ and **Co-Cl₂cat** · 2 MeCN crystallized in the triclinic space group $P-1$. In all cases, the asymmetric unit contains half of the dinuclear complex and one counterion, consistent with the expected dicationic dinuclear complex with one BPh_4^- counterion per asymmetric unit.

A bis-tetradentate bridging ligand coordinates two cobalt centres within two binding pockets via four nitrogen donor atoms. The octahedral coordination sphere of each cobalt ion is completed by two oxygen donor atoms from an *ortho*-dioxolene ligand. Importantly, the two dioxolene ligands are arranged trans to one another across the dinuclear framework. This trans disposition maximises spatial separation of the redox-active ligands and effectively minimises steric hindrance within the coordination spheres. The bridging spacer consists of a piperazine unit adopting a chair conformation,

which further increases the metal-metal separation and reduces steric repulsion between the coordination pockets.

Each cobalt centre adopts an N_4O_2 coordination, comprising two nitrogen atoms from the *ortho*-methylpyridine moieties, one nitrogen atom from the tertiary amine bridge, and one nitrogen atom of the piperazine linker, with the remaining two coordination sites occupied by the oxygen donors of the dioxolene ligand. Due to geometric constraints imposed by the distorted piperazine fragment, the Co-N bond to the piperazine nitrogen is consistently elongated relative to the remaining Co-N distances.

The oxidation and spin states of the cobalt centres were assessed from Co-N bond lengths and octahedral distortion parameters derived from continuous shape measurements (CShM), calculated using SHAPE 2.1.⁵⁵ The oxidation state of the coordinated dioxolene ligands was assessed from C-O and C-C bond lengths and quantified via the metric oxidation state (MOS) formalism⁵⁶, where values of 0, -1 and -2 correspond to quinone, semiquinonate and catecholate oxidation states, respectively.

Continuous shape analysis reveals the largest octahedral distortion for **Co-dbusq** (CShM = 1.55). In **Co-Cl₄cat**, crystallographic disorder results in two distinct octahedral environments (CShM = 0.50 and 0.77), both less distorted than **Co-dbusq**. **Co-Br₄cat** and **Co-Cl₂cat** exhibit the smallest distortion parameters (CShM = 0.49 and 0.47), approaching ideal octahedral geometry (CShM = 0).

Comparison with structurally analogous complexes from previous works underscores the significant influence of the *ortho*-methyl substituent on the coordination geometry.⁵² Complexes bearing unsubstituted innocent ligands combined with tetrahalogenated catecholates display CShM values of 0.24-0.41 and Co-N bond lengths of 1.902-1.957 Å, while meta-substituted derivatives bearing di-*tert*-butylcatecholates show CShM values of 0.24-0.33 and Co-N distances of 1.914(3)–1.959(1) Å. The substantially larger distortion parameter of **Co-dbusq** (CShM = 1.55), together with its markedly elongated Co-N bond lengths, thus directly reflects the steric perturbation imposed by the *ortho*-methyl group. Since HS Co(II) centres are characteristically associated with longer metal-donor bond lengths and greater octahedral distortion, this structural predisposition is expected to stabilise the high-spin configuration and shift the VT equilibrium temperature to lower temperatures.⁴⁸

The elongated Co-N bond lengths and increased octahedral distortion in **Co-dbusq** are consistent with a HS Co(II) (d^7) configuration, whereas the shorter bond lengths and lower distortion parameters in the halogenated derivatives support LS Co(III) (d^6) assignments. These Co-N bond lengths are consistent with values reported for HS Co(II) and LS Co(III) complexes in the literature.^{26,37,47}

Analysis of the dioxolene ligands further corroborates this interpretation. The MOS value of **Co-dbusq** is -1.003, indicating semiquinonate character. In contrast, **Co-Cl₄cat** exhibits values of -1.620 and -1.725, **Co-Br₄cat** -1.839 and **Co-Cl₂cat** -1.99, all consistent with predominantly catecholate character. This assignment is supported by the intraligand C-C bond metrics: **Co-dbusq** displays pronounced bond length alternation (1.37-1.38 Å and 1.43-1.45 Å), characteristic of semiquinonate species, whereas the halogenated derivatives show aromatic C-C bond distances of approximately 1.40 Å, indicative of catecholate character.

The solid-state structures determined at 120 K establish **Co-dbusq** as a d^7 high-spin Co(II)-semiquinonate species, while the halogenated derivatives adopt d^6 low-spin Co(III)-catecholate electronic configurations.

Across the series, a clear trend is observed in the CShM values: *ortho*-methylation leads to a markedly more distorted coordination environment compared to unsubstituted and *meta*-substituted analogues. This increased distortion is structurally significant, as the geometric reorganisation accompanying the Co(III) to Co(II) conversion during a VT interconversion requires less structural rearrangement when the ground-state coordination environment is already predistorted towards the HS geometry. Consequently, *ortho*-substitution is expected to lower the energetic barrier for VT interconversion and shift the transition to lower temperatures.^{26,57,58} In **Co-dbusq**, however, the

combination of steric perturbation and an electron-rich catecholate proves sufficiently strong that the Co(II)sq state is already stabilised at 120 K. In contrast, no systematic trend is observed between MOS values and switching behaviour across the series. **Co-Cl₂cat**, which exhibits the most complete VT transition, displays a near-ideal catecholate MOS value of -1.99, while the tetrahalogenated derivatives, despite intermediate MOS values, show only incomplete transitions. This suggests that while the MOS formalism reliably identifies the ground-state oxidation state of the dioxolene ligand, it does not serve as a reliable predictor of VT completeness in this series.

Selected bond lengths, CShM parameters, and MOS values are summarised in **Table 1** and the complete crystallographic data are provided in the ESI.

Table 1: Metal-Donor Bond Lengths of Complexes in Å at 120 K with Metric Oxidation State of the dioxolene and Continuous Shape Measurement Value.

Co-X	Co-dbusq	Co-Cl ₄ cat	Co-Br ₄ cat	Co-Cl ₂ cat
Co1-O1	2.1075(13)	1.891(6)	1.879(3)	1.8911(13)
Co1-O1A		1.97(3)		
Co1-O2	2.0182(12)	1.863(9)	1.897(3)	1.8835(13)
Co1-O2A		1.925(17)		
Co1-N1	2.1376(14)	1.939(3)	1.946(3)	1.9468(16)
Co1-N2	2.1570(15)	2.058(11)	2.002(3)	1.9876(17)
Co1-N2A		1.84(3)		
Co1-N3	2.2442(15)	1.995(3)	2.002(3)	2.0310(16)
Co1-N4	2.2738(14)	2.081(3)	2.081(3)	2.0617(17)
MOS	-1.00	-1.62 -1.73	-1.84	-1.99
CShM OC-6	1.553	0.50 0.77	0.49	0.47

Solid State Magnetism

Temperature-dependent magnetic susceptibility measurements were performed on crystalline samples **Co-dbusq**, **Co-Cl₄cat**, **Co-Br₄cat** and **Co-Cl₂cat** using a SQUID magnetometer over a temperature range 10-400 K. As **Co-dbusq** was crystallographically established to adopt a HS Co(II)sq ground-state, magnetic measurements were restricted to the temperature range of 2-300 K. The resulting χT vs. T plots are shown in **Figure 2**. Individual heating and cooling traces are provided in the ESI.

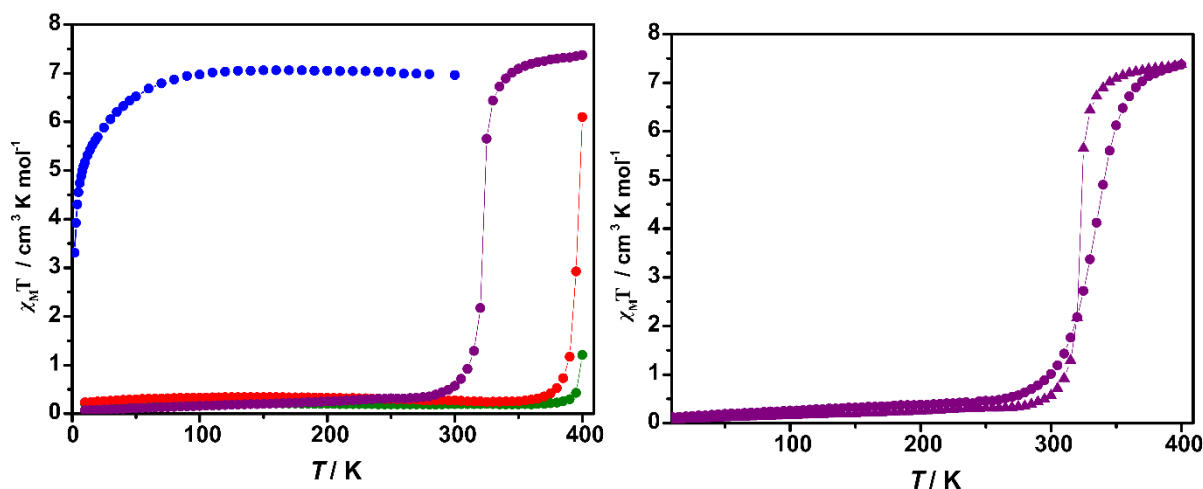


Figure 2: Left: Temperature dependent magnetic susceptibility of crystalline compounds **Co-dbusq** (blue) over the temperature window 2-300 K and **Co-Br₄cat** (green), **Co-Cl₄cat** (red) and **Co-Cl₂cat** (purple) over the temperature window 10-400 K in the heating mode. Right: Heating (triangle) and cooling (circles) cycle of a crystalline sample of **Co-Cl₂cat** (purple).

Temperature-dependent magnetic susceptibility measurements were performed on **Co-dbusq** in the temperature range of 2–300 K. In the range of 110–300 K, **Co-dbusq** exhibits nearly constant χT values of $7.06 \text{ cm}^3 \text{ K mol}^{-1}$. Below 110 K, χT gradually decreases, reaching a value of $3.31 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K. This behaviour is attributed to the depopulation of spin-orbit split energy levels of HS Co(II). The observed χT values are in good agreement with those reported for dinuclear HS Co(II) VT-complexes ranging from 6 to $8 \text{ cm}^3 \text{ K mol}^{-1}$.^{47,53} These values are consistent with two non-interacting semiquinonate radicals (spin $\frac{1}{2}$) and two HS Co(II) centres (spin $\frac{3}{2}$ and a $^4T_{1g}$ state with significant spin-orbit coupling).⁴⁷ Accordingly, **Co-dbusq** exists in a temperature-invariant HS Co(II)sq state over the entire investigated temperature range.

The temperature-invariant HS Co(II)sq state of **Co-dbusq** can be rationalised by the synergistic interplay of steric and electronic effects. The *ortho*-methyl substituents enforce elongated Co–N bond lengths, as confirmed by X-ray structural analysis, thereby reducing the ligand field splitting and favouring occupation of the antibonding eg^* orbitals, which stabilises the HS configuration.⁵⁹ This steric contribution is further reinforced by the strongly electron-donating di-*tert*-butylcatecholate, which additionally favours the Co(II)sq tautomer. The combined effect leads to a significant overstabilisation of the HS state across the entire temperature range, in contrast to previous studies employing the unsubstituted ligand, where only an incomplete VT transition was observed with the same catecholate ($\chi T = 1.25 \text{ cm}^3 \text{ K mol}^{-1}$ at 380 K).⁵²

To specifically tune the tautomeric equilibrium, electron-withdrawing tetrahalogenated catecholates were employed to stabilise the LS Co(III)cat state. Both derivatives exhibit pronounced temperature-dependent magnetic behaviour. **Co-Br₄cat** exhibits very low χT values of $0.21 \text{ cm}^3 \text{ K mol}^{-1}$ up to 390 K and remains in the diamagnetic LS Co(III)cat state within this temperature range. Above 390 K the χT values begin to increase, reaching a value of $1.21 \text{ cm}^3 \text{ K mol}^{-1}$ at 400 K, indicating an incomplete VT transition.

Co-Cl₄cat shows very similar behaviour at low temperatures. However, the VT transition sets in at lower temperatures. Above 380 K, χT increases abruptly and reaches $6.1 \text{ cm}^3 \text{ K mol}^{-1}$ at 400 K, which is close to the values typical of fully switched HS Co(II)sq states. Nevertheless, the transition profile remains incomplete in this case as well. Overall, these results confirm that tetrahalogenated catecholates effectively stabilise the LS Co(III)cat state; however, they do so too strongly to allow a complete VT transition.

Having established that tetrahalogenated catecholates shift the equilibrium too far towards the Co(III)cat state, resulting in only an incomplete VT transition, and the di-*tert*-butylcatecholate too far towards the Co(II)sq state, resulting in a temperature-invariant behaviour, a catecholate with intermediate electron-withdrawing character was targeted. The dichlorinated derivative **Co-Cl₂cat** was synthesised to probe whether a finely balanced electronic environment could restore fully reversible VT switching within the same structural framework.

Indeed, **Co-Cl₂cat** exhibits a diamagnetic LS Co(III)cat state between 10 and 300 K, analogous to the tetrahalogenated derivatives. However, above 300 K, χT rises abruptly, reaching $7.63 \text{ cm}^3 \text{ K mol}^{-1}$ at 400 K, in excellent agreement with the expected value for a fully switched dinuclear HS Co(II)sq system. This demonstrates that precise electronic tuning of the redox-active catecholate ligand, within a sterically defined framework, enables complete and reversible valence tautomeric switching.

The cooling cycle shown in **Figure 2** demonstrates the reversibility of the VT transition. The transition temperature is 322 K on heating and 333 K on cooling, with the cooling transition occurring more gradually. This behaviour is attributed to partial loss of lattice solvent upon heating to 400 K, as elemental analysis indicates the presence of 1.5 MeCN molecules per formula unit in the as-prepared material, likely resulting in a loss of crystallinity and a reduction in cooperative interactions within the lattice. Consistent with this interpretation, measurements on an independently prepared amorphous powder sample show a gradual transition in both heating and cooling modes, with no abrupt character

(Figure S44). The abrupt transition observed in the crystalline material is therefore attributed to cooperative effects arising from the ordered crystal lattice, which are diminished upon solvent loss.

Variable-Temperature Solid State NMR

The VT transition of **Co-Cl₂cat** was investigated by variable-temperature solid-state NMR spectroscopy, as its switching temperature falls within the accessible measurement range. Figure 3 shows the stacked NMR spectra recorded at different temperatures. In addition, ambient temperature solid-state NMR spectra were recorded for the remaining complexes. These spectra are provided in the SI.

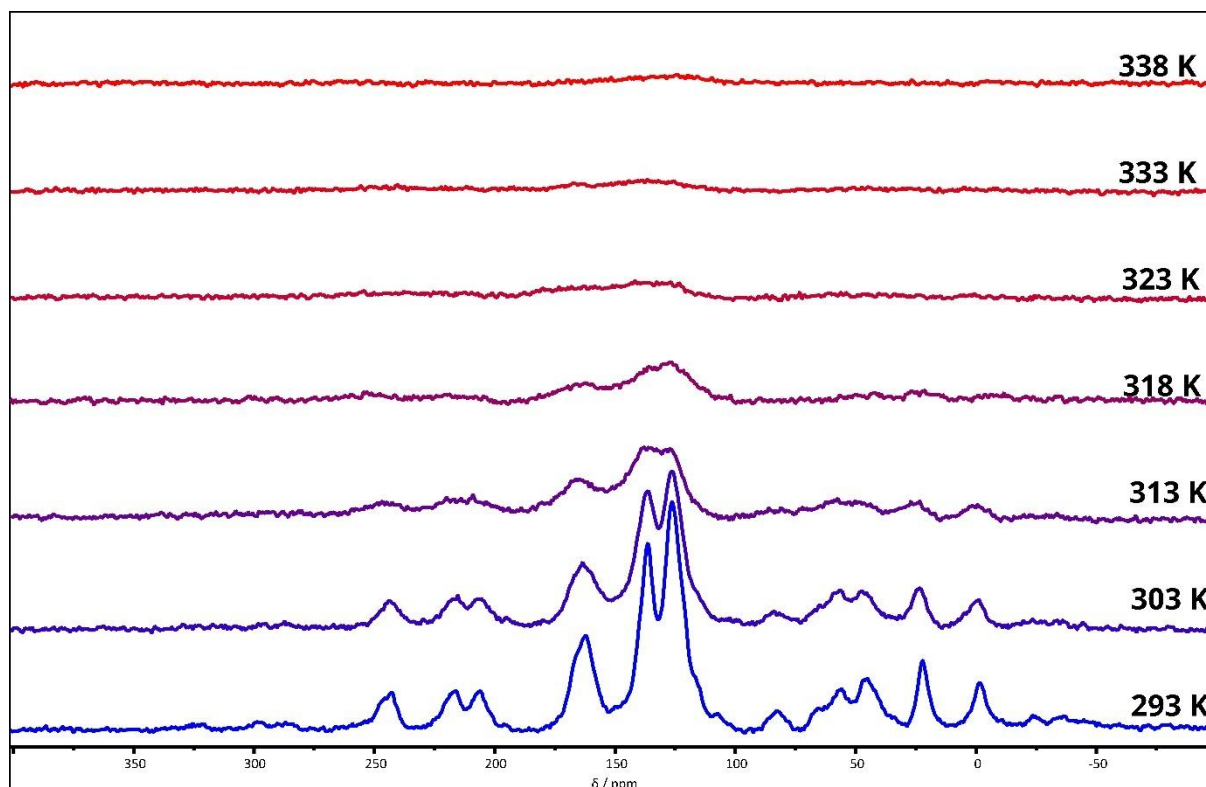


Figure 3: ¹³C MAS Solid State NMR of Cl₂cat in the temperature range of 293 K to 338 K. [101 MHz]

Variable-temperature ¹³C MAS NMR spectra were recorded over the temperature range 293–338 K. At 293 K, broad signals are observed at 160 ppm, 136 ppm, 126 ppm, 22 ppm and -1 ppm. In addition, several spinning sidebands appear approximately at ±8 kHz relative to the main signals. The signals are assigned to the tetraphenylborate anion, as confirmed by comparison with the spectrum of pure sodium tetraphenylborate (Figure S35). The complex fragment is also expected to contribute aromatic and aliphatic ¹³C signals. However, due to pronounced line broadening, a clear assignment is not possible.

Upon increasing temperature, signal intensities decrease and lines broaden further, consistent with progressive population of the paramagnetic HS Co(II)sq state, which causes increasing line broadening and attenuation of the LS Co(III)cat signals. At 338 K, a strongly broadened residual signal of low intensity remains, consistent with the incomplete conversion of the LS Co(III)cat. This is in agreement with the magnetic data in Figure 2, where the maximum χ_T value is not yet reached at this temperature.

After heating to 338 K, the sample was cooled back to 293 K, and the spectrum was recorded again, showing recovery of the signals. This confirms the reversibility of the process. **Co-Br₄cat** and **Co-Cl₄cat** exhibit similar spectra at room temperature. However, variable-temperature measurements up to 338 K were not performed, as the required temperatures for switching exceed the limits of the

instrument and sample holder. As expected for a paramagnetic HS Co(II)sq compound, **Co-dbusq** yields no observable signals (**Figure S36**). The remaining spectra can be found in the supporting information.

Overall, the valence tautomeric transition is also reflected in ^{13}C MAS NMR spectroscopy. Notably, the signals of the tetraphenylborate anion, located up to 7 Å from the nearest cobalt centre according to the crystal structure, are significantly broadened, indicating that paramagnetic relaxation effects extend beyond the first coordination sphere, affecting nuclei of the outer-sphere counter-anion.

Solution Measurements

UV-Vis spectra of the complexes **Co-dbusq**, **Co-Cl₄cat** and **Co-Br₄cat** were recorded at room temperature in the range from 230 to 1000 nm in acetonitrile (**Figure 4**). Due to its complete insolubility after synthesis, **Co-Cl₂cat** could not be studied in solution. Solid-state UV-Vis diffuse reflectance spectroscopy was therefore employed, as described in the following section.

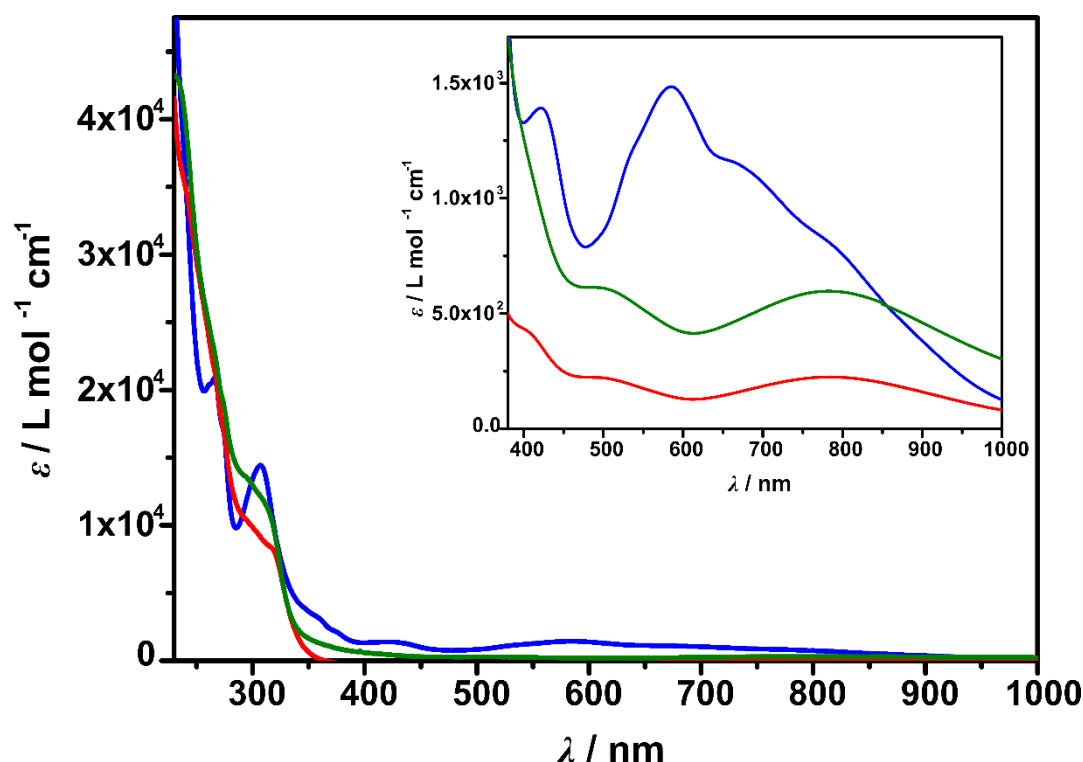


Figure 4: Room temperature UV-vis spectra of **Co-dbusq** (blue), **Co-Cl₄cat** (red) and **Co-Br₄cat** (green) recorded in acetonitrile in the range of 230 nm to 1000 nm at a concentration of 0.02mM with a zoomed in region recorded with a concentration of 1 mM.

The spectra of **Co-Br₄cat** and **Co-Cl₄cat** closely resemble the characteristic absorption patterns of LS Co(III)cat complexes. An intense $\pi\text{--}\pi^*$ transition of the aromatic ligand fragments is observed at 314 nm for **Co-Br₄cat** and at 316 nm for **Co-Cl₄cat**. The bands at 504 nm ($\epsilon = 608 \text{ L mol}^{-1}\text{cm}^{-1}$) (**Co-Br₄cat**) and 502 nm ($\epsilon = 221 \text{ L mol}^{-1}\text{cm}^{-1}$) (**Co-Cl₄cat**) are attributed to a d-d transition of an octahedrally coordinated LS Co(III) ion ($^1\text{A}_1 \rightarrow ^1\text{T}_1$). Broad bands appear at 784 nm ($\epsilon = 597 \text{ L mol}^{-1}\text{cm}^{-1}$) (**Co-Br₄cat**) and 785 nm ($\epsilon = 225 \text{ L mol}^{-1}\text{cm}^{-1}$) (**Co-Cl₄cat**), which is assigned to a ligand-to-metal-charge transfer (LMCT) in accordance with literature. In addition, a shoulder at 414 nm ($\epsilon = 442 \text{ L mol}^{-1}\text{cm}^{-1}$) is discernible for **Co-Cl₄cat** and is assigned to an LMCT transition. For **Co-Br₄cat**, a comparable feature is not clearly resolved, likely due to overlap with a more intense and rapidly increasing absorption in this region.^{47,60}

The spectrum of **Co-dbusq** differs significantly from those of **Co-Br₄cat** and **Co-Cl₄cat** and is characteristic of HS Co(II)sq species, as commonly reported in the literature.^{48,60,61} Intense absorption bands are observed at 266 nm ($\epsilon = 20860 \text{ L mol}^{-1}\text{cm}^{-1}$), and 307 nm ($\epsilon = 14365 \text{ L mol}^{-1}\text{cm}^{-1}$), which are

assigned to π - π^* transitions of the aromatic ligand fragments. Furthermore, a band at 422 nm is observed, which is assigned to a ligand-centred π - π^* transition involving the semiquinonate radical. In addition, a broad absorption at 585 nm ($\epsilon = 1484 \text{ L mol}^{-1}\text{cm}^{-1}$), assignable to a metal-to-ligand charge transfer (MLCT), is accompanied by shoulder features at longer wavelengths attributed to internal ligand transitions.^{47,60}

Solid State Diffuse Reflectance UV-Vis Spectroscopy

Solid-state diffuse reflectance UV-Vis spectroscopy was employed to probe the electronic structure of **Co-Cl₂cat**. Variable-temperature measurements were performed for **Co-Cl₂cat**, as its VT transition falls within the accessible temperature range, consistent with the magnetometry data. The remaining complexes were measured at room temperature only. These spectra are provided in the ESI. The variable-temperature spectra of **Co-Cl₂cat** recorded between 303 and 383 K are shown in **Figure 5**.

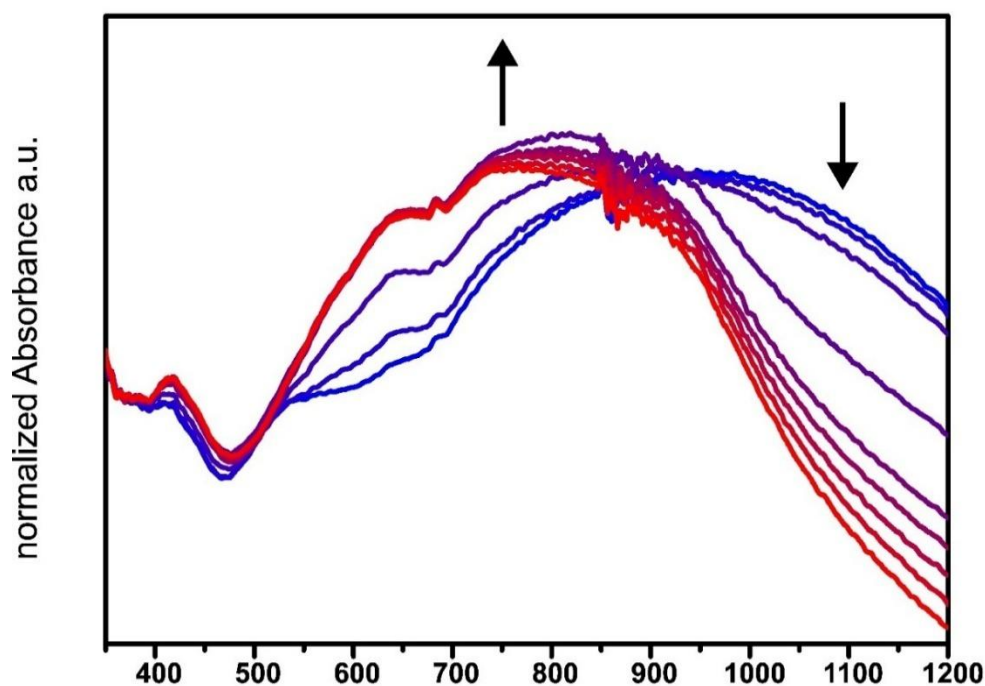


Figure 5: Variable-temperature solid-state diffuse reflectance UV-Vis spectra plotted as normalized absorbance against the wavelength of **Co-Cl₂cat** from 350 to 1200 nm in the temperature range of 303 and 383 K.

At 303 K, the spectrum exhibits the characteristic features of a LS Co(III)cat complex. An absorption band at 414 nm is assigned to a d-d transition of octahedral LS Co(III) ($^1A_{1g} \rightarrow ^1T_{1g}$), accompanied by a broad band extending from 700 to beyond 1200 nm, attributable to a ligand-to-metal charge transfer (LMCT).³⁹

With increasing temperature, the intensity of this low-energy band decreases and, from 323 K onward, the absorption undergoes a pronounced hypsochromic shift. At higher temperatures, the band progressively evolves into a broad absorption spanning from 500 to 1000 nm. Comparison with the solution UV-Vis spectra of **Co-dbusq** and structurally related HS Co(II)sq complexes reported in the literature reveals a similar broad absorption in this region. The band between 550 and 650 nm is assigned to metal-to-ligand charge transfer (MLCT) from Co(II) to the semiquinonate radical, while shoulder features extending beyond 700 nm are attributed to intraligand transitions.^{26,47,54,60}

These spectral changes provide direct optical evidence for the VT transition in **Co-Cl₂cat**, consistent with the magnetometry data.

Conclusion

In summary, four new dinuclear cobalt complexes were synthesised through rational ligand design, combining steric control via an *ortho*-methylated innocent bridging ligand with systematic electronic tuning of the redox-active catecholate. This strategy enabled the precise modulation of the VT equilibrium across the series. While the strongly electron-donating 3,5-di-*tert*-butylcatecholate stabilises a temperature-invariant HS Co(II)sq state, tetrahalogenated catecholates overstabilise the LS Co(III)cat form, yielding only incomplete transitions at elevated temperatures. The electronically optimised 4,5-dichlorocatecholate achieves the essential electronic balance, yielding a complex that undergoes a complete and reversible valence tautomeric transition.

To the best of our knowledge, this represents the first dinuclear cobalt valence tautomeric complex incorporating an innocent bridging ligand to exhibit both a complete and fully reversible transition. This outcome demonstrates that the interplay between steric demand and electronic modulation constitutes a powerful and transferable design principle. Steric perturbation through *ortho*-substitution of the innocent bridging ligand tunes the coordination geometry and ligand field strength, while the selection of commercially available catecholates with tailored electron-withdrawing character enables precise modulation of the redox-active component. Together, these two independently addressable contributions allow the rational realisation of a complete and reversible VT transition within a well-defined dinuclear framework.

Materials and Methods

Unless otherwise stated, all commercially available chemicals were used without further purification. Piperazine, chloroacetonitrile, lithium aluminium hydride, and 4,5-dichlorocatechol were purchased from *Sigma-Aldrich*. Sodium carbonate and ferrocene were obtained from *Acros Organics*. 6-Methylpyridine-2-carbaldehyde and sodium tetraphenylborate were purchased from *BLD Pharm*. Triethylamine was obtained from *Carl Roth* and dried over calcium hydride. Cobalt(II) chloride hexahydrate was purchased from *Chempur* and subsequently converted to its anhydrous form using thionyl chloride. 3,5-Di-*tert*-butylcatechol was obtained from *TCI*. Tetrachlorocatechol was purchased from *Avocado Research Chemicals*, and tetrabromocatechol from *Thermo Scientific*. Potassium hexafluorophosphate was obtained from *abcr*, and sodium triacetoxyborohydride from *Carbolution*. Anhydrous and degassed methanol was purchased from *Thermo Fisher*. All reactions were carried out under aerobic conditions with HPLC grade solvents unless stated otherwise. Dry THF was obtained from a solvent purification system (MBRAUN MG-SPS-800). Infrared spectra were recorded in a range of 4500–400 cm⁻¹ using a *Bruker ALPHA II ATR-IR* with the software *OPUS* and plotted using *Origin V7.5*. Crystallographic characterization of suitable single crystals of the complexes were measured on a *STOE STADIVARI* at the Johannes Gutenberg-University Mainz at 120 K. Solving and refinement of the crystal structures was done by *ShelXT*⁶² and *ShelXL*⁶³ in combination with *Olex2*⁶⁴ by Dr. Luca M. Carrella. The resolved structures are planned to be deposited at the CCDC database. HRes ESI mass spectra were recorded on a *Agilent 6200 series TOF/6500 series G-TOF(11.0.203.0)* at the Johannes Gutenberg-University Mainz in acetonitrile or methanol. The magnetic measurements were conducted with a *MPMS3 SQUID magnetometer*. The samples were prepared in plastic capsules placed in a brass holder and the magnetic data were collected in a temperature range of 10–400 K under an applied magnetic field of 0.1 T in a heating and cooling cycle in the settle mode, with a nominal ramp rate of 10 K/min between target temperatures. At each setpoint, the temperature was allowed to stabilise before data acquisition, followed by a 5-minute hold at 400 K prior to cooling. Measurements were performed over a length of 3 cm, every data point was measured three times and averaged. Magnetic contributions of the holder and capsule were experimentally determined by a test run of an empty capsule at the exact same position with the exact same brass holder with the exact same measuring parameters and subtracted from the measured susceptibility data with *Squidlab*⁶⁵ for *Matlab*⁶⁶. **Co-dbusq** was prepared in a gelatin capsule without eicosane and placed in a plastic straw. Here the magnetic data were obtained over a temperature range from 2–300 K. The elemental analysis (CHN) was performed at the

Department of Chemistry at the Johannes Gutenberg-University Mainz on an Elementar vario EL Cube and (CHNS) was performed at RPTU Kaiserslautern-Landau on an Elementar vario Mirco cube. NMR spectra and Evans Method NMR were conducted using an *Avance III HD 300* ($\nu(^1\text{H}) = 400.13 \text{ MHz}$ $\nu(^{13}\text{C}) = 100.1 \text{ MHz}$); *Avance II 400* ($\nu(^1\text{H}) = 400.13 \text{ MHz}$ $\nu(^{13}\text{C}) = 100.1 \text{ MHz}$); *Bruker Neo 400* ($\nu(^1\text{H}) = 400.13 \text{ MHz}$ $\nu(^{13}\text{C}) = 100.1 \text{ MHz}$). All NMR spectra were recorded in deuterated solvents. Chemical shifts are reported in ppm and referenced to the residual solvent signal of the respective deuterated solvent. The obtained spectra were evaluated by *MestReNova x64* made by *Mestrelab Research*. Solid state NMR were measured on a *Bruker Avance DSX 400* under MAS conditions with 8 kHz spinning. UV-Vis spectra in solution were measured on a *JASCO V-770*. For the measurement in solid state the *JASCO-V770* was used with a Harrick *PRAYING MANTIS* attachment and the temperature was adjusted with a *Temperature Controller (ATC)* from *Harrick Scientific Products*.

Experimental Section

The organic precursor ligands were synthesised as previously reported and can be found in the SI.^{51,52}

L^{o-Me}: *N,N'*-Bis(2-aminoethyl)piperazine (1 equiv.) was dissolved in 100 mL DCM, $\text{Na}(\text{BH}(\text{OAc})_3)$ (5 equiv.) was added in small portions. A solution of 6-Methyl-2-picolinaldehyde (4.2 equiv.) in 30 mL DCM was added dropwise in 30 minutes. It was stirred overnight at room temperature. 50 mL of a sat. aq. NaHCO_3 solution was added and stirred for 30 minutes. Phases were separated, aq. Phase was extracted twice with DCM. Combined organic phases were dried over NaSO_4 . Solvent was removed under reduced pressure. Yellow oil was recrystallized twice from MeCN. Yellow powder (3.51 g, 5.92 mmol, 44%), **IR** $\tilde{\nu}$ [cm^{-1}]: 3066 (w), 2961 (w), 2938 (m), 2826 (m), 2687 (w), 1590 (m), 1575 (s), 1459 (s), 1445 (m), 1374 (w), 1350 (m), 1315 (m), 1289 (m), 1264 (m), 1243 (m), 1219 (w), 1161 (m), 1135 (m), 1119 (m), 1087 (m), 1071 (w), 1048 (m), 1009 (m), 977 (m), 964 (m), 935 (m), 895 (w), 869 (m), 831 (m), 787 (s), 759 (m), 732 (m), 652 (w), 633 (m), 562 (w), 546 (w), 532 (w), 461 (m), 433 (m), 409 (m), **Elemental Analysis:** Found: C, 71.97%; H, 8.09%; N, 18.55%, Calc. for $\text{C}_{36}\text{H}_{48}\text{N}_8 + 0.5 \text{ H}_2\text{O}$: C, 71.85%; H, 8.21%; N, 18.62%, **Mass spectrometry** [m/z]: 593.409 [$\text{L} + \text{H}$]⁺ (calc. = 593.407), 297.208 [$\text{L} + 2\text{H}$]²⁺ (calc. = 297.207), **¹H-NMR** (CDCl_3 [400 MHz]) δ [ppm] = 7.52 (t, 4H, $J^3=7.7 \text{ Hz}$, H^{13}), 7.38 (d, 4H, $J^3=7.7 \text{ Hz}$, H^{14}), 6.98 (d, 4H, $J^3=7.6 \text{ Hz}$, H^{12}), 3.81 (s, 8H, H^8), 2.71-2.68 (m, 4H, H^6), 2.53-2.49 (m, 16H, $\text{H}^{15} + \text{H}^5$), 2.38 (s, $\text{H}^{2,3}$), **¹³C-NMR** (CDCl_3 [101 MHz]): δ [ppm] = 159(C^{11}), 157(C^9), 136(C^{13}), 121(C^{12}), 61(C^8), 56(C^5), 53($\text{C}^{2,3}$), 52(C^6), 24(C^{15}).

[Co₂(L^{o-Me})(dbusq)₂](B(Ph)₄)₂ Co-dbusq: L^{o-Me} (1 equiv.), dbucat (2 equiv.) and $\text{CoCl}_2 \times 6 \text{ H}_2\text{O}$ (2 equiv.) were dissolved in 15 mL MeOH. Triethylamine (4 equiv.) was added dropwise, it was refluxed for 1 hour. NaB(Ph)_4 (2 equiv.) were added after cooling to room temperature. It was stirred for 15 minutes. Blue precipitate was filtered and air dried. Single crystals suitable for X-Ray diffraction were grown from an acetonitrile solution with diethyl ether vapor diffusion after 4 weeks. Blue blocks (160 mg, 0.090 mmol, 90%). **IR** $\tilde{\nu}$ [cm^{-1}]: 3056 (vw), 3033 (vw), 2984 (vw), 2961 (vw), 1604 (w), 1578 (w), 1455 (s), 1432 (w), 1407 (w), 1372 (w), 1356 (w), 1344 (w), 1313 (w), 1292 (w), 1243 (w), 1218 (w), 1167 (w), 1137 (w), 1121 (w), 1099 (w), 1066 (w), 1032 (w), 1012 (w), 983 (w), 954 (w), 908 (w), 859 (w), 826 (w), 780 (m), 731 (vs), 705 (vs), 671 (w), 612 (s), 572 (w), 541 (vw), 494 (w), 466 (w), 422 (w) cm^{-1} , **Elemental Analysis:** Found: C, 74.84%; H, 7.36%; N, 6.31%, Calc. for $\text{C}_{112}\text{H}_{130}\text{N}_8\text{B}_2\text{O}_4\text{Co}_2$: C, 75.08%; H, 7.31%; N, 6.25%, **Mass spectrometry** [m/z]: 575.281 [C]²⁺ (calc. = 575.279).

[Co₂(L^{o-Me})(Cl₄cat)₂](B(Ph)₄)₂ Co-Cl₄cat: L^{o-Me} (1 equiv.), Cl₄cat (2 equiv.) were dissolved in the glovebox in 10 mL of dry and degassed MeOH. Anhydrous CoCl_2 (2 equiv.) was dissolved in 5 mL dry and degassed MeOH and added dropwise under stirring to the 1st solution. Triethylamine (4 equiv.) was added dropwise. Directly an orange suspension formed. FcBPh_4 (2 equiv.) was added, the suspension was stirred overnight and turned brown. Now every manipulation was performed outside of the glovebox under ambient conditions. The brown suspension was then centrifugated (3500 rpm, 20 minutes) and filtered. The brown precipitate was dried on air and then recrystallized from 10 mL of MeCN. Suitable single crystals were grown from the mother liquor after two days of slow evaporation. Brown plates (23 mg, 0.012 mmol, 13%) were obtained. **IR** $\tilde{\nu}$ [cm^{-1}]: 3053 (m), 2982 (m), 1610 (m),

1577 (m), 1433 (s), 1375 (m), 1291 (m), 1251 (m), 1172 (m), 1132 (m), 1020 (m), 981 (m), 953 (m), 860 (m), 802 (m), 783 (m), 733 (s), 704 (s), 611 (s), 595 (m), 576 (m), 506 (m), 468 (m), 437 (m), 411 (m), **Elemental Analysis:** Found: C, 62.44%; H, 4.91%; N, 6.20%, Calc. for $C_{96}H_{90}N_8Cl_8B_2O_4Co_2$: C, 62.57%; H, 4.92%; N, 6.08%, **Mass spectrometry** [m/z]: 600.996 [C] $^{2+}$ (calc. = 600.995).

[Co₂(L^{OMe})(Br₄cat)₂](B(Ph)₄)₂ Co-Br₄cat: Was performed similar to **Co-Cl₄cat**. Brown plates (63 mg, 0.029 mmol, 29%) were obtained. **IR** $\tilde{\nu}$ [cm^{-1}]: 3054 (m), 3035 (m), 2997 (m), 2981 (m), 1610 (m), 1577 (m), 1434 (s), 1381 (m), 1346 (m), 1298 (m), 1266 (m), 1232 (m), 1174 (m), 1150 (m), 1128 (m), 1091 (m), 1056 (w), 1020 (m), 1005 (m), 952 (m), 938 (m), 859 (m), 842 (m), 792 (m), 763 (m), 735 (s), 705 (s), 624 (m), 611 (m), 591 (m), 561 (m), 514 (m), 466 (m), 437 (m), 421 (m), 421 (m), 421 (m), 409 (m), **Elemental Analysis:** Found: C, 51.89%; H, 4.01%; N, 6.96%, Calc. for $C_{96}H_{90}N_8Br_8B_2O_4Co_2 + 1.25 CH_3CN + 1 H_2O$: C, 52.17%; H, 4.26%; N, 5.71%, **Mass spectrometry** [m/z]: 778.792 [C] $^{2+}$ (calc. = 778.792).

[Co₂(L^{OMe})(Cl₂cat)₂](B(Ph)₄)₂ Co-Cl₂cat: L^{OMe} (1 equiv.), Cl₂cat (2 equiv.) were dissolved in the glovebox in 10 mL of dry and degassed MeOH. Anhydrous CoCl₂ (2 equiv.) was dissolved in 5 mL dry and degassed MeOH and added dropwise under stirring to the 1st solution. Triethylamine (4 equiv.) was added dropwise. Directly an orange suspension formed. FcPF₆ (2 equiv.) was added, the suspension was stirred overnight and turned brown. Now every manipulation was performed outside of the glovebox under ambient conditions. The brown suspension was then centrifugated (3500 rpm, 20 minutes) and filtered. The brown precipitate was dried on air and then recrystallized from 20 mL of MeCN. It was centrifugated again and filtered to get rid of non-soluble impurities. For powder, NaBPh₄ (2.0 eq.) was added while stirring. It was stirred for 1 hour, filtered and air dried (160 mg, 0.094 mmol, 94%) For crystals, NaBPh₄ (2.0 eq.) was added while stirring. After the complete Sodium tetraphenylborate dissolved it was filtered and the solvent was allowed to slowly evaporate. After 1 day crystals suitable for single crystal XRD were obtained. Brown crystals (110 mg, 0.065 mmol, 65%). **IR** $\tilde{\nu}$ [cm^{-1}]: 3050 (m), 3033 (w), 2999 (w), 2982 (w), 1611 (w), 1578 (w), 1470 (s), 1363 (m), 1295 (w), 1256 (m), 1190 (w), 1169 (m), 1131 (w), 1100 (m), 1064 (w), 1019 (m), 1002 (m), 953 (m), 918 (w), 892 (w), 841 (m), 780 (m), 751 (m), 734 (s), 706 (s), 679 (m), 610 (s), 572 (m), 470 (m), **Elemental Analysis:** Found: C, 67.16%; H, 5.42%; N, 7.81%, Calc. for $C_{96}H_{94}N_8Cl_4B_2O_4Co_2 + 1.5 CH_3CN$: C, 67.30%; H, 5.62%; N, 7.81%.

Ferrocenium hexafluorophosphate FcPF₆

Was prepared as previously reported.⁶⁷

Ferrocenium tetraphenylborate FcBPh₄

Was prepared as previously reported.⁶⁸

Notes

The authors declare no conflict of interests.

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6.1 ESI: Unlocking Valence Tautomerism in Dinuclear Cobalt Complexes Through Steric and Electronic Design

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6.1.1 Experimental Synthesis

L^oMe

N,N'-Bis(2-aminoethyl)piperazine (1 equiv.) was dissolved in 100 mL DCM, Na(BH(OAc)₃) (5 equiv.) was added in small portions. A solution of 6-Methyl-2-picolinaldehyde (4.2 equiv.) in 30 mL DCM was added dropwise in 30 minutes. It was stirred overnight at room temperature. 50 mL of a sat. aq. NaHCO₃ solution was added and stirred for 30 minutes. Phases were separated, aq. Phase was extracted twice with DCM. Combined organic phases were dried over NaSO₄. Solvent was removed under reduced pressure. Yellow oil was recrystallized twice from MeCN.

Yellow powder (3.51 g, 5.92 mmol, 44%), **IR** $\tilde{\nu}$ [cm⁻¹]: 3066 (w), 2961 (w), 2938 (m), 2826 (m), 2687 (w), 1590 (m), 1575 (s), 1459 (s), 1445 (m), 1374 (w), 1350 (m), 1315 (m), 1289 (m), 1264 (m), 1243 (m), 1219 (w), 1161 (m), 1135 (m), 1119 (m), 1087 (m), 1071 (w), 1048 (m), 1009 (m), 977 (m), 964 (m), 935 (m), 895 (w), 869 (m), 831 (m), 787 (s), 759 (m), 732 (m), 652 (w), 633 (m), 562 (w), 546 (w), 532 (w), 461 (m), 433 (m), 409 (m), **Elemental Analysis**: Found: C, 71.97%; H, 8.09%; N, 18.55%, Calc. for C₃₆H₄₈N₈ + 0.5 H₂O: C, 71.85%; H, 8.21%; N, 18.62%, **Mass spectrometry** [*m/z*]: 593.409 [**L** + **H**]⁺ (calc. = 593.407), 297.208 [**L** + **2H**]²⁺ (calc. = 297.207), **¹H-NMR** (CDCl₃ [400 MHz]) δ [ppm] = 7.52 (t, 4H, *J*³=7.7 Hz, H¹³), 7.38 (d, 4H, *J*³=7.7 Hz, H¹⁴), 6.98 (d, 4H, *J*³=7.6 Hz, H¹²), 3.81 (s, 8H, H⁸), 2.71-2.68 (m, 4H, H⁶), 2.53-2.49 (m, 16H, H¹⁵+H⁵), 2.38 (s, H^{2,3}), **¹³C-NMR** (CDCl₃ [101 MHz]): δ [ppm] = 159(C¹¹), 157(C⁹), 136(C¹³), 121(C¹²), 61(C⁸), 56(C⁵), 53(C^{2,3}), 52(C⁶), 24(C¹⁵).

