VALENCE TAUTOMERISM AND SPIN CROSSOVER IN SWITCHABLE COBALT COORDINATION POLYMERS

by

Olga Maria Drath

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Boskovic Research Group
School of Chemistry
The University of Melbourne
“Próbowałam różnych doświadczeń opisanych w podręcznikach fizyki i chemii. Niekiedy dodawał mi otuchy jakiś drobny sukces. Kiedy indziej znów wpadałam w głęboką rozpacz z powodu wypadków i błędów, wynikających z mojego braku doświadczenia. Na ogół jednak wiedziałam, że postępy nie mogą przychodzić ani szybko, ani łatwo; te pierwsze próby utrwaliły we mnie zamiłowanie do badań eksperymentalnych z dziedziny fizyki i chemii.”

Maria Skłodowska-Curie

“I tried out various experiments described in treatises on physics and chemistry, and the results were sometimes unexpected. At times, I would be encouraged by a little unhoped-for success, at others I would be in the deepest despair because of accidents and failures resulting from my inexperience. But on the whole, though I was taught that the way of progress is neither swift nor easy, this first trial confirmed in me the taste for experimental research in the fields of physics and chemistry.”

Maria Skłodowska-Curie
Abstract

This thesis presents efforts towards the synthesis and characterization of novel coordination polymers based on cobalt centers and O- and N- donor ligands, with emphasis on investigating potential valence-tautomeric (VT) and spin crossover (SCO) properties. Valence tautomerism constitutes a stimulated electron transfer between a redox-active metal center and a redox-active ligand. The majority of known VT systems are based on Co-dioxolene complexes, where the comparable energies of the frontier orbitals of the Co center and the dioxolene ligand allow the electron transfer to be initiated and controlled by various external stimuli. Spin crossover is a phenomenon occurring for some transition metal complexes, including Co$^{II}$, wherein the d electron configuration changes due to an application of an external perturbation. Stimuli used to control VT and SCO transitions are mostly temperature and light, with reported examples of the interconversions controlled by pressure, magnetic field or X-ray. A possibility of being switched between distinguishable electronic states makes VT and SCO complexes potential candidates for data storage, sensor devices and molecular electronics. Results in the field of VT and SCO compounds suggest that coordination polymers (CPs) could show additional interesting properties such as photomechanical effect, host-guest interactions and cooperativity effects.

Four one-dimensional (1D) polymeric compounds of general formula \{Co(3,5-dbdiox)$_2$(N$_2$L)$_x$S (3,5-dbdiox = 3,5-di-tert-butylidioxolene; N$_2$L = bipyridyl-based ligand: 1,2-bis(4-pyridyl)ethane (1,2-bpe), 4,4-trans-azopyridine (azpy) and 1,3-bis(4-pyridyl)propane (1,3-bpp); S = solvent) have been synthesized and characterized crystallographically. Three compounds show a trans disposition of the
nitrôngen-donor ligands around the cobalt center, while the compound based on flexible 1,3-bpp consists of two types of chains, cis and trans. All compounds undergo thermally-induced VT transitions and in some cases, multiple heating and cooling cycles indicate a significant solvation-dependence. The VT phenomenon in all compounds can also be induced by irradiation with green light at low temperature and the achieved level of photoconversion varies from 10 to 17%.

The employment of the divergent 1,2,4,5-tetra(4-pyridyl)benzene (tpb) ligand to link \{Co(3,5-dbdiox)\}_2 units has afforded two 1D CPs. In the [Co(3,5-dbdiox)_2(tpb)]\_\infty, tpb acts as a 2-connecting linker yielding a chain with a trans disposition of the ligands around the cobalt center, while in the [Co(3,5-dbdiox)_2(tpb)_{0.5}]\_\infty it takes a role of a 4-connecting linker, giving rise to a ribbon-like topology with a cis arrangement of the ligands; both compounds were obtained as water solvates. [Co(3,5-dbdiox)_2(tpb)]\_\infty·H_2O undergoes a thermally-induced VT transition above the room temperature.

The combination of cobalt, 3,5-dbdiox and 1-hydroxy-1,2,4,5-tetra(4-pyridyl)cyclohexane (tpch) yields two CPs with different topologies: a 1D zig-zag chain and a 2D sheet. Compound \{Co(3,5-dbcat)\_2\cdot tpch\}·EtOH·5H_2O shows temperature-triggered VT behavior with a small solvent dependency. The compound \{[Co(3,5-dbcat)\_2\cdot tpch]\·2EtOH·15H_2O is a second example of a 2D CP based on \{Co(3,5-dbdiox)\}_2 units.

Four cobalt-based coordination compounds, one discrete and three polymeric, have been obtained using the 4-pyridyl-2,2':6',2''-terpyridine (pterpy) ligand. The compound [Co(3,5-dbcat)(3,5-dbcatH)terpy] (3,5-dbcat = 3,5-di-\textit{tert}-butylcatecholate) is a rare example of a cobalt-dioxolene complex with a 1:3 Co:O ratio in the metal coordination sphere. Based on bond lengths measured at 130 K, a 1D chain-like
[CoCl₂pterpy]₂·2DMSO is a high spin CoⅡ complex. Studies on two 1D CPs, 
{{[Co(pyterpy)₂Co(hfac)₂]}₃[Co(hfac)₃]₂ and {{[Co(pyterpy)₂][Zn(hfac)₂]}₃[Zn(hfac)₃]₂
(hfac = hexafluoroacetyloacetonate), show that [Co(pyterpy)₂] units can undergo a SCO transition, not only in mononuclear complexes but also in coordination polymers.

Presenting eleven novel crystal structures and eight fully characterized polymeric compounds, this work presents a significant contribution to the field of Co-based VT and SCO CPs.
Declaration

This is to certify that:

◊ the thesis comprises only my original work towards the PhD except where indicated in the Preface,

◊ the candidate contributed more than 50% to the publications that are used as Chapters in this thesis,

◊ due acknowledgement has been made in the text to all other material used,

◊ the thesis is less than 100,000 words in length, exclusive of tables, maps, bibliographies and appendices.
Preface

The magnetic measurements presented in Chapters 2-4 were performed by Dr. Giordano Poneti and Dr. Lorenzo Sorace at the University of Florence at the University of Florence, Italy.

The magnetic measurements presented in Chapter 5 were performed by Dr. Boujemaa Moubaraki and Prof. Keith Murray at Monash University, Australia.

All the photomagnetism was carried out by Dr. Giordano Poneti at the University of Florence at the University of Florence, Italy.

The EPR measurements were carried out by Dr. Lorenzo Sorace at the University of Florence at the University of Florence, Italy.

The X-ray powder diffraction data for the compound 2·EtOH·5H₂O was collected by Prof. Kay Latham at RMIT University, Australia.

This thesis includes candidate’s publications as Chapters. Co-authors included in the publications have signed agreement forms that certify the following:

◊ the candidate has contributed more than 50% to the content of the manuscripts

◊ the candidate is the "primary" author of the manuscripts, i.e. the student was responsible primarily for the planning, execution and preparation of the work for publication.

These agreement forms are found in the Appendices section of this thesis.
Acknowledgements

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◊ ‘Thermal and Light-Induced Valence Tautomerism in Co-Dioxolene Coordination Polymers’, *RACI VIC Inorganic Chemistry Symposium*, Melbourne 2016 (talk)

◊ ‘Structural and Magnetic Studies of Novel Valence Tautomeric Coordination Polymers’, *15th International Conference on Molecule-Based Magnets*, Sendai 2016 (short talk & poster)
‘Structural and Magnetic Studies of Novel Valence Tautomeric Coordination Polymers’, 13th Materials Science School for Young Chemist, Sendai 2016 (poster)

‘Valence Tautomerism in One-Dimensional Coordination Polymers, 27th International Conference on Organometallic Chemistry, Melbourne 2016 (talk)

‘Valence Tautomerism in One-Dimensional Coordination Polymers’, RACI VIC Inorganic Chemistry Symposium, Melbourne 2015 (poster)