[Co₂(L^oMe)(dbusq)₂](B(Ph)₄)₂ Co-dbusq:

L^o-Me (1 equiv.), dbucat (2 equiv.) and CoCl₂ × 6 H₂O (2 equiv.) were dissolved in 15 mL MeOH. Triethylamine (4 equiv) was added dropwise, it was refluxed for 1 hour. NaB(Ph)₄ (2 equiv.) were added after cooling to room temperature. It was stirred for 15 minutes. Blue precipitate was filtered and air dried. Single crystals suitable for X-Ray diffraction were grown from an acetonitrile solution with diethyl ether vapor diffusion after 4 weeks. Blue blocks (160 mg, 0.090 mmol, 90%). **IR** $\tilde{\nu}$ [cm⁻¹]: 3056 (vw), 3033 (vw), 2984 (vw), 2961 (vw), 1604 (w), 1578 (w), 1455 (s), 1432 (w), 1407 (w), 1372 (w), 1356 (w), 1344 (w), 1313 (w), 1292 (w), 1243 (w), 1218 (w), 1167 (w), 1137 (w), 1121 (w), 1099 (w), 1066 (w), 1032 (w), 1012 (w), 983 (w), 954 (w), 908 (w), 859 (w), 826 (w), 780 (m), 731 (vs), 705 (vs), 671 (w), 612 (s), 572 (w), 541 (vw), 494 (w), 466 (w), 422 (w) cm⁻¹, **Elemental Analysis**: Found: C, 74.84%; H, 7.36%; N, 6.31%, Calc. for C₁₁₂H₁₃₀N₈B₂O₄Co₂: C, 75.08%; H, 7.31%; N, 6.25%, **Mass spectrometry** [*m/z*]: 575.281 [**C**]²⁺ (calc. = 575.279).

[Co₂(L^oMe)(Cl₄cat)₂](B(Ph)₄)₂ Co-Cl₄cat:

L^o-Me (1 equiv.), Cl₄cat (2 equiv.) were dissolved in the glovebox in 10 mL of dry and degassed MeOH. Anhydrous CoCl₂ (2 equiv.) was dissolved in 5 mL dry and degassed MeOH and added dropwise under stirring to the 1st solution. Triethylamine (4 equiv.) was added dropwise. Directly an orange suspension formed. FcBPh₄ (2 equiv.) was added, the suspension was stirred overnight and turned brown. Now every manipulation was performed outside of the glovebox under ambient conditions. The brown suspension was then centrifugated (3500 rpm, 20 minutes) and filtered. The brown precipitate was dried on air and then recrystallized from 10 mL of MeCN. Suitable single crystals were grown from the mother liquor after two days of slow evaporation. Brown plates (23 mg, 0.012 mmol, 13%) were

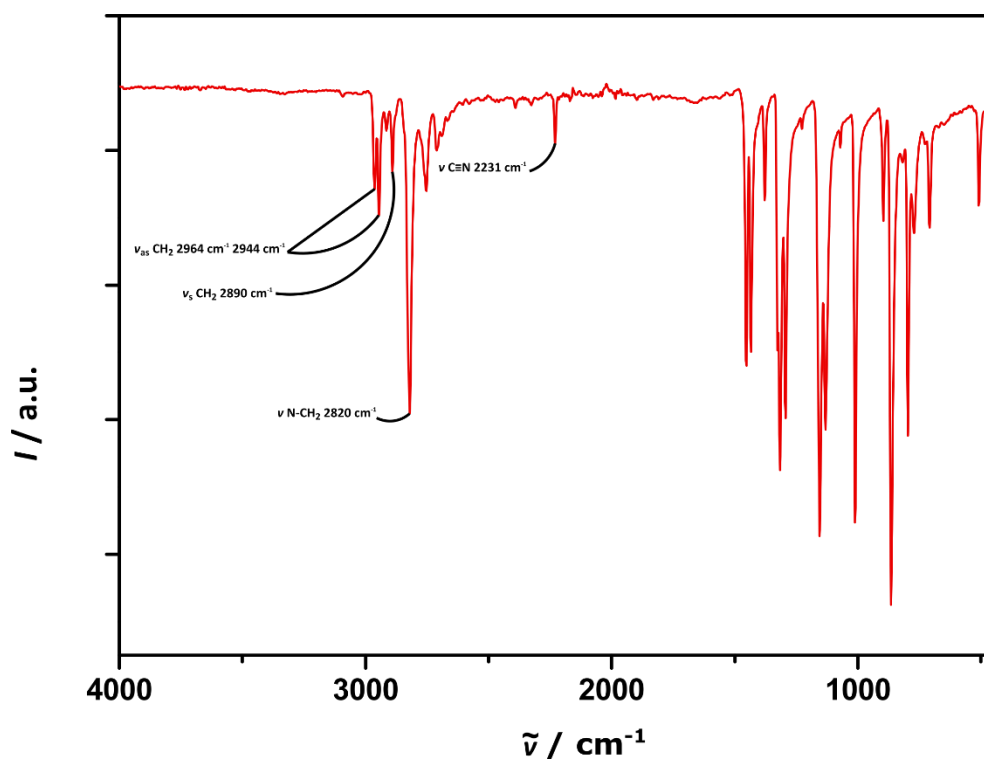
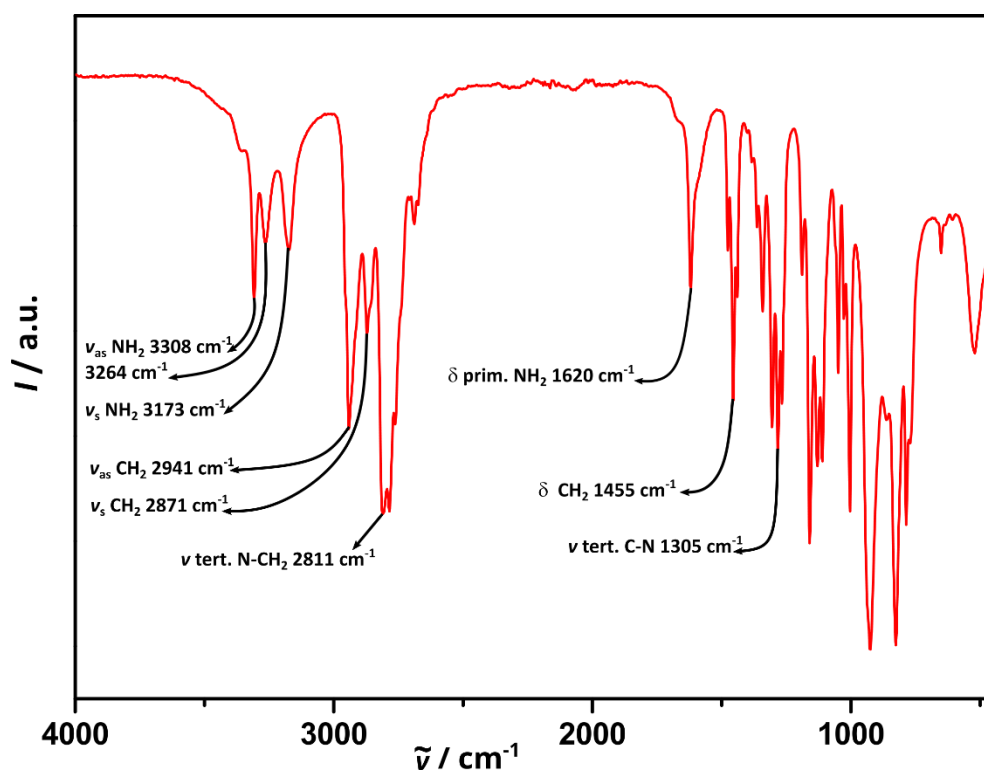
obtained. **IR** $\tilde{\nu}$ [cm⁻¹]: 3053 (m), 2982 (m), 1610 (m), 1577 (m), 1433 (s), 1375 (m), 1291 (m), 1251 (m), 1172 (m), 1132 (m), 1020 (m), 981 (m), 953 (m), 860 (m), 802 (m), 783 (m), 733 (s), 704 (s), 611 (s), 595 (m), 576 (m), 506 (m), 468 (m), 437 (m), 411 (m), **Elemental Analysis**: Found: C, 62.44%; H, 4.91%; N, 6.20%, Calc. for C₉₆H₉₀N₈Cl₈B₂O₄Co₂: C, 62.57%; H, 4.92%; N, 6.08%, **Mass spectrometry** [*m/z*]: 600.996 [C]²⁺ (calc. = 600.995).

[Co₂(L^{oMe})(Br₄cat)₂](B(Ph)₄)₂ Co-Br₄cat:

o-L-Me (59 mg, 0.1 mmol, 1eq.), Br₄cat (85 mg, 0.2 mmol, 2.0 eq.) was dissolved in the glovebox in 10 mL of dry and degassed methanol. CoCl₂ (26 mg, 0.2 mmol, 2.0 eq.) was dissolved in 5 mL of dry and degassed methanol and added dropwise during stirring. TEA (41 mg, 0.4 mmol, 4.0 eq.) was added dropwise. Directly an orange suspension formed. FcBPPH₄ (101 mg, 0.2 mmol, 2.0 eq.) was added, the suspension was stirred in the glovebox overnight. The now brown suspension was then centrifugated and filtered. The brown precipitate was dried on air. The residue was then recrystallized from 10 mL MeCN, after 2 days of slow evaporation suitable single crystals for Xray diffraction were obtained. Brown plates (63 mg, 0.029 mmol, 29%) were obtained. **IR** $\tilde{\nu}$ [cm⁻¹]: 3054 (m), 3035 (m), 2997 (m), 2981 (m), 1610 (m), 1577 (m), 1434 (s), 1381 (m), 1346 (m), 1298 (m), 1266 (m), 1232 (m), 1174 (m), 1150 (m), 1128 (m), 1091 (m), 1056 (w), 1020 (m), 1005 (m), 952 (m), 938 (m), 859 (m), 842 (m), 792 (m), 763 (m), 735 (s), 705 (s), 624 (m), 611 (m), 591 (m), 561 (m), 514 (m), 466 (m), 437 (m), 421 (m), 421 (m), 409 (m), **Elemental Analysis**: Found: C, 51.89%; H, 4.01%; N, 6.96%, Calc. for C₉₆H₉₀N₈Br₈B₂O₄Co₂ + 1.25 CH₃CN + 1 H₂O: C, 52.17%; H, 4.26%; N, 5.71%, **Mass spectrometry** [*m/z*]: 778.792 [C]²⁺ (calc. = 778.792).

[Co₂(L^{oMe})(Cl₂cat)₂](B(Ph)₄)₂ Co-Cl₂cat: L^{o-Me} (1 equiv.), Cl₂cat (2 equiv.) were dissolved in the glovebox in 10 mL of dry and degassed MeOH. Anhydrous CoCl₂ (2 equiv.) was dissolved in 5 mL dry and degassed MeOH and added dropwise under stirring to the 1st solution. Triethylamine (4 equiv.) was added dropwise. Directly an orange suspension formed. FcPF₆ (2 equiv.) was added, the suspension was stirred overnight and turned brown. Now every manipulation was performed outside of the glovebox under ambient conditions. The brown suspension was then centrifugated (3500 rpm, 20 minutes) and filtered. The brown precipitate was dried on air and then recrystallized from 20 mL of MeCN. It was centrifugated again and filtered to get rid of non-soluble impurities. For powder, NaBPh₄ (2.0 eq.) was added while stirring. It was stirred for 1 hour, filtered and air dried (160 mg, 0.094 mmol, 94%) For crystals, NaBPh₄ (2.0 eq.) was added while stirring. After the complete Sodium tetraphenylborate dissolved it was filtered and the solvent was allowed to slowly evaporate. After 1 day crystals suitable for single crystal XRD were obtained. Brown crystals (110 mg, 0.065 mmol, 65%). **IR** $\tilde{\nu}$ [cm⁻¹]: 3050 (m), 3033 (w), 2999 (w), 2982 (w), 1611 (w), 1578 (w), 1470 (s), 1363 (m), 1295 (w), 1256 (m), 1190 (w), 1169 (m), 1131 (w), 1100 (m), 1064 (w), 1019 (m), 1002 (m), 953 (m), 918 (w), 892 (w), 841 (m), 780 (m), 751 (m), 734 (s), 706 (s), 679 (m), 610 (s), 572 (m), 470 (m), **Elemental Analysis**: Found: C, 67.16%; H, 5.42%; N, 7.81%, Calc. for C₉₆H₉₄N₈Cl₄B₂O₄Co₂ + 1.5 CH₃CN: C, 67.30%; H, 5.62%; N, 7.81%.

6.1.2 IR-Spectra Ligand

Figure S1: ATR-IR-spectrum of *N, N'*-Bis(cyanomethyl)piperazine.Figure S2: ATR-IR-spectrum of *N, N'*-bis(aminoethyl)piperazine.

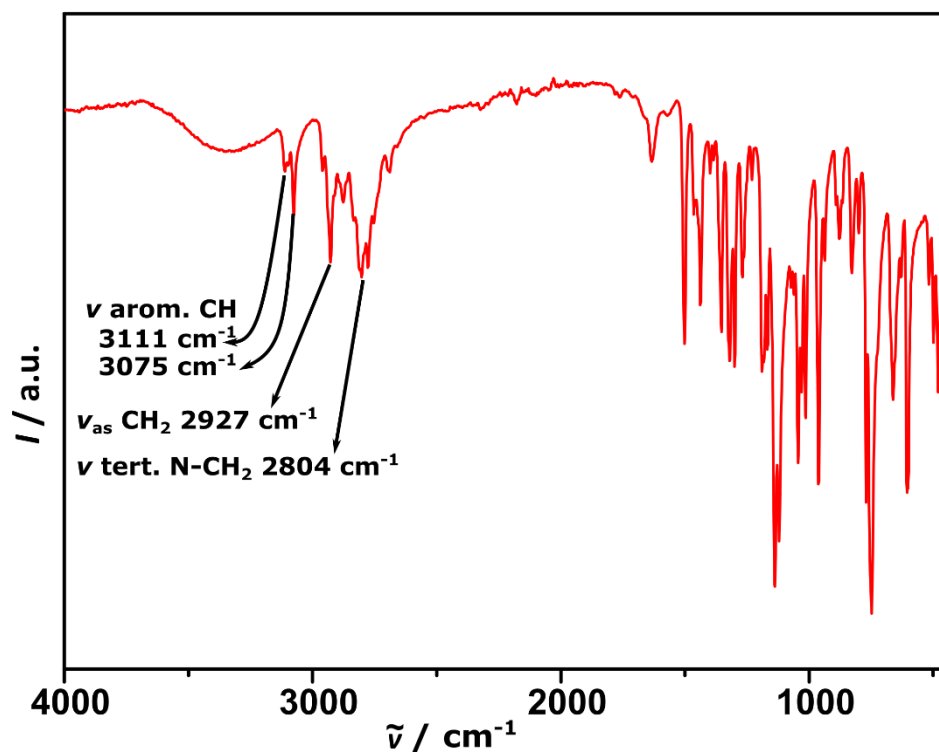


Figure S3: ATR-IR of *N, N', N'*-Tetra-2-picoly-1,4-bis(2-aminoethyl)piperazine (*L-H*).

6.1.3 Mass Spectrometry Ligand

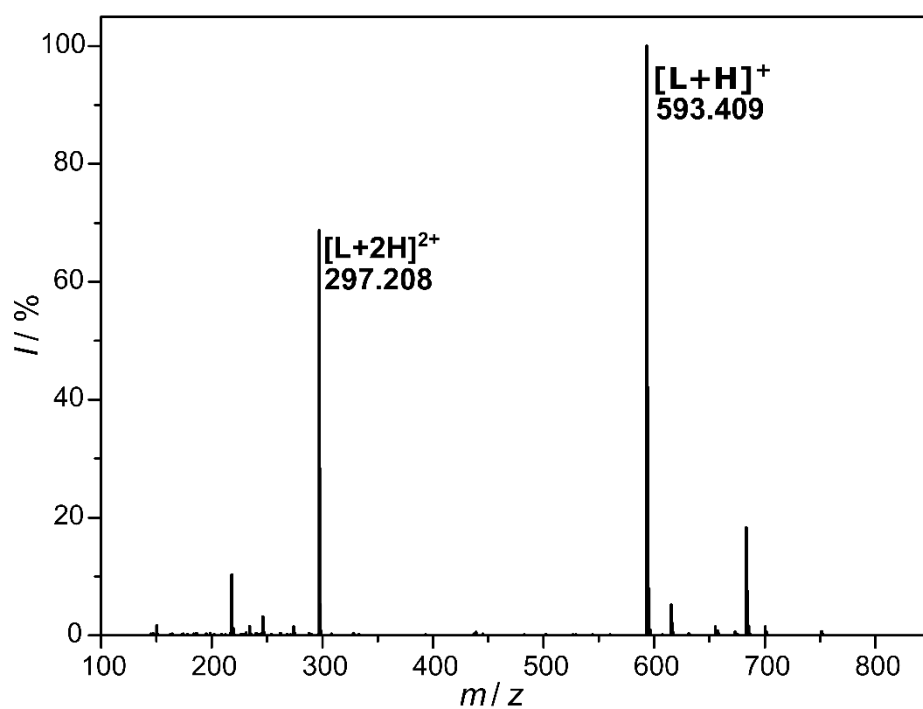
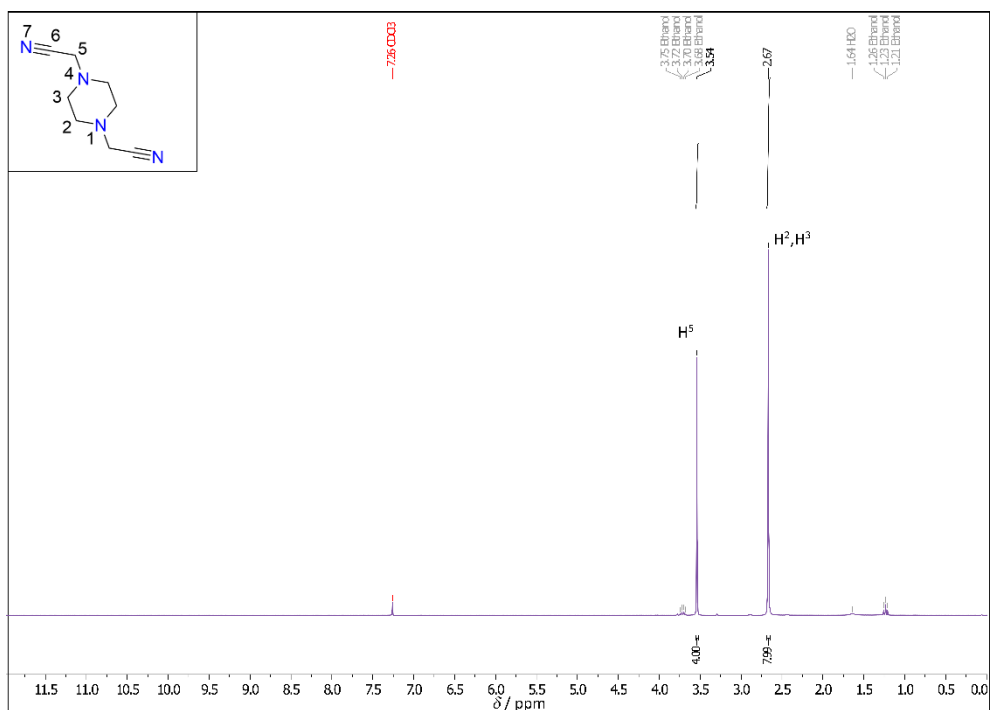
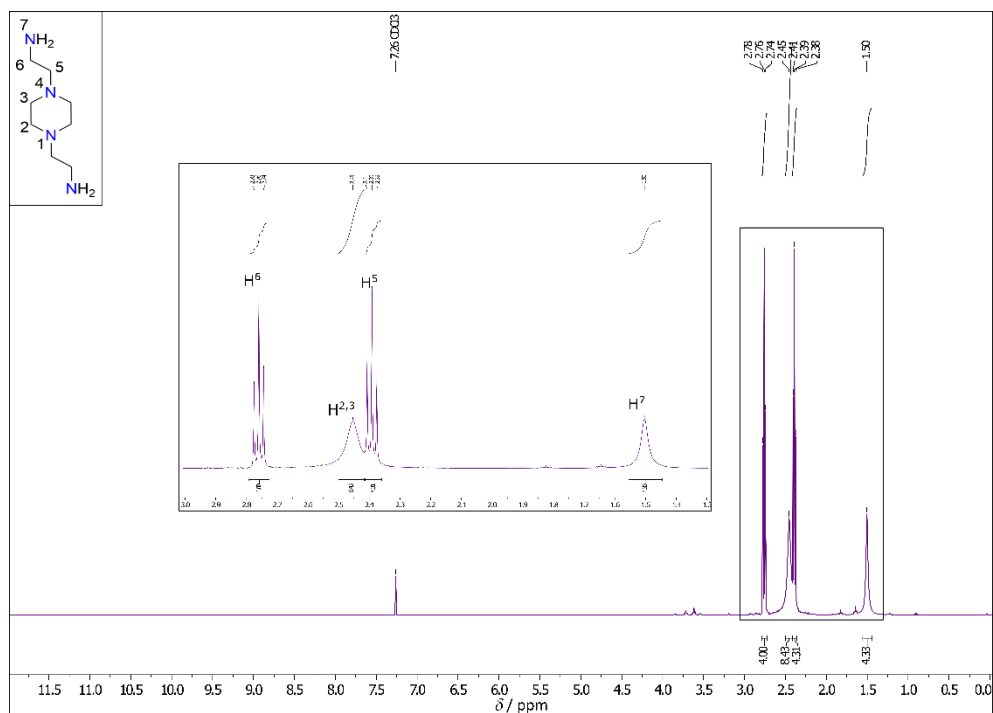


Figure S4: ESI⁺- MS of L-Me showing the double protonated adduct $[L+2H]^{2+}$ at 297.208 m/z, the protonated adduct $[L+H]^+$ at 593.409 m/z.

6.1.4 ^1H -NMR LigandFigure S5: ^1H -NMR-Spectrum of *N,N'*-bis(cyanomethyl)piperazine in CDCl_3 [400 MHz].Figure S6: ^1H -NMR-Spectrum of *N,N'*-bis(aminoethyl)piperazine in CDCl_3 [400 MHz].

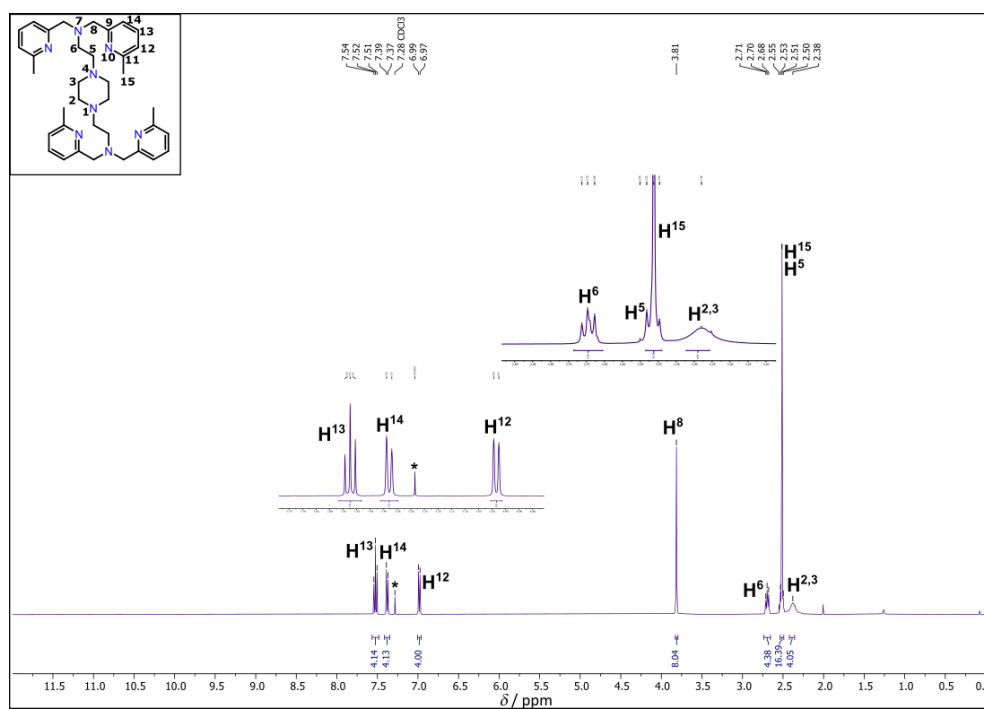


Figure S7: ^1H -NMR-Spectrum of L^{OMe} in CDCl_3 [400 MHz].

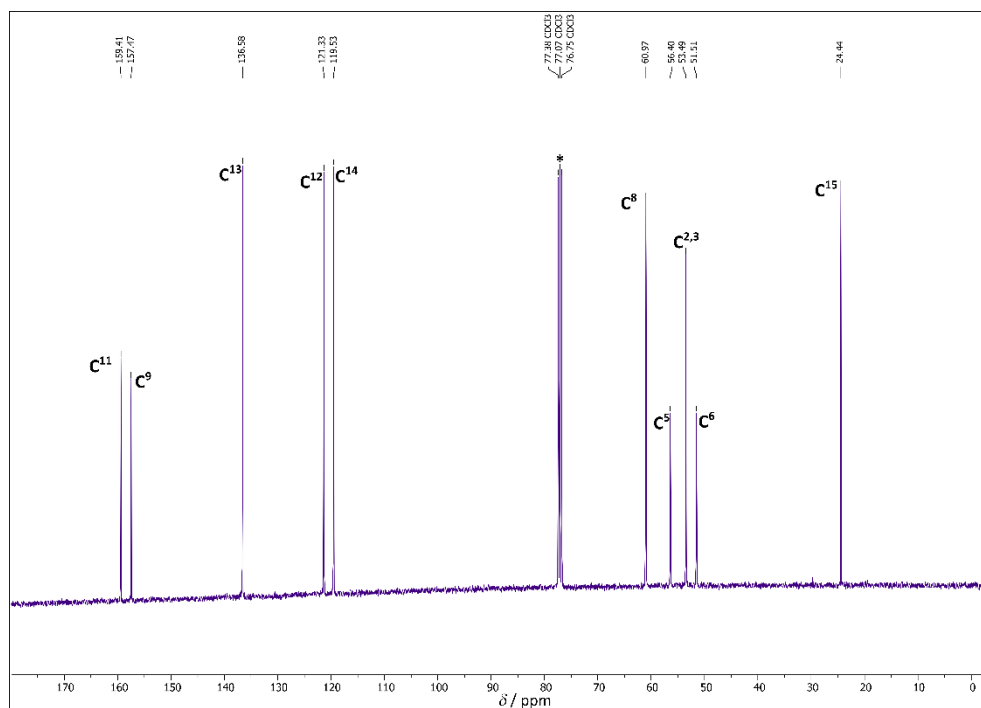
6.1.5 ^{13}C -NMR-Spectra Ligand

Figure S8: ^{13}C -NMR-Spectrum of L^{oMe} in CDCl_3 [101 MHz].

6.1.6 COSY-NMR-Spectra Ligand

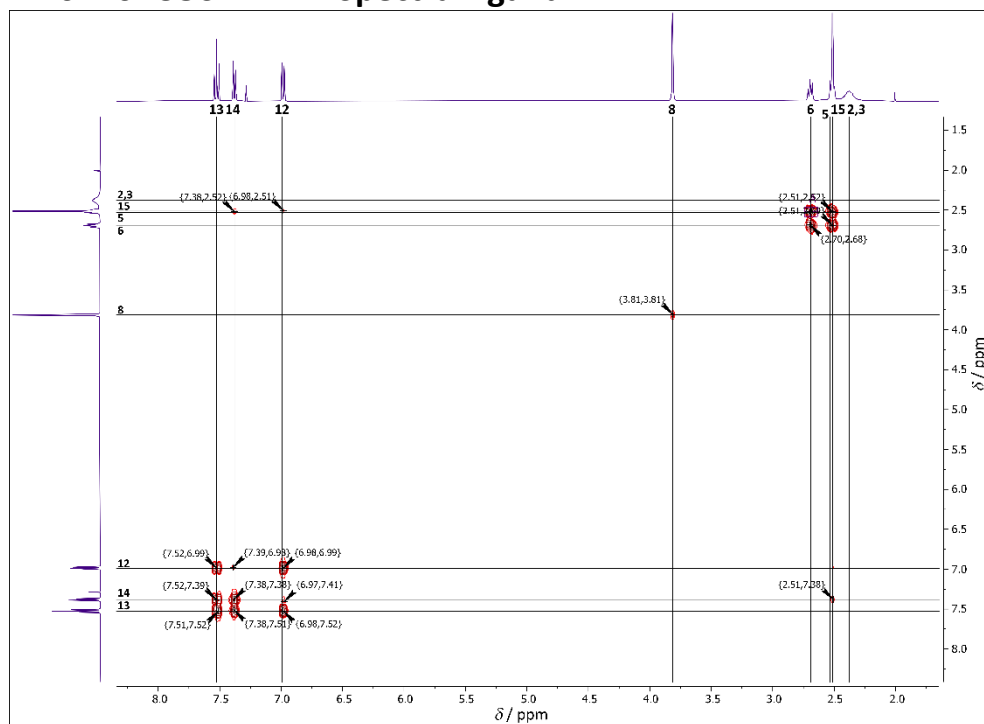


Figure S9: COSY-NMR-Spectrum of L^{OMe} in CDCl_3 .

6.1.7 HSQC-NMR-Spectra Ligand

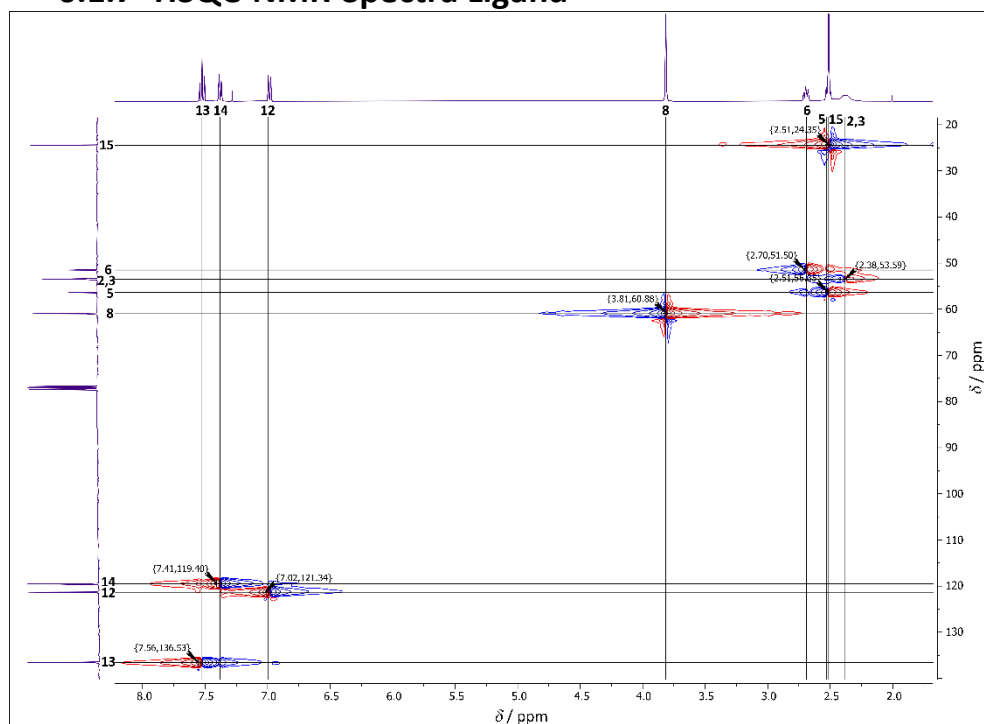


Figure S10: HSQC-NMR-Spectrum of L^{OMe} in $CDCl_3$.

6.1.8 HMBC-NMR-Spectra Ligand

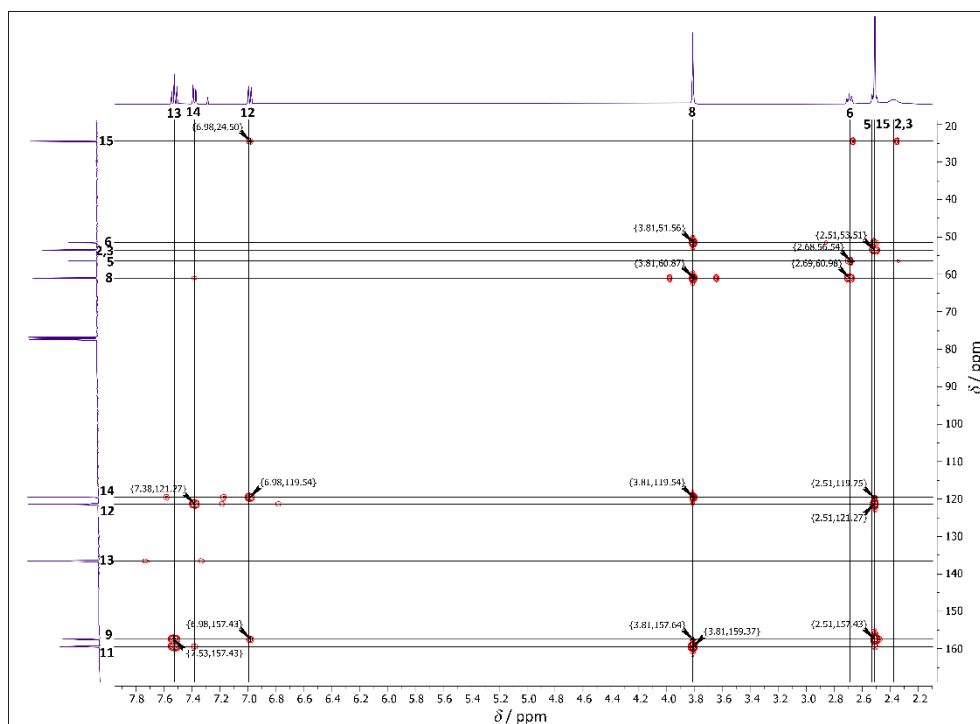
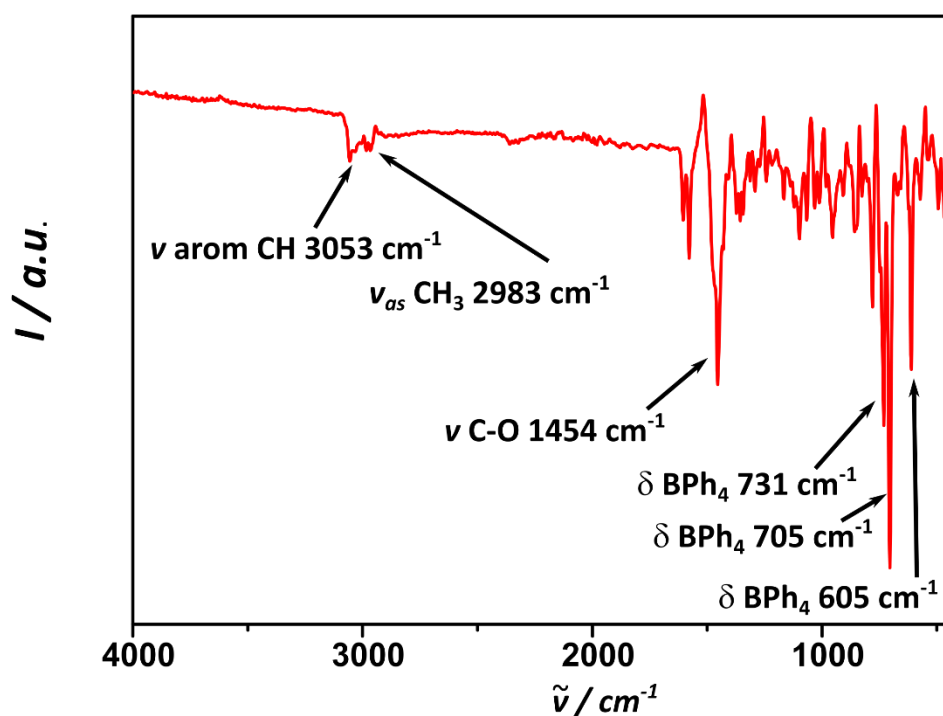
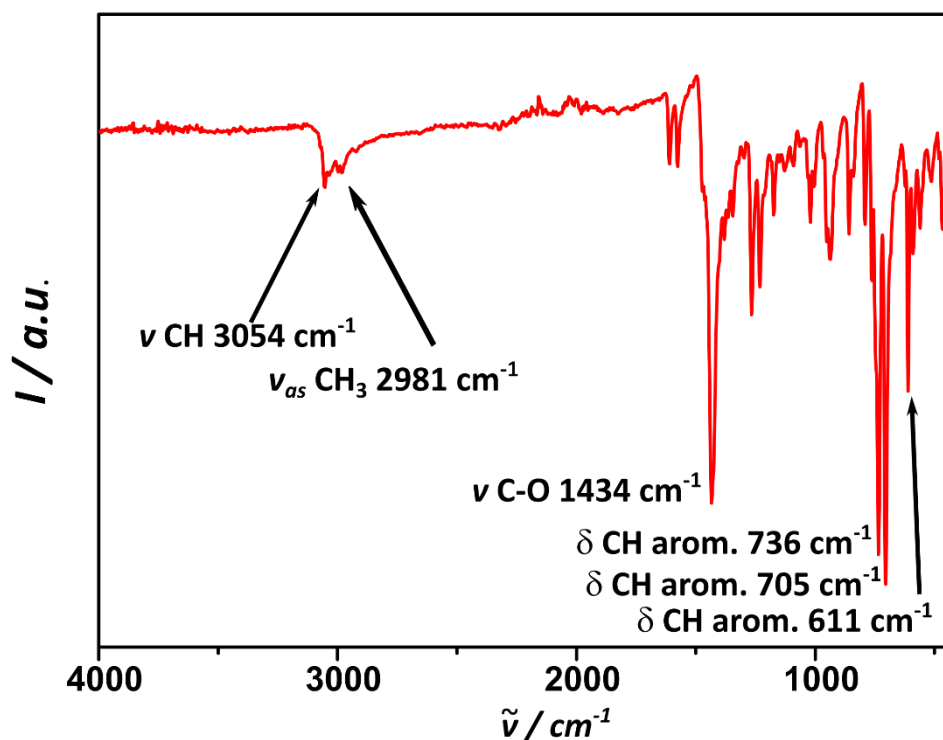


Figure S11: HMBC-NMR-Spectrum of L^{oMe} in $CDCl_3$.

6.1.9 Infrared Spectroscopy Complexes

Figure S12: ATR-IR of *Co-dbusq.*Figure S13: ATR-IR of *Co-Br₄cat.*

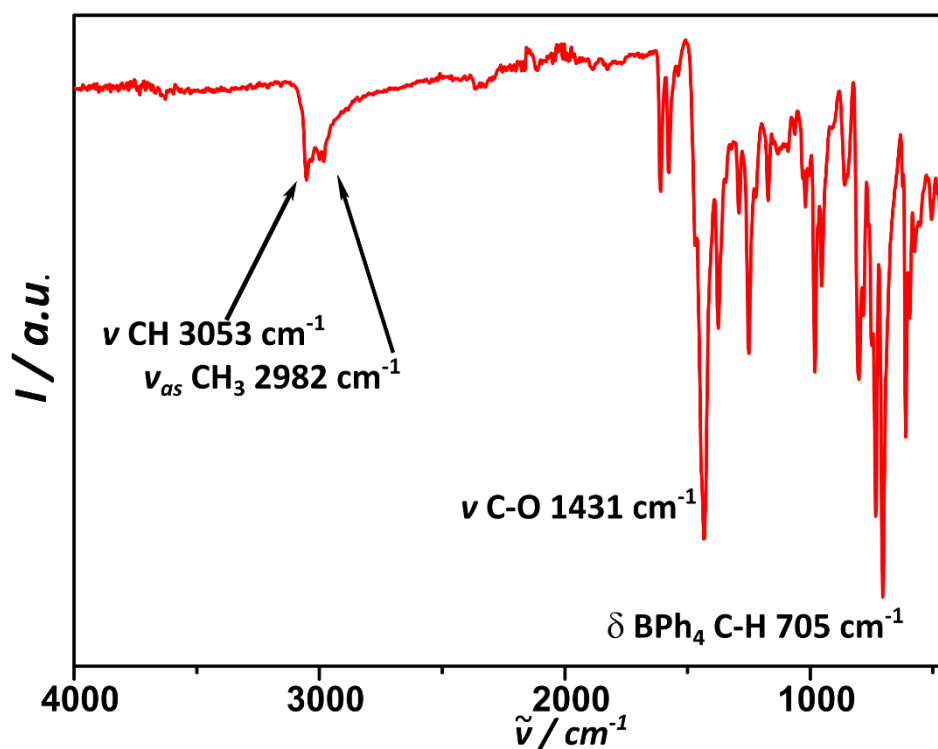


Figure S14: ATR-IR of $\text{Co-Cl}_4\text{cat}$.

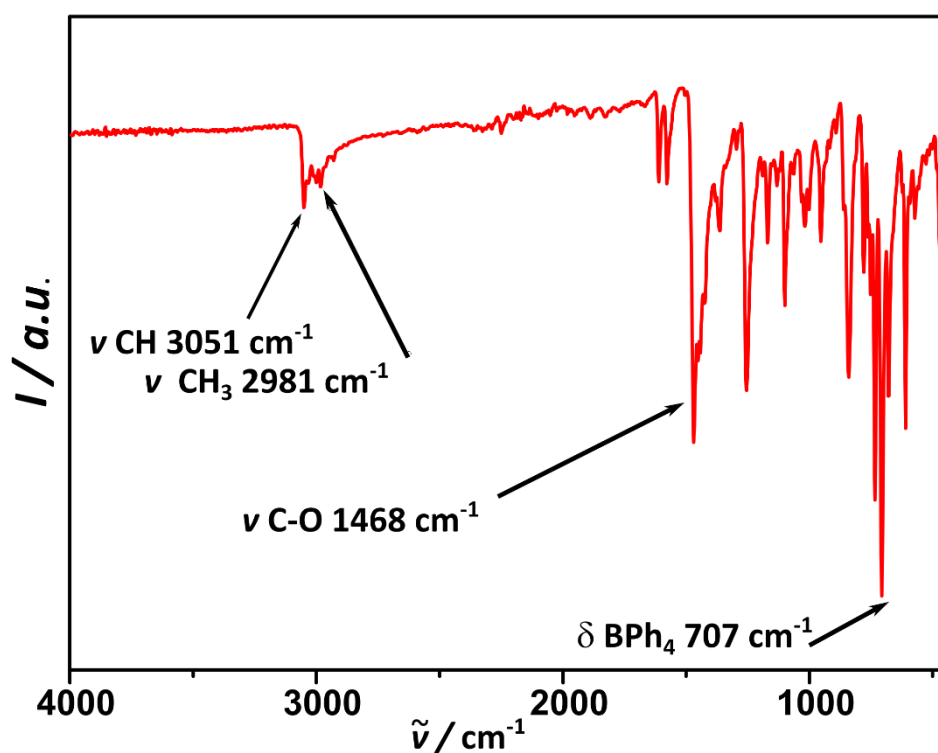


Figure S15: ATR-IR of $\text{Co-Cl}_2\text{cat}$.

6.1.10MS Spectra Complexes

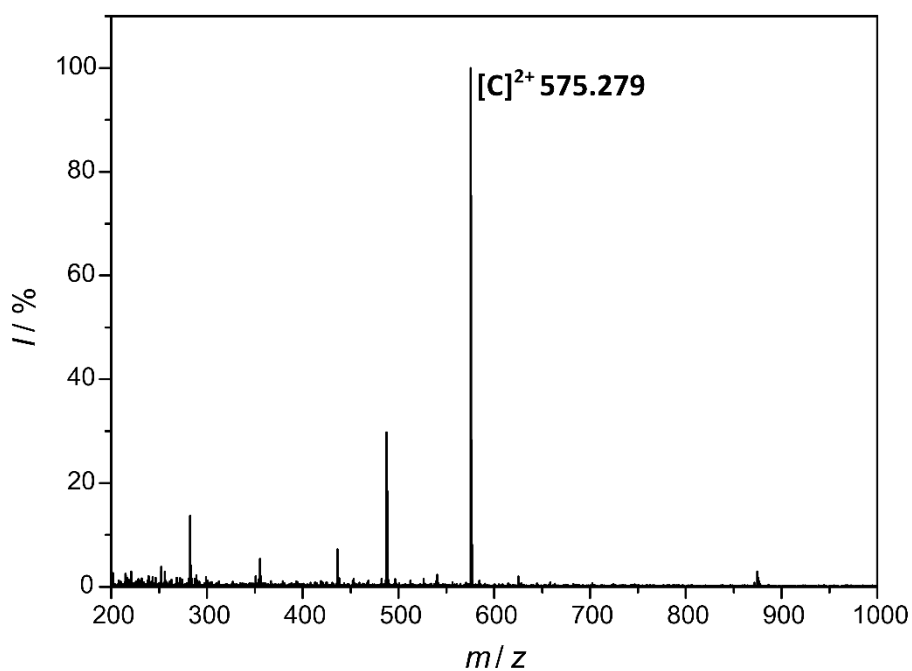


Figure S16: ESI+-mass spectrum of **Co-dbusq** with the dicationic fragment $[C]^{2+}$.

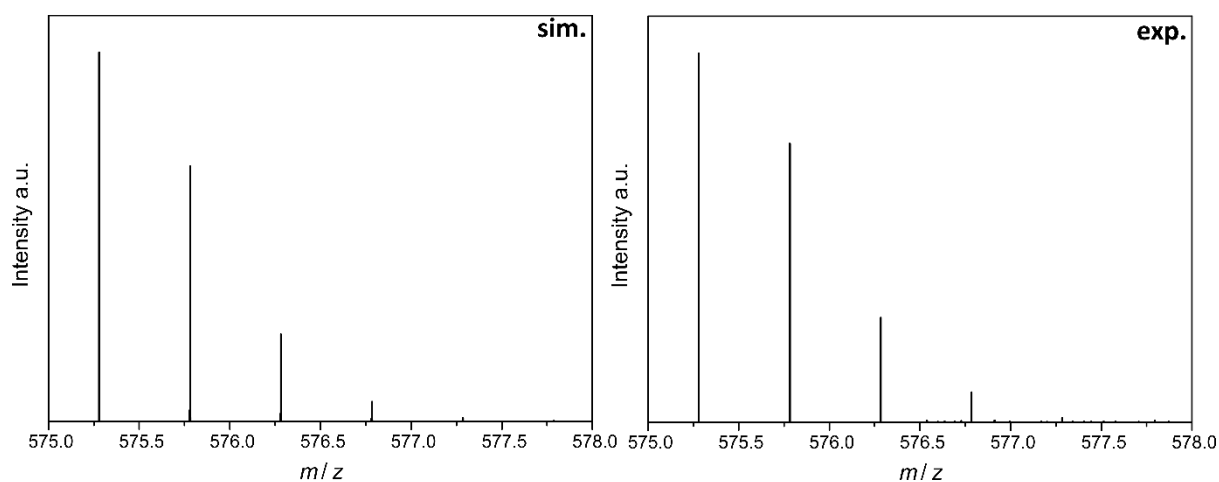


Figure S17: Comparison of the isotopic peak pattern of **Co-dbusq**.

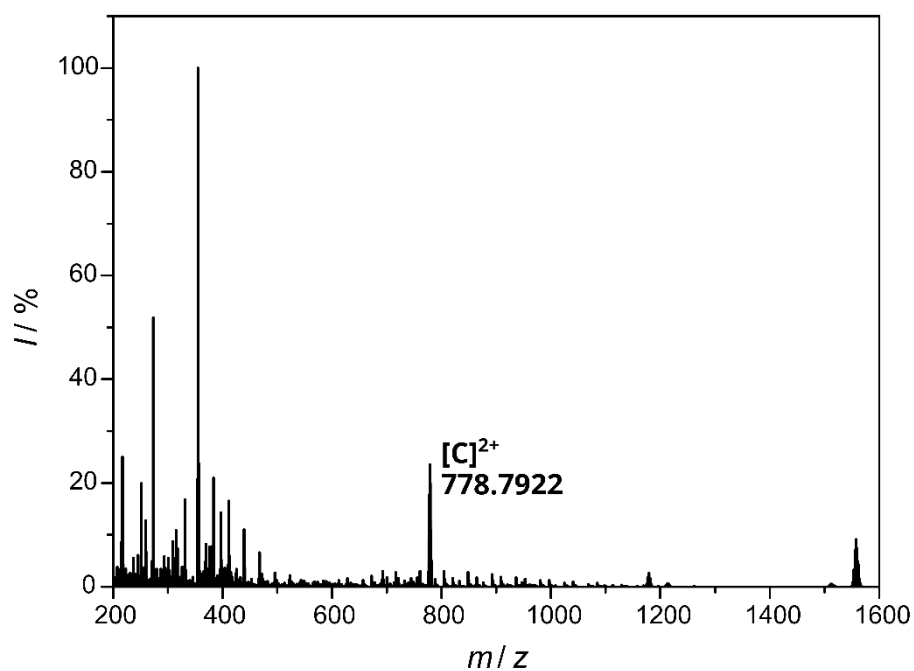


Figure S18: ESI⁺-mass spectrum of Co-Br₄cat with the dicationic fragment $[C]^{2+}$.

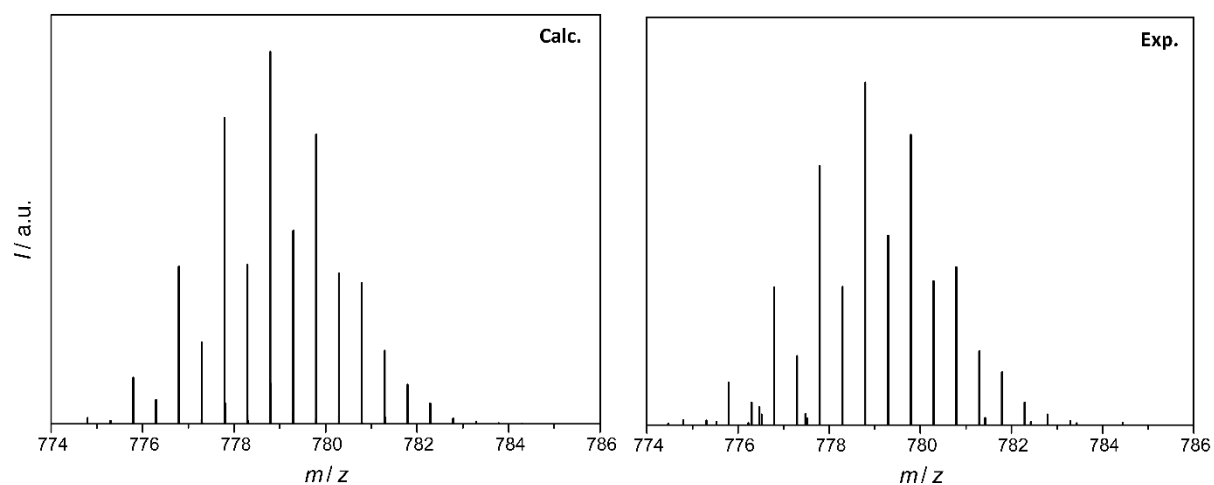


Figure S19: Comparison of the isotopic peak pattern of Co-Br₄cat.

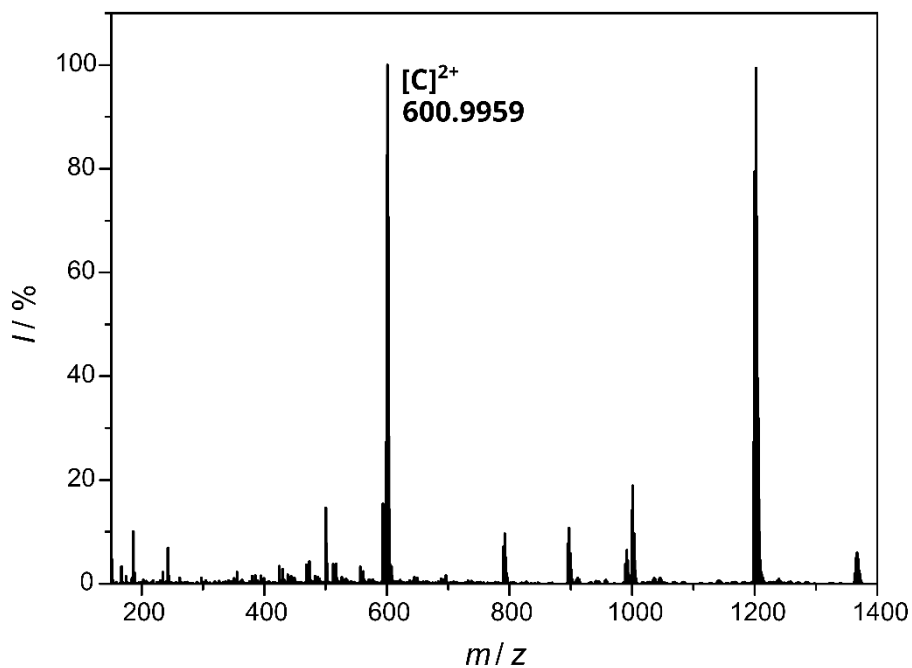


Figure S20: Esi⁺-mass spectrum of **Co-Cl₄cat** with the dicationic fragment $[C]^{2+}$.

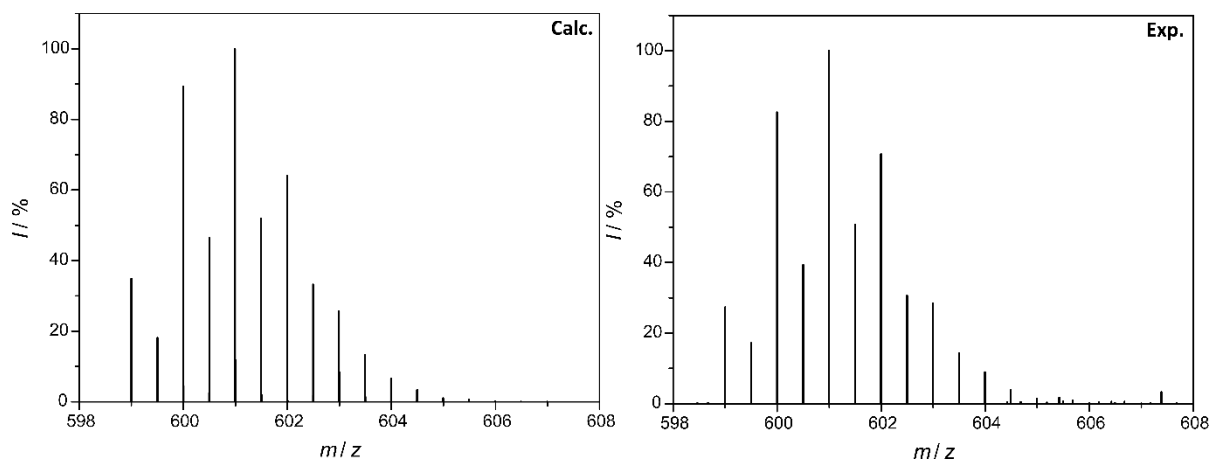


Figure S21: Comparison of the isotopic peak pattern of **Co-Cl₄cat**.

6.1.11 Crystal Structures

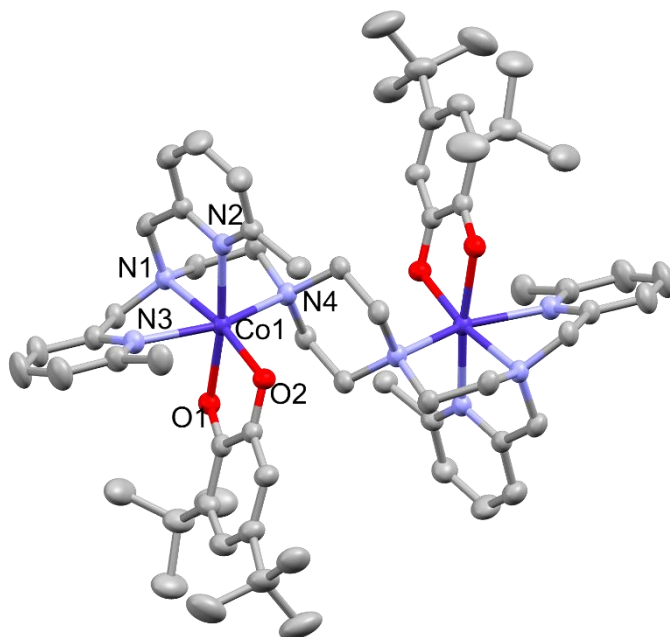


Figure S22: Complex structure of $[\text{Co}_2(\text{L}^{\text{OMe}})(\text{dbusq})_2](\text{BPh}_4)_2 \cdot 3 (\text{C}_2\text{H}_5)_2\text{O}$ at 120 K. Lattice solvent molecules, anions and hydrogen atoms are omitted for clarity. The probability level for the displacement of the ellipsoid is 50%. Colour Code: carbon (grey), cobalt (dark blue), nitrogen (light blue), oxygen (red). Three diethyl ether molecules were modelled with the SQUEEZE routine due to disorder.

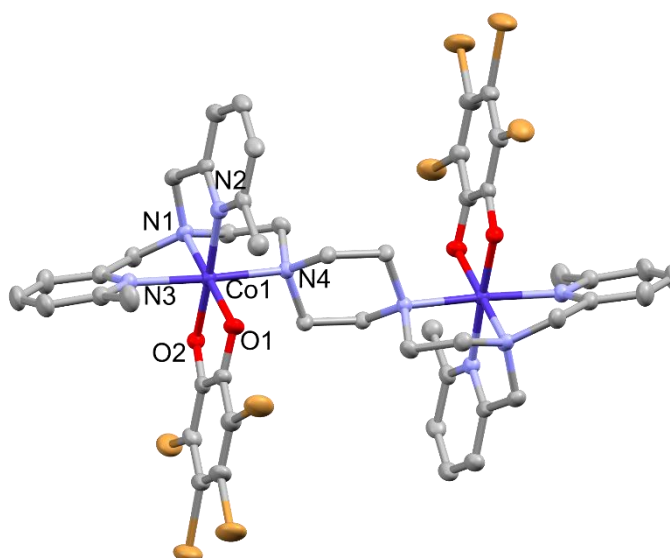


Figure S23: Complex structure of $[\text{Co}_2(\text{L}^{\text{OMe}})(\text{Br}_4\text{cat})_2](\text{BPh}_4)_2 \cdot 4 \text{MeCN}$ at 120 K. Lattice solvent molecules, anions and hydrogen atoms are omitted for clarity. The probability level for the displacement of the ellipsoid is 50%. Colour Code: carbon (grey), cobalt (dark blue), nitrogen (light blue), oxygen (red), bromine (brown).

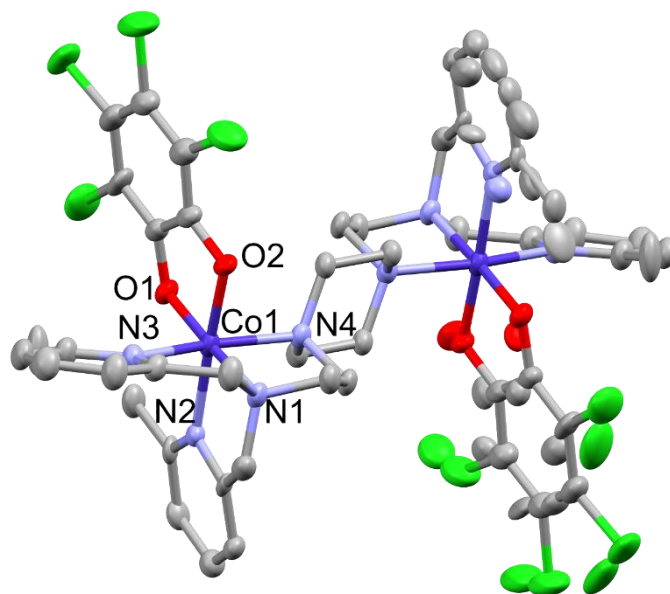


Figure S24: Complex structure of $[\text{Co}_2(\text{L}^{\text{OMe}})(\text{Cl}_4\text{cat})_2](\text{BPh}_4)_2 \cdot 4 \text{ MeCN}$ at 120 K. Lattice solvent molecules, anions and hydrogen atoms are omitted for clarity. The probability level for the displacement of the ellipsoid is 50%. Colour Code: carbon (grey), cobalt (dark blue), nitrogen (light blue), oxygen (red), chlorine (green).

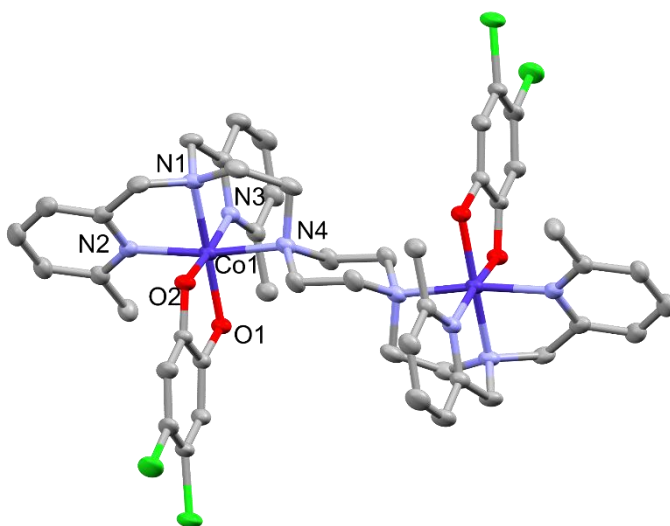


Figure S25: Complex structure of $[\text{Co}_2(\text{L}^{\text{OMe}})(\text{Cl}_2\text{cat})_2](\text{BPh}_4)_2 \cdot 2 \text{ MeCN}$ at 120 K. Lattice solvent molecules, anions and hydrogen atoms are omitted for clarity. The probability level for the displacement of the ellipsoid is 50%. Colour Code: carbon (grey), cobalt (dark blue), nitrogen (light blue), oxygen (red), chlorine (green).

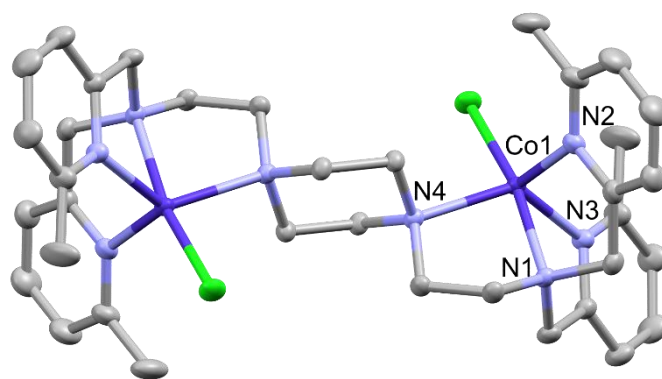


Figure S26: Complex structure of $[\text{Co}_2(\text{L}^{\text{OMe}})(\text{Cl})_2](\text{PF}_6)_2 \cdot \text{Co}_2\text{LCl}_2 \cdot 1 \text{ BuCN}$ at 120 K. Lattice solvent molecules and hydrogen atoms are omitted for clarity. The probability level for the displacement of the ellipsoid is 50%. Colour Code: carbon (grey), cobalt (dark blue), nitrogen (light blue), oxygen (red), sulphur (yellow), fluorine (light green).

6.1.12 SHAPE Measurements

Table S1: Continuous SHAPE calculation of **Co-dbusq**.

ML6	Symmetry	Name	CSHM
HP-6	D6h	Hexagon	30.22273
PPY-6	C5v	Pentagonal pyramid	25.44483
OC-6	Oh	Octahedron	1.55331
TPR-6	D3h	Trigonal prism	13.82504
JPPY-6	C5v	Johnson pentagonal pyramid	29.11935

Table S2: Continuous SHAPE calculation of **Co-Br₄cat**.

ML6	Symmetry	Name	CSHM
HP-6	D6h	Hexagon	30.03166
PPY-6	C5v	Pentagonal pyramid	26.54940
OC-6	Oh	Octahedron	0.48969
TPR-6	D3h	Trigonal prism	15.07631
JPPY-6	C5v	Johnson pentagonal pyramid	30.39016

Table S3: Continuous SHAPE calculation of **Co-Cl₄cat**.

ML6	Symmetry	Name	CSHM
HP-6	D6h	Hexagon	29.85712
PPY-6	C5v	Pentagonal pyramid	26.77689
OC-6	Oh	Octahedron	0.49969
TPR-6	D3h	Trigonal prism	15.02428
JPPY-6	C5v	Johnson pentagonal pyramid	30.65379

Table S4: Continuous SHAPE calculation of **Co-Cl₄cat**. (Disordered)

ML6	Symmetry	Name	CSHM
HP-6	D6h	Hexagon	30.74164
PPY-6	C5v	Pentagonal pyramid	26.16190
OC-6	Oh	Octahedron	0.77112
TPR-6	D3h	Trigonal prism	13.92699
JPPY-6	C5v	Johnson pentagonal pyramid	29.06427

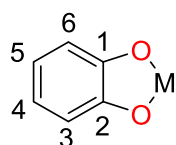
Table S5: Continuous SHAPE calculation of **Co-Cl₂cat**.

ML6	Symmetry	Name	CSHM
HP-6	D6h	Hexagon	30.26111
PPY-6	C5v	Pentagonal pyramid	27.54771
OC-6	Oh	Octahedron	0.46756
TPR-6	D3h	Trigonal prism	15.75772
JPPY-6	C5v	Johnson pentagonal pyramid	30.94015

6.1.13 Metric Oxidation State (MOS)

Table S6: The MOS of the catecholate ligands of **C1-C7**.

Compound	C-O avg.	C1-C2	C2-C3 avg.	C3-C4 avg.	C4-C5	Calc. MOS
Co-dbusq	1.286	1.457	1.432	1.375	1.43	-1.003
Co-Br ₄ cat	1.332	1.394	1.402	1.3965	1.389	-1.839
Co-Cl ₄ cat	1.332	1.398	1.3915	1.4085	1.453	-1.620
Co-Cl ₄ cat disordered	1.3895	1.352	1.374	1.34	1.537	-1.724
Co-Cl ₂ cat	1.344	1.407	1.3865	1.3995	1.374	-1.994



6.1.14 Catecholate Bond Lengths

Table S7: Catecholate Bond Lengths of Complexes *Co-dbusq*, *Co-Br₄cat* and *Co-Cl₄cat*.

Co-dbusq	Bond Length / Å	Co-Br ₄ cat	Bond Length / Å	Co-Cl ₄ cat	Bond Length / Å
C19-C20	1.445(3)	C19-C20	1.402(6)	C19-C20	1.361(9)
C20-C21	1.381(3)	C20-C21	1.395(6)	C20-C21	1.408(10)
C21-C22	1.431(3)	C21-C22	1.388(7)	C21-C22	1.413(13)
C22-C23	1.369(3)	C22-C23	1.399(7)	C22-C23	1.398(14)
C23-C24	1.419(2)	C23-C24	1.401(6)	C23-C24	1.399(10)
C24-C19	1.457(2)	C24-C19	1.395(6)	C24-C19	1.411(12)

Table S8: Catecholate Bond Lengths of Complexes *Co-Cl₄cat* disordered and *Co-Cl₂cat*.

Co-Cl ₄ cat disordered	Bond Length / Å	Co-Cl ₂ cat	Bond Length / Å
C19A-C20A	1.36(3)	C19-C20	1.389(3)
C20A-C21A	1.41(2)	C20-C21	1.401(3)
C21A-C22A	1.49(3)	C21-C22	1.373(3)
C22A-C23A	1.25(4)	C22-C23	1.398(3)
C23A-C24A	1.44(3)	C23-C24	1.384(3)
C24A-C19A	1.40(3)	C24-C19	1.407(3)

6.1.15 Metal Donor Bond Angles

Table S9: Metal Donor Bond Angles of Complexes *Co-dbusq*, *Co-Br₄cat*, *Co-Cl₄cat*, *Co-Cl₄cat* disordered and *Co-Cl₂cat*.

	Co-dbusq/°	Co-Br ₄ cat/°	Co-Cl ₄ cat /°	Co-Cl ₄ catA/°	Co-Cl ₂ cat/°
O1 Co1 N1	94.58(5)	174.89(14)	177.09(18)	80.1(7)	174.53(6)
O1 Co1 N2	172.85(5)	96.99(14)	96.3(4)	173.4(11)	99.05(6)
O1 Co1 N3	83.96(5)	99.82(14)	100.13(19)	83.4(8)	98.94(6)
O1 Co1 N4	93.10(5)	90.90(13)	90.83(18)	91.8(9)	91.36(6)
O2 Co1 O1	78.47(5)	86.39(13)	87.8(3)	82.2(8)	86.56(6)
O2 Co1 N1	170.27(5)	89.29(13)	91.0(3)	162.2(4)	88.13(6)
O2 Co1 N2	104.31(5)	176.53(14)	175.9(4)	104.3(10)	86.05(6)
O2 Co1 N3	96.74(5)	84.34(13)	85.8(3)	97.8(4)	174.50(6)
O2 Co1 N4	105.33(5)	91.16(13)	91.4(3)	91.8(4)	89.89(6)
N1 Co1 N2	81.83(5)	87.37(14)	84.9(3)	93.3(10)	81.89(7)
N1 Co1 N3	75.58(5)	82.45(14)	82.42(12)	82.42(12)	86.36(7)
N1 Co1 N4	81.65(5)	86.46(14)	86.55(11)	86.55(11)	87.30(7)
N2 Co1 N3	89.15(5)	94.27(14)	93.4(3)	94.6(10)	93.11(6)
N2 Co1 N4	92.49(5)	89.58(13)	88.6(3)	89.0(11)	168.56(7)
N3 Co1 N4	156.71(5)	168.07(14)	168.58(12)	168.58(12)	89.91(6)

6.1.16 Crystallographic Parameters

Table S10: Crystallographic Data of Complexes *Co-dbusq* and *Co-Br₄cat*.

	Co-dbusq	Co-Br₄cat
Empirical formula	C ₁₂₄ H ₁₅₈ B ₂ Co ₂ N ₈ O ₇	C ₁₀₄ H ₁₀₀ B ₂ Br ₈ Co ₂ N ₁₂ O ₄
Formula weight	2012.05	2360.71
Temperature/K	120.00	120.00
Crystal system	monoclinic	orthorhombic
Space group	P21/c	Pbca
a/Å	12.9718(3)	16.7091(2)
b/Å	19.3802(4)	17.2578(2)
c/Å	22.5795(5)	33.9953(4)
α/°	90	90
β/°	104.890(2)	90
γ/°	90	90
Volume/Å³	5485.8(2)	9803.0(2)
Z	2	4
ρ_{calc}/cm³	1.218	1.600
μ/mm⁻¹	0.362	3.658
F(000)	2156.0	4736.0
Crystal size/mm³	0.085 × 0.067 × 0.04	0.11 × 0.074 × 0.012
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	4.204 to 67.686	4.72 to 64.574
Index ranges	-18 ≤ h ≤ 18, -27 ≤ k ≤ 26, -33 ≤ l ≤ 33	-23 ≤ h ≤ 22, -24 ≤ k ≤ 24, -47 ≤ l ≤ 50
Reflections collected	63475	106071
Independent reflections	18855 [R _{int} = 0.0440, R _{sigma} = 0.0640]	16230 [R _{int} = 0.0540, R _{sigma} = 0.0497]
Data/restraints/parameters	18855/0/585	16230/0/599
Goodness-of-fit on F²	1.053	1.092
Final R indexes [I > 2σ (I)]	R ₁ = 0.0598, wR ₂ = 0.1499	R ₁ = 0.0734, wR ₂ = 0.1619
Final R indexes [all data]	R ₁ = 0.1028, wR ₂ = 0.1697	R ₁ = 0.1269, wR ₂ = 0.1889
Largest diff. peak/hole / e Å⁻³	0.74/-0.45	1.60/-1.57

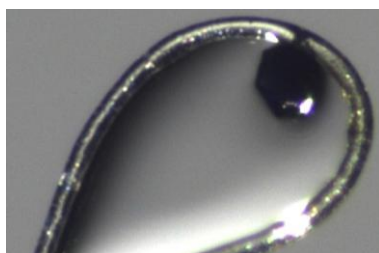
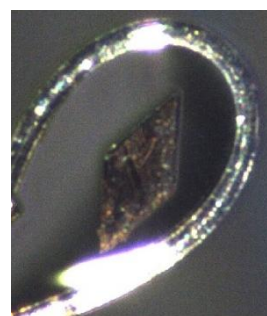
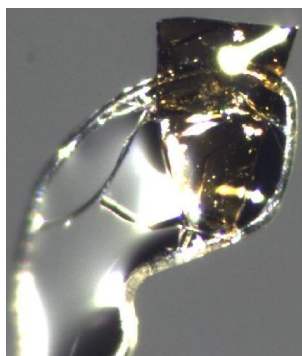


Table S11: Crystallographic Data of Complexes **Co-Cl₄cat** and **Co-Cl₂cat**.

	Co-Cl₄cat	Co-Cl₂cat
Empirical formula	C ₁₀₄ H ₁₀₀ B ₂ Cl ₈ Co ₂ N ₁₂ O ₄	C ₁₀₀ H ₉₈ B ₂ Cl ₄ Co ₂ N ₁₀ O ₄
Formula weight	2005.03	1785.16
Temperature/K	120.00	120.00
Crystal system	orthorhombic	triclinic
Space group	Pbca	P-1
a/Å	16.4624(4)	11.5577(2)
b/Å	17.2855(3)	14.1885(3)
c/Å	34.0212(6)	14.4416(3)
α/°	90	100.024(2)
β/°	90	112.147(2)
γ/°	90	93.701(2)
Volume/Å³	9681.1(3)	2137.90(8)
Z	4	1
ρ_{calc}/cm³	1.376	1.387
μ/mm⁻¹	0.623	0.575
F(000)	4160.0	932.0
Crystal size/mm³	0.46 × 0.242 × 0.037	0.088 × 0.062 × 0.012
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	4.172 to 63.818	4.726 to 67.494
Index ranges	-22 ≤ h ≤ 21, -20 ≤ k ≤ 21, -48 ≤ l ≤ 34	-17 ≤ h ≤ 16, -20 ≤ k ≤ 21, -20 ≤ l ≤ 22
Reflections collected	34378	48260
Independent reflections	10625 [R _{int} = 0.0473, R _{sigma} = 0.0415]	14708 [R _{int} = 0.0245, R _{sigma} = 0.0349]
Data/restraints/parameters	10625/384/772	14708/234/584
Goodness-of-fit on F²	1.054	1.056
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0856, wR ₂ = 0.2269	R ₁ = 0.0565, wR ₂ = 0.1351
Final R indexes [all data]	R ₁ = 0.1101, wR ₂ = 0.2519	R ₁ = 0.0817, wR ₂ = 0.1509
Largest diff. peak/hole / e Å⁻³	1.61/-0.99	0.82/-0.49



6.1.17 UV-Vis Spectroscopy

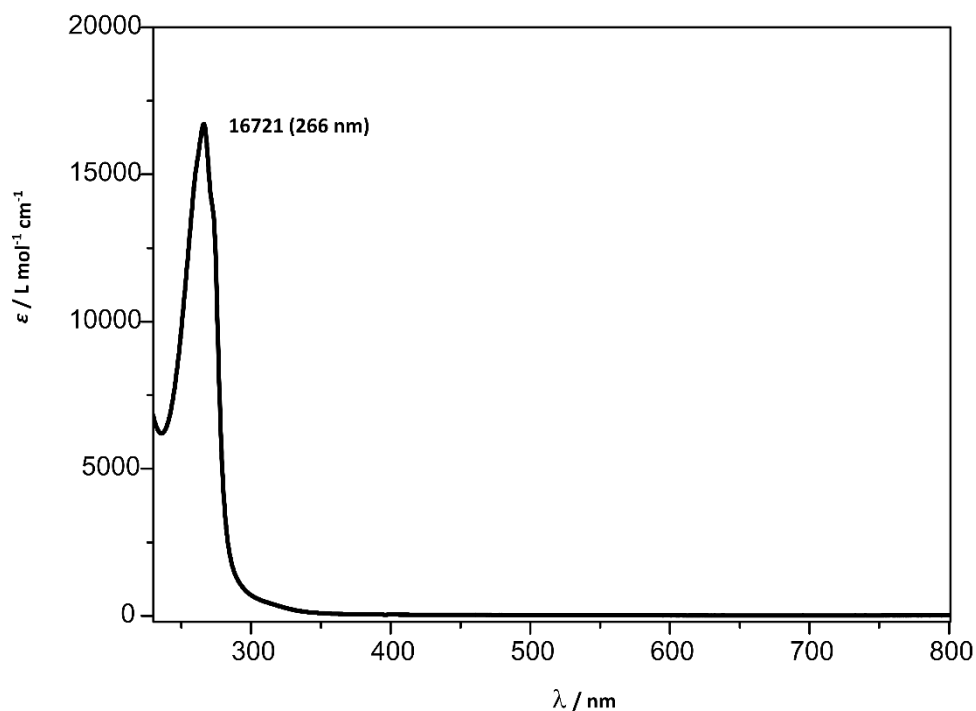


Figure S27: UV-Vis spectrum of L^{oMe} at RT in MeCN at 0.1 mM.

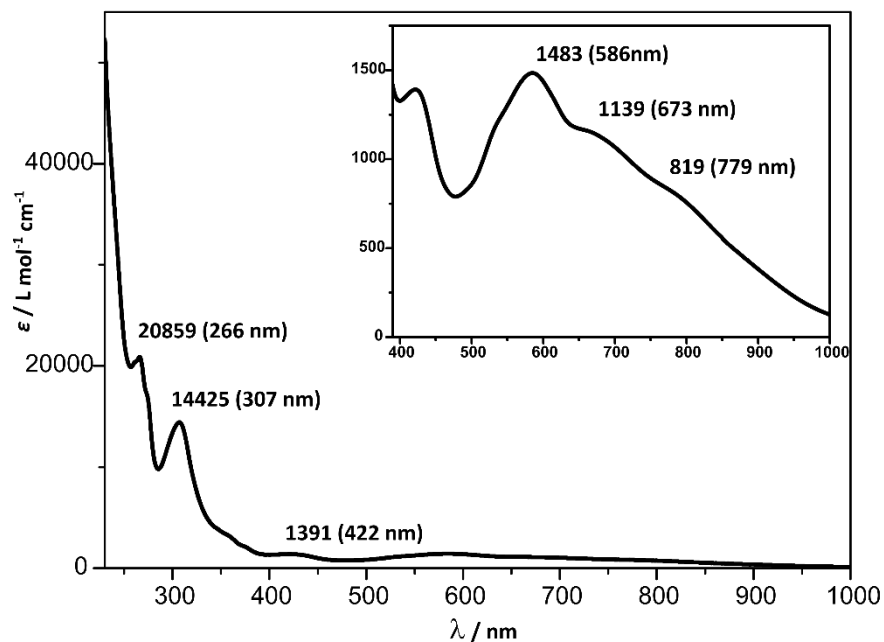


Figure S28: UV-Vis spectrum of Co-dbusq at RT in MeCN at 0.02mM with a zoomed in region at 1mM in MeCN.

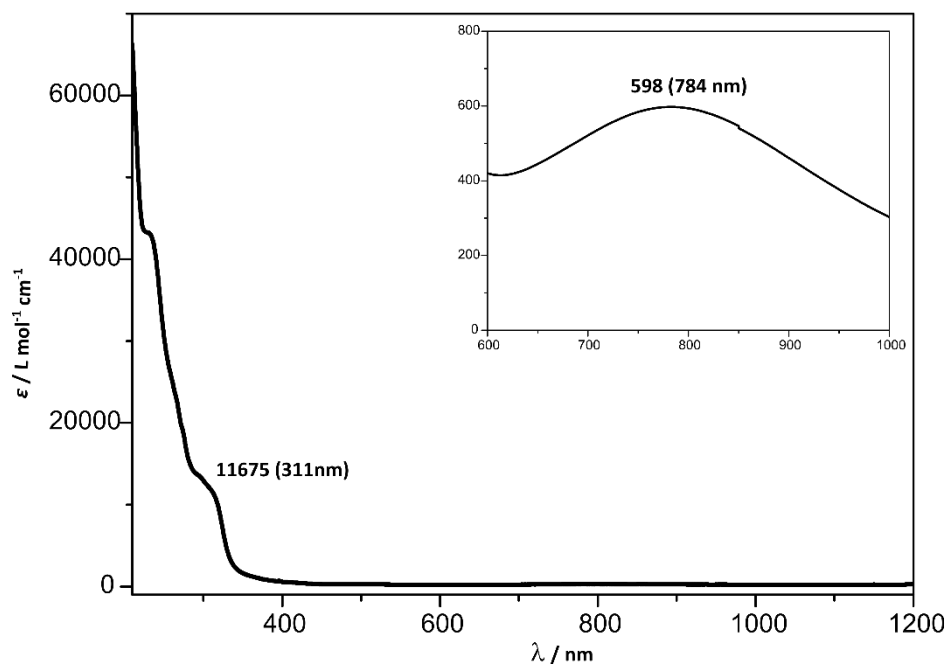


Figure S29: UV-Vis spectrum of **Co-Br₄cat** at RT in MeCN at 0.02mM with a zoomed in region at 1mM in MeCN.

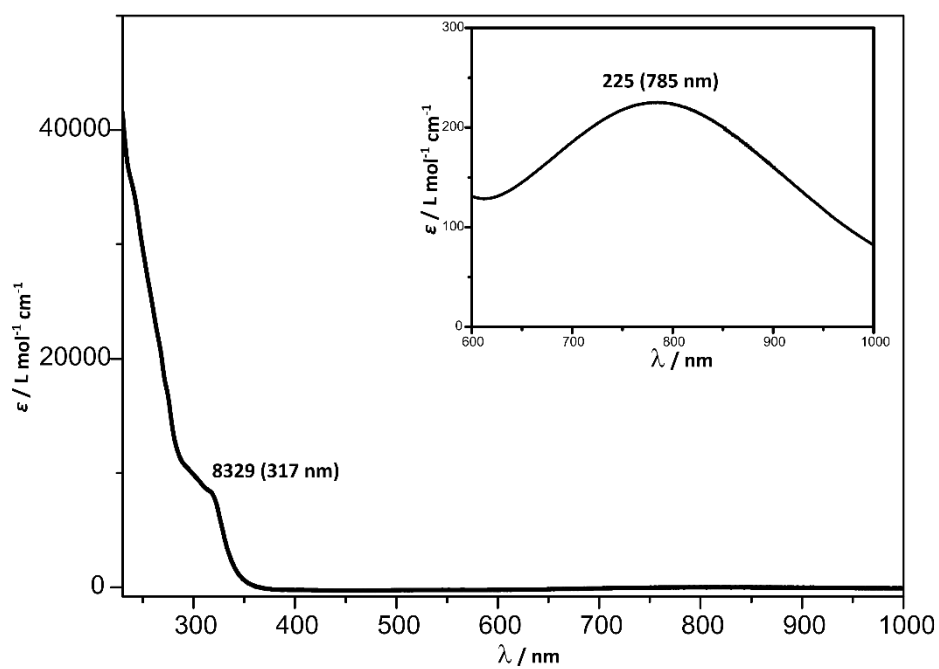


Figure S30: UV-Vis spectrum of **Co-Cl₄cat** at RT in MeCN at 0.02mM with a zoomed in region at 1mM in MeCN.

6.1.18 Solid State UV-Vis

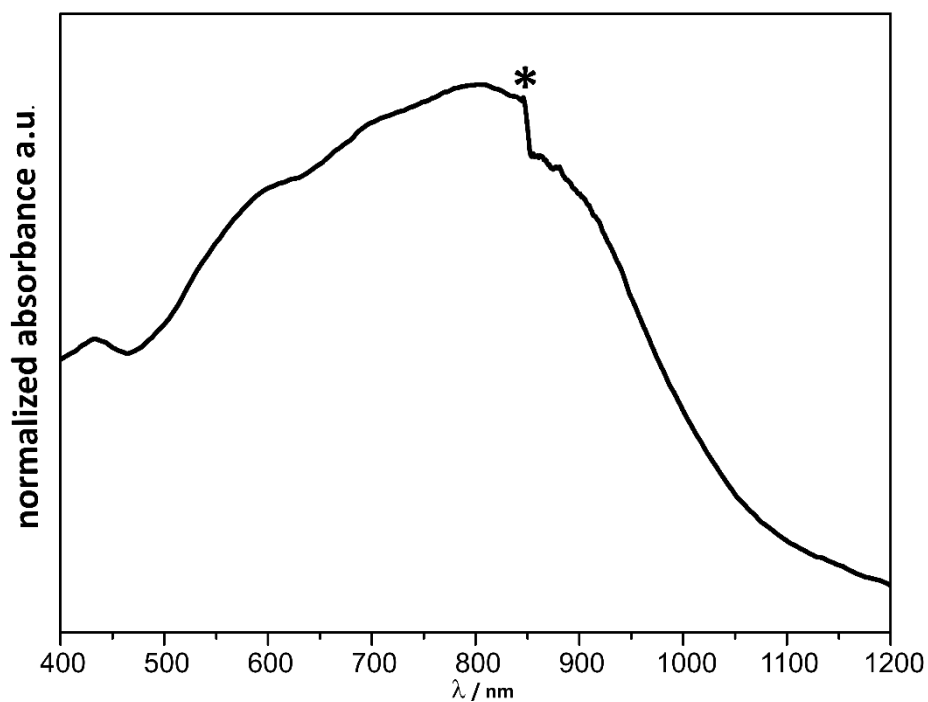


Figure S31: Normalized absorbance solid-state diffuse reflectance UV-Vis spectrum of **Co-dbusq** at 303K. Spectra were recorded using BaSO_4 as a white standard reference as well as optical dilution agent. The asterisk denotes an instrumental grating-change artefact.

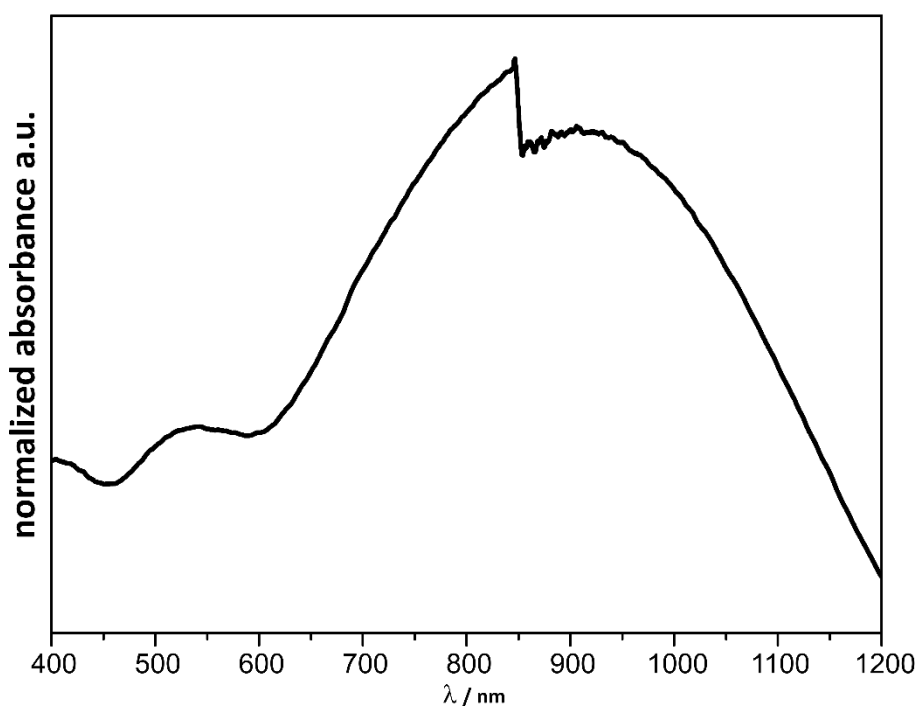


Figure S32: Normalized absorbance solid-state diffuse reflectance UV-Vis spectrum of **Co-Br₄cat** at 303K. Spectra were recorded using BaSO_4 as a white standard reference as well as optical dilution agent. The asterisk denotes an instrumental grating-change artefact.

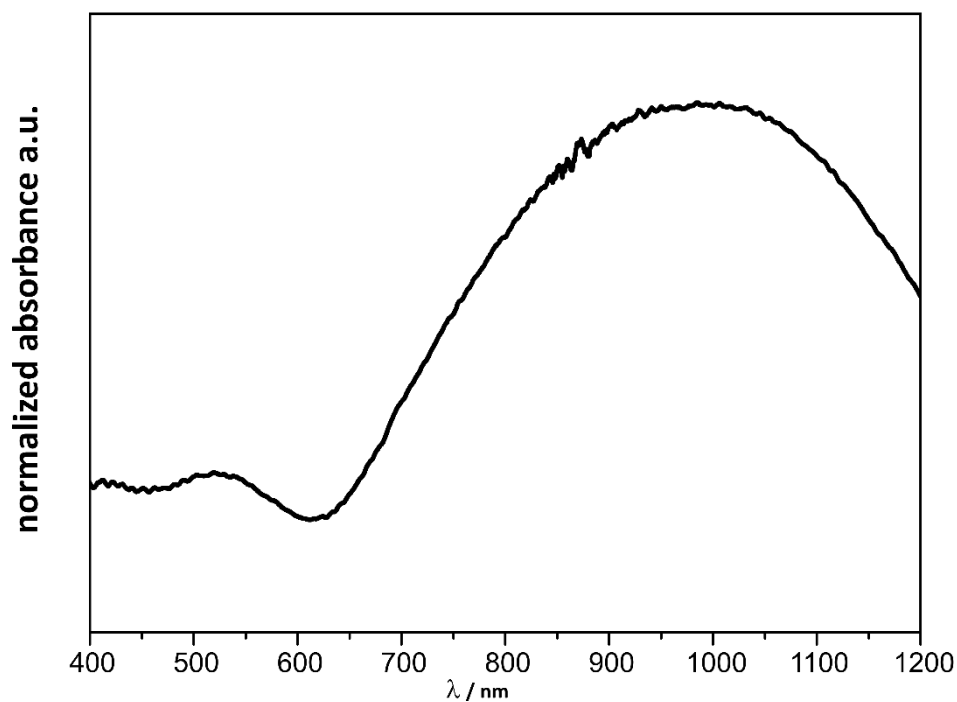


Figure S33: Normalized absorbance solid-state diffuse reflectance UV-Vis spectrum of $\text{Co-Cl}_4\text{cat}$ at 303K. Spectra were recorded using BaSO_4 as a white standard reference as well as optical dilution agent.

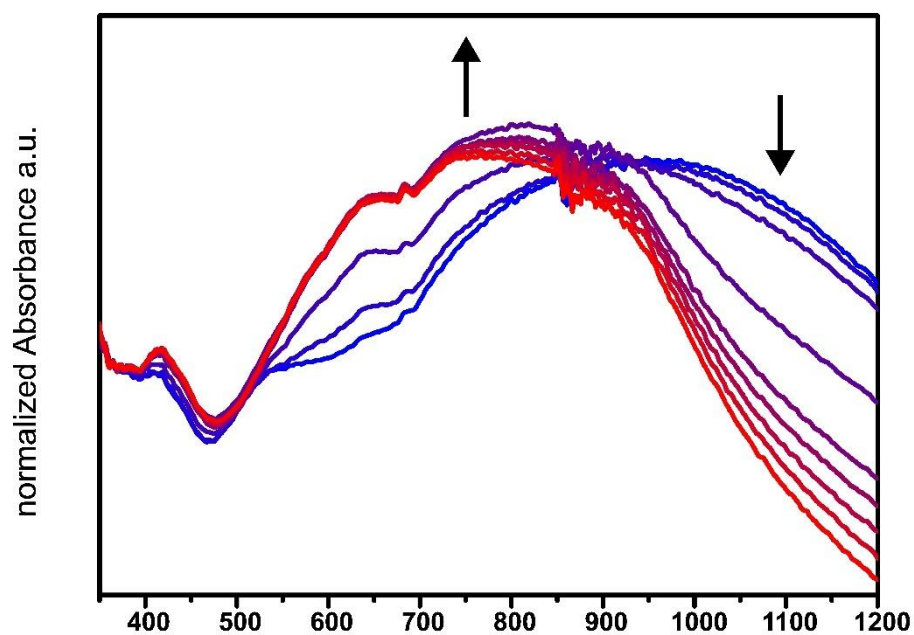


Figure S34: Normalized absorbance solid-state diffuse reflectance UV-Vis spectrum of $\text{Co-Cl}_2\text{cat}$ between 303K and 383K. Spectra were recorded using BaSO_4 as a white standard reference as well as optical dilution agent.

6.1.19 Solid State NMR

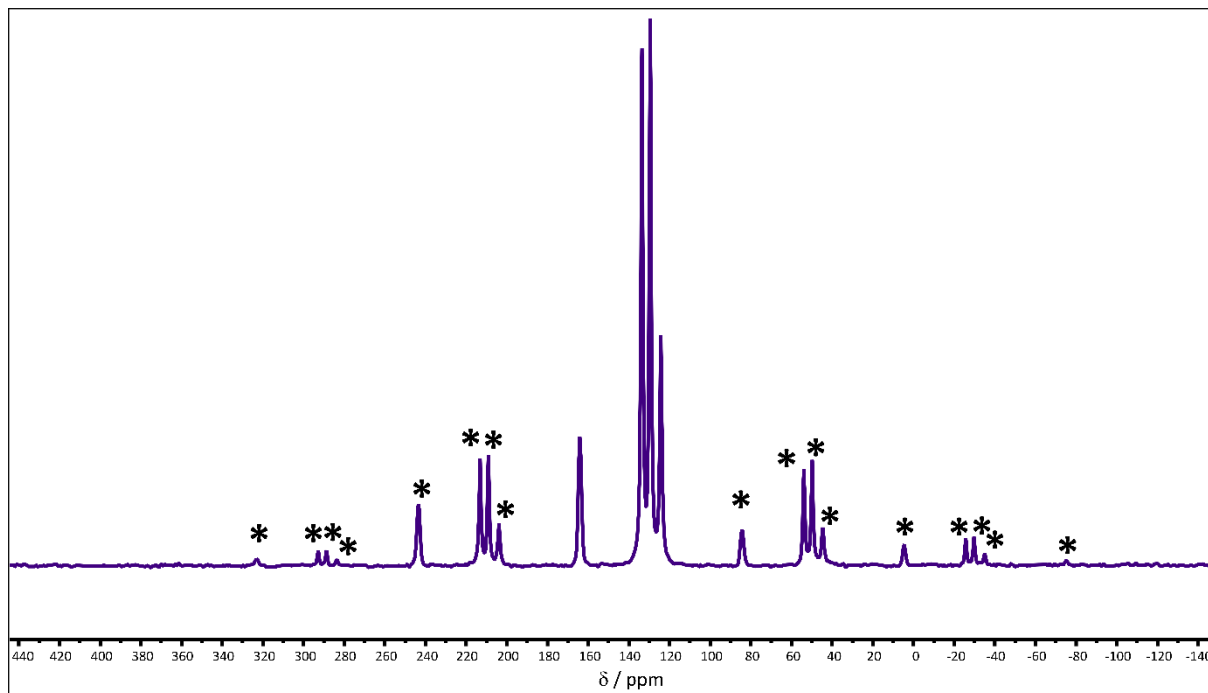


Figure S35: Solid State ^{13}C CP-MAS NMR spectrum of **NaBPh₄** measured at 293K with MAS spinning rate of 8 kHz. Spinning sidebands are denoted with an asterisk and appear at multiples of the spinning frequency (± 8 kHz and ± 16 kHz) relative to the real signals.