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<th>Description</th>
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<td>1,2-bpe</td>
<td>1,2-bis(4-pyridyl)ethane</td>
</tr>
<tr>
<td>1,3-bpp</td>
<td>1,3-bis(4-pyridyl)propane</td>
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<td>bpb</td>
<td>1,4-bis(4-pyridyl)-benzene</td>
</tr>
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<td>1,3,5-benzenetricarboxylate</td>
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<td>coordination polymer particles</td>
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<td>coordination polymers</td>
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<td>(\textit{dl})-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane</td>
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<tr>
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<td>dicyanamide</td>
</tr>
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<td>DFT</td>
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<td>dhbq</td>
<td>2,5-dihydroxy-1,4-benzoquinone</td>
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<tr>
<td>diox</td>
<td>dioxolene</td>
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<td>DLS</td>
<td>dynamic light scattering</td>
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<td>dimethylsulfoxide</td>
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<td>dpg</td>
<td>meso-alpha,beta-di(4-pyridyl)glycol</td>
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<td>E-dpss</td>
<td>2,6-bis(1H-pyrazol-1-yl)-4-styrylpyridine</td>
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<td>enbzpy</td>
<td>N,N’-bis(2-pyridinylbenzylidene)ethane-1,2-diamine</td>
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<td>EPR</td>
<td>Electron paramagnetic resonance</td>
</tr>
<tr>
<td>EtOH</td>
<td>ethanol</td>
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<td>EXAFS</td>
<td>extended X-ray absorption fine structure</td>
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<tr>
<td>hfac</td>
<td>hexafluoroacetylacetone</td>
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<tr>
<td>hs</td>
<td>high spin</td>
</tr>
<tr>
<td>LIESST</td>
<td>light-induced excited spin state trapping</td>
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<tr>
<td>LIVT</td>
<td>light induced valence tautomerism</td>
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<td>L-N4tBu2</td>
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<tr>
<td>ls</td>
<td>low spin</td>
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<tr>
<td>LTMCT</td>
<td>ligand-to-metal charge transfer</td>
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<tr>
<td>MALDI-TOF</td>
<td>matrix assisted laser desorption ionization-time of flight</td>
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<td>MeCN</td>
<td>acetonitrile</td>
</tr>
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<td>MeOH</td>
<td>methanol</td>
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<tr>
<td>MLCT</td>
<td>metal-to-ligand charge transfer</td>
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<td>MOS</td>
<td>metrical oxidation state</td>
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<td>N2L</td>
<td>bidentate nitrogen donor ligand</td>
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<tr>
<td>NITIm</td>
<td>2-(2-imidazolyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-3-oxide-</td>
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<td>Abbreviation</td>
<td>Definition</td>
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<tr>
<td>1-oxyl</td>
<td>monodentate nitrogen donor ligand</td>
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<td>OAc</td>
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<td>phen</td>
<td>4-pyridil-2,2′:6′,2″-terpyridine</td>
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<tr>
<td>pterpy</td>
<td>bis(pyridine) ether</td>
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<td>pyrazine</td>
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<td>pz</td>
<td>solvent</td>
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<tr>
<td>S</td>
<td>spin crossover</td>
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<tr>
<td>SCO</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>SEM</td>
<td>semiquinonate</td>
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<tr>
<td>SQUID</td>
<td>superconducting quantum interference device</td>
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<tr>
<td>TCNQ*</td>
<td>7,7,8,8-tetracyanoquinodimethane radical</td>
</tr>
<tr>
<td>terpy</td>
<td>2,2′:6′,2″-terpyridine</td>
</tr>
<tr>
<td>TGA</td>
<td>thermogravimetric analysis</td>
</tr>
<tr>
<td>tpa</td>
<td>tpa = tris(2-pyridylmethyl)amine</td>
</tr>
<tr>
<td>tpb</td>
<td>1,2,4,5-tetra(4-pyridyl)benzene</td>
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<td>tpch</td>
<td>1-hydroxy-1,2,4,5-tetra(4-pyridyl)cyclohexane</td>
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<tr>
<td>tpom</td>
<td>tetrakis(4-pyridyloxy)methylene methane</td>
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<td>VT</td>
<td>valence tautomeric</td>
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<td>ZFS</td>
<td>zero-field splitting</td>
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Introduction

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1.1 Electronic Lability in Metal Complexes.

The rapid growth of technology has created demand for new types of sensors, display devices and high-density memory storage. A possible approach to meeting this demand could be new molecular materials that can be switched between at least two distinguishable electronic states by applying an external stimulus, for example temperature or light. In general, three classes of compounds are known to display such properties. Worth mentioning, although they are not subject of this thesis, are heterometallic complexes that exhibit charge transfer induced spin transitions. The conversion entails two metal ions with $d$-orbitals of comparable energy and a linking ligand providing a pathway for stimulated electron transfer with an associated spin transition. This thesis focuses on the other two groups of switchable materials, primarily valence tautomeric (VT) and also spin crossover (SCO) compounds, with a focus on systems that incorporate octahedral cobalt (II) ions. Following appropriate stimulation, SCO complexes undergo a simple spin transition at the metal center, from low spin ($ls$) to high spin ($hs$) (Scheme 1-1). In valence tautomerism, stimulation induces electron transfer between a redox-active ligand and a redox-active metal center (Scheme 1-2). In the case of octahedral Co$^{II}$ complexes this is accompanied by a spin transition at the metal center. Mixed-valence systems have been classified into three groups by Robin and Day, depending on the level of electron delocalization (Scheme 1-3). Valence tautomeric (VT) complexes belong to class II, which means that interaction between the metal ion and the ligand is moderate. The activation energy barrier is high enough to localize the electron on one of the redox centers, but can be overcome by external stimuli.
**Scheme 1-1** Changes in the $d$-electron distribution at an octahedral Co$^{II}$ center for a SCO transition.

**Scheme 1-2.** Changes in the electron distribution at an octahedral Co$^{II}$ complex for a VT transition.

**Scheme 1-3.** Potential energy curves for three types of mixed-valence systems as classified by Robin and Day. In class I the interaction between two redox centers is negligible. In Class II the interaction between the redox centers is weak/moderate and can lead to an electron transfer. In Class III the electron is delocalized between two redox centers.
1.2 Valence Tautomerism.

1.2.1 Metal centers, electroactive ligands.

Although VT has been observed for various metal centers and ligands, two mandatory conditions must be satisfied: 1) a low degree of covalency between the metal ion and the redox-active ligand and, 2) a similar energy of the frontier orbitals, meaning the redox potentials associated with metal-based and ligand-based redox couples must be similar. The majority of VT transitions concern octahedral Co complexes, although VT systems have also been reported for manganese, iron, nickel, copper and ruthenium. The most commonly used type of ligands are ortho-dioxolenes, but there are examples based on other types of electroactive ligands, including: O,N,O Schiff-bases, nitroxy radicals, diimine analogues of dioxolenes, ONS- and ON- coordinated o-iminobenzoquinone, tetraphenylporphyrin, polychlorotriphenylmethyl radicals or even bis(arylimino) acenaphthene.

Dioxolene (diox) ligands have been widely used in the synthesis of valence tautomeric complexes since the first report in 1980. The ligand can exist in three redox states (Scheme 1-4): as a neutral quinone, radical semiquinone (sq) or dianionic catecholate (cat2-). Ortho-benzoquinones are weak donor ligands and are easily displaced from a coordinated metal ion. Therefore, the reported VT complexes are based instead on semiquinone and catecholate forms of the ligand. The majority of these complexes contain either 3,5- or 3,6-di-tert-butylcatecholate or semiquinonate ligands (3,5-dbcat and 3,5-dbsq). The tertiary butyl groups, as electron donating substituents, stabilize the complex and the oxidized semiquinone form. Moreover, tert-butyl groups create additional steric hindrance and affect the crystal packing of the complex, but can also reduce solvent effects in solvated complexes. Some VT transitions have also been reported for complexes with tetrahalo-dioxolene ligands (X4-diox, X = Cl, Br). The
electron withdrawing halogen groups tend to prevent the oxidation to the semiquinone state. Nevertheless, their ability to protect the complex from aerial oxidation has also been considered.\textsuperscript{25,26}

\textbf{Scheme 1-4.} Three redox forms of the dioxolene ligand.

Octahedral Co-diox complexes have yielded the best results in terms of investigating the origins and the means of controlling the VT interconversions (Eq.1). The Co\textsuperscript{III}/Co\textsuperscript{II} and sq'/cat\textsuperscript{2-} couples have similar redox potentials and belong to the type II mixed-valence systems, as described by Robin and Day.

\[
\{hs\textsuperscript{-}Co\textsuperscript{III} – \text{cat}\} \rightleftharpoons \{hs\textsuperscript{-}Co\textsuperscript{II} – sq\}\quad (1)
\]

Manganese-dioxolene complexes have also been a point of interest for researchers from the earliest studies on VT phenomena, due to their potential to exist in three different redox states and undergo two-step VT transitions per Eq.2:

\[
\{\text{Mn}^{IV} – (\text{cat})_2\} \rightleftharpoons \{hs\textsuperscript{-}\text{Mn}^{III} – (\text{cat})(\text{sq})\} \rightleftharpoons \{hs\textsuperscript{-}\text{Mn}^{II} – (\text{sq})_2\}\quad (2)
\]

Unlike cobalt-dioxolene species, the electron transfer is not accompanied by a spin transition, which means the Mn-ions remain in the high-spin state. Moreover, due to antiferromagnetic coupling between the manganese center and radical semiquinonate
ligand, the spin ground state for all three redox isomers remains \( S = \frac{3}{2} \), which prevents the detection of the VT transitions by magnetic susceptibility measurements. Instead, the two-step transition can be confirmed by optical spectral changes that occur in solution and solid state, which result in visible color changes.

### 1.2.2 Discrete valence tautomeric complexes.

Depending on the denticity of the ancillary ligands we can distinguish three main types of cobalt-dioxolene VT complexes (Table 1-1). Predominantly, ancillary ligands providing an appropriate ligand field for the VT complex are N-donor type. The first investigated VT complexes are 1:2 Co:diox complexes of general formula \([\text{Co}(\text{N}_2\text{L})(\text{sq})(\text{diox})]\), where \( \text{N}_2\text{L} \) is a bidentate nitrogen donor ancillary ligand (e.g. 2,2’-bipyridyl) and the four remaining Co coordination sites are occupied by two dioxolene ligands; one of them remains in the semiquinone form and doesn’t take part in the interconversion.\(^{23,27,28}\) The bidentate N-donor ligand enforces a cis arrangement of dioxolene ligands. Alternatively, two monodentate N-donor ligands can also afford the \([\text{Co}(\text{NL})_2(\text{sq})(\text{diox})]\).\(^{26,29}\) In this case, the ligands can be arranged around the cobalt center in either a cis or trans manner, but the trans disposition is more common. The cis/trans distinction is not without significance. Recently, Panja et al. showed noteworthy changes in the experimental VT transition profile, depending on the geometric isomerism.\(^{26}\) Khusniyarov et al. calculated a theoretical coupling constant for trans-\([\text{Co}(\text{NL})_2(\text{sq})_2]\) complex employing 4-phenylazopyridine and compared it with values obtained for cis-\([\text{Co}(\text{N}_2\text{L})(\text{sq})_2]\) involving the 4,4’-bipyridyl ligand.\(^{30}\) The calculations show the differences in magnetic exchange due to different geometries of cis and trans species. The \( \text{hs-Co}^{\text{II}} \) ion \( (S = \frac{3}{2}) \) in the cis complex is antiferromagnetically coupled with two ligand \( \pi \) radicals, while the coupling for the trans homologues is of a ferromagnetic nature.
The other well investigated compound families are 1:1 cobalt-diox complexes, incorporating tetridentate ancillary ligands, which can be a tetraazamacrocycles\textsuperscript{31} or derivatives of tris(pyridylmethyl)amine.\textsuperscript{32–34}

Table 1-1. Representations of discrete Co-dioxolene valence tautomeric coordination complexes.