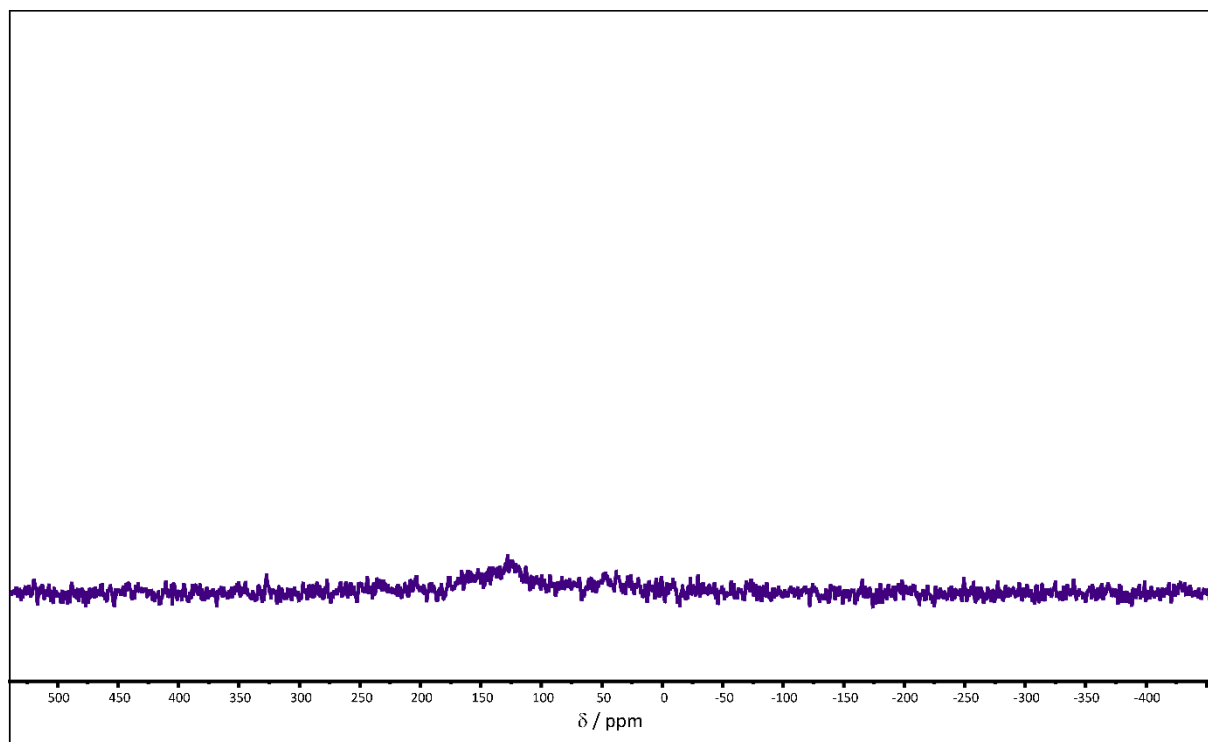


Figure S36: Solid State ^{13}C CP-MAS NMR spectrum of **Co-dbusq** measured at 293K with MAS spinning rate of 8 kHz.

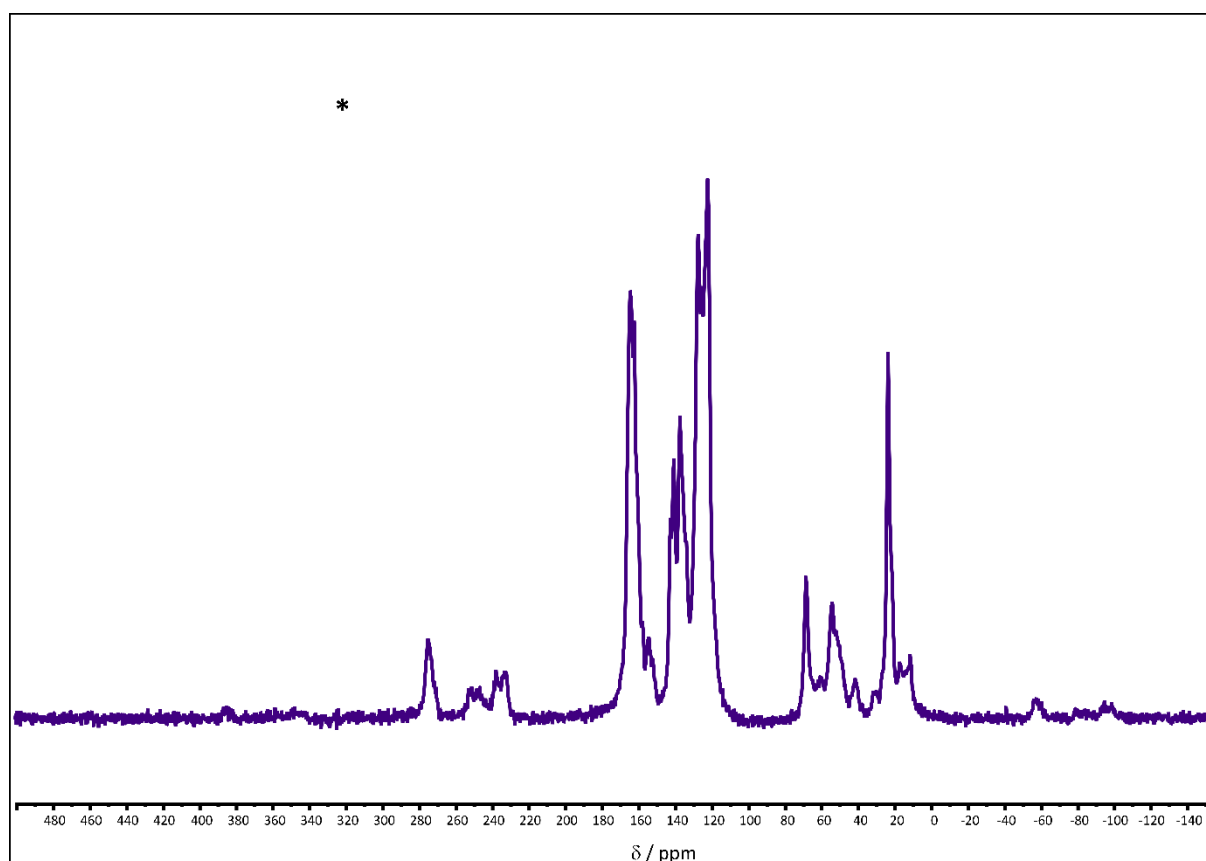


Figure S37: Solid State ^{13}C CP-MAS NMR spectrum of **Co-Cl₄cat** measured at 293K with MAS spinning rate of 8 kHz.

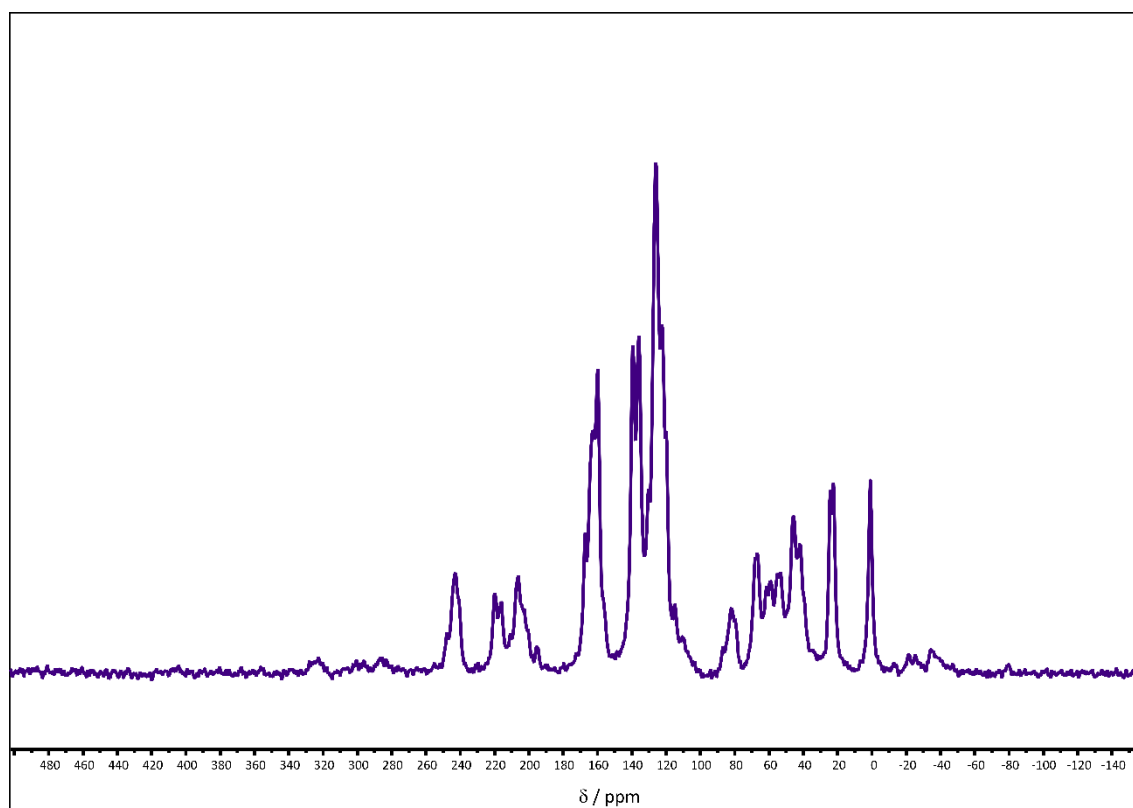


Figure S38: Solid State ^{13}C CP-MAS NMR spectrum of **Co-Br₄cat** measured at 293K with MAS spinning rate of 8 kHz.

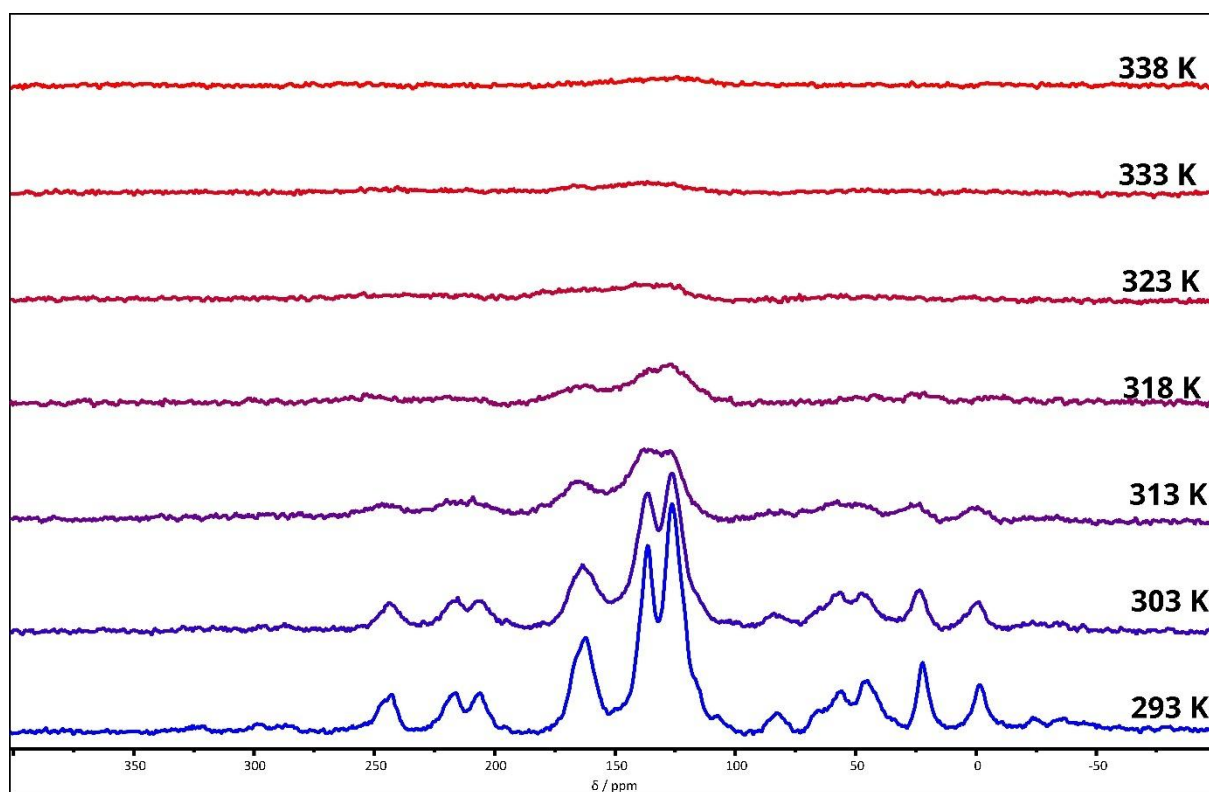


Figure S39: Solid State ^{13}C CP-MAS NMR spectrum of $\text{Co-Cl}_2\text{cat}$ measured at 293K with MAS spinning rate of 8 kHz.

6.1.20 SQUID Magnetometry

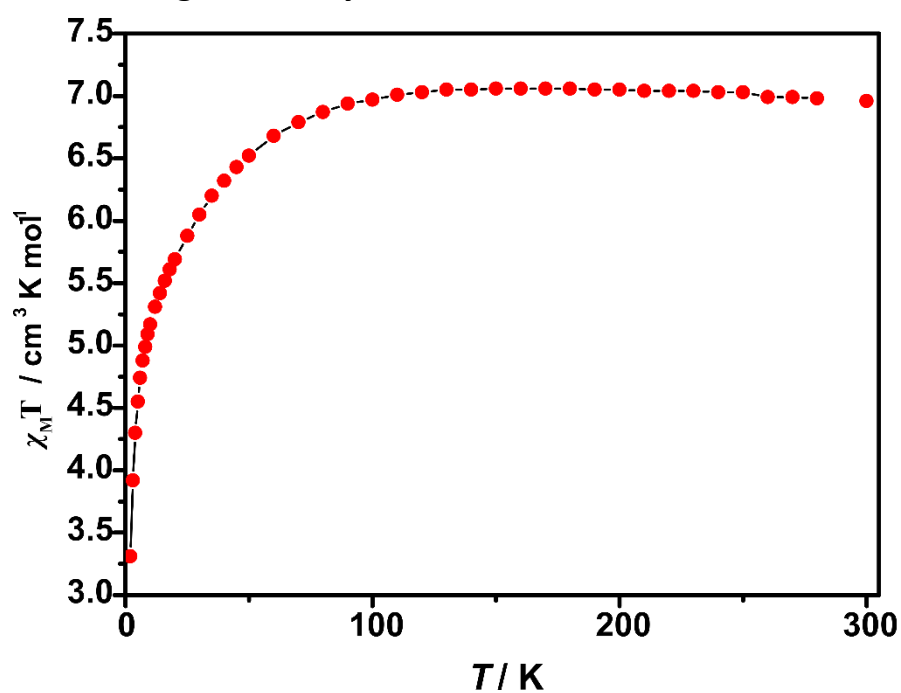


Figure S40: Temperature dependent $\chi_M T (T)$ of **Co-dbusq** in heating (red) mode over the temperature range of 2-300 K.

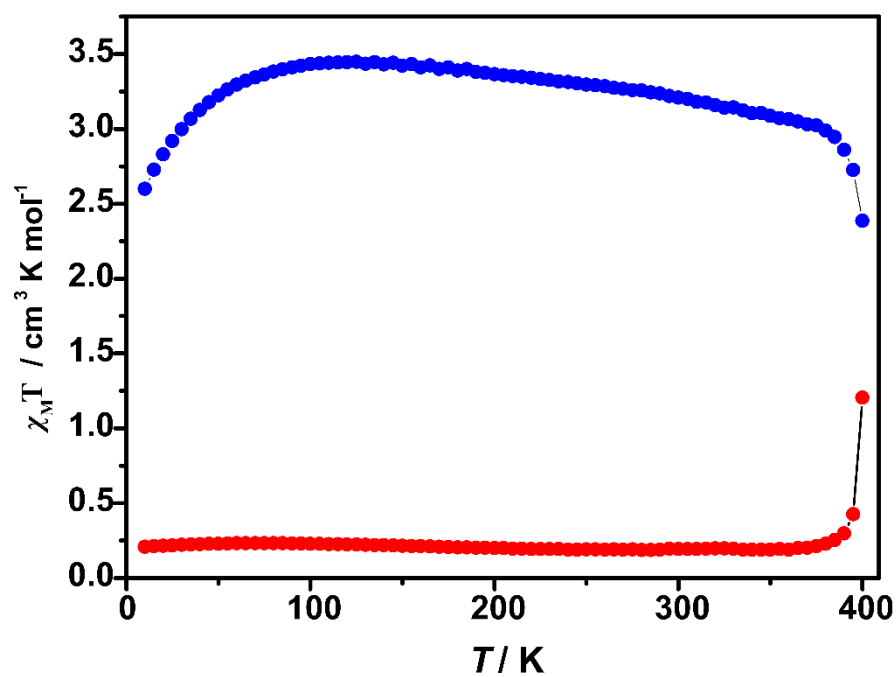


Figure S41: Temperature dependent $\chi_M T (T)$ of **Co-Br₄cat** in heating (red) and cooling (blue) mode over the temperature range of 10-400 K, waiting 5 minutes at 400 K.

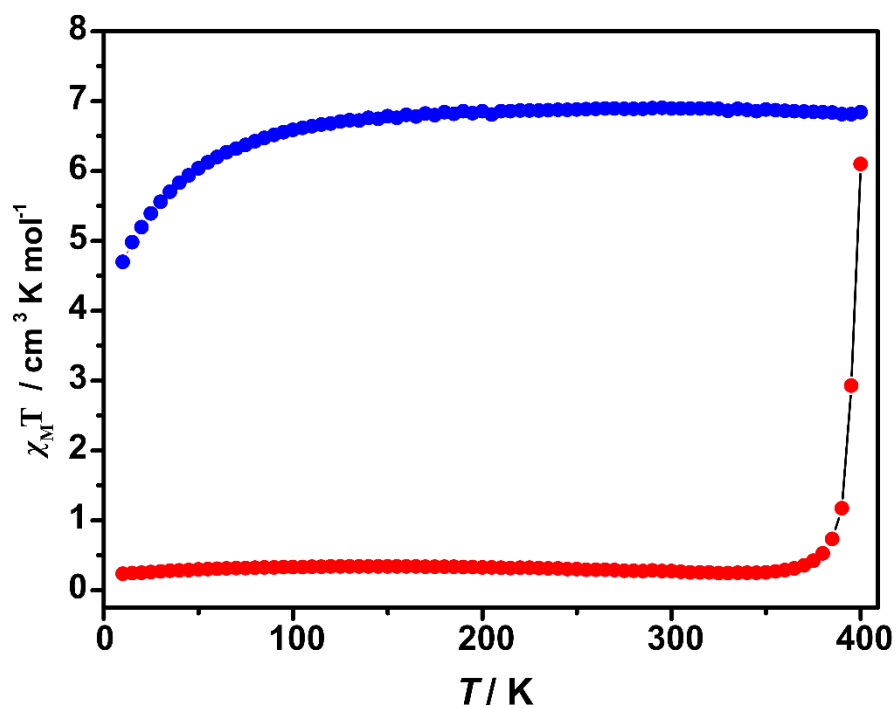


Figure S42: Temperature dependent $\chi_M T(T)$ of **Co-Cl₄cat** in heating (red) and cooling (blue) mode over the temperature range of 10–400 K, waiting 5 minutes at 400 K.

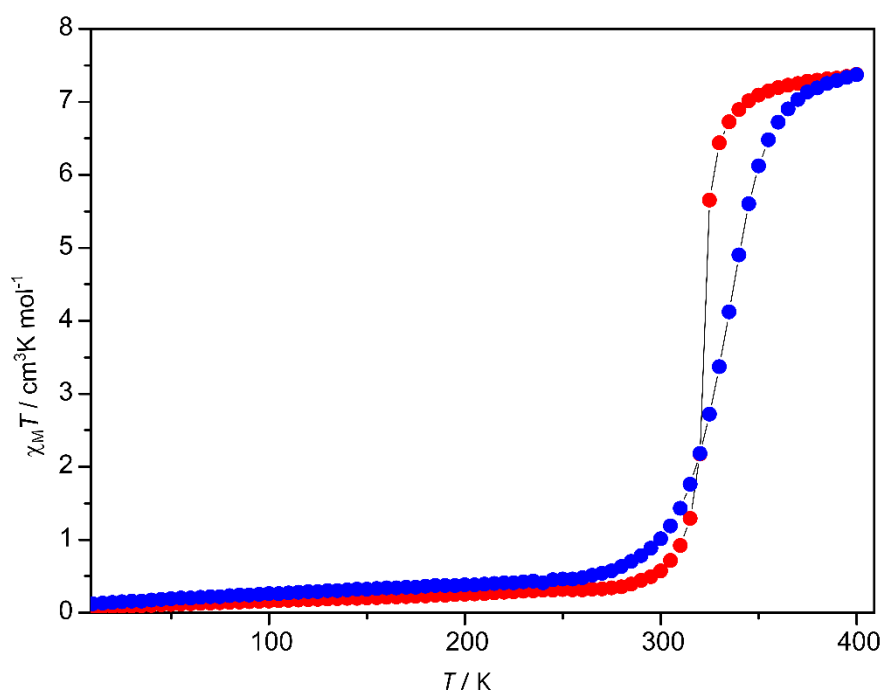


Figure S43: Temperature dependent $\chi_M T(T)$ of crystalline **Co-Cl₂cat** in heating (red) and cooling (blue) mode over the temperature range of 10–400 K, waiting 5 minutes at 400 K.

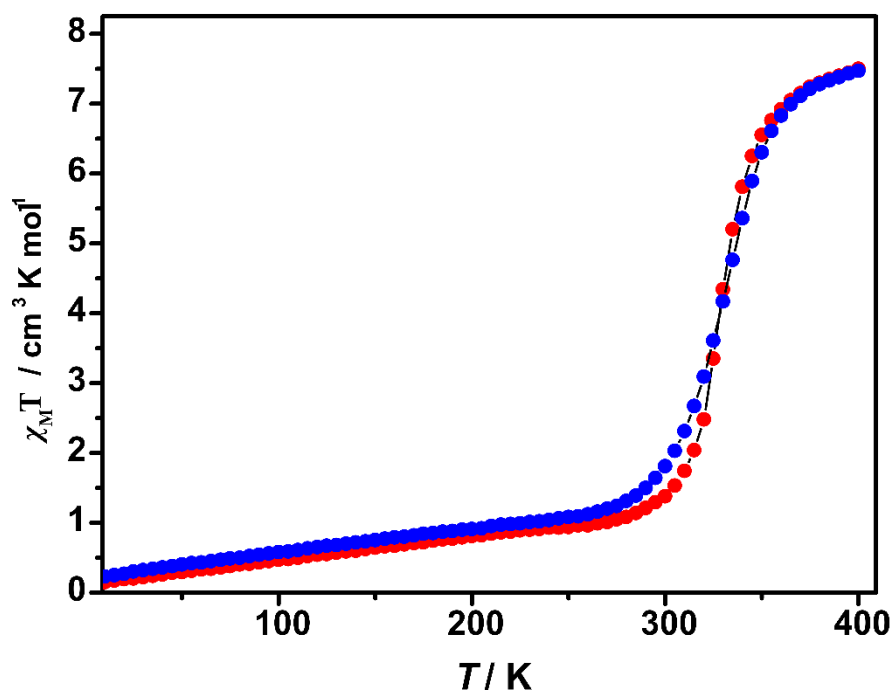


Figure S44: Temperature dependent $\chi_M T$ (T) of amorphous **Co-Cl₂cat** in heating (red) and cooling (blue) mode over the temperature range of 10–400 K, waiting 5 minutes at 400 K.

7. Chapter 4: Introducing Electronic Communication

In this chapter, the fourth adjustable parameter of the parent system is addressed: the aliphatic piperazine bridging unit of the redox-innocent ancillary ligand is replaced by an aromatic pyrazine group to introduce electronic communication between the two cobalt-dioxolene centres. The dinuclear complex incorporating the aliphatic piperazine bridge has demonstrated that a reversible and complete VT transition is achievable in a dinuclear framework, yet the two cobalt-dioxolene units switch simultaneously rather than stepwise, consistent with negligible electronic communication. Replacing the aliphatic linker with an aromatic pyrazine group is therefore intended to introduce genuine electronic coupling between the two metal centres, with the aim of promoting sequential, two-step VT behaviour in which the transition of one centre precedes and influences that of the other. Owing to the symmetry of the pyrazine ring, the linking positions are shifted to the 2- and 5-positions. Contributions to this study were made by [REDACTED] as part of her bachelor's thesis and a subsequent position as a research assistant.

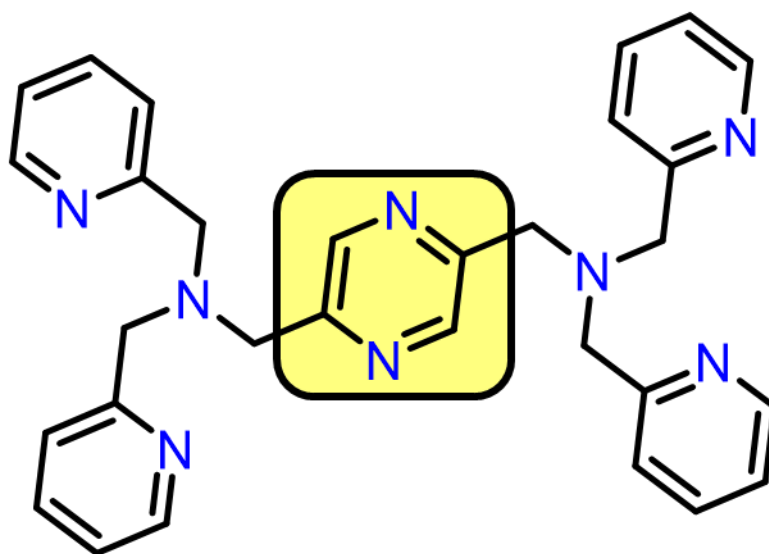


Figure 30: Structure of the redox-inactive pyrazine-bridged ancillary ligand employed in this chapter.

7.1 Ligand Synthesis

The new bis(tetradentate) pyrazine-bridged ligand 2,5-bis[*N,N*-bis(2-pyridylmethyl)aminomethyl]pyrazine (**L^{bpap}**) was synthesised following an adapted literature procedure. The original synthesis, shown at the top of the reaction scheme, involved bromination of 2,5-dimethylpyrazine via a Wohl-Ziegler reaction using carbon tetrachloride, followed by nucleophilic substitution with bis(2-pyridylmethyl)amine under basic conditions.¹ Due to the toxicity of carbon tetrachloride and the associated restrictions on its use in laboratory settings, an alternative four-step route was developed, as illustrated in the reaction scheme, drawing on literature-known procedures for the first two steps and the final step.²

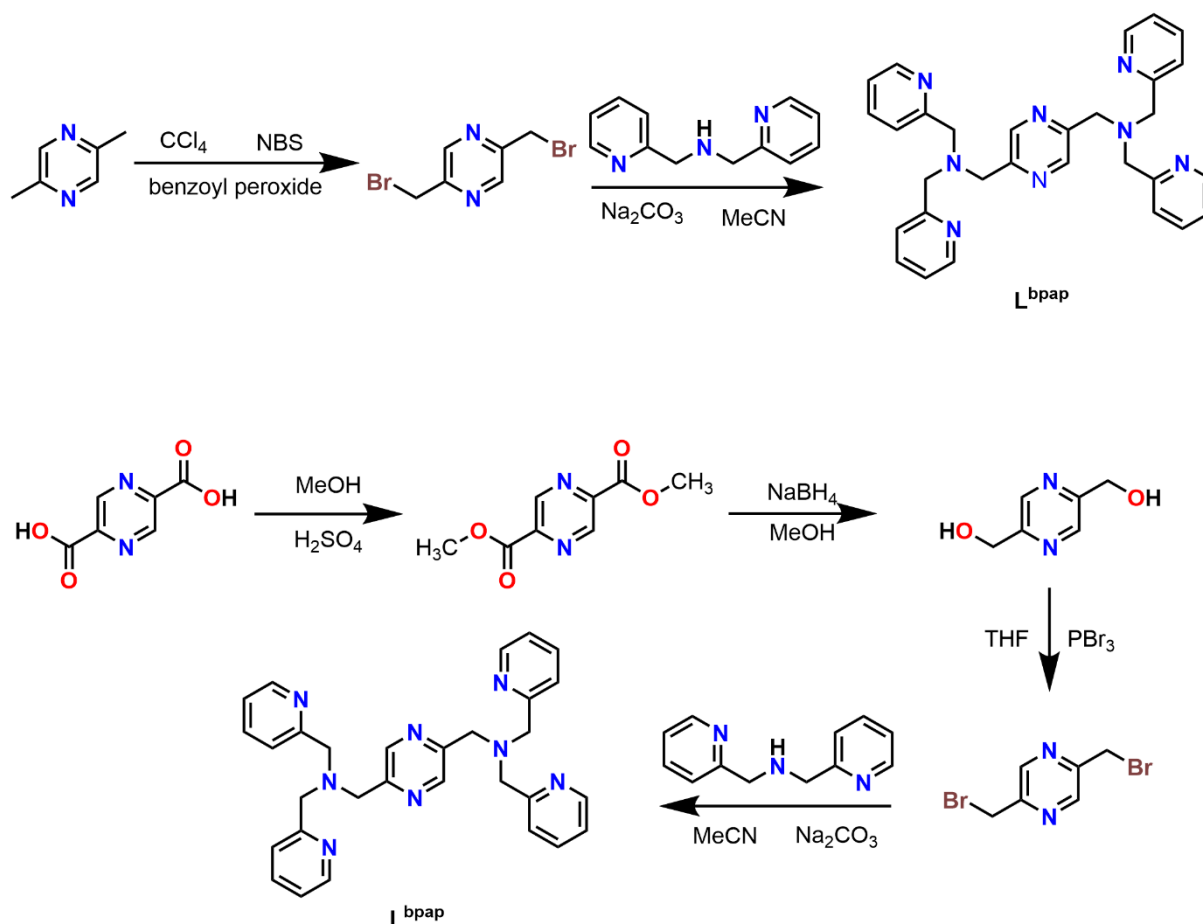


Figure 31: Comparison of the previously reported synthetic route (top) and the modified synthesis developed in this work (bottom).^{1,2}

In the first step, commercially available pyrazine-2,5-dicarboxylic acid was esterified under acidic conditions in methanol to give pyrazine-2,5-dicarboxylic acid dimethyl ester. Sulfuric acid served as the acid catalyst, and the reaction was carried out under reflux overnight. Upon cooling to room temperature, the desired product crystallised from solution as beige needles and was isolated in high yield.

In the second step, the diester was reduced to 2,5-bis(hydroxymethyl)pyrazine using sodium borohydride in methanol. The diester was suspended in methanol and sodium borohydride was added in small portions under ice-bath cooling. After stirring at room temperature overnight, the product was isolated by column chromatography.

In the third step, the hydroxymethyl groups were converted to the corresponding bromides using phosphorus tribromide in THF to give 2,5-bis(bromomethyl)pyrazine. Phosphorus tribromide was added dropwise to a solution of the diol in THF, and after stirring overnight the mixture was extracted with DCM and purified by two successive column chromatography steps to afford the product as colourless crystals.

In the final step, the target ligand was obtained by nucleophilic substitution of 2,5-bis(bromomethyl)pyrazine with bis(2-pyridylmethyl)amine, prepared according to a literature procedure.³ Bis(2-pyridylmethyl)amine was dissolved in acetonitrile with potassium carbonate as base, and 2,5-bis(bromomethyl)pyrazine was added as a solution in acetonitrile at reflux. The suspension was stirred at reflux overnight, and the product was isolated by column chromatography. The yield of this step was improved from 30% to 70% relative to the original procedure. All pre-ligand intermediates were characterised by IR and ^1H NMR spectroscopy. The final ligand was characterised by IR

spectroscopy, mass spectrometry, and ^1H , ^{13}C , COSY, HMBC, and HSQC NMR spectroscopy. Complete synthetic procedures, characterisation data, and spectroscopic details are provided in the experimental section.

7.2 Assessment of the Complexation Behaviour

To verify the complexation properties of the new pyrazine-based ligand (L^{bpap}), the neutral complex $\text{Co}_2(\text{L}^{\text{bpap}})(\text{SCN})_4$ ($\text{Co-L}^{\text{bpap-SCN}}$) was synthesised. For direct comparison, the analogous piperazine-based complex $\text{Co}_2\text{LH}(\text{SCN})_4$ (Co-LH-SCN) was prepared alongside. In both cases, each ligand was dissolved in DCM and a solution of Co(II) thiocyanate was layered on top using a 1:1 DCM/MeOH interlayer to slow diffusion and promote single-crystal growth. The obtained red single crystals were investigated by IR spectroscopy and single-crystal X-ray diffraction. Synthetic details are provided in the experimental section of this chapter.

To confirm the correct composition and complexation behaviour of the synthesised compounds, IR spectroscopy was employed. As both complexes contain thiocyanate ligands, a characteristic SCN stretching band is expected in the region of $2050\text{--}2100\text{ cm}^{-1}$. The IR spectra of both complexes and the free ligand are overlaid in **Figure 32**.

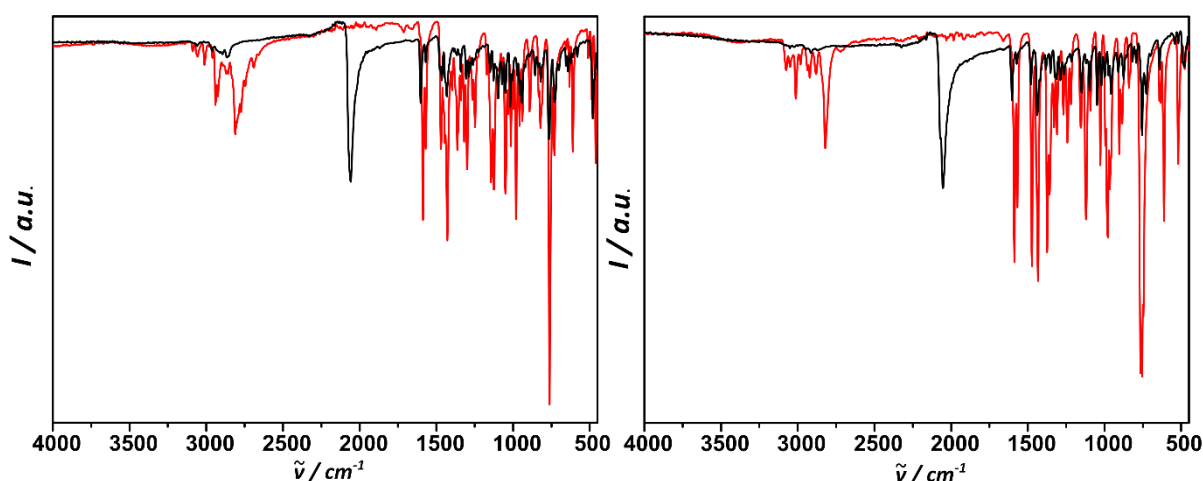


Figure 32: Left: Comparison of the IR spectra of the piperazine-based ligand **LH** (red, TH-AM-29) and complex **Co-LH-SCN** (black, TH-AM-9). Right: Corresponding IR spectra of the pyrazine-based ligand L^{bpap} (red, TH-6) and the complex **Co-L^{bpap}-SCN** (black, TH-443).

The band positions and shapes of the free ligand and the complexes are in good overall agreement. However, three distinctive differences are observed. First, the N-CH_2 stretching vibration shifts from 2810 cm^{-1} to 2861 cm^{-1} upon coordination for **Co-LH-SCN**, and analogously from 2820 cm^{-1} to 2872 cm^{-1} for **Co-L^{bpap}-SCN**. Second, nearly all C-H stretching bands shift to higher wavenumbers, and some bands become obscured upon coordination due to changes in intensity. Most significantly, a new band appears at 2058 cm^{-1} for **Co-LH-SCN** and at 2052 cm^{-1} for **Co-L^{bpap}-SCN**, assignable to the CN stretching mode of the coordinated thiocyanate.³¹ Together, these observations confirm the identity of both complexes as the desired cobalt thiocyanate species.

The crystal structures of both complexes are presented in **Figure 33**. **Co-L^{bpap}-SCN** crystallised without lattice solvent, whereas **Co-LH-SCN** crystallised with one disordered DCM molecule. Both crystal structures are monoclinic and centrosymmetric, **Co-L^{bpap}-SCN** crystallised in space group $C2/c$ and **Co-LH-SCN** crystallised in $C2_1/c$. In both cases, the asymmetric unit comprises half of the dinuclear complex, with an inversion centre located on the bridging unit. The unit cell of **Co-L^{bpap}-SCN** contains $Z = 4$ complexes, while **Co-LH-SCN** has $Z = 2$.

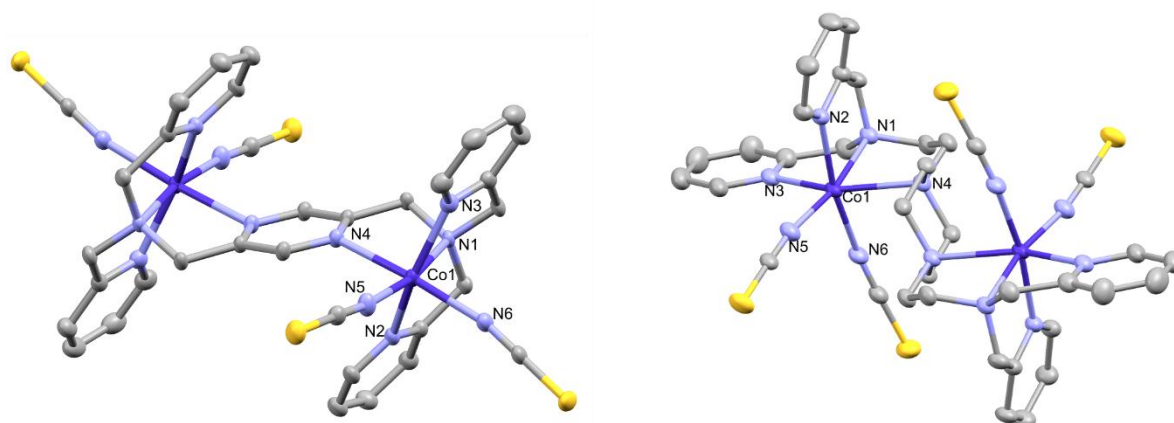


Figure 33: Crystal structures of the two complexes: **Co-L^{bpap}-SCN** and **Co-LH-SCN** (right). Hydrogen atoms and solvent molecules are omitted for clarity. The probability level for displacement of the ellipsoid is 50%. Atoms are displayed using the standard colour scheme (carbon: grey, nitrogen: light blue, cobalt: dark blue, sulfur: yellow).

The molecular structures of both complexes are closely related. Both are dinuclear cobalt complexes in which the two metal centres are coordinated by the corresponding bis(tetradentate) bridging ligand, with the coordination sphere at each cobalt centre completed by two terminal coordinating N-bound thiocyanate ligands, resulting in an N₆ coordination environment. Each cobalt is coordinated by two thiocyanate nitrogen atoms, two pyridyl nitrogen atoms from the bridging ligand arms, one tertiary amine nitrogen linking the pyridyl moieties to the bridging unit, and one nitrogen atom from the bridging heterocycle (pyrazine or piperazine). All cobalt centres adopt a distorted octahedral geometry, as reflected by SHAPE⁴ indices of 1.29 for **Co-LH-SCN** and 1.33 for **Co-L^{bpap}-SCN** (ideal octahedron: 0). The Co-N bond lengths in **Co-LH-SCN** range from 2.029 to 2.155 Å, with one significantly elongated Co-N bond of 2.407 Å attributed to the geometric constraints imposed by the piperazine unit. For **Co-L^{bpap}-SCN**, bond lengths range from 2.021 to 2.237 Å. Both sets of bond lengths are consistent with a HS Co(II) configuration.⁵

The thiocyanate ligands adopt a *cis* arrangement at each cobalt centre, but a *trans* orientation relative to the second cobalt site within the dinuclear complex. This arrangement is imposed by the bridging ligand geometry and minimises steric congestion between the two coordination spheres. In **Co-LH-SCN**, the aliphatic piperazine adopts a chair conformation, further reducing steric demand.

Co-L^{bpap}-SCN additionally exhibits intermolecular π - π interactions. As shown in **Figure 34**, the complexes stack along the *c*-axis in parallel rows, with π - π interactions between pyridyl fragments of neighbouring rows. The centroid-to-centroid distance is 3.63 Å, the inter-ring offset is 1.505 Å, and the rings are inclined at 2.38°.

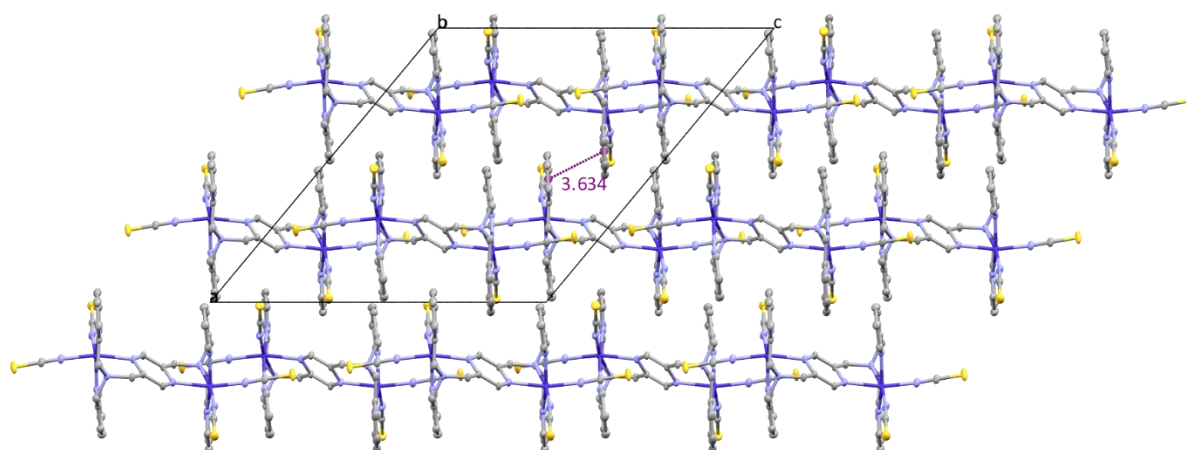


Figure 34: Crystal structure of **Co-L^{bpa}-SCN** shown in projection onto the *ac* plane, illustrating π - π stacking interactions.

In contrast, **Co-LH-SCN** shows no intermolecular interactions. As illustrated in **Figure 35**, the complexes pack as isolated units with disordered DCM solvent molecules occupying the intervening cavities.

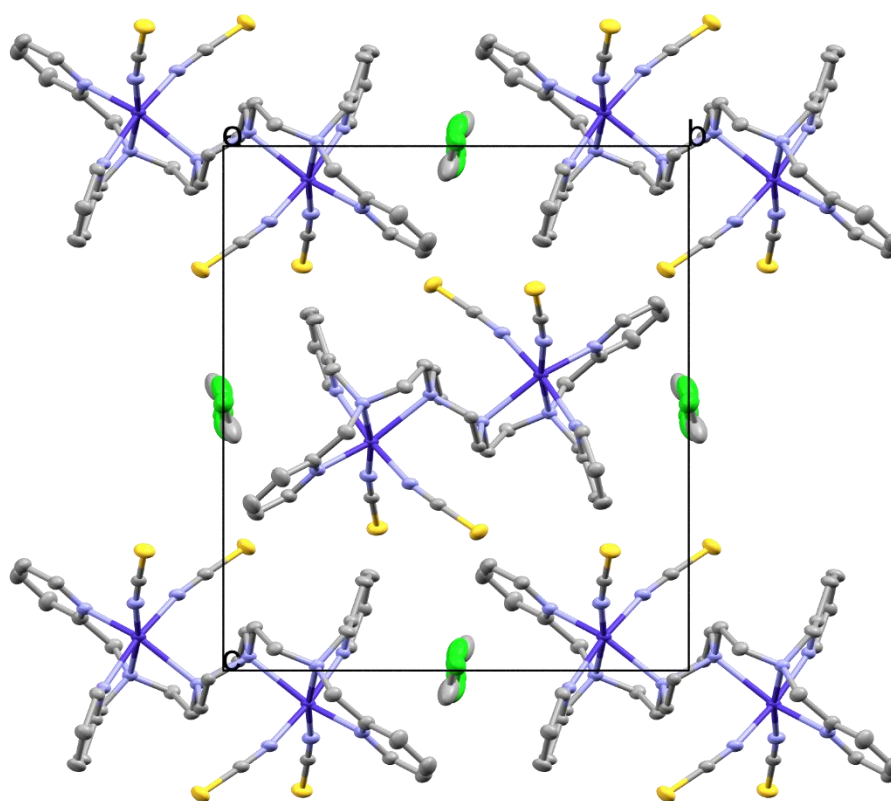


Figure 35: Crystal structure of **Co-LH-SCN** shown in projection onto the *bc*-plane, illustrating the isolated complexes.

The planar aromatic pyrazine unit thus facilitates parallel stacking and enhances intermolecular cooperativity relative to the aliphatic piperazine analogue, which is anticipated to promote valence tautomeric transitions in the target complex system. All bond lengths, angles, and crystallographic parameters are listed in the supplementary information to this chapter.

7.3 Reaction Conditions

Having established the coordination behaviour of L^{bpap} , synthesis of the target complex $[Co_2(L^{bpap})(dbcac)_2]SO_4$ was attempted. Following the procedure of M. Diehl⁶, the ligand L^{bpap} was dissolved together with 3,5-di-*tert*-butylcatecholate and Co(II) sulfate heptahydrate, triethylamine was added to deprotonate the catecholate, and the mixture was refluxed for one hour. The complex was isolated as green crystals after three days of slow evaporation under ambient conditions. Subsequent XRD structure analysis and mass spectrometry revealed that the desired complex had not been obtained under these conditions. Instead, the insertion product $Co_2(L^{bpap}-(dbcac)_2)(SO_4)_2$ was formed, in which the catecholate moieties had undergone formal insertion into the CH_2 groups connecting the pyrazine ring to the tertiary amine.

Interestingly, an analogous side reaction occurs with the piperazine-based ligand **LH** under ambient conditions, although in that case only a single oxygen atom formally inserts into the CH bonds of the methylene group. A further distinction is that with L^{bpap} the insertion is consistently complete, yielding exclusively the doubly catecholated product, whereas with **LH** the reaction yields a statistical mixture of unmodified, mono-inserted, and doubly inserted products with no selectivity. This behaviour may be attributed to the more electron-withdrawing nature of the pyrazine bridge compared to the piperazine analogue.

Both complexes resulting from the insertion reaction are shown in **Figure 36**. Both crystallise in the monoclinic centrosymmetric space group $C2/c$, with the asymmetric unit comprising half the complex and an inversion centre on the bridging heterocycle, and both have $Z = 4$ molecules per unit cell. Both structures contain extensively disordered lattice solvent methanol molecules. The piperazine analogue additionally exhibits disorder at the *tert*-butyl groups, which was not observed for $Co_2(L^{bpap}-(dbcac)_2)(SO_4)_2$.

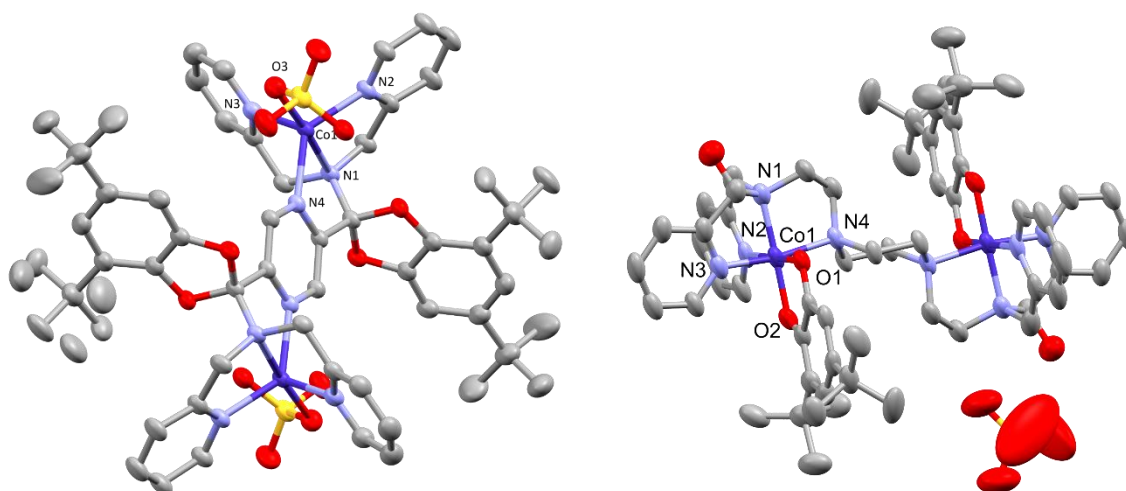


Figure 36: Crystal structures of the two complexes: $Co_2(L^{bpap}-(dbcac)_2)(SO_4)_2$ (left) and $Co-LH-OH-dbcac-SO_4$ (right). Hydrogen atoms and solvent molecules are omitted for clarity. The probability level for displacement of the ellipsoid is 50%. Atoms are displayed using the standard colour scheme (carbon: grey, nitrogen: light blue, cobalt: dark blue, sulfur: yellow).

In both complexes a distorted N_4O_2 coordination environment is present. In $Co_2(L^{bpap}-(dbcac)_2)(SO_4)_2$ the coordination sphere is completed by a coordinating sulfate anion, yielding a neutral complex with no counter anions. In $Co-LH-OH-dbcac-SO_4$, by contrast, the coordination sphere is completed by a coordinated catecholate, and a free sulfate counter anion is present, making it a cationic complex.

$Co_2(L^{bpap}-(dbcac)_2)(SO_4)_2$ adopts a severely distorted trigonal prismatic geometry with a SHAPE⁴ value of 8.07, while $Co-LH-OH-dbcac-SO_4$ is nearly ideally octahedral (SHAPE = 0.28; ideal octahedron:0).⁴ $Co_2(L^{bpap}-(dbcac)_2)(SO_4)_2$ exhibits Co-N bond lengths between 2.058 and 2.277 Å, consistent with HS Co(II)⁷, while $Co-LH-OH-dbcac-SO_4$ shows shorter Co-N bonds of 1.919 to 1.948 Å, with one elongated

bond of 2.047 Å attributed to piperazine distortion, consistent with LS Co(III).⁸ In both cases the dioxolene is in the catechol oxidation state, as indicated by the metric oxidation state (MOS) values of -2.4 and -1.96 for **Co₂(L^{bpap}-(dbcat)₂)(SO₄)₂** and **Co-LH-OH-dbcac-SO₄**, respectively. The slight deviation from -2 in the latter is attributed to the dioxolene not being coordinated to a metal centre. However, the aromatic character of the bond lengths was confirmed in the crystal structure.⁹ In both cases the catecholates are disposed in a *trans* arrangement to minimise steric strain.

No π - π interactions are observed in either structure. For **Co-LH-OH-dbcac-SO₄**, solvent and anion channels are present between rows of complexes as seen in **Figure 37**. The large displacement ellipsoids of the sulfate oxygen atoms preclude a definitive assignment of hydrogen-bonding interactions between the hydroxyl group and the sulfate anion.

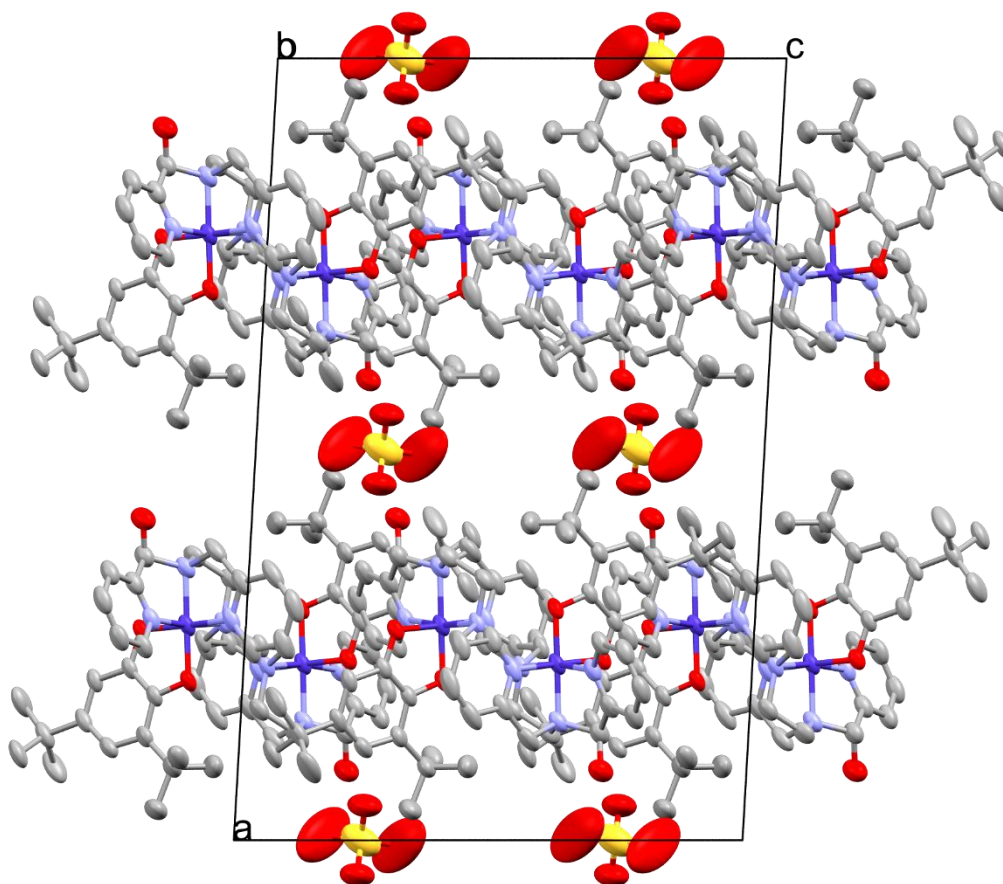


Figure 37: Crystal structure of **Co-LH-OH-dbcac** shown in projection onto the *ac*-plane, illustrating the anion and solvent molecule channels between rows of parallel complexes.). Hydrogen atoms and solvent molecules are omitted for clarity.

For **Co₂(L^{bpap}-(dbcat)₂)(SO₄)₂**, the *ac* plane projection (**Figure 38**) similarly shows rows of non-interacting complexes but with empty voids between them. The lattice solvent methanol molecules are arranged around the coordinated sulfate ligand with a similar degree of disorder.

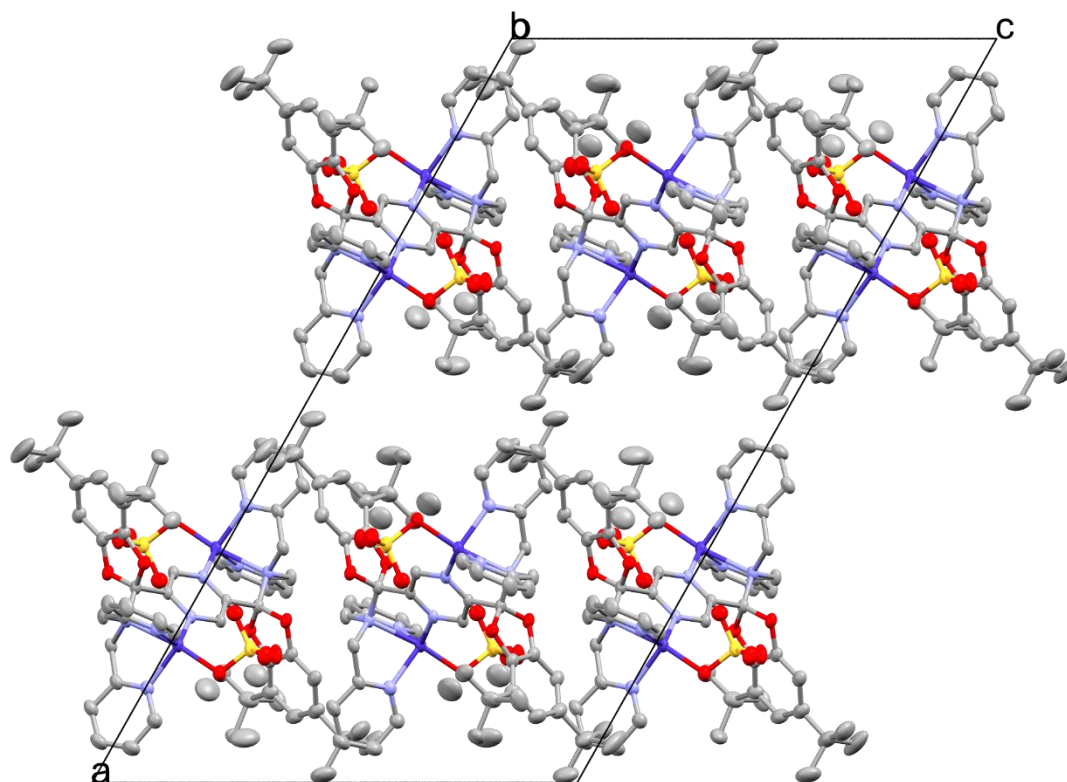


Figure 38: Crystal structure of $\text{Co}_2(\text{L}^{\text{bpop}}-(\text{dbcat})_2)(\text{SO}_4)_2$ shown in projection onto the ac -plane, illustrating empty channels between rows of parallel complexes. Hydrogen atoms and solvent molecules are omitted for clarity.

In both structures, a hydrogen-bonding network between lattice solvent methanol and the sulfate anion is observed (**Figure 39**), and no further intermolecular interactions beyond hydrogen bonding are present.

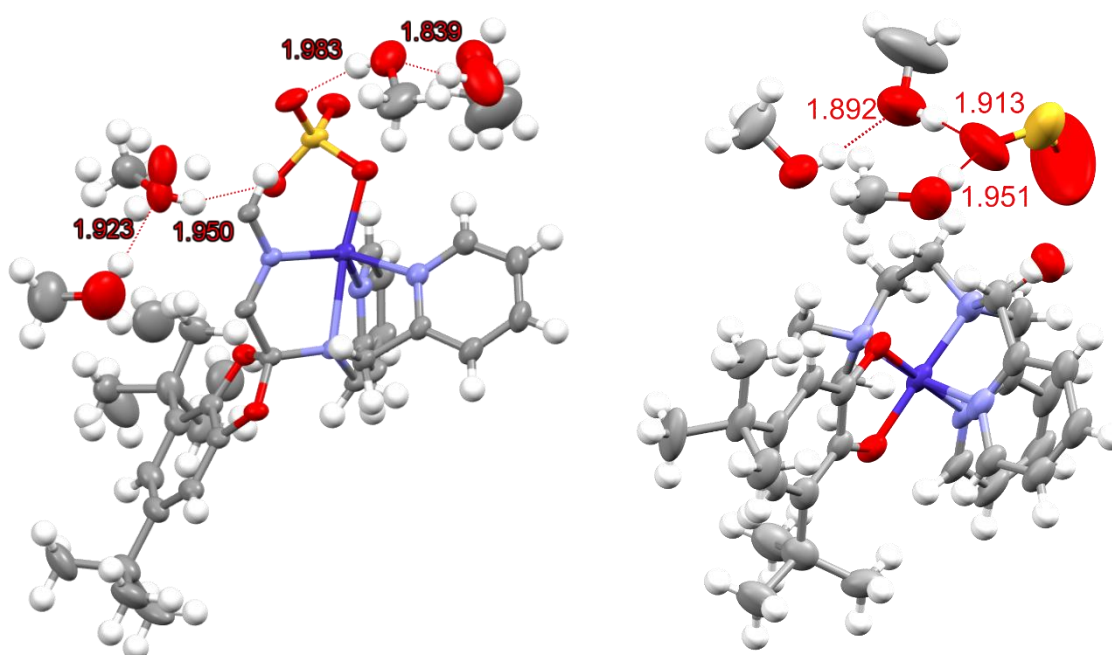


Figure 39: Crystal structures of the two complexes: $\text{Co}_2(\text{L}^{\text{bpop}}-(\text{dbcat})_2)(\text{SO}_4)_2$ (left) and $\text{Co-LH-OH-dbcat-SO}_4$ (right). The probability level for displacement of the ellipsoid is 50%. Atoms are displayed using the standard colour scheme (carbon: grey, nitrogen: light blue, cobalt: dark blue, sulfur: yellow). Illustrating the H-Bonding network.

The degree of insertion is also in agreement with ESI⁺ mass spectrometry. $\text{Co}_2(\text{L}^{\text{bpap}}\text{-(dbcac)}_2)(\text{SO}_4)_2$ was detected as the sodium adduct $[\text{Co}_2(\text{L}^{\text{bpap}}\text{-(dbcac)}_2)(\text{SO}_4)_2 + \text{Na}]^+$ at $m/z = 1271.279$ (calc. 1271.280) and as the dimeric sodium adduct $[2(\text{Co}_2(\text{L}^{\text{bpap}}\text{-(dbcac)}_2)(\text{SO}_4)_2) + \text{Na}]^+$ at $m/z = 2520.571$ (calc. 2520.574). The absence of peaks corresponding to the mono-inserted or uninserted species, together with 100% occupancy in the XRD structure, confirms quantitative insertion for L^{bpap} . For $\text{Co-LH-OH-dbcac-SO}_4$ the mass spectrum presents a different picture, with simultaneous observation of the unmodified $[\text{Co-LH}]^{2+}$ at $m/z = 547.248$ (calc. 547.248), the mono-hydroxylated species $[\text{Co-LH-OH}]^{2+}$ at $m/z = 555.244$ (calc. 555.245) and the doubly-hydroxylated species $[\text{Co-LH-(OH)}_2]^{2+}$ at $m/z = 563.248$ (calc. 563.243), as shown in **Figure 40**.

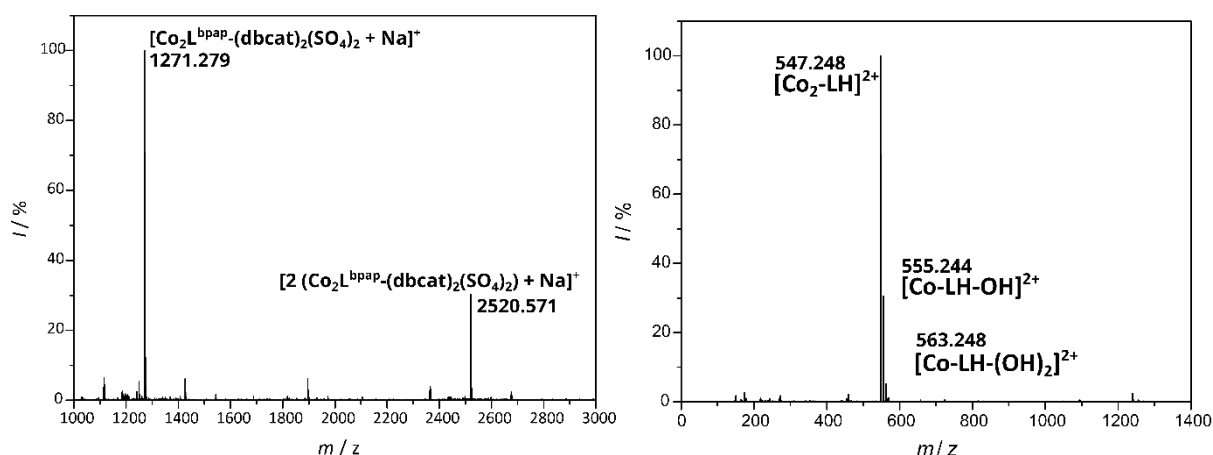


Figure 40: ESI⁺-MS spectra of $\text{Co}_2(\text{L}^{\text{bpap}}\text{-(dbcac)}_2)(\text{SO}_4)_2$ (left) and of $\text{Co-LH-OH-dbcac-SO}_4$ (right) showing the degree of insertion.

Performing the coordination reaction with LH under strictly anhydrous and inert conditions yielded the pure uninserted complex (**Figure 41**).

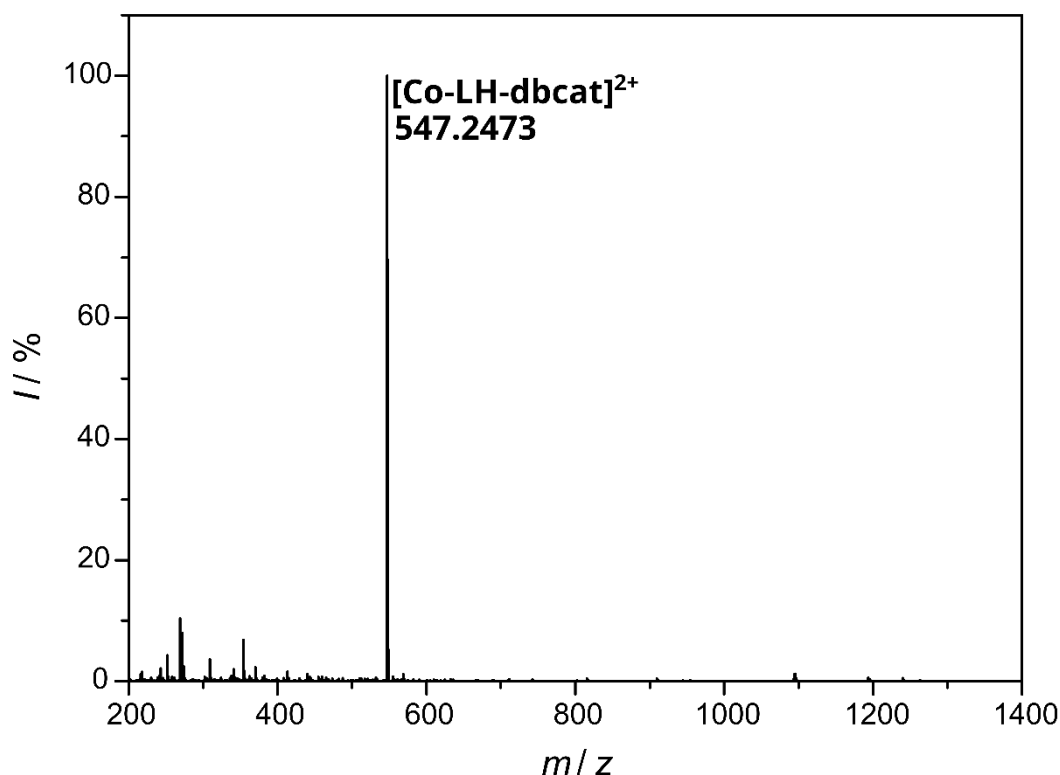


Figure 41: ESI⁺-MS of Co-LH-dbcac obtained from a reaction carried out under anhydrous and inert atmospheric conditions.

Notably, for the piperazine analogue the coordination reaction required inert conditions, while crystallisation could be carried out aerobically. For the pyrazine-based target system, by contrast, both reaction and crystallisation had to be conducted under strictly anaerobic and anhydrous conditions, as exposure to water and air during crystallisation also triggered the insertion reaction.

7.4 [Co₂(L^{bpap})(dbcat)₂] (PF₆)₂ / (BPh₄)₂

The desired complex was synthesised as the hexafluorophosphate and tetraphenylborate salts. The coordination reaction was carried out under strictly anaerobic and anhydrous conditions to suppress the insertion side reaction. As the complex proved unstable in aerated solution, crystallisation was likewise conducted under inert conditions.

Anhydrous Co(II) chloride, dried with thionyl chloride prior to use, was employed throughout. All synthetic steps were carried out in a glovebox. 3,5-Di-*tert*-butylcatecholate and L^{bpap} were dissolved in dry, degassed methanol. A solution of anhydrous Co(II) chloride in dry, degassed methanol was added dropwise with stirring, followed by dry, degassed triethylamine. Ferrocenium tetraphenylborate or ferrocenium hexafluorophosphate (both prepared according to literature procedures^{10,11}) was then added as a solid. The tetraphenylborate salt precipitated immediately, while the hexafluorophosphate remained in solution. Crystals of Co-L^{bpap}-BPh₄ were obtained by redissolving the precipitate in dichloromethane and layering with diethyl ether after four days. Crystals of Co-L^{bpap}-PF₆ were grown by slow evaporation under an inert atmosphere in the glovebox over four days. Slow evaporation under aerobic conditions yielded the insertion product instead.

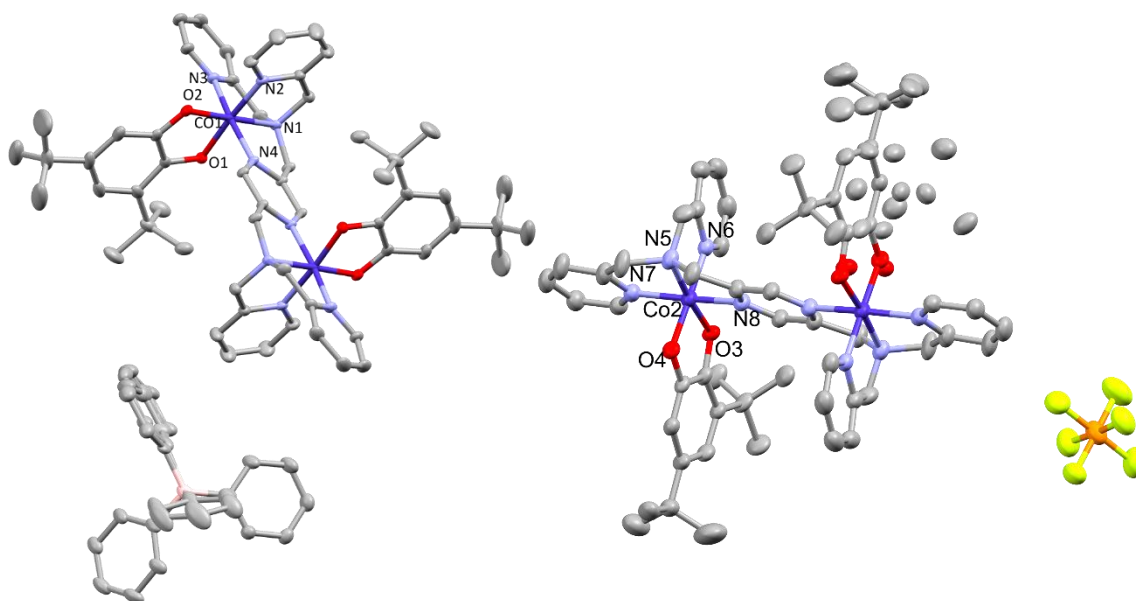


Figure 42: Crystal structures of the two complexes: Co-L^{bpap}-BPh₄ (left) and Co-L^{bpap}-PF₆ (right). Hydrogen atoms and solvent molecules are omitted for clarity. The probability level for displacement of the ellipsoid is 50%. Atoms are displayed using the standard colour scheme (carbon: grey, nitrogen: light blue, cobalt: dark blue, boron: pink, phosphorus: orange, fluorine: light green).

Co-L^{bpap}-BPh₄ crystallised in the monoclinic centrosymmetric space group *P*2₁/*n*, while Co-L^{bpap}-PF₆ crystallised in the triclinic centrosymmetric space group *P*-1. Both complexes possess an inversion centre on the pyrazine moiety. The asymmetric unit of Co-L^{bpap}-BPh₄ contains one half of a single complex cation, while that of Co-L^{bpap}-PF₆ contains two independent half-complexes. Both structures have *Z* = 2. Lattice solvent is disordered in both cases. Co-L^{bpap}-BPh₄ contains ten lattice dichloromethane molecules, while Co-L^{bpap}-PF₆ contains four lattice methanol molecules. In the latter, the 3,5-di-*tert*-butylcatecholate ligand additionally exhibits positional disorder.

Both complexes are dinuclear and are coordinated by the bis(tetradentate) pyrazine-based bridging ligand. The two remaining coordination sites at each cobalt centre are occupied by the dioxolene ligand, giving a N_4O_2 coordination motif. Each cobalt centre is coordinated by two *ortho*-oxygen atoms of the dioxolene ligand, two pyridyl-nitrogen atoms from the pyridine arms of the bridging ligand, one tertiary amine nitrogen atom connecting the pyridyl moieties to the bridging unit, and one nitrogen atom from the bridging pyrazine. The cobalt centres adopt near-ideal octahedral geometries in both cases, as indicated by the low SHAPE values of 0.185 for **Co-L^{bpap}-BPh₄** and 0.171 for **Co-L^{bpap}-PF₆**.⁴ Co-N bond lengths range from 1.908–1.956 Å for **Co-L^{bpap}-PF₆** and 1.914–1.955 Å for **Co-L^{bpap}-BPh₄**, consistent with LS Co(III) bond lengths reported in literature.¹² Metric oxidation state values of -1.95 for both complexes confirms that the dioxolene ligands are in the catecholate oxidation state at 120 K.⁹ Both complexes exist as isolated, non-interacting units in the solid state, as is evident from the packing motifs shown in **Figure 43** and **Figure 44**. Single crystal X-ray analysis at 120 K thus establishes that both complexes adopt the diamagnetic LS Co(III)cat ground state. All bond lengths, angles, and crystallographic parameters are provided in the supplementary section to this chapter.

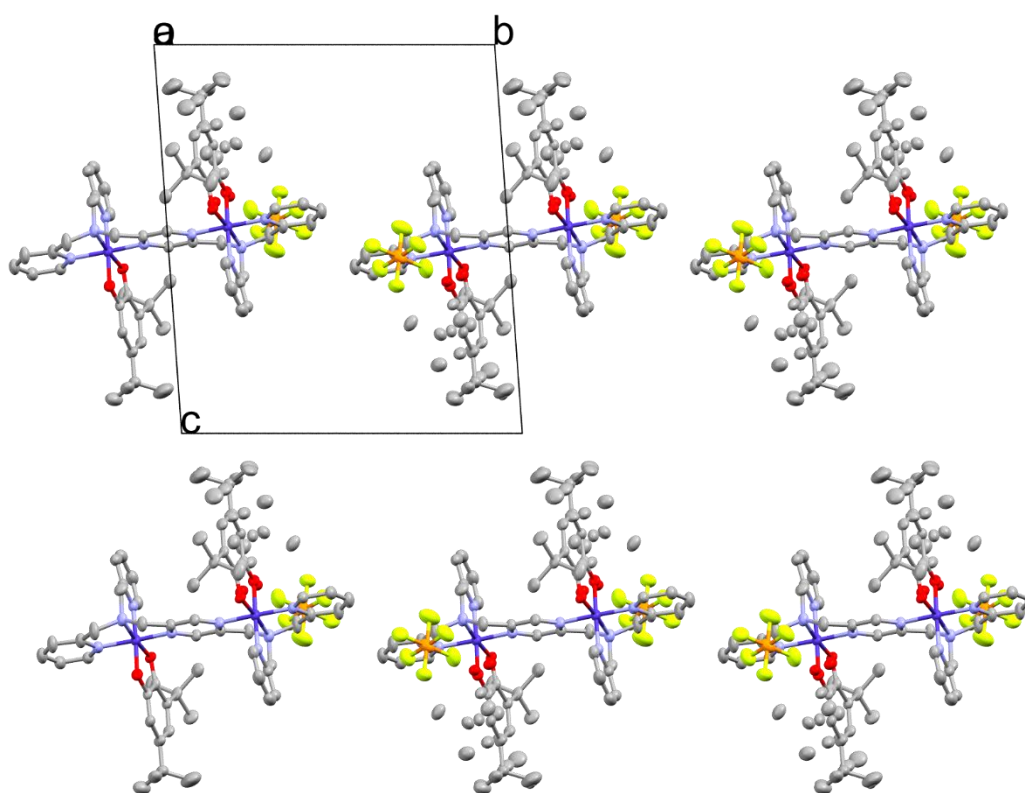


Figure 43: Crystal structure of **Co-L^{bpap}-PF₆** shown in projection onto the *bc*-plane, illustrating the isolated complexes. Hydrogen atoms and solvent molecules are omitted for clarity.

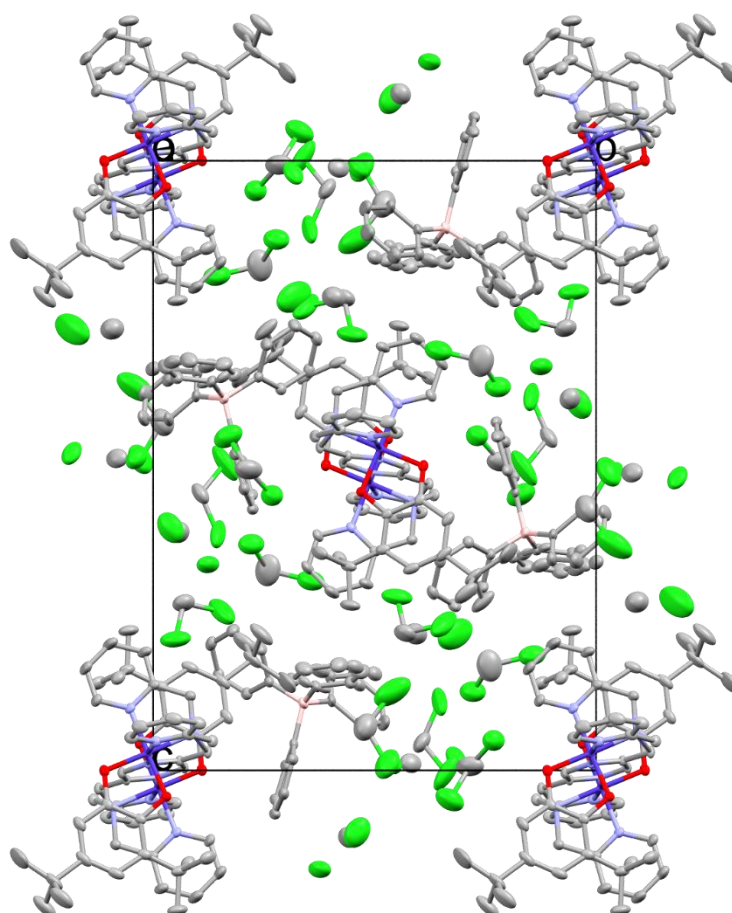


Figure 44: Crystal structure of $\text{Co-L}^{\text{bpop}}\text{-BPh}_4$ shown in projection onto the bc -plane, illustrating the isolated complexes with DCM molecules. Hydrogen atoms are omitted for clarity.

ESI⁺ mass spectrometry confirmed the identity of the complex (**Figure 45**). The observed isotope pattern matches the calculated distribution. The doubly charged fragment was detected at $m/z = 530.2087$ (calc. 530.2087).

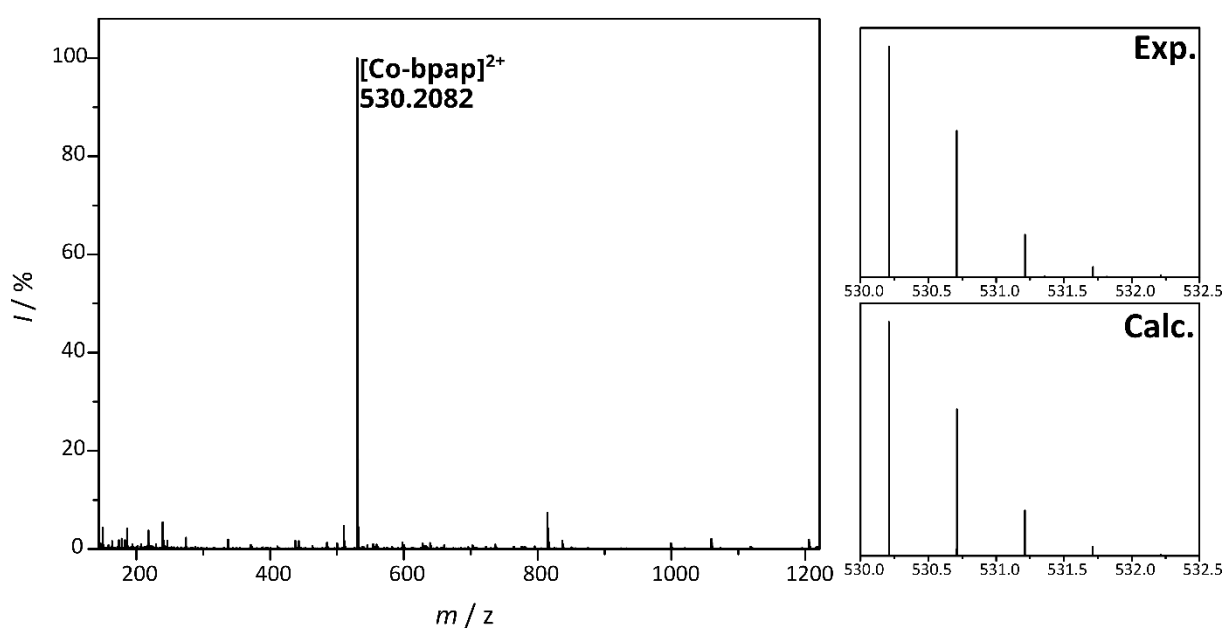


Figure 45: ESI⁺-MS of $\text{Co-L}^{\text{bpop}}\text{-PF}_6$ in MeCN with a comparison of the isotopic peak pattern of the monocationic peak at $m/z = 530.2082$ with the calculated one. (TH-AM-93)

To probe the electronic structure in solution, free from solid-state packing effects, electronic absorption spectra were recorded in acetonitrile at room temperature (**Figure 46**).

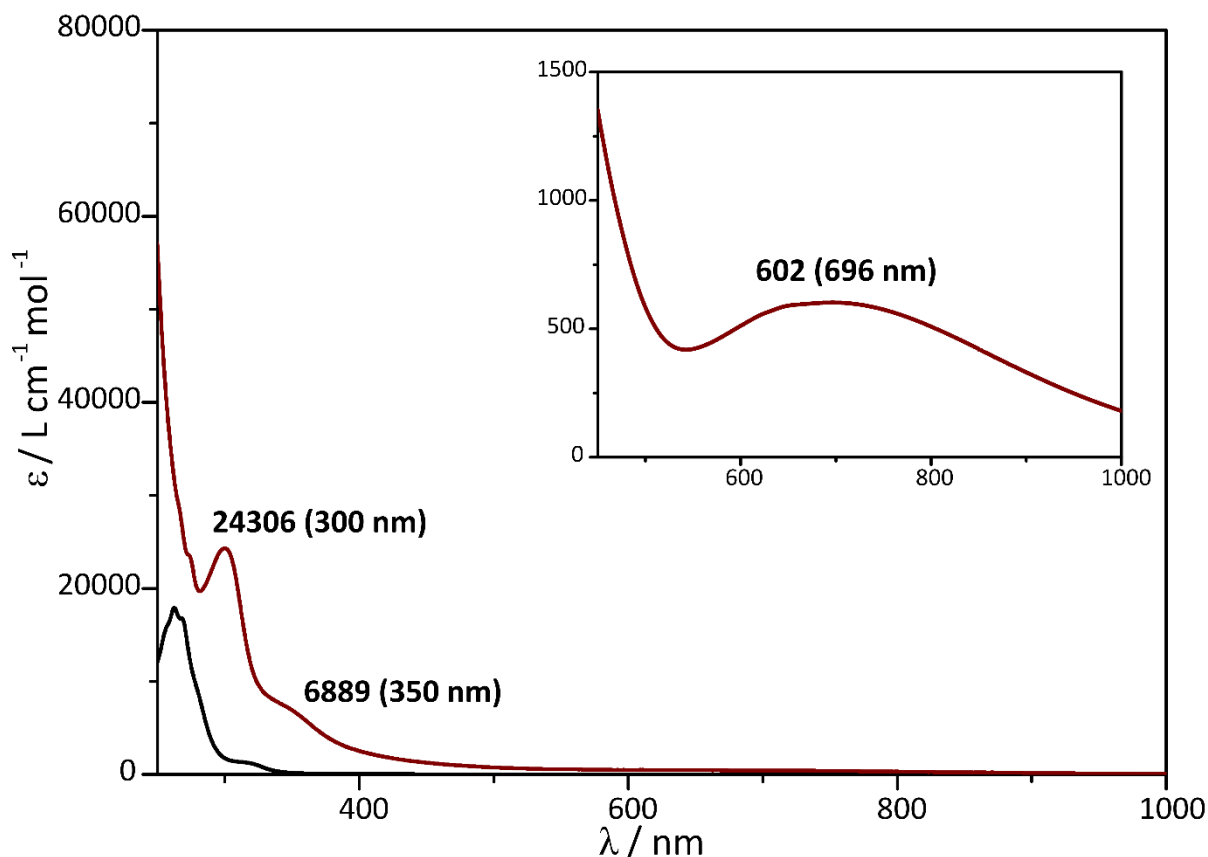


Figure 46: UV-Vis absorption spectra for acetonitrile solutions of **Co-L^{bpa}-BPh₄** (red) 0.02 mM with a zoomed-in section from 450 nm to 1000 nm at 0.9 mM with the absorption spectrum of **L^{bpa}** (black) 0.05 mM.

The spectrum is characteristic of LS Co(III)cat species as reported in the literature.¹³ A band at 300 nm ($\epsilon = 24306 \text{ L mol}^{-1}\text{cm}^{-1}$) is assigned to $\pi\text{-}\pi^*$ transitions of the coordinated ligand, red-shifted from 262 nm ($\epsilon = 17903 \text{ L mol}^{-1}\text{cm}^{-1}$) of the free ligand, due to coordination to the metal centre. A shoulder at 350 nm ($\epsilon = 6889 \text{ L mol}^{-1}\text{cm}^{-1}$) is tentatively assigned to a LMCT transition.^{14,15} However, as a corresponding feature is also present in the free ligand spectrum at 316 nm ($\epsilon = 1256 \text{ L mol}^{-1}\text{cm}^{-1}$), a contribution from an intraligand transition (pyrazine/pyridine) cannot be excluded. A broad, weak band at 696 nm ($\epsilon = 602 \text{ L mol}^{-1}\text{cm}^{-1}$) is assigned to a symmetry-forbidden LMCT transition characteristic of LS Co(III)cat species, as described by literature.¹⁶

In **Figure 47**, the LMCT bands of **Co-L^{bpa}-BPh₄** are compared with those of the piperazine-based complex **Co-LH-dbcac-ClO₄**.¹²

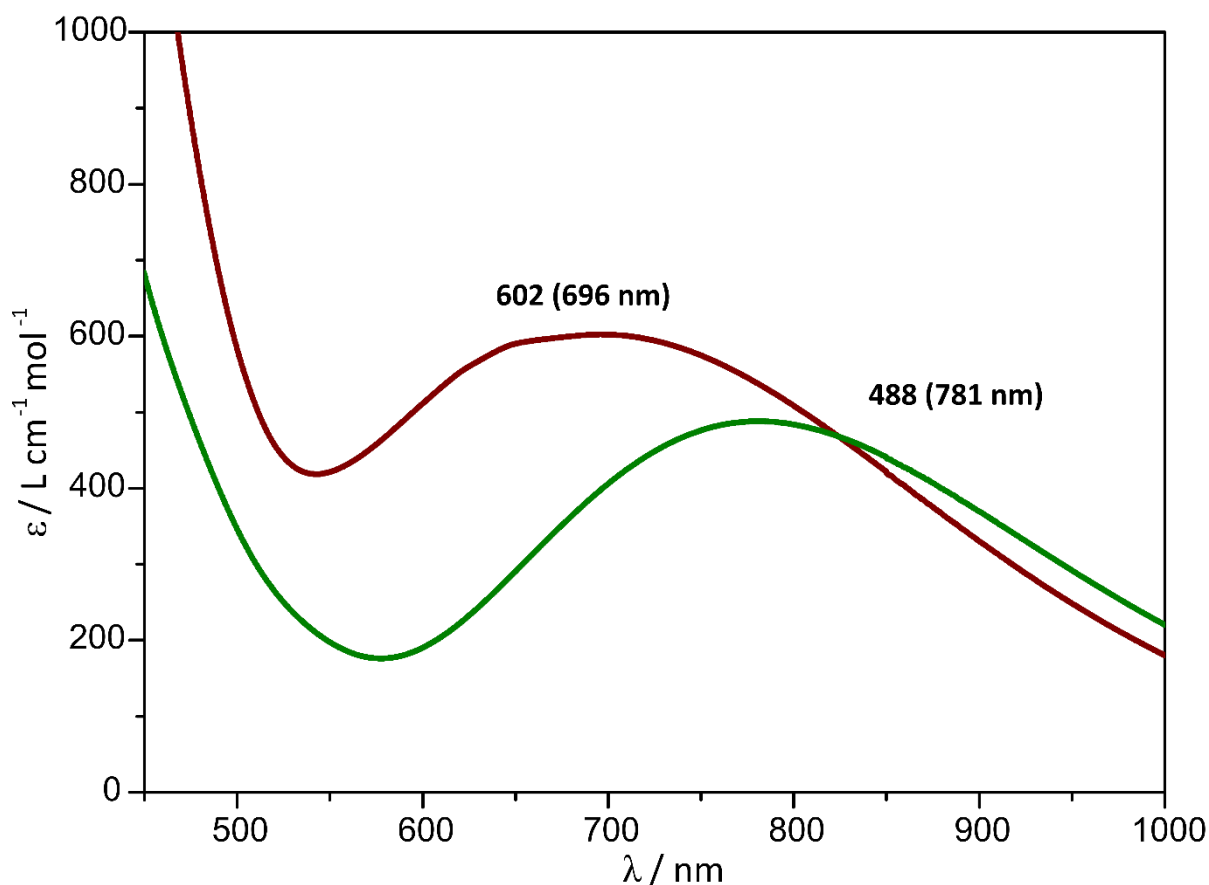


Figure 47: UV-Vis absorption spectra for acetonitrile solutions of **Co-bpap-BPh₄** (red) 0.9 mM and **Co-LH-dbcats-SO₄** (green) 1mM.

As the LMCT transition reflects electron density transfer from the catecholate ligand to the cobalt centre, its energy is directly related to the intramolecular electron-transfer process underlying valence tautomerism and thus serves as an indicator of the energetic separation between the tautomeric states. The LMCT band of **Co-L^{bpap}-BPh₄** is blue-shifted relative to **Co-LH-dbcats-SO₄** (696 nm vs. 781 nm), suggesting a larger energetic gap between the tautomeric states and therefore a less thermally accessible VT transition.^{17,18}

The cyclic voltammetry data provide complementary insights into the energetic accessibility of the tautomeric states. The separation between the Co(II)/Co(III) and cat²/sq[•] redox potentials serves as an approximate measure of the activation barrier for intramolecular electron transfer, where a smaller separation generally indicates a lower barrier for VT.¹⁸

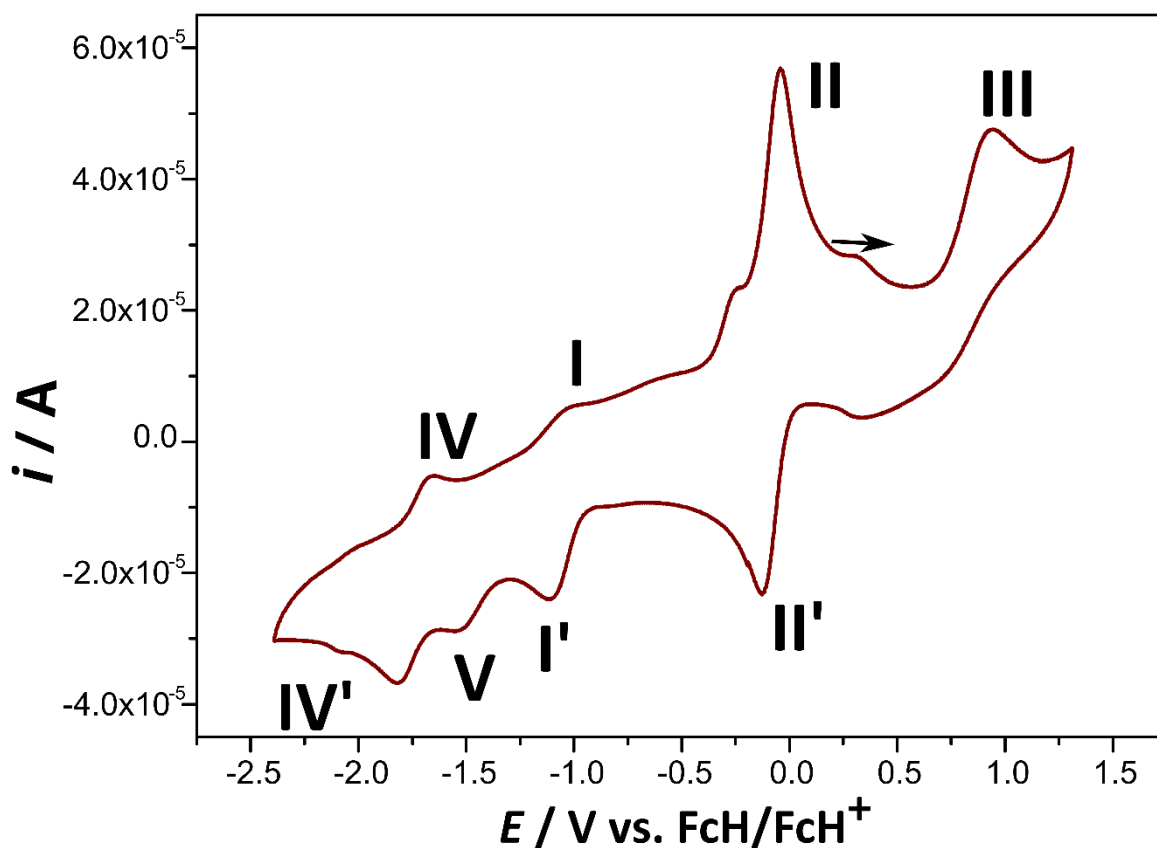


Figure 48: Cyclic voltammogram for $\text{Co-L}^{\text{bpap}}\text{-PF}_6$ (1 mM with 0.1 M $n\text{-Bu}_4\text{PF}_6$ in acetonitrile obtained with a scan rate of 0.1 Vs^{-1} , with a glassy carbon electrode, a silver / silver nitrate reference electrode, platinum counter electrode, referenced internally against the redox pair ferrocene / ferrocenium.)

Half-wave potentials (E_m) and peak-to-peak separations (ΔE_p) are compiled in **Table 3**, together with peak potentials (E_p) for irreversible processes, and compared to the previously reported **Co-LH-dbcac-ClO₄**.⁸

Table 3: CV data for reported **Co-LH-dbcac-ClO₄** and **Co-L^{bpap}-PF₆** in MeCN referenced against Fc/Fc^+ . (E_m is the experimentally determined average potential between the potentials of the corresponding anodic and cathodic events of a reversible or quasi-reversible electrochemical event, while E_p is the peak potential of an irreversible electrochemical event), E_m or E_p/V ($\Delta E_p/\text{mV}$).