<table>
<thead>
<tr>
<th>General formula</th>
<th>Structural representation</th>
<th>Co:diox</th>
<th>Representative compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(N\textsubscript{2}L)(sq)(diox)]</td>
<td><img src="image" alt="Structural representation" /></td>
<td>1:2</td>
<td>[Co(phen)(3,5-dbsq)(3,5-dbdiox)]\textsuperscript{28} phen = phenanthroline</td>
</tr>
<tr>
<td>[Co(NL)\textsubscript{2}(sq)(diox)]</td>
<td><img src="image" alt="Structural representation" /></td>
<td>1:2</td>
<td>[Co(4-papy)(3,5-dbsq)(3,5-dbdiox)]\textsuperscript{30} 4-papy = 4-phenylazopyridine</td>
</tr>
<tr>
<td>[Co(N\textsubscript{4}L)(diox)]</td>
<td><img src="image" alt="Structural representation" /></td>
<td>1:1</td>
<td>[{Co(cth)}\textsubscript{2}(dhbq)]\textsuperscript{+}\textsuperscript{35} cth = (dl)-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane dhbq = 2,5-dihydroxy-1,4-benzoquinone</td>
</tr>
</tbody>
</table>

1.2.3 Ancillary ligands.

Although the choice of the electroactive metal center - ligand system is the crucial step in synthesizing valence tautomeric complexes, the role of other factors cannot be underestimated. As mentioned above, the denticity of the ancillary ligand determines geometry, and hence, the electronic structure and properties of the compound. However, it is not the only factor related to the coligand which can affect transitions in the VT complex. The role of the donor strength of the bidentate diimine ancillary ligand in
shifting the valence tautomeric transition temperature was observed in several studies of 1:2 cobalt:dioxolene complexes of general formula [Co(NL)₂(diox)]₂.²⁷,³⁶–³⁹ The important role of tuning the system cooperativity was also reported for [Co(Cnbpy)(3,5-dbdiox)]₂ (Cnbpy = 4,4’-dialkyl-2,2’-bipyridine).⁴⁰ More recently, studies conducted on the 1:1 cobalt:dioxolene complexes showed interesting behavior for two families based on different tetradeutate nitrogen donor ligands.⁴¹,⁴² For the [Co(L)(diox)]⁺, where L is a tetrazamacroyclic ligand, it was found that ligands containing secondary amine donors stabilize the \{Co^{III} – cat\} form, while those with tertiary amine donors stabilize the \{Co^{II} – sq\} form of the complex.⁴¹ No less important changes were observed for [Co(Meₙtpa)(3,5-diox)]⁺ (Meₙtpa; n = 0–3, tpa = tris(2-pyridylmethyl)amine). The successive introduction of methyl groups into the 6-position of the pyridine moieties resulted in shifting the thermally induced transition to lower temperatures and changing the lifetime of the photoinduced metastable \{hs-Co^{II} – sq\} tautomers.⁴² Similarly, for the series of dinuclear complexes based on 3,3,3’,3’-tetramethyl-1,1’-spirobisindane (diox-spiro-diox), VT properties were tuned by the variation of the ancillary ligand Meₙtpa (Figure 1-1). When n = 0, the complex stays in the \{hs-Co^{II}-sq\} state in the 5 -350 K range, while n = 3 variant exhibits a stable \{ls-Co^{III}-cat\} state similarly not undergoing any transition. Only the complex incorporating Me₂tpa shows a thermally-induced VT interconversion.
Figure 1-1. Variable temperature magnetic susceptibility data for the complexes based on Me₃tpa (green squares), Me₂tpa (red triangles) and tpa (blue circles) ligands.³³

1.3 Spin Crossover.

Spin-crossover (SCO), also referred to as spin transition or spin equilibrium, consists of a rearrangement of the $d$-electrons of the metal ion upon the application of an external stimulus (temperature, light, pressure or magnetic field). Temperature-triggered SCO was reported for the first time in 1930s by Cambi et al., for Fe$^{III}$ derivatives of dithiocarbamates, which initiated almost a century of studies on the phenomenon. It has been observed for several d-block ions with $d^4$ (Cr$^{II}$, Mn$^{III}$), $d^5$ (Mn$^{II}$, Fe$^{III}$), $d^6$ (Fe$^{II}$, Co$^{III}$) and $d^7$ (Co$^{II}$, Ni$^{III}$) configuration. Hitherto, the most investigated systems have been coordination complexes incorporating Fe$^{II}$ and Fe$^{III}$, with a smaller group of Co$^{II}$ and individual cases of SCO complexes based on other ions. Similar to VT, SCO transitions can be affected by several parameters, with often drastic changes to the nature of the transition. Nitrogen-donor ligands have been shown to be crucial in providing an
appropriate crystal field, but within these ligands even a slight change of the substituents can alter the conversion significantly.\textsuperscript{43,44} For cationic SCO complexes changing the counteranion can change the packing and affect short-range interactions, creating additional hydrogen bonding or $\pi$-$\pi$ stacking. These changes have been shown to shift the transition temperature, as well as making the transition more gradual or abrupt.\textsuperscript{43} Sometimes a change of anion can induce or remove hysteresis. Similar effects can also be seen upon changes in the solvation of the SCO complex.\textsuperscript{45,46}

1.3.1 Spin Crossover in Cobalt (II) complexes.

Upon a SCO transition, one electron from the $t_{2g}$ energy level of the Co\textsuperscript{II} center is promoted to the $e_g$ energy level, changing the overall spin from $S = 1/2$ to $S = 3/2$ (Scheme 1-1), while for Fe\textsuperscript{II} this change is greater ($\Delta S = 2$, from $S = 0$ to $S = 2$). Due to spin-orbit coupling in octahedral Co\textsuperscript{II}, there is a significant chance of interactions between wavefunctions corresponding to different spin states. This results in much less defined and more gradual transitions for Co\textsuperscript{II}-based SCO compounds in comparison to the Fe\textsuperscript{II}-based, as well as shorter relaxation times from the excited $hs$ state. The typical coordination environment for SCO complexes is six nitrogen donor atoms around the metal center, which can be realized using combinations of monodentate and chelating nitrogen-donor ligands. In octahedral complexes, the ligand field required for the spin-pairing in Co\textsuperscript{II} is bigger than that for Fe\textsuperscript{II}. Consequently, a ligand which may be appropriate for a Fe\textsuperscript{II}-based SCO complex may not be suitable for the synthesis of SCO materials employing cobalt centers. The other property distinguishing SCO Co\textsuperscript{II} is the stronger Jahn-Teller effect seen in the $ls$ state, which arises from the singly occupied $e_g$ orbital. In general, the coordination sphere of the octahedral Co\textsuperscript{II} SCO complex in the $ls$ state consists of two elongated bonds and four shorter bonds, lying in the equatorial plane of the octahedron. The increase in bond lengths associated with the spin transition can be
observed mostly for the four equatorial bonds, while the axial bonds elongate to a very small extent. The N-donor ligands employed in Co\textsuperscript{II} SCO complexes can be divided into three main groups: bis(tridentate) systems, tris(diimine) systems and tetradeionate Schiff base systems.\textsuperscript{47} Regarding the first group, it has been established by several examples that tridentate planar ligands, such as terpyridine (terpy), are particularly good at providing an appropriate coordination environment for the SCO transition on the octahedral Co\textsuperscript{II} cation.\textsuperscript{48,49} There have been numerous reports of substituted terpy systems in Co\textsuperscript{II} SCO. Predominantly, the terpy ligands reported are substituted in the fourth position with groups such as: hydroxyl,\textsuperscript{50} methoxy\textsuperscript{51} or pyridyl rings.\textsuperscript{52} An interesting way of accessing new functionalities in SCO complexes is using terpy ligands with long branched alkyl chains.\textsuperscript{48} These soft materials exhibit novel physical properties, such as liquid crystal transitions, and when applied into SCO systems can lead to unique ‘reverse spin transitions’.