Compound	I/I'	II/II'	III	IV	V	$\Delta \text{I/I}' - \text{II/II}'$
Co-bpap-PF₆	-1.065 (68)	-0.081 (83)	0.94	-1.74 (170)	-1.52	0.984
Co-LH-dbcac-ClO₄	-1.022(147)	-0.027(91)	1.07			0.995

The cyclic voltammogram resembles those of related compounds.⁸ Two distinct redox processes (**I/I'**) and (**II/II'**) are observed, corresponding to the $\text{Co(II)}/\text{Co(III)}$ and $\text{cat}^{2-}/\text{sq}^{\bullet-}$ redox couples, respectively, assigned according to literature precedent.^{8,14,19} Both processes are quasi-reversible, as evidenced by the scan-rate-dependent peak divergence and peak separation exceeding the theoretical 59 mV expected for a fully reversible one-electron process (**Figure 49**).²⁰ The third process (**III**) is irreversible and assigned to the oxidation of the semiquinonate radical anion to the benzoquinone form.^{5,7,8} The irreversibility arises from the poor coordination ability of the benzoquinone oxidation state, which frequently leads to ligand dissociation and complex decomposition.¹⁴

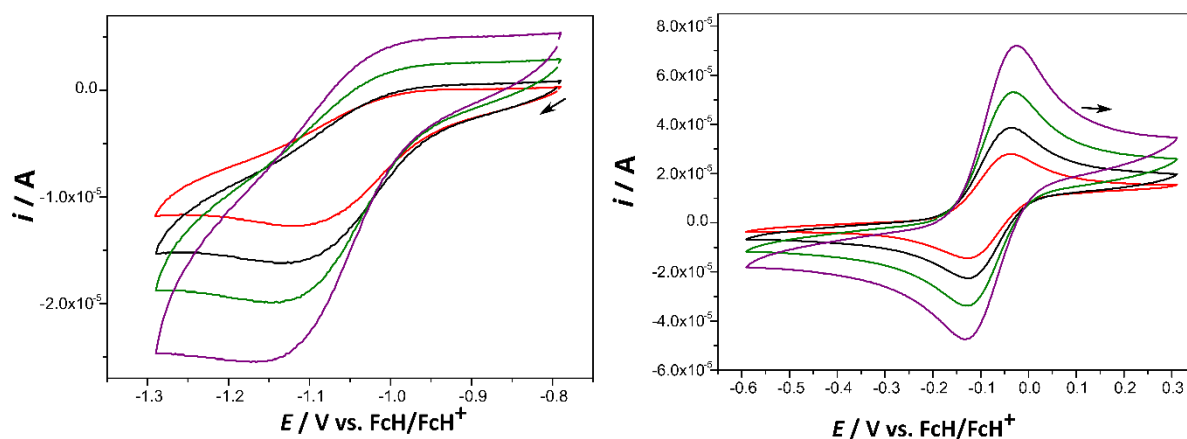


Figure 49: Cyclic voltammogram of **Co-L^{bpaP}-PF₆** in acetonitrile (1 mM, 0.1 M *n*-Bu₄PF₆) obtained with different scan rates (50 mV s⁻¹ (red), 100 mV s⁻¹ (black), 150 mV s⁻¹ (green), 200 mV s⁻¹ (purple)) of redox processes (I/I') left and (II/II') right, measured with a glassy carbon working electrode and a silver / silver nitrate reference electrode, referenced internally against the redox pair of Fc/Fc⁺.

The irreversible features flanking processes (II/II') and process (V) are attributed to redox events at more extreme potentials, as these features are absent in the scan-rate studies. Process (IV) occurs at a strongly cathodic potential, is absent in the piperazine-based complex, and is tentatively assigned to a ligand-centred reduction of the pyrazine ring

Comparison of the two complexes reveals closely similar redox potentials. The energy difference ($\Delta I/I' - II/II'$) is 984 mV for **Co-L^{bpaP}-PF₆** and 995 mV for **Co-LH-dbcac-ClO₄**, indicating a marginally lower activation barrier for the pyrazine-based system.

At first glance, the hypsochromic shift of the LMCT band appears inconsistent with the slightly reduced separation of the metal- and ligand-centred redox processes observed in the cyclic voltammogram. However, both techniques probe different aspects of the electronic structure. The LMCT transition reflects the energy required for a vertical excitation from the LS Co(III)cat ground state into an excited charge-transfer state and therefore does not directly correspond to the energy of the thermally accessible HS Co(II)sq valence tautomer. Following photoexcitation, the system undergoes a series of relaxation processes, before reaching the corresponding valence-tautomeric state, if it reaches that state at all. In contrast, the separation of the metal- and ligand-based redox couples obtained from cyclic voltammetry provides a more direct measure of the thermodynamic energy difference between the involved redox states and, consequently, of the driving force for intramolecular electron transfer. Therefore, a higher-energy LMCT transition can coexist with a smaller electrochemical energy gap across different complex systems without representing a contradiction.^{17,21,22}

To probe the VT transition directly in solution, the Evans method was employed. In this technique, a capillary of pure solvent is co-inserted into an NMR tube containing the complex solution. The paramagnetic susceptibility of the complex shifts the solvent resonance relative to the reference capillary, and from this shift the molar magnetic susceptibility can be calculated. Measurements were performed from 273 K to 343 K in 10 K steps and the spectra are shown in **Figure 50** in stacked mode. The inherent uncertainty of the Evans method is 5-10% as it is based on NMR spectroscopy.^{23,24} At low temperatures, the solvent reference peak is unchanged, consistent with a diamagnetic LS Co(III)cat ground state. Upon heating, a shoulder develops progressively until at 343 K two partially overlapping signals are observed, indicative of a small but detectable increase in paramagnetic moment and a small but real VT contribution.

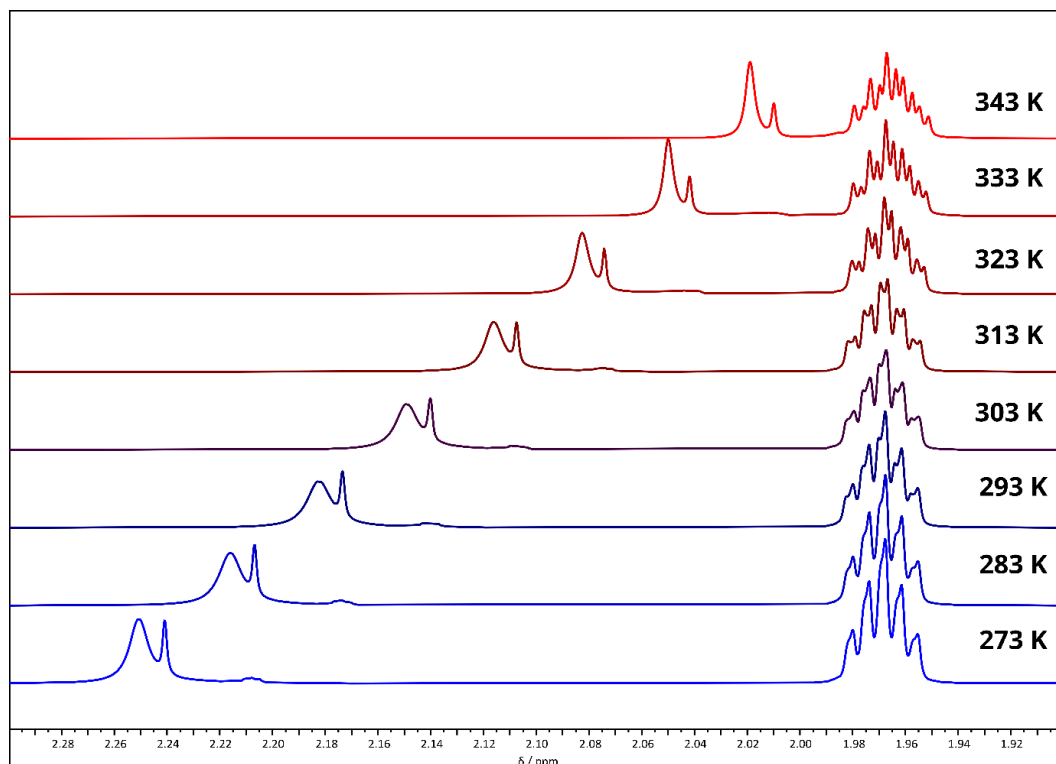


Figure 50: Evans method NMR of $\text{Co-L}^{\text{bpop}}\text{-PF}_6$ in CD_3CN in the temperature range from 273 K to 343 K [400 MHz].

As shown in Figure 51, both the pyrazine- and piperazine-based complexes show a weak, gradual, and incomplete increase in magnetic moment with temperature.

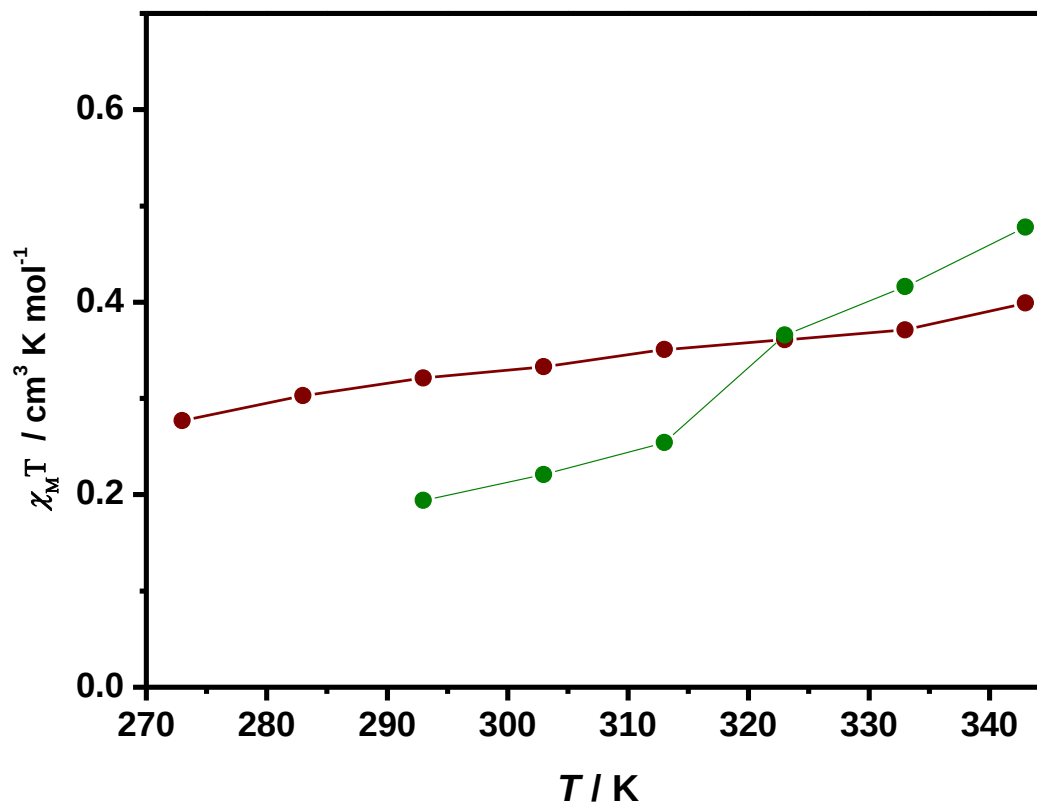


Figure 51: Evans method ^1H NMR (6 mM) at variable temperatures of previously reported $\text{Co-LH-dbcacat-ClO}_4$ (green) and $\text{Co-L}^{\text{bpop}}\text{-PF}_6$ (red) in acetonitrile in 10 K steps. [400MHz]

The piperazine complex rises marginally faster, but the overall behaviour is similar for both systems. The incomplete nature of the transition precludes determination of a transition temperature or thermodynamic parameters (ΔH , ΔS). It is well established that the valence tautomeric equilibrium is strongly influenced by the solvent environment. Less polar solvents, such as butyronitrile, preferentially stabilise the more apolar HS Co(II)sq state and can therefore shift the equilibrium towards the paramagnetic form. However, insufficient solubility in butyronitrile and DCM precluded this approach for the present systems.

Complementary to the solution-state measurements, the magnetic properties were also investigated in the solid state by SQUID magnetometry. The $\chi_M T$ vs. T data for both complexes are shown in **Figure 52** over the range of 10–400 K, with the tetraphenylborate salt measured over 200–400 K only. Below 300 K, both complexes remain essentially diamagnetic, consistent with the LS Co(III)cat ground state established by X-ray crystallography.

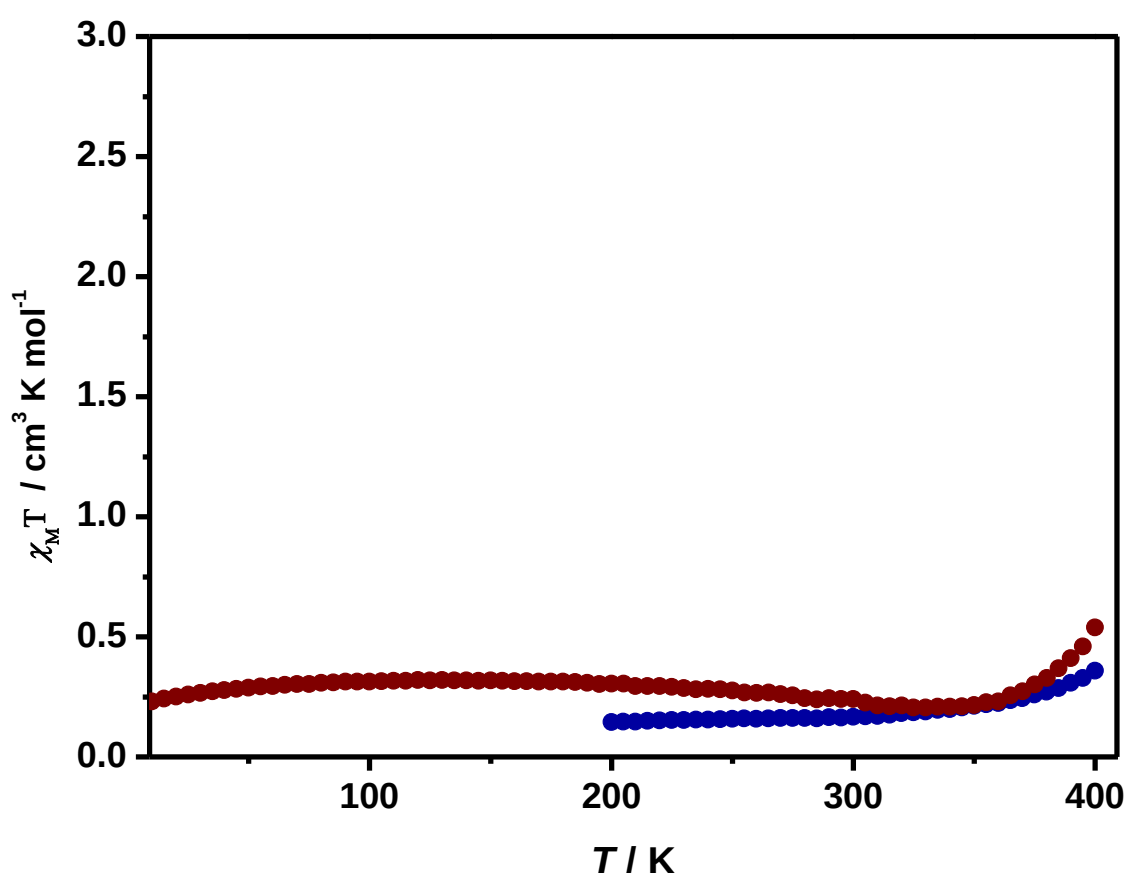


Figure 52: Temperature dependent magnetic susceptibility of Co-L^{bpap}-PF₆ (red) and Co-L^{bpap}-BPh₄ (blue).

Above 300 K both complexes show a gradual increase in $\chi_M T$, reaching maximum values of 0.539 cm³Kmol⁻¹ and 0.359 cm³Kmol⁻¹ for Co-L^{bpap}-PF₆ and Co-L^{bpap}-BPh₄, respectively. While this is indicative of a VT transition, it remains incomplete within the accessible temperature window and no $T_{1/2}$ could be determined. In comparison, the piperazine-based analogue reaches a maximum value of 1.26 cm³Kmol⁻¹ at 380 K, though that transition is also incomplete.^{6,12} In all cases, the observed magnetic moment remains well below the spin-only value of 2.25 cm³K mol⁻¹ expected for an uncoupled HS Co(II) ($S=3/2$) and semiquinonate radical ($S=1/2$), as well as comparable dinuclear systems, which reach values between 6 and 8 cm³K mol⁻¹.^{5,7} In fully converted systems, substantially larger values are typically observed owing to the significant orbital contribution from the ⁴T₁ ground state of octahedral Co(II) centres, as also discussed in previous chapters.

Unfortunately, the incomplete transition precludes assessment of whether the aromatic bridging unit enables the two-step transition profile that might be expected for an electronically coupled dinuclear system. Nonetheless, the cyclic voltammogram displays a single, unresolved Co(II)/Co(III) redox event rather than two separated waves, indicating negligible electronic communication between the two metal centres.

Summary

To introduce electronic communication between the metal centres, the aliphatic piperazine bridge was replaced by an aromatic pyrazine unit. Based on the ligand L^{bpap} , a new family of dinuclear cobalt-dioxolene complexes was developed and characterised, including an improved, carbon tetrachloride-free four-step synthesis of the ligand backbone. Since the pyrazine system was found to undergo a previously unreported catecholate insertion reaction under ambient conditions. Both the hexafluorophosphate and tetraphenylborate salts were thoroughly characterised, with X-ray diffraction confirming the LS Co(III)cat ground state at low temperature. Magnetic studies in solution and the solid state revealed a weak, gradual, and incomplete VT transition above 300 K. To conclusively establish whether the aromatic bridge enables the two-step transition profile expected for an electronically coupled system, future work should aim to shift the transition temperature into an experimentally accessible range and to systematically vary the bridging unit to modulate the degree of electronic communication between the two metal centres.

8. Experimental Part Chapter 4

8.1 General

The chemicals were purchased from TCI, Alfa Aesar, Acros Organics, BLD Pharm, Thermo scientific, Sigma Aldrich, Deutero, VWR, Roth, and Titolchimica and used without further purification unless stated otherwise. Anhydrous cobalt(II) chloride was dried by treatment with thionyl chloride. Triethylamine was dried over calcium hydride and freshly distilled. Dry THF was obtained from a solvent purification system (MBRAUN MG-SPS-800).

8.2 IR Spectroscopy

Infrared spectra were recorded at room temperature on a Bruker ALPHA II ATR-IR spectrometer. Data were processed using the OPUS software package and plotted using Origin V7.5.

8.3 NMR Spectroscopy and Evans Method

NMR spectra were recorded on the following instruments: Bruker *Avance III HD 300* ($\nu(^1\text{H}) = 400.13$ MHz $\nu(^{13}\text{C}) = 100.1$ MHz); Bruker *Avance II 400* ($\nu(^1\text{H}) = 400.13$ MHz $\nu(^{13}\text{C}) = 100.1$ MHz); Bruker *Neo 400* ($\nu(^1\text{H}) = 400.13$ MHz $\nu(^{13}\text{C}) = 100.1$ MHz). All spectra were recorded in deuterated solvents, and chemical shifts are reported in ppm relative to the residual solvent signal of the respective deuterated solvent. Spectra were processed and evaluated using *MestReNova x64* (Mestrelab Research).

8.4 UV-Vis Spectroscopy

UV-Vis absorption spectra were recorded on a JASCO V-770 spectrophotometer at a scan rate of 400 nm per minute in 0.2 nm increments. Data were plotted using Origin 7.5 V5.

8.5 Elemental Analysis

The elemental analysis (CHN) was carried out at the Department of Chemistry, Johannes Gutenberg-University Mainz, using an Elementar vario EL Cube. CHNS analysis was performed at RPTU Kaiserslautern-Landau on an Elementar vario Micro cube.

8.6 Mass Spectrometry

High-resolution ESI mass spectra were recorded on an *Agilent 6200 series TOF/6500 series G-TOF(11.0.203.0)* at Johannes Gutenberg-University Mainz, using acetonitrile or methanol as solvent. Spectra were plotted with Origin 7.5 V5. Isotope pattern calculations and comparison were performed using enviPat.²⁵

8.7 X-Ray Crystallography

Single-crystal X-ray diffraction data were collected on a *STOE STADIVARI* diffractometer at Johannes Gutenberg-University Mainz at 120 K. Structure solution and refinement were performed using *ShelXT*²⁶ and *ShelXL*²⁷ in combination with *Olex2*²⁸ by Dr. Luca M. Carrella. Structures were further analysed using *Olex2* and *Mercury* 4.2.0.

8.8 Cyclic Voltammetry

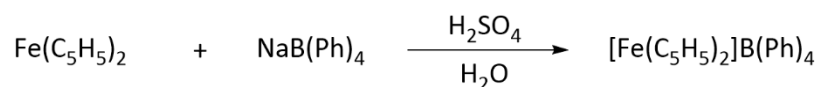
Cyclovoltammetry measurements were performed using a Metrohm Autolab potentiostat and controlled by Nova 2.1.4 software. A standard three-electrode setup was employed, consisting of a glassy carbon working electrode, a Ag/AgNO₃ reference electrode, and a platinum counter electrode. Prior to each measurement series, the glassy carbon electrode was immersed in nitric acid for 20 minutes, rinsed with distilled water, polished with aluminium oxide polishing paste (Buehler) on a microfiber cloth using a figure-of-eight motion, and rinsed thoroughly again. All solutions were degassed with argon prior to measurement and kept under a continuous argon atmosphere throughout. Tetrabutylammonium hexafluorophosphate (0.1 mol L⁻¹) was used as the supporting electrolyte. All potentials were referenced to the ferrocene/ferrocenium redox couple at the end of each measurement series. Voltammograms were plotted using Origin V7.5.

8.9 SQUID Magnetometry

Magnetic measurements were performed on a *Quantum Design MPMS3 EC SQUID magnetometer*. Samples were prepared in plastic capsules placed in a brass sample holder. Magnetic data were collected over a temperature range of 10-400 K under an applied field of 0.1 T, in both heating and cooling cycles using settle mode with a nominal ramp rate of 10 K/min between target temperatures. The temperature was allowed to stabilise at each setpoint before data acquisition, with an additional 5-minute hold at 400 K prior to cooling. All measurements were performed over a scan length of 3 cm, with each data point averaged over three consecutive measurements. The diamagnetic contributions of the sample holder and capsule were determined experimentally by measuring an empty capsule under identical conditions and at the same position, and subtracted from the raw susceptibility data using *Squidlab*²⁹ for *Matlab*³⁰.

8.10 Precursor Synthesis

8.10.1 Ferrocenium tetraphenylborate



Substance	<i>M</i> / g mol ⁻¹	<i>m</i> / g	<i>n</i> / mmol	<i>V</i> / mL	equiv.
Ferrocene	186.03	1.50	8.06	-	1.00
Sodium Tetraphenylborate	342.22	3.28	9.59	-	1.19
Conc. Sulfuric Acid	98.08	-	-	30	-
Water	37.83	-	-	450	Solvent

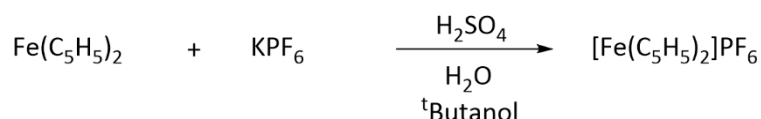
Reaction: REN-TH-AM-39

Procedure¹⁰:

Ferrocene (1.50 g, 8.06 mmol, 1.00 equiv.) was dissolved in 30 mL of concentrated sulfuric acid and stirred for 30 minutes at room temperature. The resulting blue solution was carefully poured into 300 mL of water, and followed by the addition of 150 mL of an aqueous sodium tetraphenylborate solution (3.28 g, 9.59 mmol, 1.19 equiv.). The resulting light blue precipitate was stirred for 2 hours and collected by filtration. The solid was washed sequentially with water (300 mL), ethanol (100 mL) and diethyl ether (150 mL), dried under reduced pressure, and stored at -25°C owing to its temperature sensitivity.

Yield: 3.91 g light blue powder (7.74 mmol, 96%)

8.10.2 Ferrocenium hexafluorophosphate



Substance	<i>M</i> / g mol ⁻¹	<i>m</i> / g	<i>n</i> / mmol	<i>V</i> / mL	equiv.
Ferrocene	186.03	2.79	15.00	-	1.00
KPF₆	184.06	5.50	30.00	-	2.00
Conc. Sulfuric Acid	98.08	-	-	10	-
Water	37.83	-	-	450	Solvent

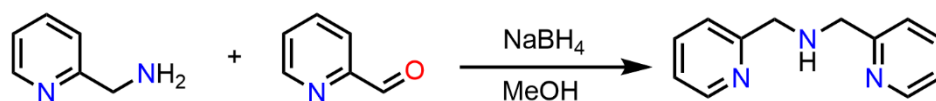
Reaction: REN-TH-AM-80

Procedure¹¹:

Ferrocene (2.79 g, 15.00 mmol, 1.00 equiv.) was dissolved in 10 mL of concentrated sulfuric acid and stirred for 45 minutes at room temperature. The resulting blue solution was carefully poured into 300 mL of water and *tert*-butanol (2.50 g), and followed by the addition of 150 mL of an ice-cooled aqueous potassium hexafluorophosphate solution (5.50 g, 30.00 mmol, 2 equiv.). The resulting light blue precipitate was stirred for 2 hours and collected by filtration. The solid was washed sequentially with ice-cold water (100 mL), ethanol (50 mL) and diethyl ether (150 mL), dried under reduced pressure, and stored at -25°C owing to its temperature sensitivity.

Yield: 4.17 g blue powder (12.60 mmol, 84%)

8.10.3 Bispyridylmethanamine



Substance	<i>M</i> / g mol ⁻¹	<i>m</i> / g	<i>n</i> / mmol	<i>V</i> / mL	equiv.
2-Methylaminopyridine	108.14	3.40	31.40	-	1.00
2-Pyridinecarboxaldehyde	107.11	3.36	31.40	-	1.00
NaBH ₄	37.83	2.54	79.76	-	2.54
MeOH	32.04	-	-	25	Solvent

Reaction: REN-TH-587

Procedure³:

2-Methylaminopyridine (3.4 g, 31.40 mmol, 1.00 equiv.) was dissolved in 25 mL of methanol and 2-pyridinecarboxaldehyde (3.36 g, 31.40 mmol, 1.00 equiv.) was added dropwise. After stirring for four hours at room temperature, sodium borohydride (2.54 g, 79.76 g, 2.54 equiv.) was added portionwise under ice-bath cooling. The resulting suspension was stirred overnight at room temperature. Water (50 mL) was added and the methanol was removed under reduced pressure. The aqueous residue was extracted twice with dichloromethane (20 mL each). The combined organic phases were dried over sodium sulfate and the solvent was removed under reduced pressure. The product was obtained as a yellow oil.

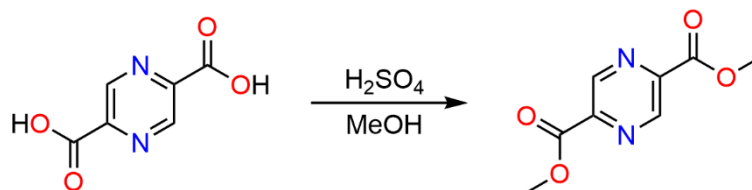
Yield: 6.00 g yellow oil (30.11 mmol, 96%)

IR $\tilde{\nu}$ [cm⁻¹]: 3306 (m, ν (-N-H)), 3052 (m, ν (=C-H)), 3009 (m, ν (-C-H)), 2915 (w, ν (-CH₂)), 2834 (m, ν (-CH₂)), 2371 (w), 2319 (w), 1590 (ss), 1569 (s), 1473 (s), 1432 (ss, d (-CH₂)), 1359 (m), 1299 (m), 1223 (m), 1148 (s), 1048 (s), 994 (s), 891 (m), 846 (s), 750 (ss), 680 (s), 627 (s), 593 (s), 501 (s), 473 (s), 402 (ss).

¹H-NMR [ppm]: 8.58 (dd, J = 5.0, 1.9, 1.0 Hz, 2H, H3), 7.66 (td, J = 7.7, 1.9 Hz, 2H, H4), 7.38 (d, J = 7.8 Hz, 2H, H6), 7.18 (ddd, J = 7.6, 4.9, 1.2 Hz, 2H, H5), 4.00 (s, 4H, H2). [400 MHz, CDCl₃]

8.11 Ligand Synthesis

8.11.1 Pyrazine-2,5-dicarboxylic acid dimethyl ester



Substance	<i>M</i> / g mol ⁻¹	<i>m</i> / g	<i>n</i> / mmol	<i>V</i> / mL	equiv.
Pyrazine-2,5-dicarboxylic acid	168.11	5.00	29.7	-	1.00
Conc. Sulfuric acid	98.08	-	-	0.5	Cat
MeOH	32.04	-	-	175	Solvent

Reaction: REN-TH-AM-1

Procedure:

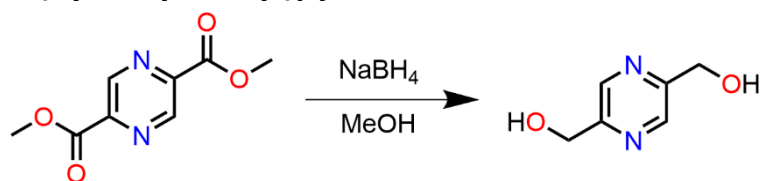
Pyrazine-2,5-dicarboxylic acid (5.00 g, 29.7 mmol, 1.00 equiv.) was suspended in 175 mL of methanol and a catalytic amount of sulfuric acid was added. The suspension was heated to reflux overnight. Upon cooling to room temperature, the product crystallised from the solution. The beige needles were collected by filtration and washed with cold methanol.

Yield: 4.82 g beige needles (24.57 mmol, 83%)

IR $\tilde{\nu}$ [cm⁻¹]: 3425 (w), 3077 (w, $\nu(\text{C-H})$), 3015 (w, $\nu(\text{C-H})$), 2961 (w, $\nu(\text{CH}_3)$), 2854 (w, $\nu(\text{CH}_3)$), 1713 (m, $\nu(\text{C=O})$), 1581 (w, $\nu(\text{C=N})$), 1471 (w, $d(\text{CH}_3)$), 1446 (w), 1427 (m), 1357 (m), 1346 (m), 1274 (m), 1200 (m), 1180 (m), 1136 (m), 1017 (s), 958 (s), 821 (m), 756 (s), 492 (m), 463 (m), 422 (m).

¹H-NMR [ppm]: 9.42 (s, 2H, H1), 4.11 (s, 6H, H2). [300 MHz, CDCl₃]

8.11.2 2,5-Bis(hydroxymethyl)pyrazine



Substance	<i>M</i> / g mol ⁻¹	<i>m</i> / g	<i>n</i> / mmol	<i>V</i> / mL	equiv.
Pyrazine-2,5-dicarboxylic acid dimethyl ester	196.16	4.00	20.39	-	1.00
Sodium borohydride	37.83	6.17	163.13	-	8.00
MeOH	32.04	-	-	160	Solvent

Reaction: REN-TH-AM-54

Procedure adapted from²:

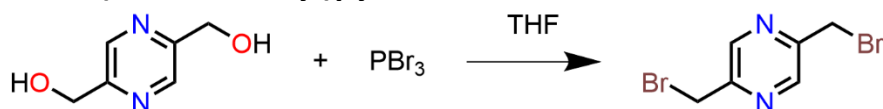
Pyrazine-2,5-dicarboxylic acid dimethyl ester (4.00 g, 20.39 mmol, 1.00 equiv.) was suspended in 160 mL of methanol and sodium borohydride (6.17 g, 163.13 mmol, 8.00 equiv.) was added portionwise under ice-bath cooling. The suspension was allowed to warm to room temperature and stirred overnight. The reaction was quenched by addition of 20 mL of water and the solvent was removed under reduced pressure. The crude product was first purified by a short plug of silica gel eluting with pure methanol, followed by a column chromatography using a gradient elution starting from dichloromethane/methanol (5:1, v/v) with increasing methanol content. The product was obtained as a yellow oil.

Yield: 2.50 g yellow oil (17.85 mmol, 88%)

IR $\tilde{\nu}$ [cm⁻¹]: 3228 (ss, ν (O–H)), 2930 (s, ν (–CH₂)), 2848 (s, ν (–CH₂)), 1733 (w), 1631 (m, ν (C=N)), 1495 (m), 1482 (m), 1438 (s), 1346 (ss), 1283 (s), 1213 (s), 1191 (s), 1152 (s), 1133 (s), 1064 (ss, ν (C–O)), 1028 (ss), 968 (s), 911 (m), 881 (w), 868 (w), 787 (m), 726 (s), 604 (s), 530 (m), 482 (w), 444 (m), 407 (ss).

¹H-NMR [ppm]: 8.67 (s, 2H, H1), 4.77 (s, 4H, H2). [300 MHz, MeOD]

8.11.3 2,5-Bis(bromomethyl)pyrazine



Substance	$M / \text{g mol}^{-1}$	m / g	n / mmol	V / mL	equiv.
2,5-Bis(hydroxymethyl)pyrazine	140.14	0.78	5.57	-	1.00
Phosphorus tribromide	170.69	3.01	11.13	-	2.00
Tetrahydrofuran	72.11	-	-	100	Solvent

Reaction: REN-TH-AM-28

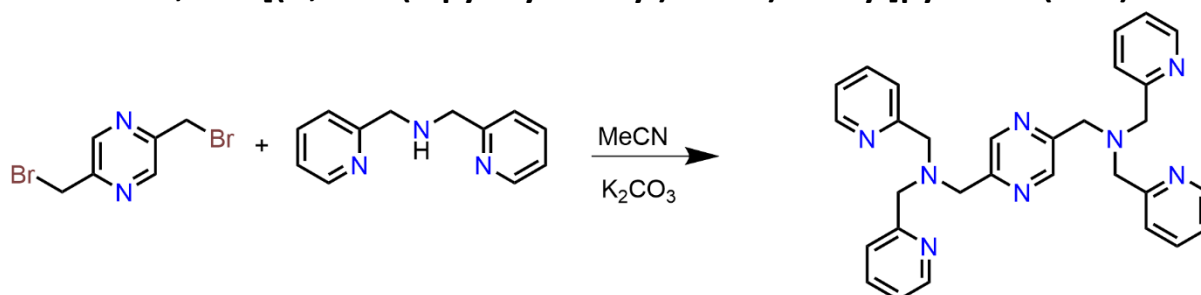
Procedure:

2,5-Bis(hydroxymethyl)pyrazine (0.78 g, 5.57 mmol, 1.00 equiv.) was dissolved in tetrahydrofuran (100 mL). Phosphorus tribromide (3.01 g, 11.13 mol, 2.00 equiv.) was added dropwise to the red solution under ice-bath cooling, upon which a light brown precipitate formed. Dichloromethane (20 mL) was added and the suspension was stirred overnight at room temperature. Water (160 mL) was added, the organic phase was separated, and the aqueous phase was extracted five times with dichloromethane (50 mL each). The combined organic phases were dried over sodium sulfate, and the solvent was removed under reduced pressure. The crude product was first purified by a short plug of silica gel eluting with dichloromethane, followed by column chromatography using dichloromethane/*n*-heptane (3:1, v/v) as the eluent. The product was obtained as a colourless solid.

Yield: 0.77 g colourless crystals (2.90 mmol, 52%)

IR $\tilde{\nu}$ [cm^{-1}]: 3036 (w, $\nu(\text{C-H})$), 1484 (m), 1427 (m, $d(-\text{CH}_2)$), 1347 (m), 1261 (m), 1198 (m), 1178 (m), 1075 (m), 1034 (s), 915 (m), 864 (m), 765 (m), 634 (s, $\nu(\text{C-Br})$), 489 (s), 400 (s).

$^1\text{H-NMR}$ [ppm]: 8.69 (s, 2H, H1), 4.59 (s, 4H, H2). [300 MHz, CDCl_3]

8.11.4 2,5-Bis[(*N,N*-bis(2-pyridylmethyl)amino)methyl]pyrazine (**L^{bpap}**)

Substance	<i>M</i> / g mol ⁻¹	<i>m</i> / g	<i>n</i> / mmol	<i>V</i> / mL	equiv.
2,5-Bis(bromomethyl)pyrazine	265.94	0.77	2.90	-	1.00
Bis(2-pyridylmethyl)amine	199.20	1.15	5.79	-	2.00
Potassium Carbonate	138.20	2.00	14.48	-	5.00
Acetonitrile	41.05	-	-	180	Solvent

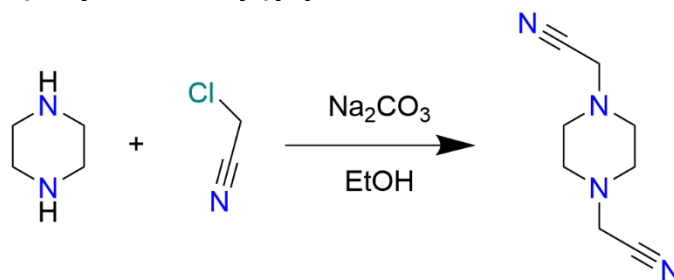
Reaction: REN-TH-AM-29

Procedure¹:

Bis(2-pyridylmethyl)amine (1.15 g, 5.79 mmol, 2.00 equiv.) and potassium carbonate (2.00 g, 14.48 mmol, 5.00 equiv.) were suspended in acetonitrile (150 mL) and heated to 75°C. A solution of 2,5-bis(bromomethyl)pyrazine (0.77 g, 2.90 mmol, 1.00 equiv.) in acetonitrile (30 mL) was then added to the reaction mixture. The resulting suspension was stirred at reflux overnight and subsequently filtered hot. The solvent was removed under reduced pressure and the crude product was purified by column chromatography using chloroform/methanol (92/8, v/v) as the eluent. The resulting yellow oil was dissolved in chloroform (4 mL) and the product was precipitated by addition of *n*-hexane (50 mL). The product was collected by filtration as a colourless solid.

Yield: 1.02 g colourless crystals (2.03 mmol, 70%)

IR	$\tilde{\nu}$ [cm ⁻¹]: 3075 (w, ν (C–H)), 3049 (w), 3013 (w, ν (C–H)), 2982 (w), 2922 (w, ν (–CH ₂)), 2881 (w, ν (–CH ₂)), 2821 (m, ν (N–CH ₂)), 1588 (s), 1568 (s), 1473 (s), 1434 (s, d (–CH ₂)), 1374 (s), 1358 (s), 1329 (m), 1310 (m), 1268 (m), 1242 (m), 1219 (w), 1154 (m), 1120 (s), 1092 (m), 1047 (w), 1028 (m), 995 (m), 979 (s), 965 (s), 904 (m), 884 (m), 841 (w), 766 (ss), 756 (ss), 746 (s), 642 (w), 634 (w), 612 (s), 520 (m), 477 (w), 408 (s).
¹H-NMR	[ppm]: 8.69 (s, 2H, H1), 8.52 (ddd, <i>J</i> = 4.9, 1.9, 0.9 Hz, 4H, H6), 7.64 (td, <i>J</i> = 7.6, 1.8 Hz, 4H, H7), 7.55 (dt, <i>J</i> = 7.8, 1.1 Hz, 4H, H9), 7.13 (ddd, <i>J</i> = 7.4, 4.9, 1.3 Hz, 4H, H8), 3.89 (s, 6H, H3, H4). [400 MHz, CDCl ₃]
¹³C-NMR	[ppm]: 159 (C5), 153 (C2), 149 (C6), 144 (C1), 137 (C7), 122.9 (C9), 122.2 (C8), 60 (C4), 58 (C3). [101 MHz, CDCl ₃]
2D-NMR	COSY, HSQC, HMBC (Supplementary Part)
ESI⁺-MS	252.1373 [L+2H] ²⁺ (calc. 252.1370); 503.2667 [L+H] ⁺ (calc. 503.2667); 525.2486 [L+Na] ⁺ (calc. 525.2486).
EA	Found: 70.45%, H: 6.31%, N: 21.77% calc. for C ₃₀ H ₃₀ N ₈ · 0.5 H ₂ O: C: 70.45%, H: 6.11%, N: 21.90%.

8.11.5 *N,N'*-Bis(2-cyanomethyl)piperazine

Substance	<i>M</i> / g mol ⁻¹	<i>m</i> / g	<i>n</i> / mmol	<i>V</i> / mL	equiv.
Piperazine	86.14	6.45	75.0	-	1.00
Chloroacetonitrile	75.50	13.59	180	-	2.40
Ethanol	46.07	-	-	300	Solvent
Sodium Carbonate	105.99	31.80	300	-	4.00

Reaction: REN-TH-0052

Procedure^{6,12}:

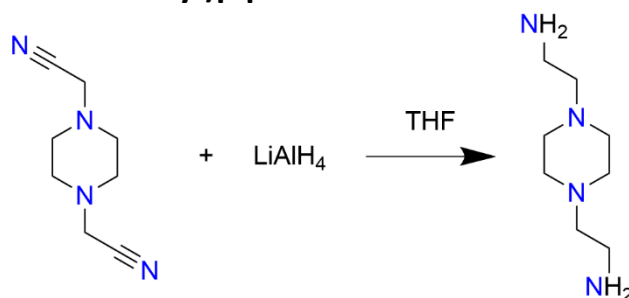
To a solution of piperazine (6.45 g, 75.0 mmol, 1.00 equiv.) in ethanol (150 mL), a solution of chloroacetonitrile (13.59 g, 180.0 mmol, 2.40 equiv.) in ethanol (150 mL) was added with stirring. Sodium carbonate (31.80 g, 300 mmol, 4.00 equiv.) was added portionwise, upon which a colourless suspension formed. The suspension was heated to reflux overnight, during which a colour change to beige was observed. The hot suspension was filtered and the filtrate was allowed to cool, whereupon colourless crystals formed. The residue was washed with ethanol. The crystals were collected by filtration and dried on air. The product was observed as colourless crystals.

Yield: 9.73 g colourless crystals (59.3 mmol, 79%)

IR $\tilde{\nu}$ [cm⁻¹]: 2964 (m, *v*_{as} CH₂), 2944 (m, *v*_{as} CH₂), 2890 (m, *v*_s CH₂), 2820 (s, *v* N-CH₂), 2753 (m), 2711 (w), 2231 (w, *v* CN), 1453 (s), 1434 (s), 1377 (m), 1316 (ss), 1294 (s), 1155 (ss), 1131 (ss), 1010 (ss), 896 (m), 864 (ss), 796 (ss), 771 (m), 709 (m), 508 (m).

¹H-NMR [ppm]: 3.54 (s, 4H, H₅), 2.67 (s, 8H, H_{2,3}) [300 MHz, CDCl₃].

Analytics: Chapter 1 ESI

8.11.6 *N,N'*-Bis(2-aminoethyl)piperazine

Substance	<i>M</i> / g mol ⁻¹	<i>m</i> / g	<i>n</i> / mmol	<i>V</i> / mL	equiv.
<i>N,N'</i> -bis(2-cyanomethyl)piperazine	164.21	2.50	15.2	-	1.00
Lithium Aluminium Hydride	37.95	2.66	70.1	-	4.60
Tetrahydrofuran	72.11	-	-	200	Solvent

Reaction: REN-TH-005

Procedure^{6,12}:

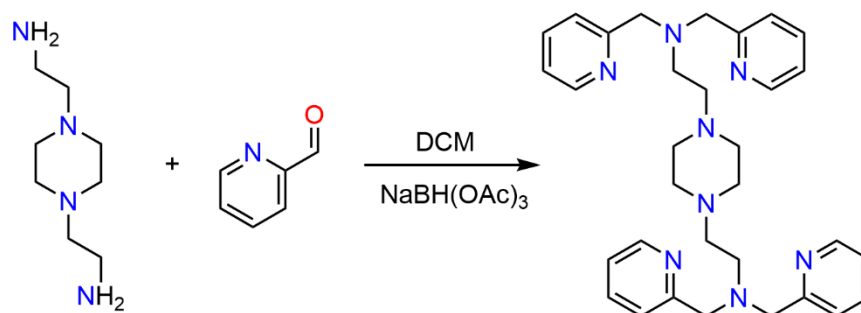
To a grey suspension of lithium aluminium hydride (2.66 g, 70.1 mmol, 4.60 equiv.) in dry tetrahydrofuran (100 mL) under a nitrogen atmosphere, a solution of *N,N'*-bis(cyanomethyl)piperazine (2.50 g, 15.2 mmol, 1.00 equiv.) was added dropwise under ice-bath cooling with vigorous stirring. Gas evolution and a moderate rise in temperature were observed. The reaction mixture was subsequently heated to reflux for three hours, with reaction progress monitored by TLC. The suspension was cooled in an ice bath and quenched by the sequential dropwise addition of water (2.35 mL), aqueous KOH solution (15%, 2.35 mL), and water (7 mL) via syringe. The suspension was filtered and the residue was washed with tetrahydrofuran (300 mL) in small portions. The combined organic phases were dried over sodium sulfate and the solvent was removed under reduced pressure. The resulting yellow oil crystallised upon standing overnight at 4°C to afford the product as yellow crystals.

Yield: 1.81 g yellow crystals (10.5 mmol, 69%)

IR $\tilde{\nu}$ [cm⁻¹]: 3308 (ν_{as} NH₂, s), 3264 (ν_{s} NH₂, m), 3173 (ν_{s} NH₂, m), 2941 (ν_{as} CH₂, ss), 2871 (ν_{s} CH₂, s), 2811 (ν''' N-CH₂, ss), 2785 (ν N-CH₂, ss), 2689 (m), 1620 (δ' NH₂, m), 1476 (m), 1455 (δ' CH₂, s), 1440 (s), 1363 (m), 1341 (s), 1305 (ν''' C-N, ss), 1282 (s), 1266 (ss), 1189 (m), 1159 (ss), 1130 (ss), 1111 (ss), 1049 (m), 1027 (m), 1004 (s), 926 (ss), 826 (ss), 786 (s), 651 (w), 521 (m).

¹H-NMR [ppm]: 2.76 (t, 4H, $J^3 = 6.3\text{Hz}$, H6), 2.45 (s, 8H, H2,3), 2.39 (t, 4H, $J^3 = 6.3\text{Hz}$, H5), 1.50 (s, 4H, N-H7). [400 MHz, CDCl₃]

Analytics: Chapter 1 ESI

8.11.1 *N, N', N', N'*-Tetra-2-picolyl-1,4-bis(aminoethyl)piperazine

Substance	$M / \text{g mol}^{-1}$	m / g	n / mmol	V / mL	equiv.
<i>N,N'</i> -bis(2-aminoethyl)piperazine	172.28	1.0	5.80	-	1.00
Sodium Triacetoxyborohydride	212.05	6.15	29.0	-	5.00
Dichloromethane	84.93	-	-	160	Solvent
2-Pyridinecarboxaldehyde	107.11	2.61	24.4	-	4.21

Reaction: REN-TH-006

Procedure^{6,12}:

To a solution of *N,N'*-bis(2-aminoethyl)piperazine (1.00 g, 5.80 mmol, 1.00 equiv.) in dichloromethane (150 mL), sodium triacetoxyborohydride (6.15 g, 29.0 mmol, 5.00 equiv.) was added portionwise. A solution of 2-pyridinecarboxaldehyde (2.61 g, 24.4 mmol, 4.21 equiv.) in dichloromethane (10 mL) was subsequently added over 30 minutes. The reaction mixture was stirred overnight at room temperature. Saturated aqueous sodium hydrogen carbonate solution (50 mL) was added and the mixture was stirred for a further 30 minutes, during which gas evolution was observed. The phases were separated and the aqueous phase was extracted twice with dichloromethane (50 mL each). The combined organic phases were dried over sodium sulfate, and the solvent was removed under reduced pressure. The resulting yellow oil was recrystallised from twice from acetone. The product was obtained as colourless crystals.