Apart from the typical N\textsubscript{6} coordination sphere around the Co center, a SCO complex with a different structure has also been reported. Kruger et al. synthesized a cobalt complex containing di-\textit{tert}-butyl derivative of the tetraazamacrocyclic ligand 2,11-diaza[3.3](2,6)pyridinophane (L-\textit{N}4\textit{t}Bu\textsubscript{2}) and 3,5-di-\textit{tert}-butylsemiquinone.\textsuperscript{53} The complex [Co\textsuperscript{II}(L-\textit{N}4\textit{t}Bu\textsubscript{2})(3,5-dbsq)] is the first known Co-diox complex that undergoes a temperature-induced SCO transition, rather than a VT process. The macrocyclic ligand, together with the semiquinonate radical, provides sufficient ligand-field strength to stabilize the \textit{ls}-Co\textsuperscript{II} state. The \textit{tert}-butyl groups on the L-\textit{N}4\textit{t}Bu\textsubscript{2} ligand cause additional steric hindrance leading to significant elongation of the axial Co-N bonds, which stays in good agreement with the Jahn-Teller effect in the \textit{ls}-Co\textsuperscript{II} ion. The spin conversion has been monitored by various techniques, such as variable-temperature crystallography, temperature-dependent UV-Vis and IR spectroscopy, and magnetic susceptibility
measurements. The SCO properties can be observed in the solid state, as well as in solution. Femtosecond time-resolved experiments have also been used, to elucidate the ultrafast photoinduced process. This study gives a unique insight into the nature of the Co$^{II}$ SCO phenomenon and the use of π-radical ligands in the synthesis of SCO with ultrafast relaxation processes. Furthermore, an analogous complex employing the dimethyl derivative of the macrocyclic ligand (L-$N_4$Me$_2$) has also been reported. The complex [Co$^{II}$($L$-$N_4$Me$_2$)(3,5-dbsq)] stays in the diamagnetic Co$^{III}$ state and does not undergo either VT or SCO transitions. These results reveal that the electronic ground state of the metal center can be adjusted by applying very small changes in the ligand. In addition to the more prevalent hexa-coordinate octahedral complexes, SCO behavior can also be observed in penta-coordinate Co$^{II}$ complexes. Examples include complexes based on tetradeutate Schiff bases like salem ($N,N'$-ethylenebis(salicyladimine)) or saloph ($N,N'$-phenylenebis(salicyladimine)).

1.4 External Stimuli

1.4.1 Thermally induced valence tautomerism and spin-crossover.

The most common method of stimulating both VT and SCO transitions is by application of heat. For systems based on Co, VT transitions involve a change in oxidation state, as well as a spin transition on the Co center. For SCO in Co$^{II}$ complexes, the transition only involves the change of spin state. Each of these processes is associated with a large entropy gain upon heating. The major components of that change are: 1) electronic – the higher spin state degeneracy of the $hs$-Co$^{II}$ form; 2) vibrational – the higher density of vibrational states of the $hs$-Co$^{II}$ form, related to its longer metal-ligand bonds. From the Gibbs free energy equation (Eq.3), we can see that at low temperatures
$T\Delta S$ (where $\Delta S$ – change of entropy) is negligible and, if $\Delta H > kT$ ($\Delta H$ - change of enthalpy), only the $ls$-Co$^{III}$ state can be populated. As temperature increases, the entropy contribution prevails and the $hs$-Co$^{II}$ fraction increases.

$$\Delta G = \Delta H - T\Delta S$$  \hspace{1cm} (3)

The increase in metal-ligand bond length can be confirmed using variable-temperature X-ray crystallography.\textsuperscript{56} The average change in Co-ligand bonds related to the VT transition in Co complexes has been estimated by Hedrickson and Pierpoint to be $\sim 0.2$ Å\textsuperscript{24}, but in most reported cases the increase is between 0.15 and 0.1 Å. In Co SCO the transition is associated with an increase in the metal-ligand bond lengths of $\sim 0.10$ Å. This, compared to the $\sim 0.20$ change in metal-ligand bonds for Fe$^{II}$ systems, renders a much smaller energy barrier between the $ls$ and $hs$ state of the Co centre.\textsuperscript{47} For a SCO transition in Co complexes the increase usually involves only 4 out of 6 bonds.\textsuperscript{53}

Traditional way of tracking temperature-dependent magnetic properties of the compound is plotting a product of a molar magnetic susceptibility and temperature ($\chi M T$) versus temperature. The key parameter used to describe a thermal SCO or VT transition is the temperature in which the two spin states of the metal center are present in equal fractions – the transition (critical temperature) $T_c$ or $T_{1/2}$. The main features of a temperature-stimulated VT conversion, which would allow the compound to be considered as a potential molecular memory storage material, are a well-defined sharp transition and a hysteresis loop. The hysteresis means there is a delay response to the temperature change, affording bistability; such that within a delivered temperature range, the complex can exist in two different states, $ls$ or $hs$, depending on the history. Like in conventional magnetic materials we can associate the two states as 0/1 (in binary code) or on/off modes. In 1997 Jung at al. reported a hysteresis loop width of 230 K, which
remains the record for VT complexes (Figure 1-2), but the majority of thermally-induced VT transitions do not exhibit bistability. In the more established field of SCO, the parameters affecting the hysteresis loop have been studied in more detail. Solvation, sample homogeneity and age can all change magnetic properties. No less important are the experimental conditions for investigating hysteresis. Brooker et al. specifically pointed out the scan-rate dependency of the hysteresis loop width. Figure 1-3 and Figure 1-4 show examples of thermal hysteresis in FeII and CoII SCO complexes, respectively. Due to the small energy barrier between ls-CoII and hs-CoII states, hysteresis loops in thermal SCO conversions in Co-based systems are rather difficult to achieve and less common than in Fe-based species.

Figure 1-2. Hysteresis for the VT transition in [Co(py$_2$O)(3,6-dbdiox)$_2$].

(py$_2$O = bis(pyridine) ether)
Figure 1-3. Hysteresis loop for the SCO transition in {Fe(pz)[Pt(CN)₄]}·0.5(CS(NH₂)₂) (orange) and {Fe(pz)[Pd(CN)₄]}·1.5H₂O·0.5(CS(NH₂)₂) (green). (pz = pyrazine)

Figure 1-4. Hysteresis loop for the SCO transition in two polymorphs of [Co(4-terpyridone)₂(CF₃SO₃)₂·H₂O].
1.4.2 Photo-induced valence tautomerism and spin crossover.

The possibility of triggering the VT or SCO interconversion by light implies that the compound could potentially be used in photorecording or photoswitching molecular devices. Beginning with McGarvey and Lawthers research,\textsuperscript{61} it has been shown that at low temperature electronically labile Fe SCO complexes can be switched by light between the $ls$-complex and metastable $hs$-complex via the light-induced excited spin state trapping (LIESST) phenomenon. The process takes place at low temperatures and irradiation is with green light. The LIESST effect has been reported for numerous iron-based complexes,\textsuperscript{62} however, has not been observed in SCO systems based on cobalt due to a smaller energy gap which leads to short $hs$–$ls$ relaxation time (see section 1.3.1). The biggest challenge of the LIESST process is the dependence on the temperature. While at low temperature the sample can be kept in the metastable $hs$ state for hours, increase of the temperature immediately triggers thermal relaxation. Hauser \textit{et al.} proposed the inverse-energy-gap law, explaining the relation between the thermal SCO temperature ($T_c$) and the life-time of the light induced metastable state. This relation is inversely proportional, which means that for SCO compounds undergoing the transition at higher temperatures, the rate of photoconversion is lower and the relaxation process faster.

Similarly to SCO research, LIVT (light induced valence tautomerism) can be investigated by irradiation of a ligand-to-metal charge transfer (LMCT) band of a Co VT complex at low temperatures (5-9 K).\textsuperscript{63,64} This results in an increase in $\chi_m T$, suggestive for a photo-induced VT transition and formation of the meta-stable $\{hs$-Co$^{II}$-sq$\}$ state (Figure 1-5). The laser is then switched off and subsequently, the sample is slowly heated (0.3 K – 1 K min$^{-1}$) until full relaxation into non-irradiated state. The temperature at which the irradiated curve starts re-joining the non-irradiated profile is referred as a $T_{\text{LIESST}}$ or $T_{\text{LIVT}}$ and for VT complexes values between 38 K and 80 K.\textsuperscript{65} The percentage of
photoconversion typically doesn’t exceed 40%.\textsuperscript{33,35,65,66} This is often attributed to the sample’s opacity, preventing penetration of the light beyond the surface, but also strongly depends on the way the sample is prepared. Pressing the VT complex into a pellet may apply too much pressure and quench the VT transition.\textsuperscript{67} These changes are mostly monitored using photomagnetic measurements (the laser is coupled to a SQUID magnetometer), but can also be examined by infra-red\textsuperscript{68}, X-ray (Co K-edge XANES)\textsuperscript{69} and EPR\textsuperscript{70} spectroscopy. Regarding the potential use of VT systems as molecular switches, a reverse LIESTT effect, discovered for Fe\textsuperscript{II} SCO compounds,\textsuperscript{71} has also been investigated in valence tautomeric complexes. To accelerate the relaxation of the metastable high-spin state, the metal-to-ligand charge transfer (MLCT) band is irradiated with red light. For some complexes the process of alternating irradiation of the LMCT and MLCT can be repeated multiple times, making them promising systems for applications in devices.\textsuperscript{72}

![Figure 1-5](image-url)  

**Figure 1-5.** $\chi_T$ vs $T$ plot for irradiated (squares) and non-irradiated (triangles) VT transition in $[(\text{Co(cth)})_2(\text{dbhq})](\text{PF}_6)_3$. The crosses indicate the increase of the $\chi_T$ product after an irradiation at 647 nm.\textsuperscript{35} (cth = (dl)-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, dbhq = deprotonated 2,5-dihydroxy-1,4-benzoquinone).
As mentioned previously, the main obstacle that prevents the use of photo-switchable VT complexes in real life devices is the short lifetime of the excited state at room temperature. Most of the observed LIESST effects in VT systems have been measured at temperatures close to 5 K. A possible solution to the problem may involve employing ligands that undergo photo-isomerization in the VT systems. The ligand isomerization process affects the geometry of the complex; changing the energy barrier and inducing the intramolecular energy transfer. It is important to choose a ligand for which both initial and photogenerated forms are stable at ambient temperature. In 2015 Khusniyarov et al. reported a VT coordination complex based on cobalt-dioxolene system and a photoactive trans-4-phenylazopyridine as a terminal ligand. The reversible trans ↔ cis photoisomerisation of the ligand drives the VT transfer and stabilizes the hs product. Their compound is the first example of the documented light-induced VT transition at room temperature with a conversion rate of 28% and the photoinduced state lasting for several hours, in comparison to the nanosecond lifetimes reported previously. The phenomenon has been named Ligand-Driven Light-Induced Valence Tautomerism and is a big step towards incorporating VT complexes into real-life devices.