Yield: 2.41 g yellow crystals (4.47 mmol, 77%)

IR $\tilde{\nu} [\text{cm}^{-1}]$: 3088 (v arom. CH, w), 3056 (v arom. CH, m), 3011 (v arom. CH, m), 2959 (ν_{as} CH_2 , m), 2939(w), 2924 (m), 2858 (m), 2810 (ν N- CH_2 , m), 2773(m), 2690 (w), 1587 (s), 1569 (m), 1470 (m) 1443 (m), 1429 (CH_2 , s), 1397 (m), 1362 (m), 1339 (m), 1318 (m), 1299 (m), 1265 (m), 1247 (m), 1172 (w), 1143 (m), 1123 (m), 1071 (w), 1049 (m), 1031 (m) 1014 (m), 996(m), 980 (s), 957 (m), 939 (m), 891 (m), 833 (m), 821 (m), 762 (δ CH arom. ss), 730 (m), 654 (w), 632 (w), 610 (m), 510 (w) 485 (m), 461 (m), 424 (m), 409 (s).

$^1\text{H-NMR}$ [ppm]: 8.51 (ddd, $^3J = 4.9, 1.8, 0.9$ Hz, 4H, H^{11}), 7.63 (td, $^3J = 7.6, 1.8$ Hz, 4H, H^{13}), 7.52 (dt, $^3J = 7.9, 1.1$ Hz, 4H, H^{14}) 7.13 (ddd, $^3J = 7.6, 4.9, 1.2$ Hz, 4H, H^{12}), 3.84 (s, 8H, H^8), 2.71 (t, 7.0, 4H, H^5), 2.52 (t, 7.0, 4H, H^6), 2.39 (s, 8H, $\text{H}^{2,3}$). [400 MHz, CDCl_3].

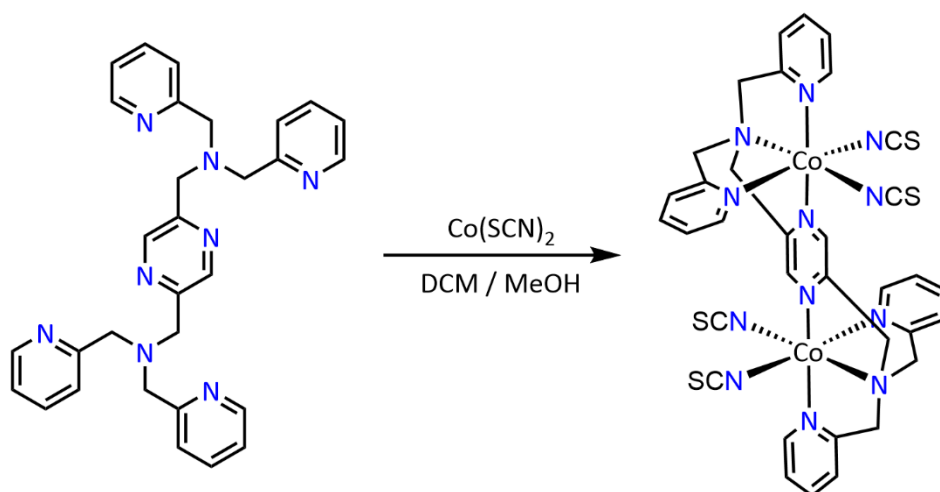
$^{13}\text{C-NMR}$ [ppm]: 160 (C9), 149 (C11), 136 (C13), 123 (C14), 122 (C12), 61 (C8), 56 (C5), 53 (C2,3), 51 (C6) [101 MHz, CDCl_3].

2D-NMR COSY, HSQC, HMBC

Analytics: Chapter 1 ESI

8.12 Complex Synthesis

8.12.1 $\text{Co}_2(\text{L}^{\text{bpap}})(\text{SCN})_4$ ($\text{Co-L}^{\text{bpap}}\text{-SCN}$)



Substance	$M / \text{g mol}^{-1}$	m / mg	n / mmol	V / mL	equiv.
L^{bpap}	502.61	50	0.1	-	1.00
Co(II) thiocyanate	175.10	35	0.2	-	2.00
Methanol	32.04	-	-	3	Solvent
Dichloromethane	84.93	-	-	10	Solvent

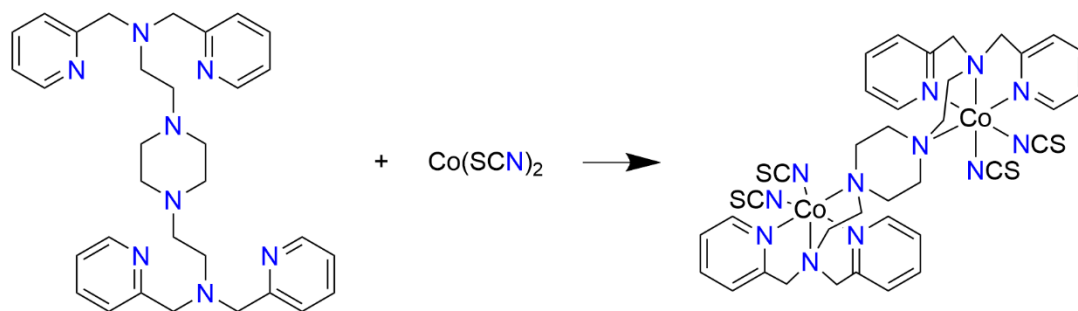
Reaction: REN-TH-AM-9

Procedure:

A solution of L^{bpap} (50 mg, 0.1 mmol, 1.00 equiv.) in dichloromethane (10 mL) was carefully layered with a solution of cobalt(II) thiocyanate (35 mg, 0.2 mmol, 2.00 equiv.) in methanol (3 mL). After three days, the product was obtained as red crystals.

Yield: 20 mg red crystals (0.023 mmol, 23%)

IR	$\tilde{\nu} [\text{cm}^{-1}]$: 2913 (w, $\nu(\text{C-H})$), 2869 (w, $\nu(\text{C-H})$), 2054 (ss, $\nu(\text{C}\equiv\text{N})$), 1603 (m, $\nu(\text{C}=\text{C})$), 1573 (w), 1479 (w), 1455 (w), 1438 (s), 1420 (w), 1381 (w), 1352 (w), 1323 (w), 1314 (w), 1288 (w), 1265 (w), 1215 (w), 1150 (m), 1120 (w), 1098 (m), 1048 (s), 1020 (w), 999 (w), 974 (w), 957 (m), 910 (w), 875 (w), 857 (w), 818 (w), 793 (w), 756 (s), 728 (m), 700 (w), 641 (w), 490 (w), 482 (w), 466 (w), 439 (w), 418 (m), 404 (w).				
EA	Found:	46.37%,	H:	3.48%,	N: 18.97%, S: 14.42%
					calc. for $\text{C}_{34}\text{H}_{30}\text{N}_{12}\text{S}_4\text{Co}_2 \cdot 0.5 \text{ DCM}$: C: 46.29%, H: 3.49%, N: 18.77%, S: 13.32%.

8.12.2 Co₂(LH)(SCN)₄ (Co-LH-SCN)

Substance	<i>M</i> / g mol ⁻¹	<i>m</i> / mg	<i>n</i> / mmol	<i>V</i> / mL	equiv.
LH	536.73	64	0.119	-	1.00
Co(II) thiocyanate	175.10	42	0.238	-	2.00
Methanol	32.04	-	-	10	Solvent
Dichloromethane	84.93	-	-	10	Solvent

Reaction: REN-TH-443

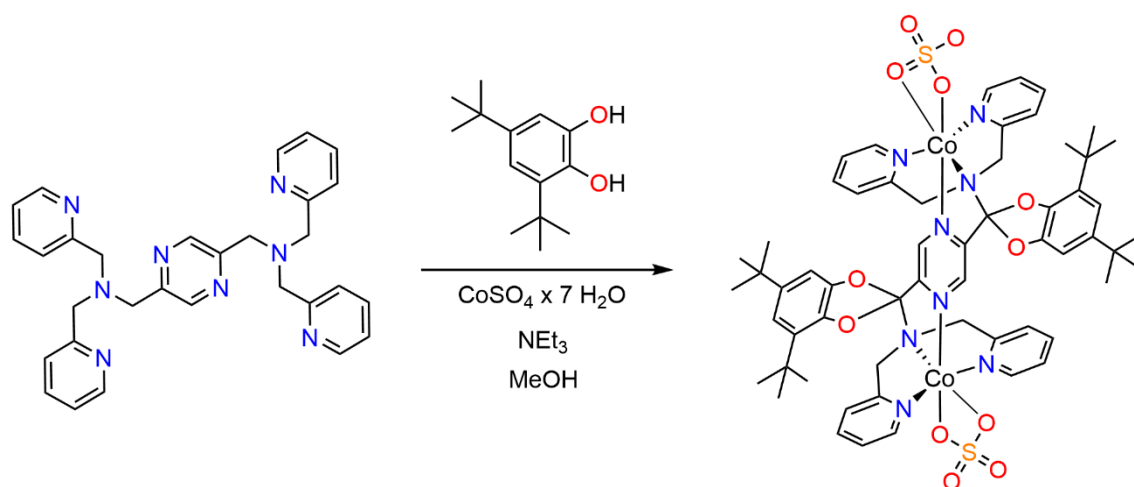
Procedure:

A solution of **LH** (64 mg, 0.119 mmol, 1.00 equiv.) in dichloromethane (10 mL) was carefully layered with a 1:1 (v/v) dichloromethane/methanol mixture (2mL) as a buffer layer. A solution of cobalt(II) thiocyanate (42 mg, 0.238 mmol, 2.00 equiv.) in methanol (10 mL) was then carefully layered on top. After three days, the product was obtained as red crystals. Red crystals were obtained after 6 days.

Yield: 75 mg red crystals (0.085 mmol, 85%)

IR $\tilde{\nu}$ [cm⁻¹]: 3061(w), 2962(w), 2894(w), 2865(w), 2059 (m), 1603 (w), 1570 (w), 1477 (w), 1465 (w), 1432 (w), 1385 (w), 1366 (w), 1342 (w), 1306 (w), 1289 (w), 1276 (w), 1261 (w), 1225 (w), 1149 (w), 1127 (w), 1097 (w), 1071 (w), 1050 (w), 1019 (w), 1005 (w), 973 (w), 956 (w), 942 (w), 921 (w), 894 (w), 857 (w), 835 (w), 820 (w), 766 (m), 731 (w), 701 (w), 655 (w), 642 (w), 623 (w), 610 (w), 581 (w), 480 (m), 444 (w), 419 (w), 404 (w).

EA Found: C, 45.84%; H, 4.50%; N, 17.29%, Calc. for C₃₆H₄₀N₁₂S₄Co₂ + 1 CH₂Cl₂: C, 45.73%; H, 4.36%; N, 17.30%.

8.12.3 $\text{Co}_2(\text{L}^{\text{bpap}}-(\text{dbcat})_2)(\mu^2-\text{SO}_4)_2$ 

Substance	$M / \text{g mol}^{-1}$	m / mg	n / mmol	V / mL	equiv.
L^{bpap}	502.61	50	0.1	-	1.00
3,5-ditertbutylcatechol (dbcat)	222.32	44	0.2	-	2.00
Triethylamine	101.19	40	0.4	-	4.00
Co(II)sulfate heptahydrate	237.93	56	0.2	-	2.00
Methanol	32.04	-	-	15	Solvent

Reaction: REN-TH-AM-30

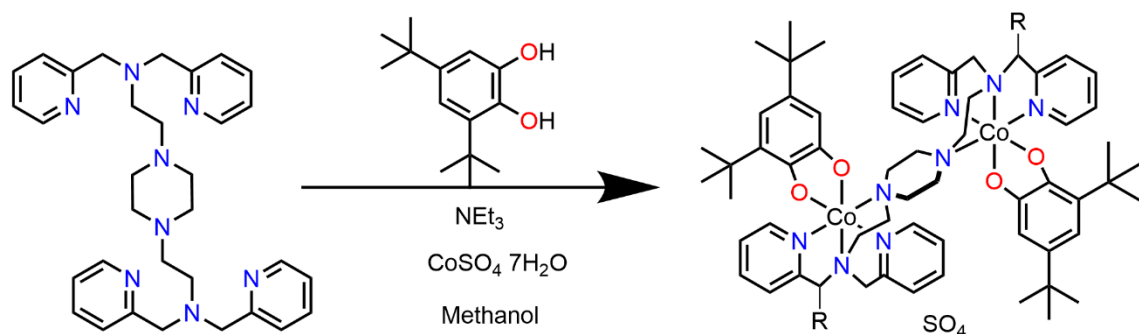
Procedure:

L^{bpap} (50 mg, 0.1 mmol, 1.00 equiv.), dbcat (44 mg, 0.20 mmol, 2.00 equiv.), and cobalt(II) sulfate heptahydrate (56 mg, 0.20 mmol, 2.00 equiv.) were dissolved in methanol (15 mL). Triethylamine (40 mg, 0.40 mmol, 4.00 equiv.) was added dropwise to the green solution, upon which a colour change to brown was observed. The reaction mixture was heated to reflux for one hour and, after cooling to room temperature, the resulting green solution was filtered. Green crystals were obtained by slow evaporation of the filtrate after three days.

Yield: 17 mg green crystals (0.007 mmol, 7%)

IR $\tilde{\nu} [\text{cm}^{-1}]$: 3646 (w, $\nu(\text{O-H})$), 3334 (w), 2960 (m, $\nu(\text{C-H})$), 2872 (w), 1634 (w), 1610 (m), 1574 (w, $\nu(\text{C=N})$), 1488 (m), 1447 (m), 1435 (m), 1412 (m), 1380 (w), 1364 (m, $\nu(\text{C-O})$), 1324 (w), 1292 (m), 1185 (m, $\nu(\text{S-O})$), 1129 (s), 1077 (m), 1060 (m), 993 (s), 923 (m), 853 (w), 832 (m), 803 (w), 769 (m), 736 (m), 701 (w), 641 (m), 615 (m), 595 (m), 545 (w), 533 (w), 503 (w), 448 (w), 417 (w).

MS m/z = 1271.279 [$\text{Complex}+\text{Na}$]⁺ (calc. m/z = 1271.280); 2520.571 [$2\cdot\text{Complex}+\text{Na}$]⁺ (calc. m/z = 2520.573).

8.12.4 [Co₂LH-(OH)_x(dbcat)₂]SO₄ (X = 0, 1, 2)

R = H / OH

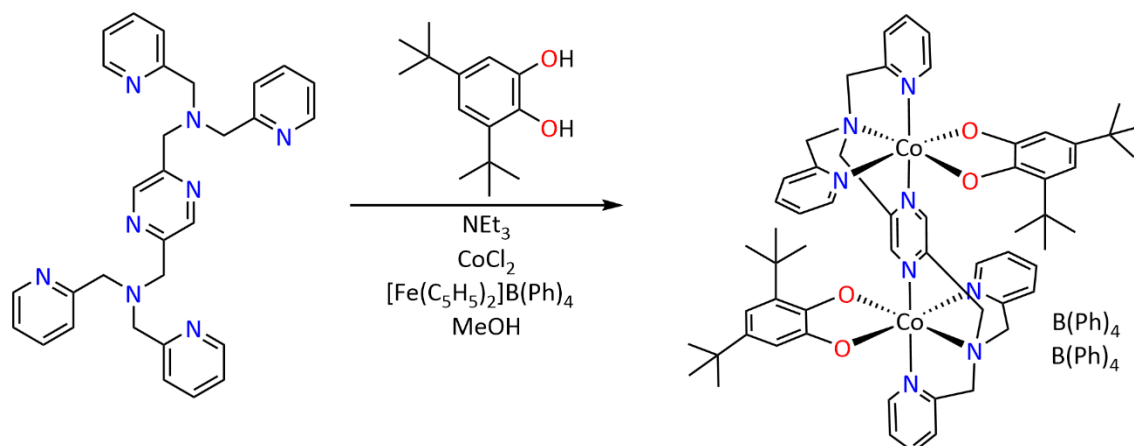
Substance	<i>M</i> / g mol ⁻¹	<i>m</i> / mg	<i>n</i> / mmol	<i>V</i> / mL	equiv.
LH	536.72	54	0.1	-	1.00
3,5-ditertbutylcatechol (dbcat)	222.32	44	0.2	-	2.00
Triethylamine	101.19	40	0.4	-	4.00
Co(II)sulfate heptahydrate	237.93	56	0.2	-	2.00
Methanol	32.04	-	-	15	Solvent

Reaction: REN-TH-467

Procedure:

LH (54 mg, 0.1 mmol, 1.00 equiv.), **dbcat** (44 mg, 0.20 mmol, 2.00 equiv.), and cobalt(II) sulfate heptahydrate (56 mg, 0.20 mmol, 2.00 equiv.) were dissolved in methanol (15 mL). Triethylamine (40 mg, 0.40 mmol, 4.00 equiv.) was added dropwise to the green solution, upon which a colour change to brown was observed. The reaction mixture was heated to reflux for one hour and, after cooling to room temperature, the resulting green solution was filtered. Green crystals were obtained by slow evaporation of the filtrate after one day.

MS $m/z = 547.248$ [Co-LH]²⁺ (calc. 547.248), $m/z = 555.244$ [Co-LH-OH]²⁺ (calc. 555.245), $m/z = 563.248$ [Co-LH-(OH)₂]²⁺ (calc. 563.243),

8.12.5[Co₂(L^{bpap}(dbcat)₂)(B(Ph)₄)₂ (Co-L^{bpap}-B(Ph)₄)

Substance	<i>M</i> / g mol ⁻¹	<i>m</i> / mg	<i>n</i> / mmol	<i>V</i> / mL	equiv.
L ^{bpap}	502.61	50	0.1	-	1.00
3,5-ditertbutylcatechol (dbcat)	222.32	44	0.2	-	2.00
Triethylamine	101.19	40	0.4	-	4.00
Co(II) chloride	129.84	26	0.2	-	2.00
[Fe(C ₅ H ₅) ₂]B(Ph) ₄	505.27	101	0.2	-	2.00
Methanol	32.04	-	-	15	Solvent

Reaction: REN-TH-AM-87

Procedure:

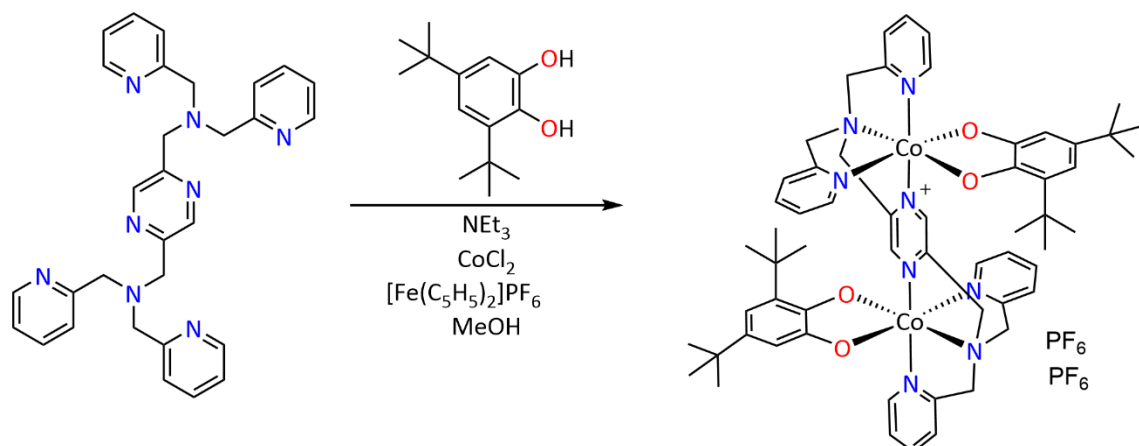
Under an argon atmosphere L^{bpap} (50 mg, 0.1 mmol, 1.00 equiv.), dbcat (44 mg, 0.20 mmol, 2.00 equiv.), and cobalt(II) chloride (26 mg, 0.20 mmol, 2.00 equiv.) were dissolved in degassed, dry methanol (15 mL). Degassed and dry triethylamine (40 mg, 0.40 mmol, 4.00 equiv.) was added dropwise to the green solution, upon which a colour change to red was observed. Ferrocenium tetraphenylborate (101 mg, 0.2 mmol, 2.00 equiv.) was added as a solid and the reaction mixture changed colour to green. The reaction mixture was stirred overnight under an inert atmosphere. The resulting green precipitate was isolated by centrifugation followed by filtration and dried in air. To remove residual yellow/orange ferrocene, the crude green powder was washed with toluene. Green crystals were obtained by carefully layering a dichloromethane solution of the crude product (118 mg) with diethyl ether, after which crystals formed within four days.

Yield: 18 mg green crystals (0.005 mmol, 5%)

IR $\tilde{\nu}$ [cm⁻¹]: 3054 (w), 3039 (w), 2981 (w, ν (C–H)), 2951 (w), 2906 (w), 2865 (w), 2623 (w), 2603 (w), 2498 (w), 1608 (w, ν (C=C)), 1579 (w, ν (C=N)), 1559 (w), 1478 (m), 1438 (m), 1427 (m), 1411 (m), 1358 (w), 1318 (w), 1276 (m), 1241 (m), 1201 (w), 1170 (w), 1158 (w), 1105 (w), 1083 (w), 1054 (w), 1031 (w), 975 (m), 937 (w), 910 (w), 881 (w), 845 (m), 829 (w), 809 (w), 766 (m), 750 (m), 732 (m), 705 (s), 663 (w), 650 (w), 625 (w), 612 (m), 549 (w), 521 (w), 504 (w), 464 (w), 442 (w), 423 (w).

MS m/z = 530.209 [C]²⁺ (calc. 530.209), 1379.586 [C + B(Ph)₄]⁺ (calc. 1379.584).

EA Found: C, 71.58%; H, 6.49%; N, 6.24%, Calc. for C₁₀₆H₁₁₀B₂Co₂N₈O₄ + 4 H₂O: C, 71.86%; H, 6.71%; N, 6.32%.

8.12.6[Co₂(L^{bpap}(dbcat)₂)(PF₆)₂ (Co-L^{bpap}-PF₆)

Substance	<i>M</i> / g mol ⁻¹	<i>m</i> / mg	<i>n</i> / mmol	<i>V</i> / mL	equiv.
L ^{bpap}	502.61	50	0.1	-	1.00
3,5-ditertbutylcatechol (dbcat)	222.32	44	0.2	-	2.00
Triethylamine	101.19	40	0.4	-	4.00
Co(II) chloride	129.84	26	0.2	-	2.00
[Fe(C ₅ H ₅) ₂]PF ₆	331.00	66	0.2	-	2.00
Methanol	32.04	-	-	15	Solvent

Reaction: REN-TH-AM-99

Procedure:

Under an argon atmosphere L^{bpap} (50 mg, 0.1 mmol, 1.00 equiv.), dbcat (44 mg, 0.20 mmol, 2.00 equiv.), and cobalt(II) chloride (26 mg, 0.20 mmol, 2.00 equiv.) were dissolved in degassed, dry methanol (15 mL). Degassed and dry triethylamine (40 mg, 0.40 mmol, 4.00 equiv.) was added dropwise to the green solution, upon which a colour change to red was observed. Ferrocenium hexafluorophosphate (66 mg, 0.2 mmol, 2.00 equiv.) was added as a solid and the reaction mixture changed colour to green. The reaction mixture was stirred overnight under an inert atmosphere. The resulting green solution was filtered and then slow evaporated. After four days green crystals formed, they were collected by filtration and dried in air.

Yield: 57 mg green crystals (0.042 mmol, 42%)

IR $\tilde{\nu}$ [cm⁻¹]: 3646 (w), 3606 (w), 3528 (w), 3443 (w), 3111 (w), 2952 (w), 2906 (w), 2865 (w), 1610 (w), 1574 (w), 1556 (w), 1479 (w), 1439 (m), 1409 (m), 1360 (w), 1318 (w), 1280 (m), 1237 (m), 1202 (w), 1173 (w), 1161 (w), 1112 (w), 1056 (w), 1039 (w), 1026 (w), 978 (w), 911 (w), 877 (w), 832 (s), 767 (m), 740 (m), 719 (m), 664 (w), 653 (w), 625 (w), 582 (w), 556 (s), 524 (w), 493 (m), 471 (w), 458 (w), 439 (m).

MS m/z = 530.209 [C]²⁺(calc. 530.209),

9. References Chapter 4

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10. Supplementary Data Chapter 4

10.1 IR Spectra Ligands

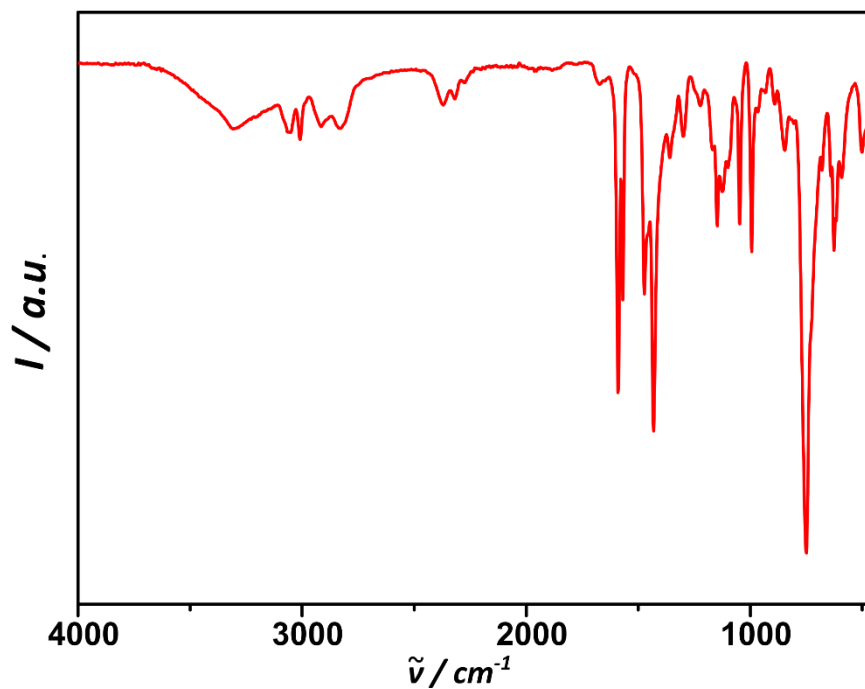


Figure S1: IR-spectrum of bis(pyridylmethyl)amine.

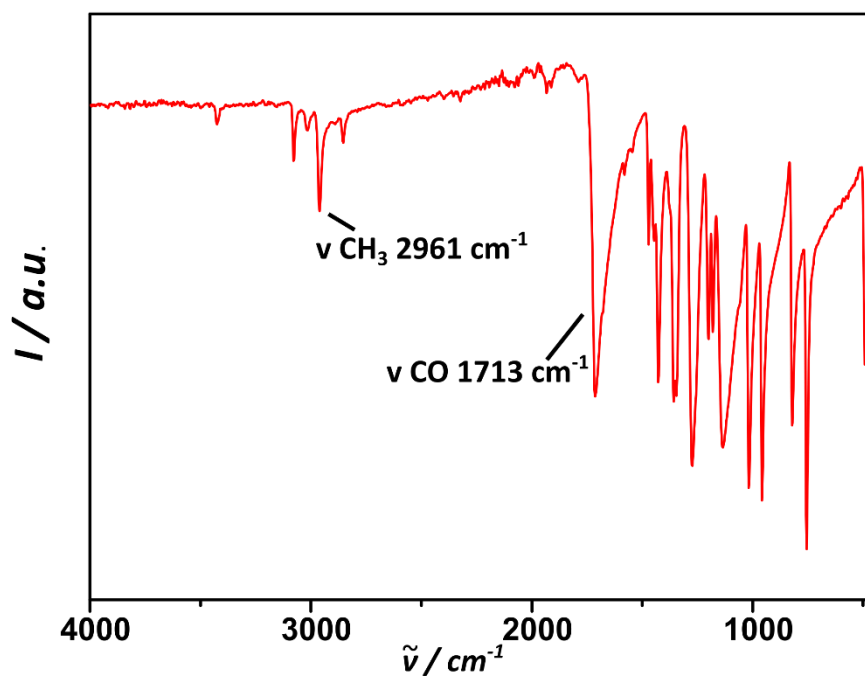


Figure S2: IR-spectrum of pyrazine-2,5-dicarboxylic acid dimethyl ester.

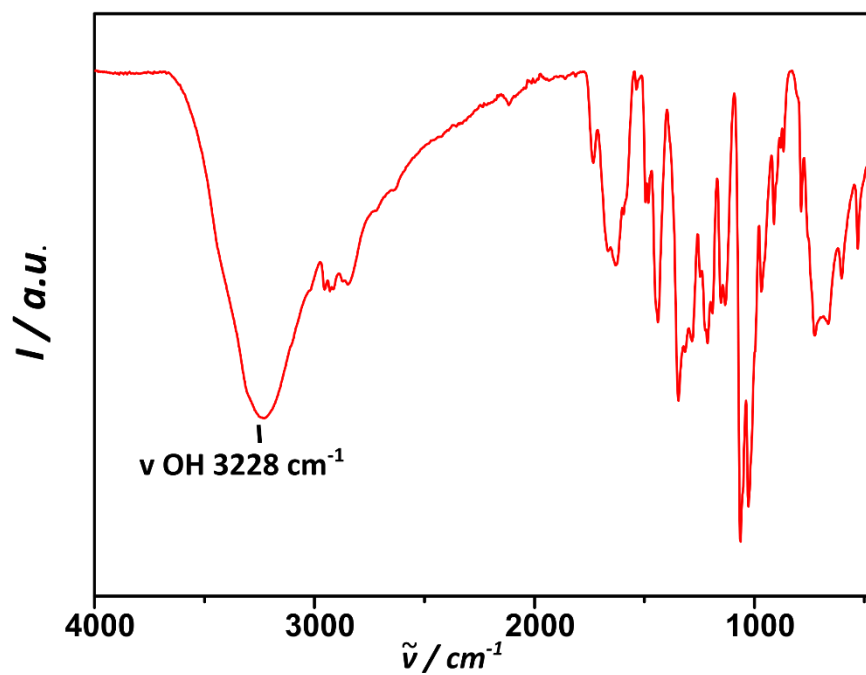


Figure S3: IR-spectrum of 2,5-bis(hydroxymethyl)pyrazine.

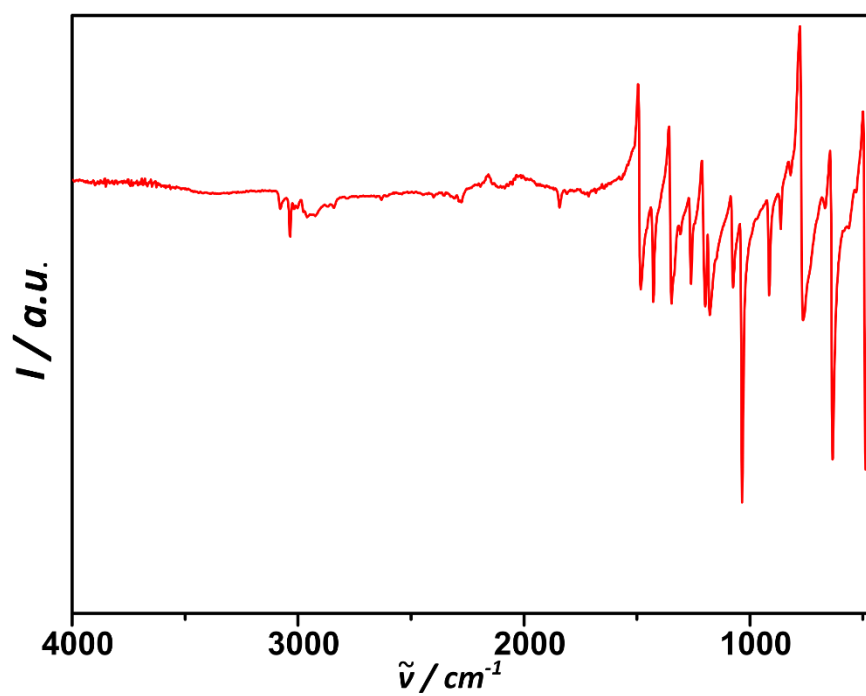


Figure S4: IR-spectrum of 2,5-Bis(bromomethyl)pyrazine.

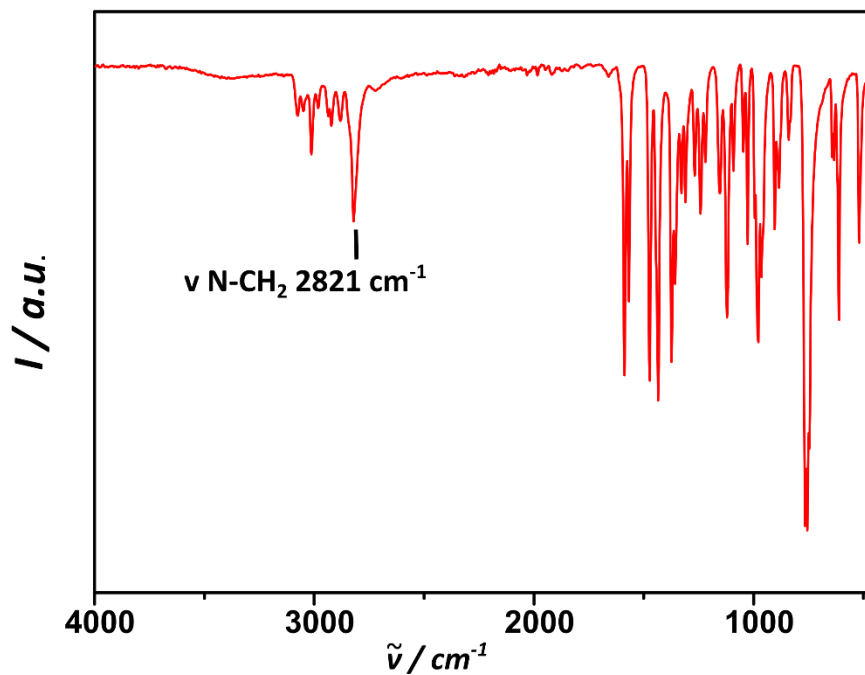


Figure S5: IR-spectrum of 2,5-Bis[(N,N-bis(2-pyridylmethyl)amino)methyl]pyrazine.

10.2 IR Spectra Complexes

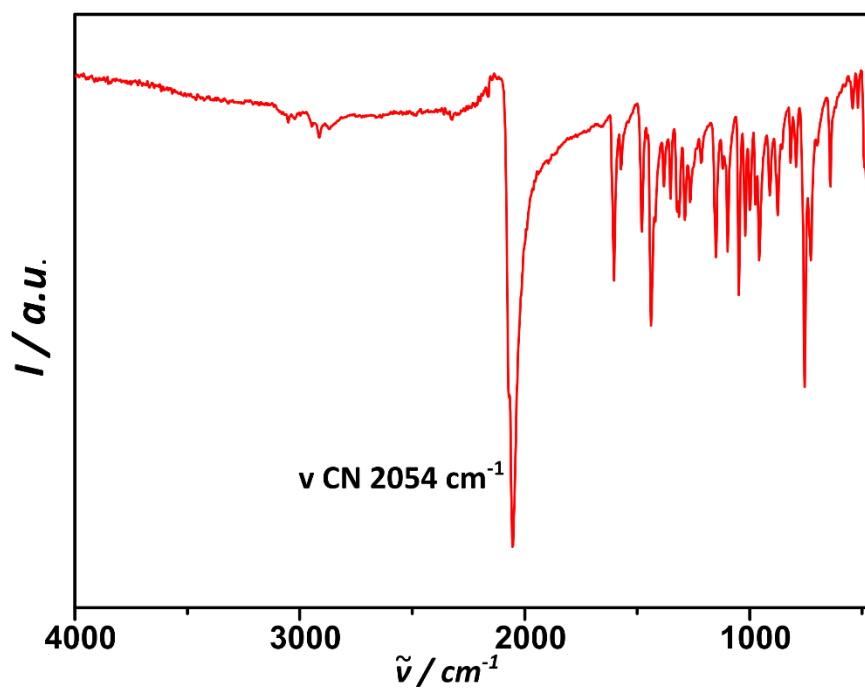


Figure S6: IR-spectrum of $Co_2(L^{bpa})(SCN)_4$.

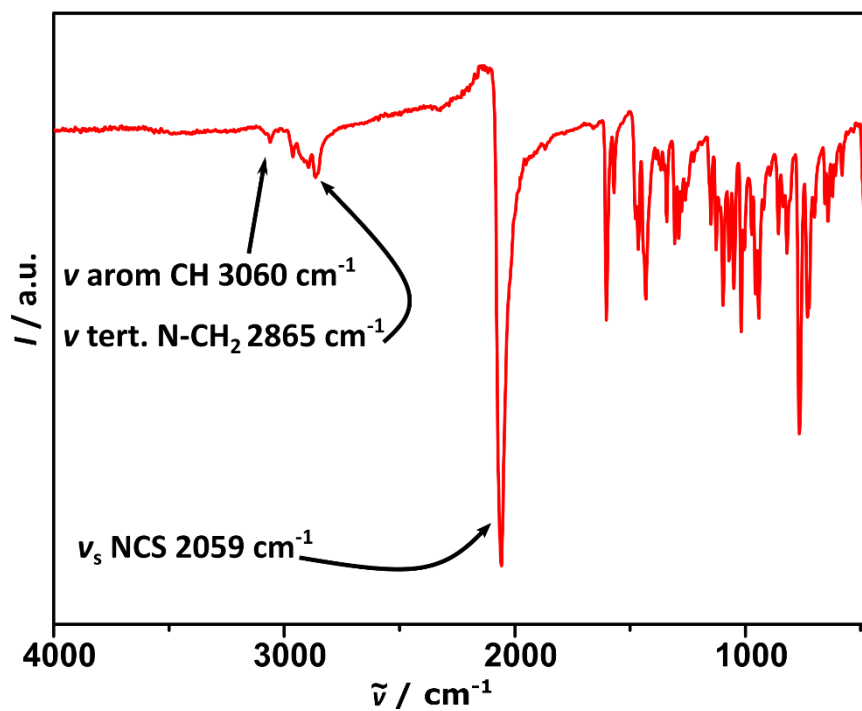


Figure S7: IR-spectrum of $\text{Co}_2(\text{LH})(\text{SCN})_4$.

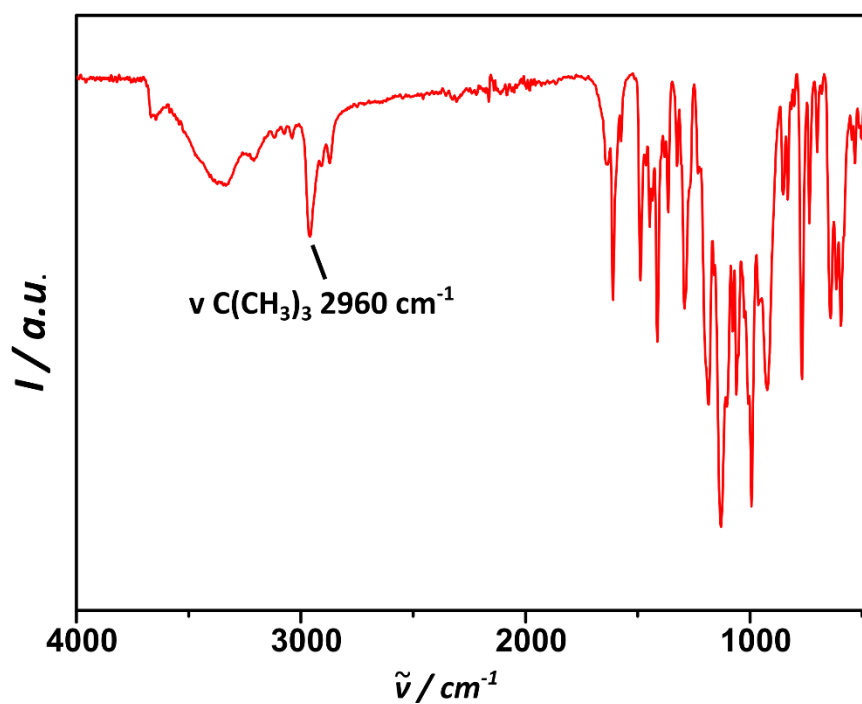


Figure S8: IR-spectrum of $\text{Co}_2(\text{L}^{\text{bpop}}-(\text{dbcat})_2)(\mu^2-\text{SO}_4)_2$.

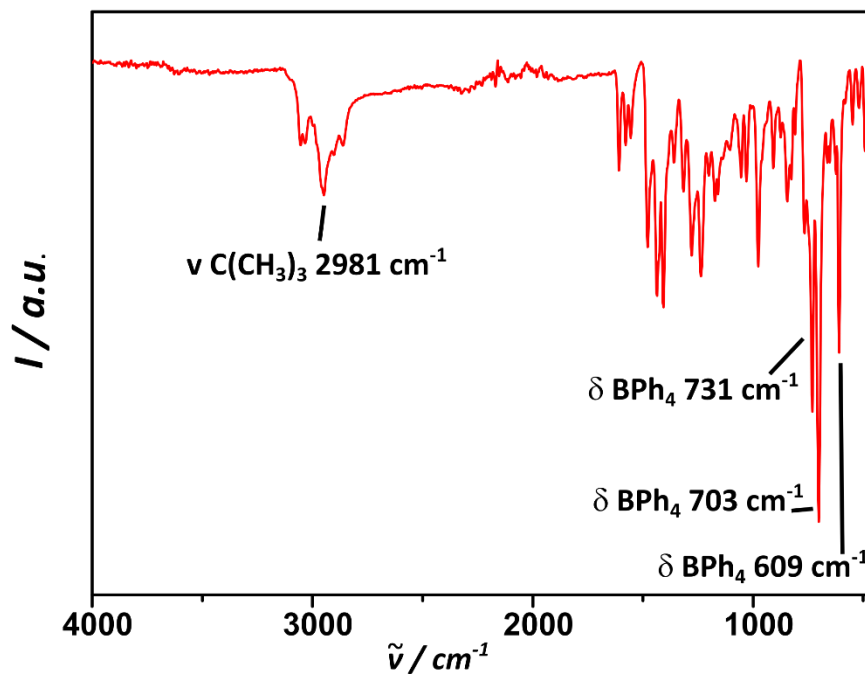


Figure S9: IR-spectrum of $[Co_2(L^{bpop}(dbcac)_2)(B(Ph)_4)_2]$.

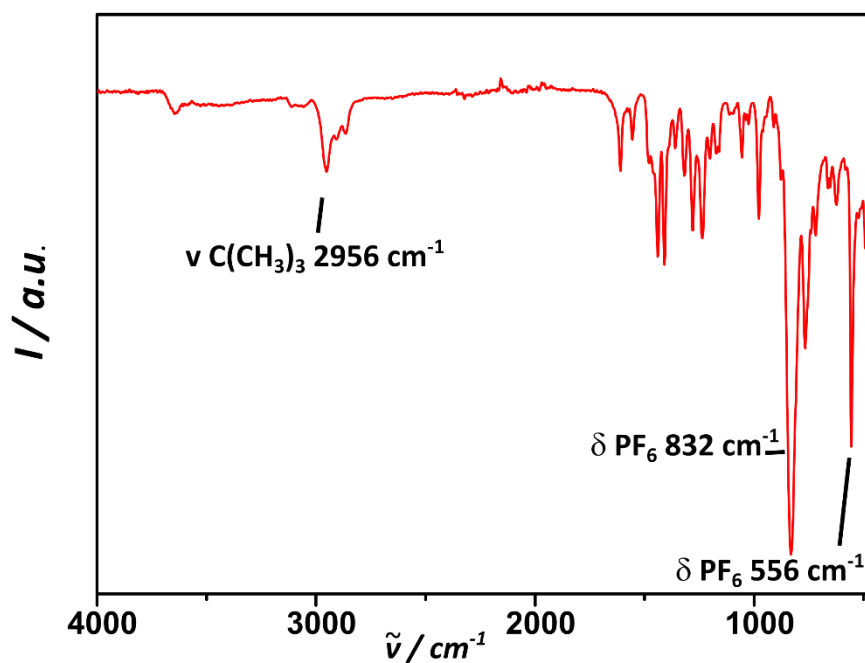


Figure S10: IR-spectrum of $[Co_2(L^{bpop}(dbcac)_2)(PF_6)_2]$.

10.3 NMR-Spectra

10.3.1 ^1H -NMR Spectra

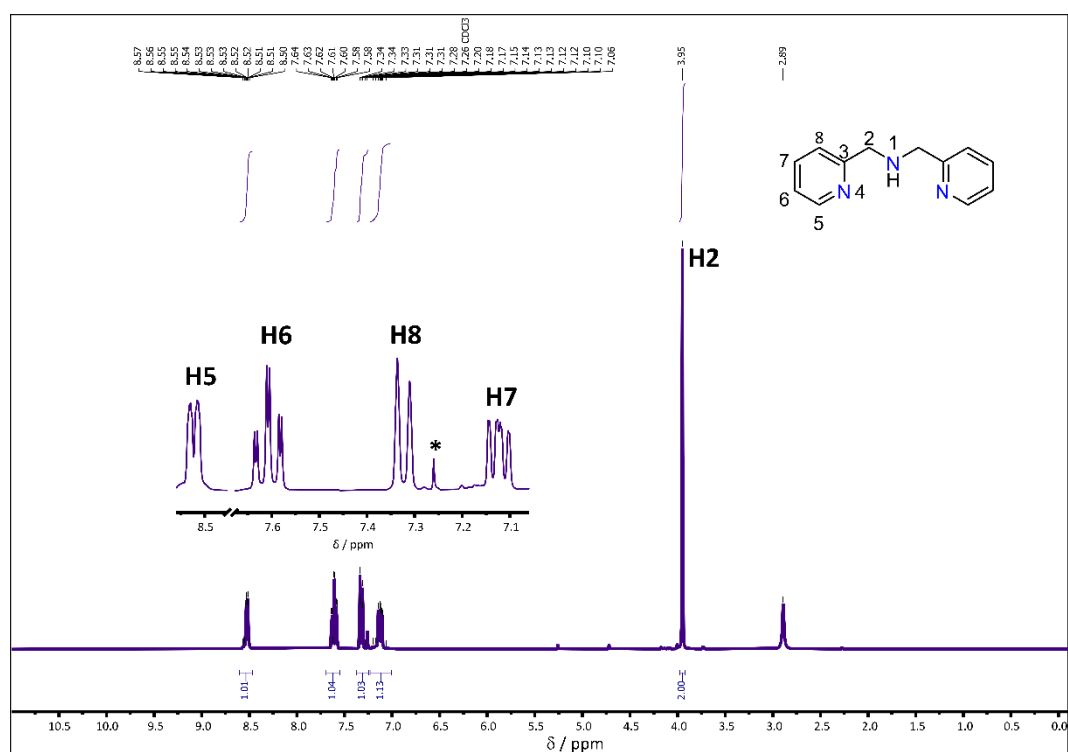


Figure S11: ^1H -NMR of bis(pyridylmethyl)amine in CDCl_3 [400 MHz].