1.4.3 Other stimuli to valence tautomeric and spin crossover transitions.

Although temperature and light have been the main focus of the research in the last twenty years, other stimuli able to affect a VT and SCO interconversion have also been investigated. Since the VT and SCO transformations are both associated with a change in bond lengths, the application of an external pressure should favor the more compact hs form in both processes. Several studies confirm that the VT or SCO $T_{1/2}$ increases with increasing pressure and the whole process becomes more gradual. On the other hand, application of a magnetic field has been proved to stabilize the hs form of the metal ion and decrease the $T_{1/2}$, either for Fe$^{II}$ SCO, Co$^{II}$ SCO or Co VT phenomena. Soft
X-rays have been shown to trigger the same LIESST process as when a sample is irradiated with visible laser light. The X-ray induced excited spin state trapping has been proven to be completely reversible in Fe^{II} SCO and Co VT transitions.\textsuperscript{78–80} Finally, Pinheiro et al. have shown recently that hard X-rays can also be used induce VT transitions, which may be especially useful for samples less prone to optical excitation.\textsuperscript{81}

1.5 Other Factors.

1.5.1 Solvation and counterion effects.

The inclusion of solvent molecules into the crystal lattice plays an important role in modifying VT transitions in the solid state. Such an effect can be found when comparing ethanol and toluene solvates of [Co(Me\textsubscript{2}tpa)(3,5-dbdiox)]PF\textsubscript{6}.\textsuperscript{42,72} The toluene solvate exhibits a complete interconversion between 100 K and 300 K, with two clearly separated steps ($T_{c1} = 125$ K, $T_{c2} = 185$ K), which suggests that the two non-equivalent Co centers in the crystal lattice undergo VT interconversion separately. On the contrary, for the ethanol solvent, the transition process does not start before about 280 K and does not reach completion in the measured temperature range. Moreover, the change of solvent also affects the relaxation time of the photoinduced fraction, which is shorter for the toluene derivative, compared with the ethanol solvate.

Another example of a similar effect was presented by Ruiz-Molina et al. in a study on five different solvates of [Co(phen)(3,5-dbdiox)]\textsubscript{2}.\textsuperscript{82} The VT transition temperature shifts to higher values according to the order toluene < acetonitrile < acetone < methylene chloride < ethanol, which is not consistent with the results obtained in solution state.

Solvation effects on the valence tautomeric transitions were also studied for trans-[Co(py)\textsubscript{2}(3,5-dbdiox)].\textsuperscript{29} Whereas the thermally driven VT transition for both pyridine and acetonitrile solvates occurs around 250 K, the temperature-variable single-crystal X-
ray crystallographic studies of the hexane solvate show no transformation below 350 K. Moreover, the loss of acetonitrile molecules from the crystal lattice shifts the $T_c$ from around 250 K to 310 K and makes it more abrupt. The results indicate a significant dependence of the VT transition on solvation-induced packing effects. A possible explanation is that loss of the solvent eliminates the steric hindrance and allows an elongation of the Co-N and Co-O bonds, hence unlocking conversion to the $hs$-$Co^{II}$ form.

Finally, Panja et al. recently reported a $[Co(Br_{Cat})_2(py)_2]$ complex showing a $cis/trans$ isomerism dependent on solvent presence. The compound isolated from methanol adopts a $cis$ configuration, whereas crystallization from acetone leads to the $trans$ arrangement of the ligands. Moreover, the halogen-bonding interactions between the brominated dioxolene ligand and solvent are manifested only when the compound is recrystallized from acetone, which makes the acetone solvate a thermodynamically stable product. Temperature-dependent magnetic susceptibility studies show how the solvation and crystal packing affect the valence tautomeric transition. While the methanol solvate undergoes 40% conversion below 380 K, the transition of the acetone solvate is almost complete in the same temperature range.

A drastic solvent dependence of SCO properties has been shown for $\{[Fe(E-dpsp)_2](BF_4)\} \cdot S$ ($E$-dpsp = 2,6-bis(1H-pyrazol-1-yl)-4-styrylpyridine, $S$ = acetone, propylene carbonate, nitromethane, diethylether). The acetone solvate of the complex exhibits a sharp SCO transition $c.a.$ 170 K, with a 15 K wide hysteresis loop, whereas propylene carbonate and diethylether solvates stay in the $ls$ state in the measured temperature range. Lastly, when the complex is crystallized from nitromethane, the resulted compound retains the $hs$ state throughout the whole temperature range.

A counterion effect, although difficult to isolate from solution and environmental effects, has been proposed to modify the valence tautomerism of the family of compounds
of general formula \([\text{Co(eth)(phen dio x)}]Y\) \((Y = \text{PF}_6^-, \text{I}^-, \text{BPh}_4^-)\). The studies showed an increase of the transition temperature, depending on volume and coulombic interaction of the counterion, in the order \(\text{PF}_6^- < \text{I}^- < \text{BPh}_4^-\). Cador et al. reported for \([\text{Co(terpy)(diox-N-diox)}]Y\) \((\text{terpy} = 2,2':6',2''\text{-terpyridyne}; \text{diox-N-diox} = \text{Shiff base diquinone ligand})\) a change in interconversion temperature depending on the counterion used\(^{31,41}\). While the \(\text{PF}_6^-\) exhibits a VT transformation around 500 K, no VT process was observed for the \(\text{BPh}_4^-\) analogue.

Similar behavior can be also observed in SCO complexes, including materials based on \(\text{Co}^{\text{II}}\) and neutral ligands. Real et al. reported a family of complexes with general formula \([\text{Co}(4\text{-terpyridone})_2]X_y\cdot nS\), where \(X = \text{BF}_4^-, \text{SiF}_6^{2-}, [\text{Co(NCS)}_4]^{2-}, \text{I}^-, \text{NO}_3^-, \text{PF}_6^-\), and \(S = \text{H}_2\text{O}, \text{CH}_3\text{OH}\).\(^{50}\) The results show differences in the magnetic behavior of the compound depending on the type of non-coordinating anion. For example, compounds incorporating \(\text{BF}_4^-\) showed gradual SCO transitions between 200 K and 300 K, whereas compounds incorporating \(\text{I}^-\) stayed in the low spin state in the measured temperature range, while the presence of \(\text{SiF}_6^{2-}, [\text{Co(NCS)}_4]^{2-}\) and \(\text{PF}_6^-\) seems to stabilize the high spin state of the complex. Those results, however, were obscured by additional solvent influence and could not offer any simple prediction on the nature of the SCO processes based on the employed counterion. In a later study, Murray et al. presented a group of complexes employing 2,2':6',2''-terpyridine ligand with an additional alkyl chain in the 4' position. The compounds \([\text{Co(terpyRX)}_2]Y_2\cdot n\text{H}_2\text{O}\) \((X = 4,8,12\) and \(Y^- = \text{BF}_4^-, \text{ClO}_4^-, \text{PF}_6^-, \text{BPh}_4^-)\) were studied. For the series of compounds containing the \(\text{BF}_4^-\) anion, the start of the SCO transition shifted toward lower temperatures with an increase in length of the RX alkyl chain. Interestingly, that trend cannot be seen for the other counterions. The role of the \(\text{PF}_6^-\) in favoring the high spin state of the \(\text{Co}^{\text{II}}\) center was also observed.\(^{50}\)
1.5.2 Cooperativity.

The very important aim of creating molecular materials that can be used in real-life devices requires bistability (hysteresis) and more abrupt transitions. These features could be achieved by creating cooperative systems, in which the electronic and steric changes are propagated throughout the crystal lattice. Higher cooperativity can be realized by a combination of short-range and long-range interactions. Short-range interactions consist of van der Waals interactions, hydrogen bonds and $\pi-\pi$ stacking, while long-range interactions incorporate covalent linkages and synthesis of coordination polymers.

Weber et al. presented a detailed study on one-dimensional Fe$^{II}$ SCO coordination polymers with zig-zag structures. Analysis of the correlations between the crystal structure and magnetic properties revealed that short-range interactions play a larger role in the cooperative effect than longer ones. The group proposed a crystal contact index parameter, being the sum of all intermolecular contacts. Compounds with a low value of the parameter exhibit gradual magnetic transitions and an increase in the number of contacts leads to more abrupt SCO behavior, and ultimately, to hysteresis loops. Another interesting finding concerned the zig-zag nature of synthesized coordination polymers. Flexible linking ligands, which lead to the formation of the zig-zag polymer, limit interactions between adjacent chains, causing steps in the SCO transition profile.85 The interesting insight in the structural origins of the magnetic inequivalence of two (or more) of the metal sites was given by Kepert et al.86 A three-step SCO transition reported for a three-dimensional Fe$^{II}$ metal-organic framework is closely associated with a series of structural rearrangements, involving also long-range configurations of ordered high spin and low spin sites.