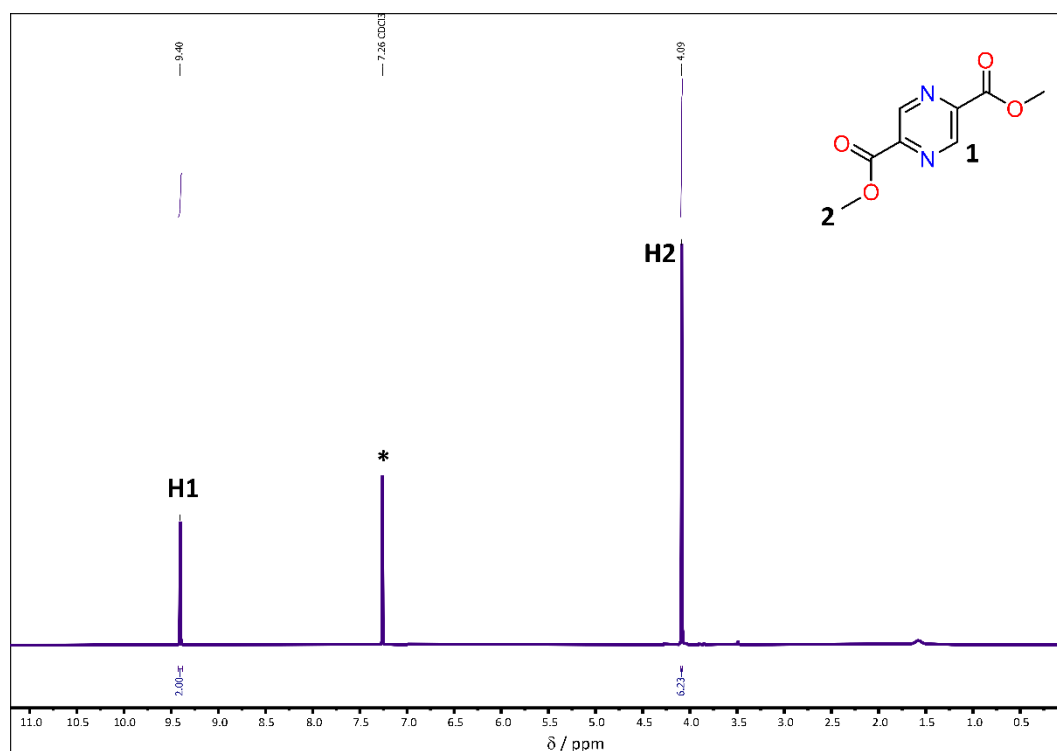


Figure S12: ^1H -NMR of pyrazine-2,5-dicarboxylic acid dimethyl ester in CDCl_3 [300 MHz].

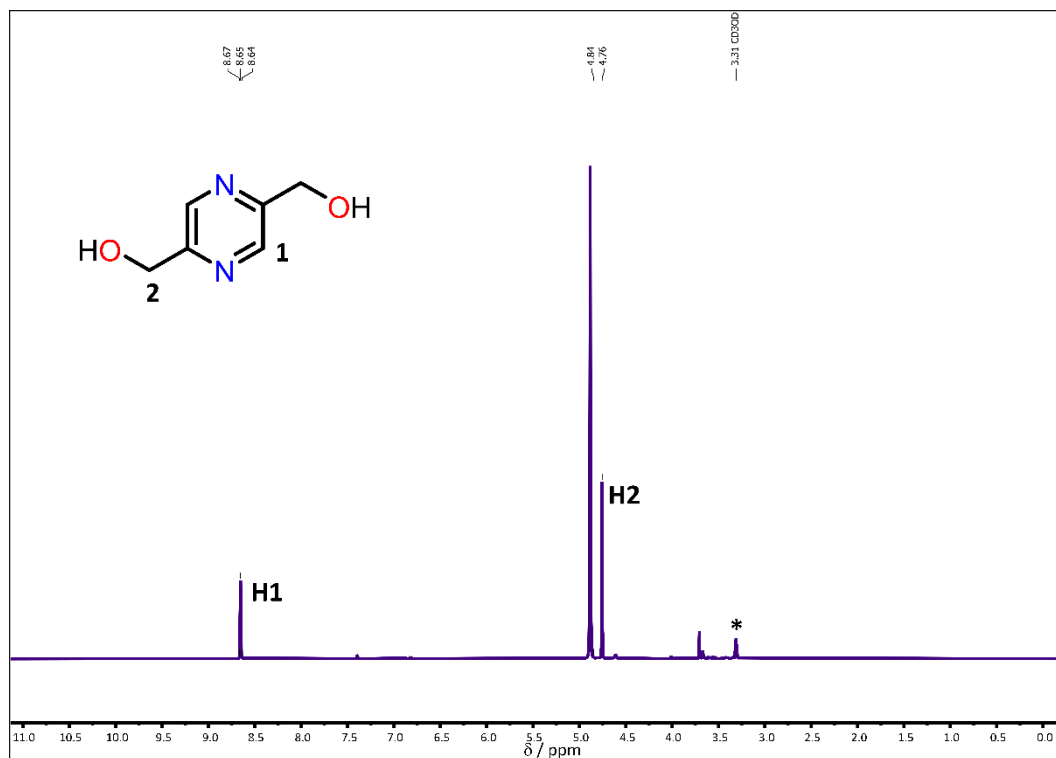


Figure S13: ^1H -NMR of pyrazine-2,5-bis(hydroxymethyl)pyrazine in MeOD . [300 MHz].

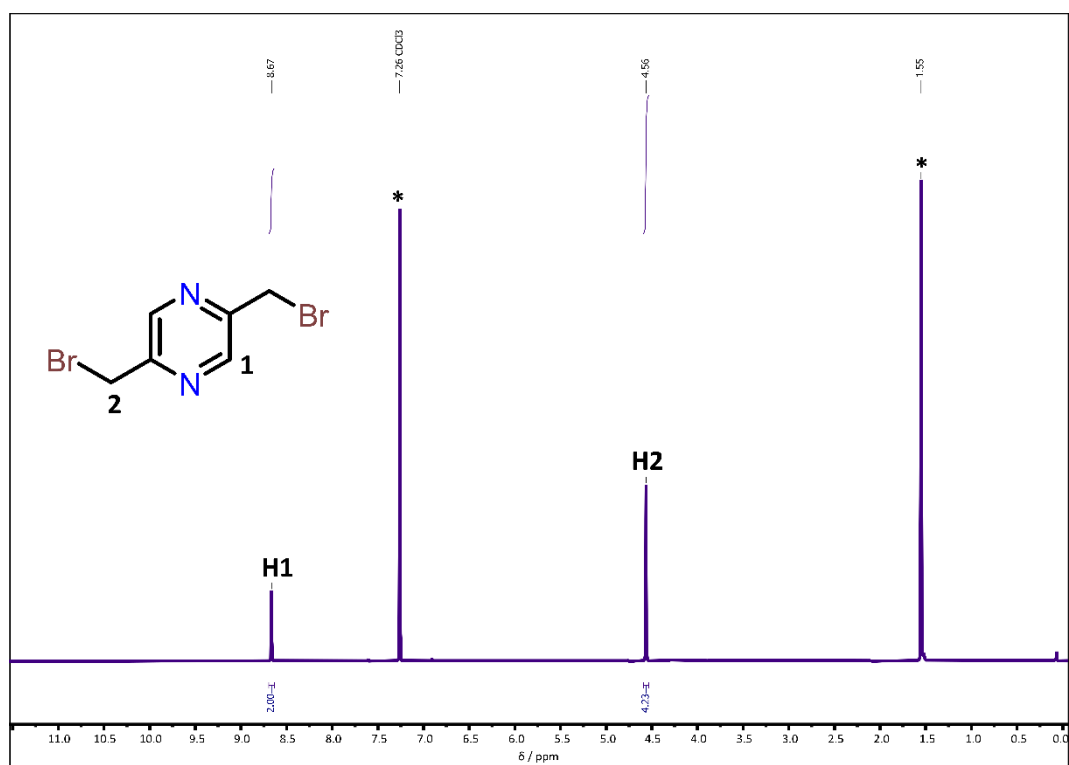


Figure S14: ^1H -NMR of pyrazine-2,5-bis(bromomethyl)pyrazine in CDCl_3 [300 MHz].

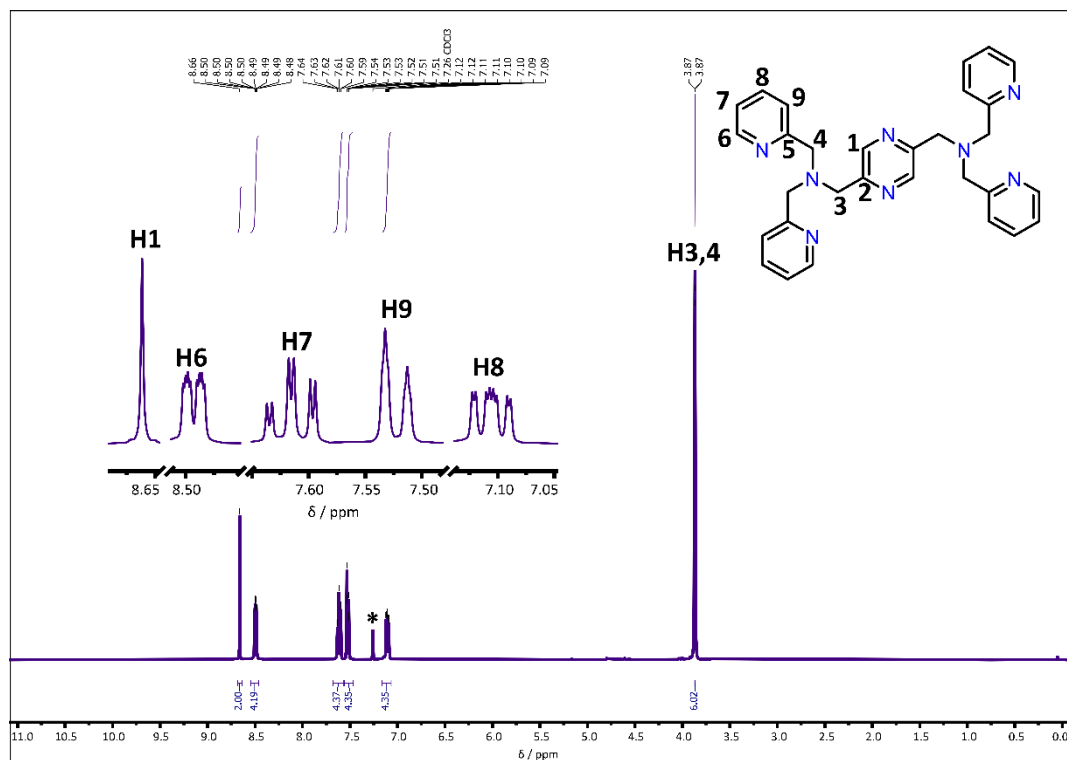


Figure S15: ¹H-NMR of 2,5-Bis[(N,N-bis(2-pyridylmethyl)amino)methyl]pyrazine (*L^{bpap}*) in CDCl₃ [400 MHz].

10.3.2 ¹³C-NMR Spectrum

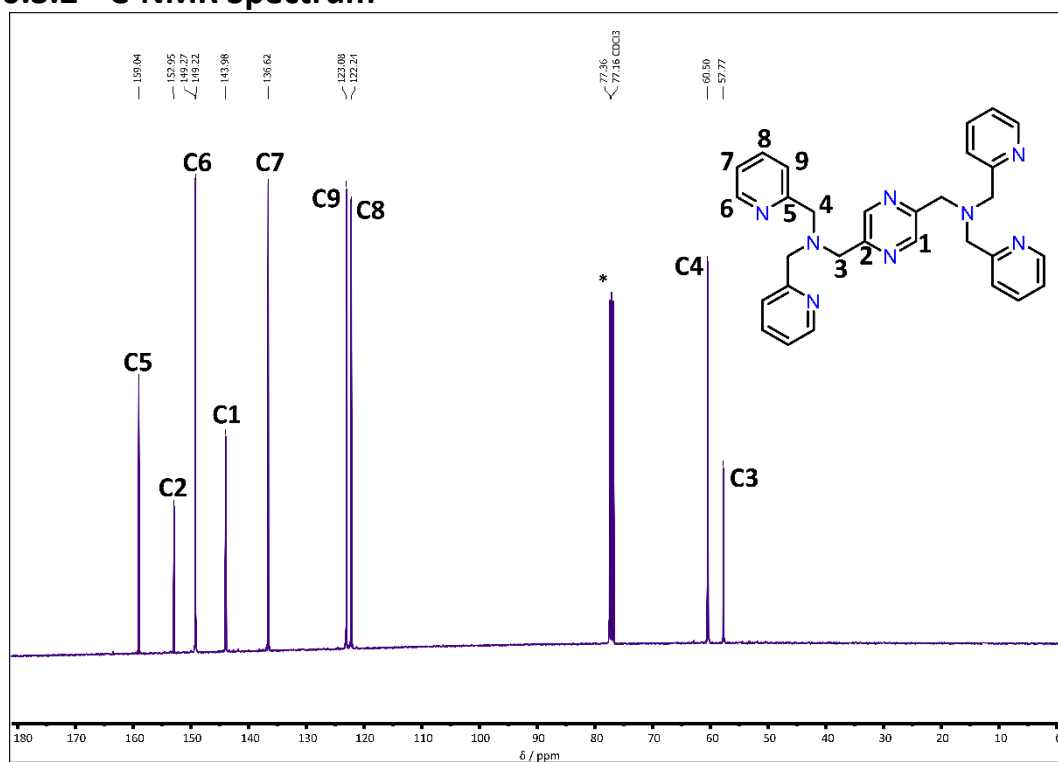


Figure S16: ¹³C-NMR of 2,5-Bis[(N,N-bis(2-pyridylmethyl)amino)methyl]pyrazine (*L^{bpap}*) in CDCl₃ [400 MHz].

10.3.3 2D-NMR Spectra

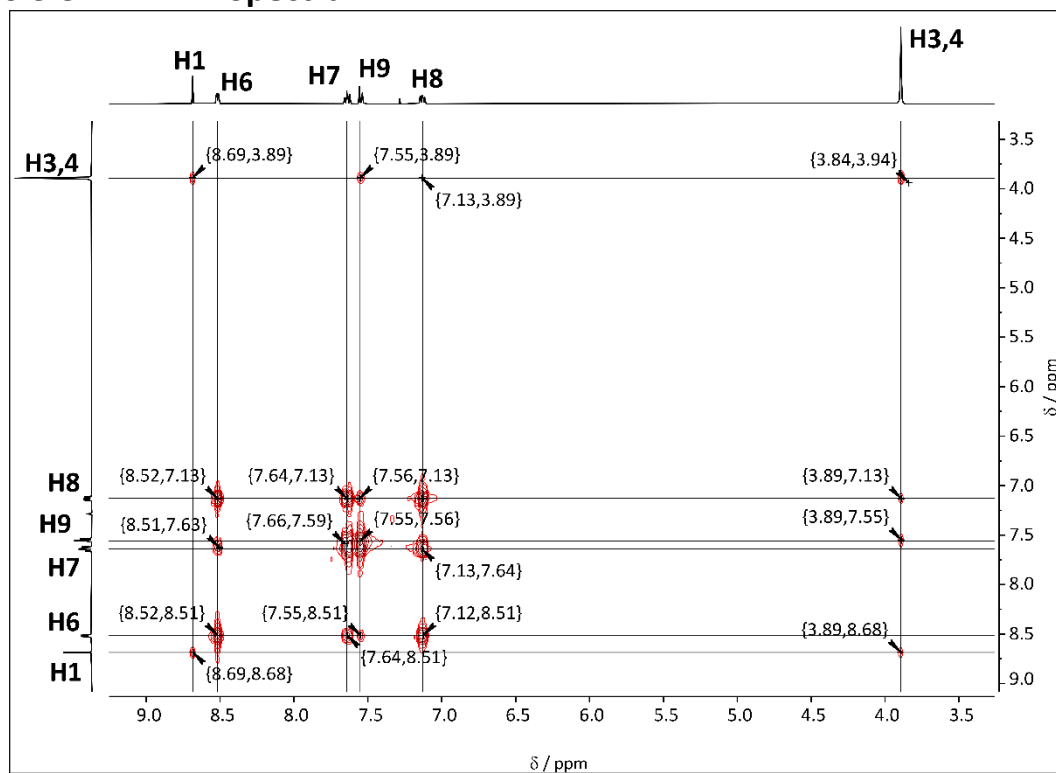


Figure S17: COSY of 2,5-Bis[(N,N-bis(2-pyridylmethyl)amino)methyl]pyrazine (L^{bpop}) in $CDCl_3$ [400 MHz].

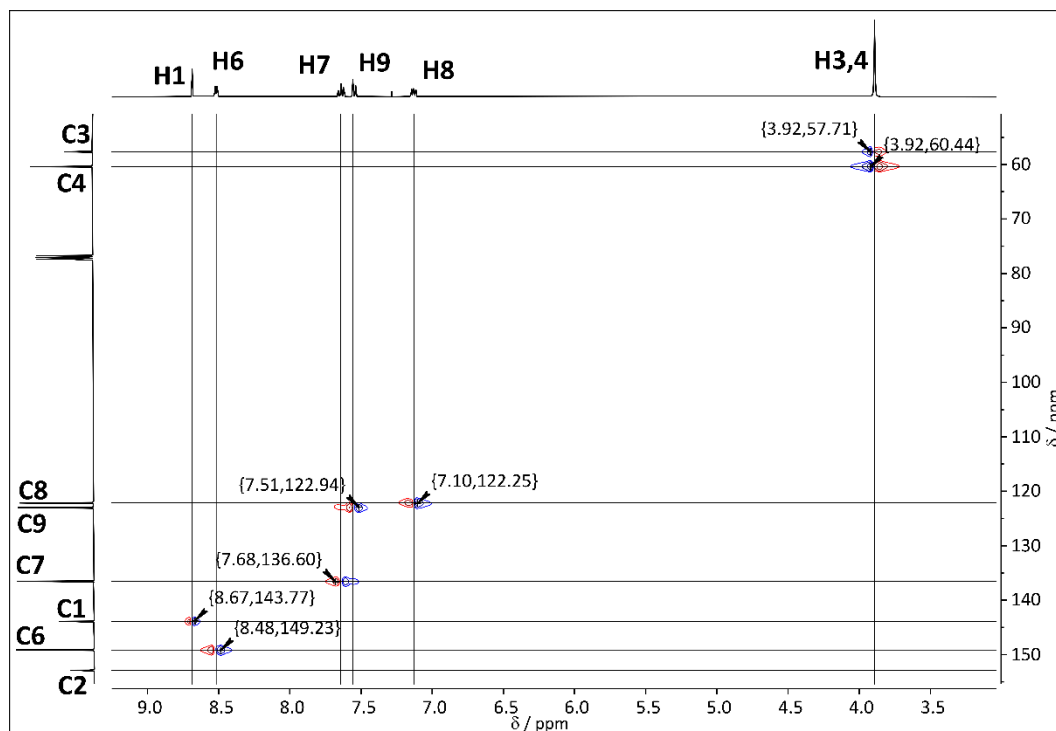


Figure S18: HSQC of 2,5-Bis[(N,N-bis(2-pyridylmethyl)amino)methyl]pyrazine (L^{bpop}) in $CDCl_3$ [400 MHz].

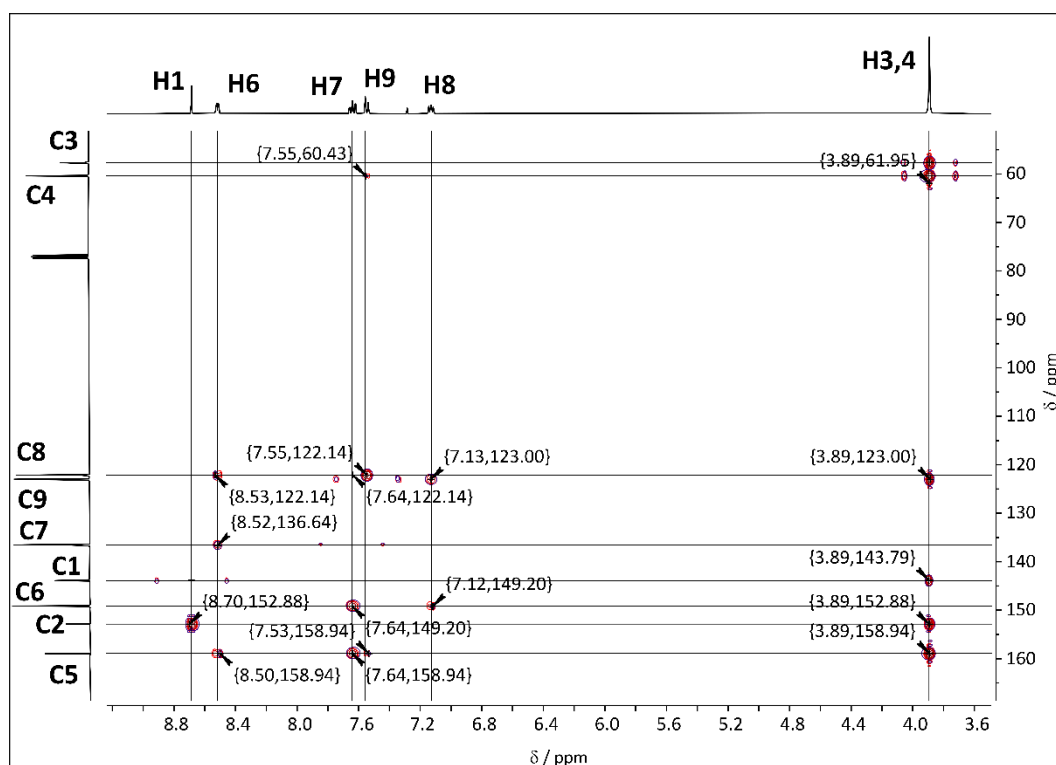


Figure S19: HMBC of 2,5-Bis[(N,N-bis(2-pyridylmethyl)amino)methyl]pyrazine (L^{bpop}) in $CDCl_3$ [400 MHz].

10.4 Mass Spectrometry

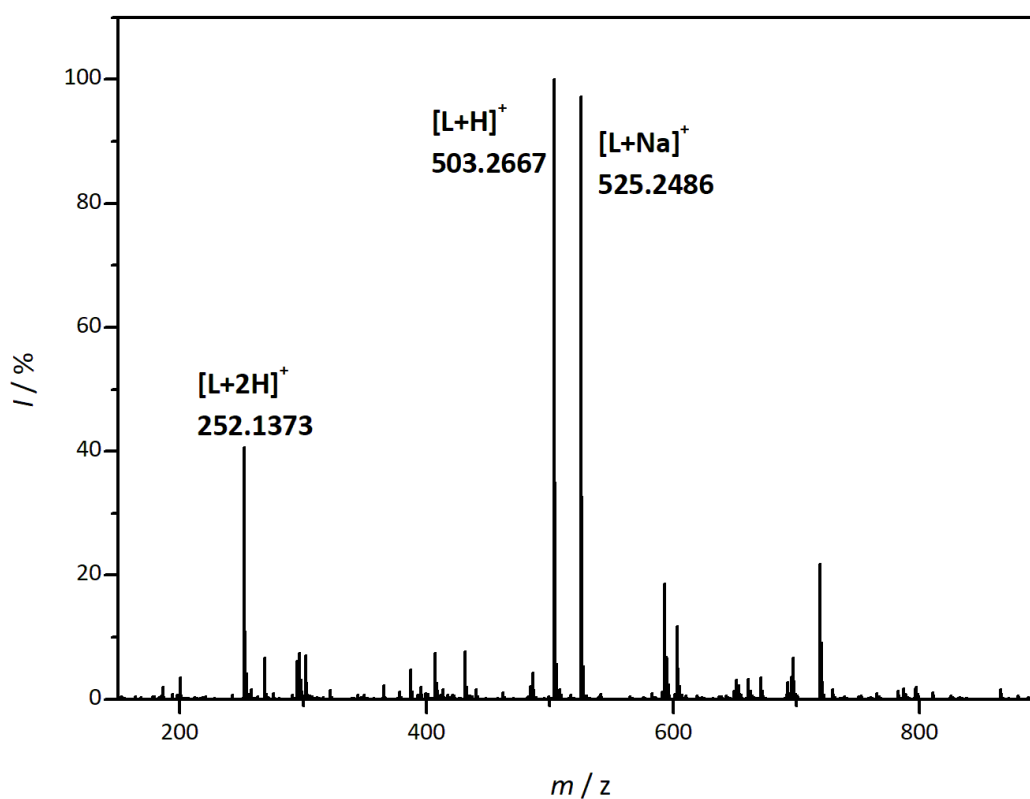
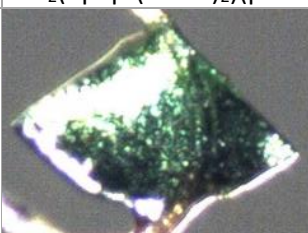
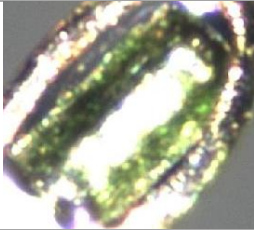
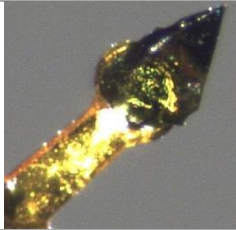
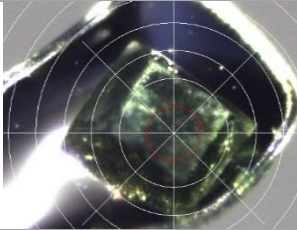
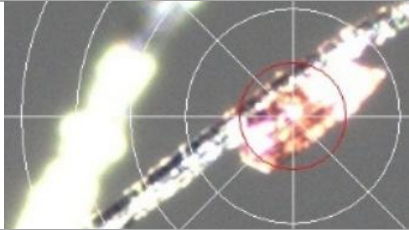


Figure S20: ESI⁺ MS-spectrum of 2,5-Bis[(N,N-bis(2-pyridylmethyl)amino)methyl]pyrazine (L^{bpop}).

10.5 Crystallographic Data

Komplex	$\text{Co}_2(\text{L}^{\text{bpap}})(\text{SCN})_4$	$\text{Co}_2(\text{bpap}-(\text{dbcat})_2)(\mu^2-\text{SO}_4)_2$
		
Ansatz	TH-AM-9	TH-AM-30
Summenformel	$\text{C}_{34}\text{H}_{30}\text{Co}_2\text{N}_{12}\text{S}_4$	$\text{C}_{58}\text{H}_{66}\text{Co}_2\text{N}_8\text{O}_{12}\text{S}_2, 8(\text{CH}_4\text{O})$
Molekulargewicht / g mol^{-1}	852.80	1505.50
Temperatur / K	120.0	120.00
Kristallsystem	monoclinic	monoclinic
Raumgruppe	C2/c	C2/c
a / Å	20.7796(6)	32.5357(8)
b / Å	11.6383(2)	13.7303(4)
c / Å	19.5677(5)	18.4544(5)
$\alpha / ^\circ$	90	90
$\beta / ^\circ$	129.778(2)	119.390(2)
$\gamma / ^\circ$	90	90
Volume / Å ³	3636.86(17)	7183.0(4)
Z	4	4
$\rho_{\text{calc}} / \text{g cm}^{-3}$	1.558	1.392
m / mm ⁻¹	1.187	0.596
F(000)	1744.0	3184.0
Kristallgröße / mm ³	$0.17 \times 0.133 \times 0.07$	$0.21 \times 0.15 \times 0.04$
Strahlung	MoK α ($\lambda = 0.71073$)	MoK α ($\lambda = 0.71073$)
2 θ Bereich für die Datenerfassung / °	4.154 to 67.424	4.432 to 65.462
Indexbereich	$-31 \leq h \leq 32, -15 \leq k \leq 18, -28 \leq l \leq 28$	$-41 \leq h \leq 44, -13 \leq k \leq 19, -25 \leq l \leq 25$
Gesammelte Reflexe	20894	35027
Unabhängige Reflexe	6245 [$R_{\text{int}} = 0.0155, R_{\text{sigma}} = 0.0165$]	10889 [$R_{\text{int}} = 0.0248, R_{\text{sigma}} = 0.0214$]
Daten / Einschränkungen / Parameter	6245/0/235	10889/118/518
Goodness-of-fit on F^2	1.028	1.039
Finaler R Index [$I \geq 2\sigma(I)$]	$R_1 = 0.0370, wR_2 = 0.0974$	$R_1 = 0.0626, wR_2 = 0.1805$
Finaler R Index [alle Daten]	$R_1 = 0.0419, wR_2 = 0.1016$	$R_1 = 0.0698, wR_2 = 0.1891$
Größte diff. peak/hole / e Å ⁻³	0.68/-0.50	1.35/-1.00

Complex	$[\text{Co}_2(\text{L}^{\text{bpap}})(\text{dbcat})_2](\text{B}(\text{Ph})_4)_2$	$[\text{Co}_2(\text{L}^{\text{bpap}})(\text{dbcat})_2](\text{PF}_6)_2$
		
Reaction Number	TH-AM-47-1	TH-AM-99
Empirical formula	$\text{C}_{58}\text{H}_{70}\text{Co}_2\text{N}_8\text{O}_4 \cdot 2(\text{C}_{24}\text{H}_{20}\text{B}), 10(\text{CH}_2\text{Cl}_2)$	$\text{C}_{62.3}\text{H}_{87.19}\text{Co}_2\text{F}_{12}\text{N}_8\text{O}_{9.3}\text{P}_2$
Formula weight	2548.75	1504.79
Temperature/K	120.00	120
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P-1$
$a/\text{\AA}$	14.6823(2)	11.4796(3)
$b/\text{\AA}$	17.3498(4)	16.5678(4)
$c/\text{\AA}$	24.3895(3)	19.1353(4)
$\alpha/^\circ$	90	85.071(2)
$\beta/^\circ$	101.5840(10)	80.434(2)
$\gamma/^\circ$	90	84.375(2)
Volume/ $\text{\AA}^3$	6086.31(18)	3562.49(15)
Z	2	2
$\rho_{\text{calc}}/\text{g/cm}^3$	1.391	1.403
μ/mm^{-1}	0.765	0.6
$F(000)$	2636.0	1567
Crystal size/ mm^3	$0.18 \times 0.103 \times 0.035$	$0.22 \times 0.14 \times 0.08$
Radiation	$\text{MoK}\alpha$ ($\lambda = 0.71073$)	$\text{MoK}\alpha$ ($\lambda = 0.71073$)
2θ range for data collection/ $^\circ$	4.14 to 65.442	4.328 to 67.6
Index ranges	$-19 \leq h \leq 22, -24 \leq k \leq 23, -34 \leq l \leq 34$	$-17 \leq h \leq 16, -24 \leq k \leq 23, -28 \leq l \leq 28$
Reflections collected	65558	79133
Independent reflections	18931 [$R_{\text{int}} = 0.0161, R_{\text{sigma}} = 0.0196$]	24796 [$R_{\text{int}} = 0.0185, R_{\text{sigma}} = 0.0194$]
Data/restraints/parameters	18931 / 379 / 795	24796/24/1055
Goodness-of-fit on F^2	1.059	1.055
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0953, wR_2 = 0.2839$	$R_1 = 0.0773, wR_2 = 0.2248$
Final R indexes [all data]	$R_1 = 0.1079, wR_2 = 0.2972$	$R_1 = 0.0936, wR_2 = 0.2416$
Largest diff. peak/hole / $e \text{\AA}^{-3}$	2.81/-2.54	1.81/-0.96

Complex	[Co ₂ LH-(OH) _x (dbcat) ₂] ₂ SO ₄	Co ₂ (LH)(SCN) ₄
		
Reaction Number	TH-467	TH-443
Empirical formula	C ₆₆ H ₁₀₄ Co ₂ N ₈ O _{14.89} S	C ₃₇ H ₄₂ Cl ₂ Co ₂ N ₁₂ S ₄
Formula weight	1397.81	971.82
Temperature/K	120	120.00
Crystal system	monoclinic	monoclinic
Space group	C2/c	P2 ₁ /c
a/Å	26.3589(11)	8.6326(2)
b/Å	17.2160(6)	14.7740(3)
c/Å	17.1203(7)	16.9918(4)
α/°	90	90
β/°	93.222(3)	101.879(2)
γ/°	90	90
Volume/Å ³	7756.8(5)	2120.69(8)
Z	4	2
ρ _{calc} /g/cm ³	1.197	1.522
μ/mm ⁻¹	0.517	1.150
F(000)	2981	1000.0
Crystal size/mm ³	0.28 × 0.227 × 0.16	0.141 × 0.08 × 0.047
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	4.732 to 54	4.822 to 65.18
Index ranges	-33 ≤ h ≤ 33, -17 ≤ k ≤ 21, -21 ≤ l ≤ 17	-13 ≤ h ≤ 11, -20 ≤ k ≤ 20, -25 ≤ l ≤ 23
Reflections collected	31872	28340
Independent reflections	8437 [R _{int} = 0.0246, R _{sigma} = 0.0241]	6548 [R _{int} = 0.0188, R _{sigma} = 0.0177]
Data/restraints/parameters	8437/0/434	6548/2/265
Goodness-of-fit on F ²	1.054	1.049
Final R indexes [I > 2σ (I)]	R ₁ = 0.0694, wR ₂ = 0.1975	R ₁ = 0.0481, wR ₂ = 0.1288
Final R indexes [all data]	R ₁ = 0.0833, wR ₂ = 0.2147	R ₁ = 0.0568, wR ₂ = 0.1362
Largest diff. peak/hole / e Å ⁻³	1.01/-1.06	1.42/-0.80

10.5.1 Bond Lengths and Angles

Table S1: Selected Metal-Donor Bond-Lengths.

$\text{Co}_2(\text{L}^{\text{bpap}})(\text{SCN})_4$	Bond Length / Å	$\text{Co}_2(\text{LH})(\text{SCN})_4$	Bond Length / Å
Co1–N1	2.1870(13)	Co1 N1	2.1552(17)
Co1–N2	2.1424(13)	Co1–N2	2.1284(15)
Co1–N3	2.1380(14)	Co1–N3	2.1374(18)
Co1–N4	2.2372(12)	Co1–N4	2.4072(16)
Co1–N5	2.0211(14)	Co1–N5	2.0288(19)
Co1–N6	2.0893(13)	Co1–N6	2.0709(16)

Table S2: Selected Bond Angles.

$\text{Co}_2(\text{L}^{\text{bpap}})(\text{SCN})_4$	Angle / °	$\text{Co}_2(\text{LH})(\text{SCN})_4$	Angle / °
N1 Co1 N4	79.60(4)	N1 Co1 N4	79.78(6)
N2 Co1 N1	77.44(5)	N2 Co1 N1	80.09(6)
N2 Co1 N4	79.00(5)	N2 Co1 N3	94.07(6)
N3 Co1 N1	76.90(5)	N2 Co1 N4	84.22(6)
N3 Co1 N2	154.31(5)	N3 Co1 N1	77.59(7)
N3 Co1 N4	97.37(5)	N3 Co1 N4	157.26(6)
N5 Co1 N1	69.67(5)	N5 Co1 N1	170.10(7)
N5 Co1 N2	103.61(6)	N5 Co1 N2	92.84(7)
N5 Co1 N3	101.84(6)	N5 Co1 N3	96.16(7)
N5 Co1 N4	90.46(5)	N5 Co1 N4	106.57(6)
N5 Co1 N6	96.98(6)	N5 Co1 N6	95.35(7)
N6 Co1 N1	93.28(5)	N6 Co1 N1	92.34(6)
N6 Co1 N2	90.19(5)	N6 Co1 N2	170.46(6)
N6 Co1 N3	90.20(5)	N6 Co1 N3	89.92(6)
N6 Co1 N4	168.09(5)	N6 Co1 N4	88.75(6)

Table S3: Selected Metal-Donor Bond-Lengths.

$\text{Co}_2(\text{L}^{\text{bpap}}-(\text{dbcat})_2)(\mu^2-\text{SO}_4)_2$	Bond Length / Å	$[\text{Co}_2\text{LH}-(\text{OH})_x(\text{dbcat})_2]\text{SO}_4$	Bond Length / Å
Co1 O3	1.9686(16)	Co1 O1	1.870(2)
Co1 O4	2.568(2)	Co1 O2	1.8773(19)
Co1 N1	2.2772(17)	Co1 N1	1.948(3)
Co1 N2	2.0583(17)	Co1 N2	1.922(2)
Co1 N3	2.0686(19)	Co1 N3	1.919(3)
Co1 N4	2.1029(17)	Co1 N4	2.047(2)

Table S4: Selected Dioxolene Bond Lengths.

$\text{Co}_2(\text{L}^{\text{bpap}}-(\text{dbcat})_2)(\mu^2-\text{SO}_4)_2$	Bond Length / Å	$[\text{Co}_2\text{LH}-(\text{OH})_x(\text{dbcat})_2]\text{SO}_4$	Bond Length / Å
C16 C17	1.382(3)	O1 C17	1.365(3)
C16 C21	1.374(3)	O2 C22	1.350(3)
C17 C18	1.410(4)	C17 C18	1.405(4)
C18 C19	1.389(4)	C17 C22	1.398(4)
C19 C20	1.410(4)	C18 C19	1.396(4)
C20 C21	1.373(3)	C19 C20	1.396(5)

O1 C16	1.399(3)	C20 C21	1.394(4)
O2 C21	1.381(3)	C21 C22	1.396(4)

Table S5: Selected Metal-Donor Bond Lengths.

$[\text{Co}_2(\text{L}^{\text{bpap}})(\text{dbcat})_2](\text{B}(\text{Ph})_4)_2$	Bond Length / Å	$[\text{Co}_2(\text{L}^{\text{bpap}})(\text{dbcat})_2](\text{PF}_6)_2$	Bond Length / Å
Co1 O1	1.877(2)	Co1 O1	1.861(2)
Co1 O2	1.860(2)	Co1 O2	1.885(2)
Co1 N1	1.955(2)	Co1 N1	1.956(2)
Co1 N2	1.922(2)	Co1 N2	1.920(2)
Co1 N3	1.914(2)	Co1 N3	1.908(2)
Co1 N4	1.919(2)	Co1 N4	1.928(2)

Table S6: Selected Bond Angles.

$[\text{Co}_2(\text{L}^{\text{bpap}})(\text{dbcat})_2](\text{B}(\text{Ph})_4)_2$	Angle / °	$[\text{Co}_2(\text{L}^{\text{bpap}})(\text{dbcat})_2](\text{PF}_6)_2$	Angle / °
O1 Co1 N1	91.13(9)	O1 Co1 O2	88.46(9)
O1 Co1 N2	175.87(9)	O1 Co1 N1	179.61(10)
O1 Co1 N3	91.40(10)	O1 Co1 N2	93.14(10)
O1 Co1 N4	86.35(9)	O1 Co1 N3	94.32(9)
O2 Co1 O1	89.41(9)	O1 Co1 N4	94.63(9)
O2 Co1 N1	179.15(9)	O2 Co1 N1	91.30(10)
O2 Co1 N2	92.79(10)	O2 Co1 N2	177.29(9)
O2 Co1 N3	94.49(10)	O2 Co1 N3	89.52(9)
O2 Co1 N4	95.27(9)	O2 Co1 N4	88.12(9)
N2 Co1 N1	86.71(10)	N2 Co1 N1	87.09(10)
N3 Co1 N1	84.84(10)	N2 Co1 N4	93.92(9)
N3 Co1 N2	91.92(10)	N3 Co1 N1	85.36(10)
N3 Co1 N4	169.96(11)	N3 Co1 N2	88.18(9)
N4 Co1 N1	85.43(9)	N3 Co1 N4	170.68(10)
N4 Co1 N2	89.97(10)	N4 Co1 N1	85.68(9)

Table S7: Selected Dioxolene Bond Lengths.

$\text{Co}_2(\text{L}^{\text{bpap}}-(\text{dbcat})_2)(\mu^2-\text{SO}_4)_2$	Bond Length / Å	$[\text{Co}_2\text{LH}-(\text{OH})_x(\text{dbcat})_2]\text{SO}_4$	Bond Length / Å
C16 C17	1.390(4)	C16 C17	1.403(4)
C16 C21	1.412(4)	C16 C21	1.406(5)
C17 C18	1.402(5)	C17 C18	1.415(5)
C18 C19	1.395(6)	C18 C19	1.360(6)
C19 C20	1.413(5)	C19 C20	1.404(5)
C20 C21	1.407(4)	C20 C21	1.392(4)
O1 C21	1.359(3)	O1 C16	1.355(3)
O2 C16	1.357(4)	O2 C21	1.366(4)

11. Summary and Outlook

The aim of this work was to systematically investigate valence tautomeric behaviour in dinuclear cobalt-dioxolene complexes and to establish rational design principles for tuning the VT transition through four independently adjustable molecular parameters: dioxolene electronics, ancillary ligand substitution, counteranion and lattice effects, and bridging unit modification. Building on earlier work by M. Diehl, this study demonstrates that the VT response in such systems is governed by a delicate interplay of electronic structure, redox tuning, and solid-state environment.

In the first chapter, electronic modulation of the catecholate was achieved through halogen substitution, and packing effects were systematically varied through anion exchange. Eight new complexes containing either tetrachlorocatecholate or tetrabromocatecholate with sulfate, perchlorate, hexafluorophosphate, and tetraphenylborate counter anions were synthesised and fully characterised by XRD, IR, MS, and EA. All complexes adopted a LS Co(III)cat configuration at low temperature. UV-Vis spectroscopy confirmed the electron-withdrawing nature of the halogenated catecholates through a hypsochromic shift of the LMCT band, and cyclic voltammetry showed an increase in the electrochemical gap between the Co(III)/Co(II) and catecholate/semiquinonate redox couples of nearly 200 mV relative to the unsubstituted system, both indicating a higher activation barrier for VT. Evans method measurements confirmed that complexes bearing tetrahalogenated catecholates do not switch within the accessible temperature window up to 343 K in acetonitrile. Notably, complexes bearing the sulfate anion exhibited a small and incomplete VT transition in the solid-state at elevated temperatures, complexes bearing different anions did not exhibit any switching behaviour in the solid-state at all. This was attributed to co-crystallisation with a large number of solvent molecules in the complexes bearing the sulfate anions, establishing an extensive intermolecular hydrogen-bonding network that softens the crystal lattice and facilitates the tautomeric transition. Unfortunately, no halogen-based intermolecular interactions could be induced and the dominant influence of the tetrahalogenated catecholates is therefore purely electronic, disfavouring the transition and shifting to higher temperatures.

In the second chapter, the catecholate was set as the electron-donating 3,5-di-*tert*-butylcatecholate to shift the VT transition to lower temperatures, and electronic modification of the pyridyl arms of the redox-innocent bridging ligand was investigated. Fluoro, bromo, and methyl substituents were introduced in the meta position of the pyridine arms, and complexes were synthesised with sulfate and hexafluorophosphate counter anions. All complexes adopted the LS Co(III)cat form at low temperature. UV-Vis measurements revealed a bathochromic shift of the LMCT band in the order methyl, unsubstituted, and fluoro, and the electrochemical gap between relevant redox couples narrowed in the same order. Evans method measurements confirmed this trend in solution, demonstrating that electronic modulation of the redox-innocent bridging ligand represents a viable strategy to promote VT transitions. In the solid state, sulfate-bearing complexes showed a clear trend in which electron-withdrawing substituents promote VT, with the fluoro substituted complex reaching the highest magnetic moment, while the methyl-substituted analogue switches least effectively. While the transitions remained incomplete, the transition temperature could successfully be pushed to lower temperatures.

In the third chapter, a sterically demanding *ortho*-methyl group was introduced at the pyridine arms of the bridging ligand to favour elongated metal-ligand bond lengths and thereby stabilise the HS Co(II)sq state. In combination with the electron-donating 3,5-di-*tert*-butylcatecholate, this yielded a temperature-invariant HS Co(II)sq complex across the full temperature window. Substitution with tetrahalogenated catecholates restored the LS Co(III)cat ground state but yielded only incomplete transitions in SQUID magnetometry at 400 K. Introduction of the moderately electron-withdrawing 4,5-dichlorocatecholate proved decisive and yielded a LS Co(III)cat complex that undergoes a fully reversible VT transition in an abrupt, concerted one-step profile. Subsequent measurements indicated slightly more gradual behaviour due to loss of crystallinity. The transition could be followed in the solid state by ^{13}C CP-MAS NMR spectroscopy and UV-Vis diffuse reflectance spectroscopy providing direct

solid-state evidence for the switching process. These results confirm that a complete and reversible VT transition in the dinuclear innocent-bridged motif is achievable through the concerted application of steric and electronic design principles.

Having successfully demonstrated that a fully reversible, concerted VT transition can be achieved and fine-tuned within the innocent-bridged dinuclear motif, the fourth chapter addresses whether the introduction of electronic communication between the two cobalt-dioxolene centres can break the concerted switching mechanism and give rise to a sequential, two-step VT profile. Therefore, the aliphatic piperazine bridge was replaced by an aromatic pyrazine unit to introduce electronic communication between the two cobalt centres. Based on the bis(tetradentate) ligand $\mathbf{L}^{\text{bpap}}$, a new family of dinuclear cobalt-dioxolene complexes was designed, synthesised and characterised. An improved four-step synthetic route avoiding the use of carbon tetrachloride was developed to access the ligand backbone. The synthesis of the target VT complexes required strictly anaerobic and anhydrous conditions, as the pyrazine system was found to undergo an unreported catecholate insertion reaction under ambient conditions. Both the hexafluorophosphate and tetraphenylborate salts were comprehensively characterised, and single-crystal X-ray diffraction established the LS Co(III)cat ground state at low temperature. Magnetic investigations in solution and in the solid state revealed a weak, gradual, and incomplete VT transition above 300 K, with magnetic moments remaining well below those expected for complete conversion. To assess whether the aromatic bridging unit enables the two-step transition profile anticipated for an electronically coupled dinuclear system, future work should target a shift of the transition temperature to experimentally accessible ranges.

Taken together, the results demonstrate that all four tuneable parameters can be applied in a controlled and predictive manner to govern VT behaviour in dinuclear cobalt-dioxolene complexes. The successful realisation of a complete and reversible VT transition in selected systems highlights the potential of the innocent-bridged motif as a versatile platform for molecular switching, while the pyrazine-bridged system represents a first step towards the targeted development of two-step VT profiles with non-catecholate bridged systems.

Building on these findings, the cobalt-dioxolene framework established in this work opens a broad and well-defined space for future exploration. The systematic variation of steric demand, electronic bias, and bridging unit communication has demonstrated that the VT equilibrium can be rationally addressed across multiple independent axes. Showing a level of synthetic control that is rarely achievable and now provides a robust foundation for targeted design.

Most directly, the steric and electronic design principles developed in chapters two and three are immediately transferable to the pyrazine-based framework. The introduction of sterically demanding *ortho*-methyl substituents on the pyridyl arms, in combination with an appropriately tuned catecholate, should shift the VT transition into a fully accessible temperature window and potentially reveal the two-step switching profile anticipated for an electronically coupled dinuclear system, which is the central open question emerging from this work. A fully substituted pre-ligand has already been synthesised within the group, providing a direct starting point.³

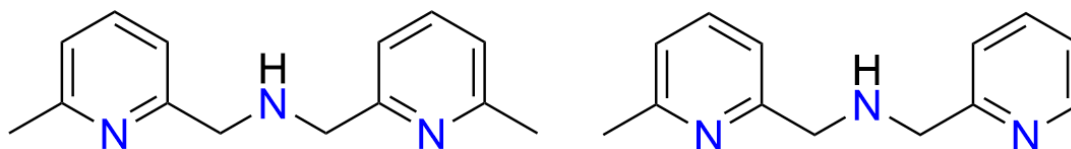


Figure 53: Possible pre-ligands for lowering the tautomeric transition temperatures of the pyrazine-bridged dinuclear cobalt complex.

Beyond this immediate next step, the modular nature of the platform invites broader application. Asymmetric mono-substitution at only one coordination site offers an elegant route to local symmetry breaking, with potentially profound consequences for both VT behaviour and inter-centre electronic communication. Further extension to related aromatic bridging units with systematically varied degrees of conjugation would directly probe the role of electronic delocalisation as a design parameter.

Nutzung von *KI*-Tools

<i>KI</i> -Tool	Genutzt für:	Warum?	Wann?
Claude AI	Sprachliche Korrektur	Bessere Lesbarkeit	Während der Formulierung der Arbeit