The most spectacular example of the cooperative effect in VT compounds was reported by Jung et al., who investigated a series of complexes involving bis(pyridyl) ether
derivates.\[^{36}\] [Co(py\textsubscript{2}O)(3,6-dbdiox)\textsubscript{2}] (py\textsubscript{2}O = bis(pyridyl) ether) exhibits a hysteretic valence tautomeric transition with a 230 K difference between heating (330 K) and cooling (100 K) transition temperatures. Such a wide hysteresis loop (Figure 1-2) is a result of a structural (planar/folded) change accompanying the electron transfer between metal and quinonate ligands (Figure 1-6), which creates an energy barrier to the intramolecular electron transfer.

![Figure 1-6. A structural change affecting the nature of a VT transition.\[^{36}\]](image)

The work from Schultz \textit{et al.} on [Co(3,5-diox)\textsubscript{2}](4-X-py)\textsubscript{2}] (4-X-py =4-(X)pyridine, X = H, OMe, Me, CN, Br, NO\textsubscript{2}) established the important role of hydrogen bonding connecting the metal complexes directly (without the inclusion of solvent molecules) in cooperativity.\[^{38,39}\] Such hydrogen bonds are present in CN-py, Br-py and NO\textsubscript{2}-py analogues, resulting in 5 K hysteresis loops upon heating-cooling cycles. The phenomenon is additionally confirmed by intercalating different solvent molecules in the crystal structure, which ‘softens’ the lattice and perturbs the hysteretic VT behavior. Moreover, these complexes can be thermally trapped in the high temperature stable \{hs-Co\textsuperscript{II}\} form when quenched from room temperature to 2 K.
1.6 **Electronically Labile Coordination Polymers.**

The motivations for synthesizing switchable coordination polymers are threefold. Firstly, infinite nets may increase the cooperativity arising from long-range interactions with the aim to induce bistability in the material. Secondly, synthesis of porous (mostly 2D and 3D) materials allows exploration of host-guest interactions and their effect on the electronic transition. It can also add an additional mode of functionality to the material. Finally, polymeric compounds can be functionalized and implemented onto new hybrid molecular platforms, facilitating the transfer of VT/SCO properties into real-life devices.

In order to design new VT/SCO polymers with switching and memory effects, one should look to the most explored switchable systems - spin-crossover coordination polymers based on Fe$^{II}$. The research field has experienced significant development in recent years and in the period 2004-2011 alone was the subject of nine reviews and in each of the following years new examples of 1D-, 2D- and 3D-SO coordination polymers were described in more than 150 academic publications.\(^\text{87–94}\)

With regard to previous VT and SCO Co-based complexes, the group of most potential for generating coordination polymers (CPs) are N-donor bridging ligands. 1D-SO-CPs based on 1,2,4-triazole based were the subject of intensive studies on transferring the Fe$^{II}$ SCO properties to technologically convenient platforms such as composites and gels,\(^\text{95}\) liquid-crystalline materials,\(^\text{96}\) dendrimers,\(^\text{97}\) Langmuir-Blodgett films\(^\text{98}\) and nanoparticles,\(^\text{99,100}\) which employed lipophilic functionalization of the triazole ring.\(^\text{2}\)

Moreover, these materials typically display abrupt and hysteretic thermally-induced magnetic and chromatic spin-transitions with \(T_c\) near room temperature, which makes them attractive candidates for memory and sensor applications. This type of ligand has

\*According to SciFinder® database search from 2.06.2017.
been also successfully used in the synthesis of 2D- and 3D-SCO-CPs. Whereas the triazole rings act as bidentate ligands, tetrazole rings tend to coordinate only through one nitrogen and a much smaller number of tetrazole based SCO-CPs has been reported in comparison to other N-donor bridging ligands. On the contrary, using bis-monodentate and polydentate pyridine-like bridges has proved to be a particularly prolific approach, starting with 1D zig-zag chains, through 2D layers, to 3D networks.85,88,101,102 A big breakthrough came with the synthesis and characterization of new functional porous SCO compounds constituted of interpenetrating 2D layers. The combination of covalent linkers and weak inter-framework interactions can have an interesting effect on the SCO transition, such as creating an additional intermediate hs-Is step.103 Finally, the employment of 1-3D-SCO-CPs based on metallocyanates has given rise to Hoffman-type materials86 with new interesting features, such as structural diversity and flexibility, porosity, host-guest interactions, physi- and chemisorption, metallophilic interactions and reversible solid-state chemical reactions.87,104,105

1.7 Valence Tautomerism in Coordination Polymers.

1.7.1 One-dimensional Co-based valence tautomeric coordination polymers.

As mentioned in Section 1.5.2, an important approach to attain a high level of cooperativity in spin transition materials is the synthesis of coordination polymers showing long-range interactions. The first polymeric VT compound was reported by Jung and Pierpoint more than two decades ago (Table 1-2).37 The anaerobic reaction between Co2(CO)8, 3,6-di-tert-butyl-1,2-benzoquinone and pyrazine in hexane resulted in the formation of the 1D VT [Co(pyz)(3,6-dbsq)(3,6-dbdiox)]∞ polymer (Figure 1-7a), which shows a temperature-induced VT transition. Between 350 K and 5 K, the magnetic
moment of the solid polymer sample decreases from the value characteristic for the Co\textsuperscript{II} from (5.86 $\mu$B) to 1.71 $\mu$B, typical for $S = \frac{1}{2}$ (Co\textsuperscript{III} form). The interconversion was additionally confirmed by near-IR spectroscopy (1700 – 3200 nm) and the observation of the disappearance of a band at 2700 nm at 350 K, characteristic for the $ls$-Co\textsuperscript{III}-cat form of complex. An important discovery associated with the light-induced transition from [Co\textsuperscript{III}(pz)(3,6-dbsq)(3,6-cat)] to [Co\textsuperscript{II}(pz)(3,6-dbsq)\textsubscript{2}] was the observation of photomechanical properties. Irradiation with a tungsten-halogen lamp at reduced temperature (-35 °C) under N\textsubscript{2} flow leads to approximately 0.2 Å change in the Co-N bond length, which propagated along the $a$ and $b$ crystallographic axes, resulting in a change of 0.06 mm per millimeter of polymer length.
Table 1-2. Co VT CPs reported prior to this work.

<table>
<thead>
<tr>
<th>Linking ligand</th>
<th>Compound molecular formula</th>
<th>Thermal transition</th>
<th>Photo-transition</th>
<th>Stereoisomer</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>pyrazine (pyz)</td>
<td>[Co(pz) (3,6-dbdiox)₂] ·C₆H₁₄</td>
<td>$T_c \geq 150$ K, gradual.</td>
<td>-</td>
<td>trans</td>
<td>37</td>
</tr>
<tr>
<td>4,4'-bipyridyl (4,4'-bpy)</td>
<td>[Co (4,4'-bpy)(3,5-dbdiox)₂]</td>
<td>$T_c \geq 330$ K, abrupt.</td>
<td>-</td>
<td>trans</td>
<td>106</td>
</tr>
<tr>
<td>meso-alpha,beta-di(4-pyridyl)glycol (dpg)</td>
<td><a href="3,5-H%E2%82%82dbcat">Co(3,5-dbdiox)₂(dpg)</a>₂</td>
<td>$T_c \geq 100$ K, gradual.</td>
<td>-</td>
<td>cis</td>
<td>107</td>
</tr>
<tr>
<td>Solvent dependent.</td>
<td>Solvated:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$T_c \geq 340$ K, abrupt.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Desolvated:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$T_c \geq 253$ K, gradual.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$T_{LIESST} = 52$ K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>bis(4-pyridyl)ethylene (bpe)</td>
<td>[Co(3,5-dbdiox)₂(bpe)]·2CH₃CN·2H₂O</td>
<td></td>
<td></td>
<td>trans</td>
<td>56</td>
</tr>
<tr>
<td>Compound</td>
<td>Formula</td>
<td>Transition Temperature and Behavior</td>
<td>$T_{LIESST}$</td>
<td>Conformation</td>
<td></td>
</tr>
<tr>
<td>------------------------------------------------------------------------</td>
<td>------------------------------------------------------------------------</td>
<td>-------------------------------------------------------</td>
<td>--------------</td>
<td>--------------</td>
<td></td>
</tr>
<tr>
<td>4,4'-azopyridine (azpy)</td>
<td>[Co(3,5-dbldiox)$_2$(azpy)]·2CH$_3$CN·2H$_2$O</td>
<td>$T_c \geq 350$ K, abrupt.</td>
<td>$T_{LIESST} = 60$ K</td>
<td>cis</td>
<td></td>
</tr>
<tr>
<td>1,4-bis(4-pyridyl)-benzene (bpb)</td>
<td>[Co(3,5-dbldiox)$<em>2$(bpb)]$</em>{0.5}$·2CH$_3$CN·2H$_2$O</td>
<td>$T_c \geq 212$ K, gradual</td>
<td>-</td>
<td>trans</td>
<td></td>
</tr>
<tr>
<td>4,4'-bipyridyl (4,4'-bpy)</td>
<td>[Co(2,3-LH)$_2$(4,4'-bpy)]·2H$_2$O·4,4'-bpy</td>
<td>$T_c \geq 212$ K, gradual</td>
<td>-</td>
<td>trans</td>
<td></td>
</tr>
<tr>
<td>tetrakis(4-pyridyl oxymethylene)methane (tpom)</td>
<td>{[Co$^{III}$(3,5-dbcat)(3,5dbsq)]$_2$(tpom)}·8H$_2$O·2C$_2$H$_5$OH</td>
<td>Solvent dependent. Solvated: $T_c \geq 325$ K, abrupt. Desolvated: Very gradual.</td>
<td>-</td>
<td>cis</td>
<td></td>
</tr>
</tbody>
</table>
More than a decade later, following on from the studies of Jung and Pierpoint, Ruiz-Molina et al. used different divergent N-donor ligands, 4,4'-bipyridine and 1,4-bis(imidazol-1-ylmethyl)benzene (bix), to link cobalt-dioxolene building blocks.\(^\text{106}\) Single crystals of \([\text{Co}(4,4'\text{-bpy})(3,5\text{-dbsq})(3,5\text{-dbdio})]_\infty\) were obtained and characterized by X-ray diffraction studies, confirming the 1D chain structure, characteristic for N-aromatic N-donor bridging ligands. Although the bis-linked material is amorphous, the polymerization of \{Co(3,5-dbsq)(3,5-dbcat)\} was confirmed by various additional studies, including elemental analysis, infrared spectroscopy, energy-dispersive X-ray spectroscopy and MALDI-TOF mass spectrometry. Both materials show valence tautomeric interconversion confirmed by magnetic susceptibility studies (Figure 1-8). For the 4,4'-bpy linked crystalline coordination polymer, the transition is abrupt and occurs over a narrow temperature range, between 275 K and 340 K. For the amorphous material the transition is more gradual, which is common for non-crystalline materials.\(^\text{110}\)

Another N-donor linking ligand - *meso*-alpha,beta-di(4-pyridyl)glycol – was used by Tao et al. to synthesize 1D zig-zag chains (Figure 1-7c), which undergo both thermally and optically induced VT interconversions.\(^\text{107}\) This compound is the first example of a VT CP with a *cis* arrangement of the ligands around the Co center. Changes in the \(\chi_mT\) vs. \(T\) plot measured under different external pressures confirm the role of the pressure as a stimulus for the VT transition and the two-step nature of this process. Increasing the applied pressure stabilizes the *ls* - Co\(^{II}\) form, shifting the transition to higher temperatures and making it more gradual.

In 2014 the same group published a series of three 1D chains linked by different bipyridyl-based linking ligands: *trans*-bis(4-pyridyl)ethylene, *trans*-4,4’-azopyridine, and 1,4-bis(4-pyridyl)- benzene (Figure 1-7b).\(^\text{56}\) All the compounds undergo a thermally-
induced VT transition, which in two cases is strongly dependent on solvation. One complex can be photo-excited at low temperature to show a light-induced VT transition.

**Figure 1-7.** Structural representations of VT CPs based on Co centers, 3,5-dbdiox and bipyridyl derivatives: a) [Co(pz)(3,6-dbdiox)$_2$], b) [Co(3,5-dbdiox)$_2$(bpb)], c) [Co(3,5-dbdiox)$_2$(dpg)].
Figure 1-8. Magnetic susceptibility data for the amorphous metal-organic nano-spheres (black squares) and for crystalline coordination polymer (triangles).\textsuperscript{106}

Linking \{Co-bis(diox)\} units by bipyridyl derivatives has been the predominant approach to synthesizing 1D VT CPs, however alternative approaches can also deliver interesting results. It has been shown that prolonged polymeric structures could be also realized by using bis-bidentate bis-dioxolene ligands.\textsuperscript{110–112} Both ligands presented in Scheme 1-5 may connect two different metal ions, giving rise to systems with 1D cooperative properties. All systems present a temperature-induced VT transition and one shows a light-triggered transition.\textsuperscript{111} The 12 K hysteresis, observed for [Co(phen)L]-0.5CH\textsubscript{2}Cl\textsubscript{2} (L = 3,5-bis(3’,4’-dihydroxy-5’-tert-butylphenyl)-1-tert-butylbenzene) suggest strong cooperativity and a promising improvement towards bistable magnetomolecular switches, while extended kinetic studies of the relaxation time for metastable photoconverted fractions have helped elucidate the physical properties of this class of compounds. Finally, the synthesis of materials formed by the 3,3,3’,3’-
tetramethyl-5,5’,6,6’-tetrahydroxy-1,1’spiro-bis(indane) gave an opportunity to investigate the behavior of Robin and Day class I valence tautomeric species.\textsuperscript{111}

\begin{scheme}
\centering
\includegraphics[width=\textwidth]{scheme}
\caption{Bis-bidentate bis-dioxolene ligands used in synthesis of polynuclear VT coordination complexes.\textsuperscript{110–112}}
\end{scheme}

Although the idea of combining two different 2-linking ligands in order to achieve higher-dimensional VT CPs seems appealing, a crystal structure of the targeted 2- or 3-dimensional complexes based on two types of linkers is yet to be reported. Sato \textit{et al.} have obtained a 1D VT chain containing both bis-dioxolene and bipyridyl-based ligands. The synthesized complex has a formula \([\text{Co}(2,3\text{-LH}_2)2(4,4’\text{-bpy})]_\infty\), where \(2,3\text{-LH}_2 = 2,3\text{-tetrahydroxy-9,10-dimethyl-9,10-dihydro-9,10-ethanoanthracene.}\textsuperscript{108}\) The polymeric compound formed as a chiral left-handed helical chain and undergoes a temperature dependent VT transition above 100 K.

Finally, Ruiz-Molina in 2015 joined redox-active O-donor ligand properties and ancillary N-donor properties and synthesized a multi-topic catechol-pyridine ligand presented in Scheme 1-6.\textsuperscript{113}\ As anticipated, the reaction of 4-(2-(pyridin-4-yl)ethyl)benzene-1,2-diol with a Co\textsuperscript{II} salt leads to the formation of cobalt-based coordination polymer nanoparticles. The compound is amorphous, but elemental analysis and energy dispersive X-ray spectroscopy corroborate the Co:ligand ratio as 1:2 and suggest a polymeric structure. Additionally, IR data confirms ligand coordination to the metal center.
Scheme 1-6. A multifunctional catechol-pyridine ligand.¹¹³

1.7.2 One-dimensional Mn-based valence tautomeric coordination polymers.

The family of 1D VT CPs based on bipyridyl ligands can be expanded with manganese analogues. The early research of Pierpont et al. focused on series of complexes with a general formula \([\text{Mn}(N_2L)(3,6\text{-dbdiox})_2]\).¹¹⁴ Temperature-dependent electronic spectroscopy was used to follow entropically driven VT transitions. The 1D polymeric complex employs the pyrazine ligand as a bridge between \{Mn-bis(diox)\} units, analogous to the previously reported Co structure. The Mn-N and Mn-O bond lengths suggest the +3 oxidation state of the Mn cation, which is further confirmed by the electronic spectra of the solid sample. The intense band at 2090 nm can be attributed to interligand charge transfer characteristic for a \{\text{Mn}^{\text{III}}(\text{sq})(\text{cat})\} species. The band decreases with increasing temperature, indicating a VT transition from \([\text{Mn}^{\text{II}}(\mu-pz)(3,6\text{-dbsq})(3,6\text{-dbcat})]_\infty\) to \([\text{Mn}^{\text{II}}(\mu-pz)(3,6\text{-dbsq})_2]_\infty\). Later Panja, Banerjee and co-workers followed with research on \([\text{Mn}(N_2L)(\text{Cl}_4\text{-diox})_2]_\infty\) (\(N_2L = \text{N,N-bis(2-pyridyl-methyl)-1,2-ethanediamine and N,N-bis(2-pyridylmethyl)-1,3-propanediamine}\)) and \{[\text{Mn}(N_2L)(X_4\text{-sq})(X_4\text{-diox})][\text{Mn}(X_4\text{-sq})(X_4\text{-diox})(\text{solvent})_2]_\infty\} (N_2L = \text{N,N-bis(2-pyridylmethyl)-1,4-butanediamine or N,N’-bis(2-pyridylmethyl)-1,6-hexanediamine, X = Cl or Br, solvent = H}_2\text{O or DMF}), successfully reporting examples of thermally induced reversible valence tautomeric transitions."
1.7.3 Two-dimensional valence tautomeric coordination polymers.

Higher dimensionality in CPs can increase the impact of the long-range interactions and enhance cooperative effects. Moreover, 2D and 3D structures are characterized by higher porosity and can be good platforms for observing host-guest interactions.

The first example of a higher dimensional VT coordination polymer was reported by Tao, Zhang et al. (Table 1-2).109 The polypyridyl ligand tetrakis(4-pyridyloxymethylene)methane (tpom) acts as a 4-connecting linker for cobalt-dioxolene units (Figure 1-9, right). The resulting 2D structure can be described as a layer of bridging tpom ligand 'sandwiched' between two layers of Co centers. (Figure 1-9, left) The presence of solvent molecules in the crystal lattice affects the magnetic properties, which were studied in two full cooling/heating cycles. During the first cycle the polymer undergoes an abrupt transition starting above 250 K, but because of the desolvation process associated with heating the sample, the cycle cannot be repeated. In the second cycle, the magnetic susceptibility versus temperature curve of the desolvated sample does not show a well-defined interconversion temperature and therefore the VT conversion is assumed to be incomplete. However, once the sample is completely desolvated, the transition becomes reversible. An interconversion between {[Co$^{II}$(3,5-dbsq)(3,5-dbcat)]$_2$tpom} and {[Co$^{II}$(3,5-dbsq)$_2$]tpom} can also be achieved by optical irradiation with blue light. Due to loss of crystallinity, the desolvated sample cannot be analyzed crystallographically. This limits the insight that may be gained into the nature of the solvent-complex interactions and their influence on the compound’s magnetic properties.
Recently Luneau et al. published the first example of a Mn-based 2D VT CP and also the first example of a VT polymeric complex employing a redox-active nitroxide radical (Figure 1-10). The redox forms of the ligand 2-(2-imidazolyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-3-oxide-1-oxyl (NITIm) are presented in Scheme 1-7. The compound obtained by Luneau et al. undergoes a thermally-induced VT transition. Upon heating, two Mn$^{3+}$ ions are reduced to Mn$^{3+}$ and two of three ligands are oxidized from their
diamagnetic aminoxyl form to a nitroxide radical. The most significant finding of the study is a 20 K hysteresis loop at room temperature associated with the interconversion. This makes the complex an attractive candidate for a switchable magnetic material.

\[
\begin{align*}
\text{O} & \text{N} - \text{N}^2\text{O} & \text{O} & \text{N} - \text{N}^\text{O}^- \\
\text{HN} & \text{N} & \text{HN} & \text{N}
\end{align*}
\]

**Scheme 1-7.** Redox isomers for NITImH free radical.\textsuperscript{15}

**Figure 1-10.** Structural representation of the Mn 2D VT CP. Hydrogen atoms omitted for clarity.\textsuperscript{15}
1.7.4 Functionalization of valence tautomeric coordination polymers.

As mentioned above, coordination polymers can be suitable materials for integrating VT or SCO properties into functional devices. The main challenge in designing VT micro-/nanostructures is the very nature of the VT/SCO transition. Any change in supramolecular packing or solvation can affect the transition significantly. Despite the obstacles, a few notable approaches have been proposed.\textsuperscript{106} A first approach to VT coordination polymer particles (CPPs) was reported by the Ruiz-Molina group using a fast precipitation method. The particle size was determined by scanning electron microscopy (SEM) and dynamic light scattering (DLS) methods, giving an average diameter of $76 \pm 9$ nm. The study shows that the particle size could be controlled by the rate of addition of the poor solvent (Figure 1-11). Later on, the group followed with a much more detailed study on controlling the compound’s spin-transition through monitored synthesis of different crystalline phases.\textsuperscript{115} The reagent concentration, synthesis temperature, use of surfactants and solvent effects were studied. The obtained micro particles of the coordination polymer [Co(4,4'-bpy)(3,5-dbdiox)$_2$] were grouped into two distinctive crystalline phases or a mixture of them. Magnetic studies revealed significant differences in the VT transition characteristics between the phases.
Figure 1-11. Upper panel: SEM images of micro/nanostructures of the VT CPPs obtained in different solvents, at different concentrations and temperatures. Color code: α-phase (blue), α+β-phase (violet), β-phase (orange). Lower panel: Magnetic measurements for the different crystalline phases as a function of temperature. The inset shows UV-Vis spectra of the α-phase between 253 and 333 K.115

A bis-catechol ligand containing an imine group was used to obtain pH-sensitive VT CPPs.116 Although the lower (~5) pH does affect the polymer matrix and magnetic
properties of the particles, the process was irreversible. Nevertheless, the study opened a new perspective regarding using pH-responsive VT CPPs as sensors or drug delivery systems. Hernando et al. synthesized two types of VT coordination polymers based systems containing a fluorescent guest. The chosen VT CP was the previously reported \([\text{Co(bix)(3,5-dbsq)(3,5-dbcat)}]_{n}\), where bix is a flexible bis-imidazole ligand. The optical properties of the complex were expected to quench the guest fluorescence when captured inside the nanoparticle, therefore enabling the easy detection of the released guest molecules. Magnetic studies show that both synthetic strategies; bonding the fluorescent backbone to the complex and encapsulating the fluorescent molecule in the polymer matrix, gave materials of similar magnetic properties and the coordination sphere of the Co center had not been modified. Concurrently, two different synthetic designs resulted in two distinctive guest-release mechanisms. Physically entrapped molecules are released by a fast diffusion process, while the delivery of the molecules covalently bonded to the metal is achieved through slow nanoparticle degradation. This shows the variety of approaches that have potential for use of the VT CPPs as drug-delivery platforms. More recently, based on successful attempts with discrete VT coordination complexes by Schultz et al. and Poneti et al., attention has been brought to the synthesis of self-assembled monolayers of VT CPs. The nanoparticles were obtained by mixing the linking bix ligand with the Co salt and the semiquinonate and catecholate forms of 3,4-dihydroxycinnamic acid. The carboxylic acid groups attach to the gold surface previously decorated with a monolayer of amino-terminated alkyl chains through a carbodiimide-mediated amide coupling reaction. Ultimately, a uniform (85% - 90% coverage) 2D monolayer of the VT CPs is obtained. XPS studies confirm that the attached nanoparticles retain their VT properties (Figure 1-12).
Figure 1-12. a) Scheme of the formation of polymeric chains for CPP-Co and assembly into nanostructure by fast precipitation process, b) Scheme of the attachment of carboxyl-functionalized nanoparticles onto a gold surface previously covered with monolayer of amino-terminated alkyl chains through a carbodiimine-mediated coupling reaction.

1.8 Spin crossover Coordination Polymers Based on Co$^{II}$.

As mentioned previously, compared to the extensive research on Fe$^{II}$ based SCO coordination polymers, Co-based SCO materials have received much less attention. The first polymeric Co SCO compound was not reported until 2004 by Hayami et al.$^{121}$ Using the chloride salt of Co$^{II}$ and 4’-(4’’’-pyridyl)-2,2’:6’,2”-terpyridine (pterpy), a 1D coordination polymer was synthesized (Figure 1-13, left) (Table 1-3). Solvent exchange experiments, followed by magnetic studies, show a significant solvation effect on the nature of the SCO transition. Compound [Co(pyterpy)Cl$_2$]·MeOH stays in the hs-Co$^{II}$ state throughout the measured temperature range. In contrast, when co-crystallized
methanol is replaced by water, to form \([\text{Co(pyterpy)Cl}_2 \cdot 2\text{H}_2\text{O}]\), an abrupt thermally-driven SCO transition can be observed. Repeated heating-cooling cycles reveal a reversible hysteresis loop \((\Delta T = 1 \text{ K})\). Later on, bromide analogs, \([\text{Co(pyterpy)Br}_2 \cdot \text{MeOH}]\) and \([\text{Co(pyterpy)Br}_2 \cdot 2\text{H}_2\text{O}]\), have been obtained and their structural and magnetic properties studied.\(^{122}\) The compound \([\text{Co(pyterpy)Br}_2 \cdot 2\text{H}_2\text{O}]\) shows, as per the chloride analog, a cooperative effect associated with the desolvation process. This time, however, the desolvated curve shows a two-step SCO transition. The research also indicated the effect of the halo ligand on the compound’s porosity and adsorption behavior. While the complex employing bromo ligands retains its porosity upon removal of guest molecules allowing a rapid CO\(_2\) uptake, the structure containing chloro ligands can be described as “closing up” upon desolvation.

In 2012, Ghosh et al. reported a 1D SCO CP that exhibits crystallographic symmetry-breaking.\(^{123}\) The magnetic susceptibility of the compound \([\text{Co-(enbzpy)(dca)}]_n(\text{ClO}_4)_n\) (enbzpy = \(N,N’\)-bis(2-pyridinylbenzylidene)ethane-1,2-diamine, dca = dicyanamide) was measured in multiple cooling-heating cycles over the temperature range 2-300 K (Figure 1-13, right). A very well defined SCO transition can be seen at around 190 K, with a reversible hysteresis loop of a 3 K width. This suggests a non-negligible cooperative effect associated with long-range and short-range interactions within the polymeric structure. Low temperature (100 K) crystallographic studies reveal a structural phase transition associated with a significant rearrangement of the crystal packing and intermolecular interactions. In particular, the reorientation of the perchlorate counterion, affecting its anion-\(\pi\) interactions with the dicyanamide bridge, seems to play a significant role in the cooperative character of the SCO transition. The phenomenon was later confirmed by the synthesis of a hexafluorophosphate salt of the complex. The compound \([\text{Co-(enbzpy)(dca)}]_n(\text{PF}_6)_n\) undergoes a very gradual spin transition, in contrast to the
abrupt one seen in the compound involving a perchlorate anion. The non-coordinating bulky PF$_6^-$ does not take part in the intermolecular interactions around the cobalt center, the result being a much less defined SCO conversion.$^{124}$

Figure 1-13. 1 D SCO coordination polymers: [Co(pyterpy)Cl$_2$] (left) and [Co-(enbzpy)(dca)] (right).$^{48,125}$
Table 1-3. Previously reported crystal structures of one-dimensional Co SCO coordination polymers.

<table>
<thead>
<tr>
<th>Linking ligand</th>
<th>Ancillary ligand</th>
<th>Compound molecular formula</th>
<th>Thermal transition</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="pterpy" /></td>
<td>Cl(^{-})</td>
<td>[Co(pyterpy)Cl(_2)](\cdot)MeOH, [Co(pyterpy)Cl(_2)](\cdot)H(_2)O</td>
<td>Solvent dependent: Gradual for H(_2)O solvate. MeOH solvate stays in the (hs) state.</td>
<td>121</td>
</tr>
<tr>
<td><img src="image" alt="pterpy" /></td>
<td>Br(^{-})</td>
<td>[Co(pyterpy)Br(_2)](\cdot)MeOH, [Co(pyterpy)Br(_2)](\cdot)H(_2)O</td>
<td>Solvent dependent: Gradual for H(_2)O solvate, two steps. MeOH solvate stays in the (hs) state.</td>
<td>122</td>
</tr>
<tr>
<td><img src="image" alt="dca" /></td>
<td><img src="image" alt="enbzpy" /></td>
<td><a href="ClO(_4)">Co-(enbzpy)(dca)</a></td>
<td>Abrupt with a 3K wide hysteresis loop.</td>
<td>123</td>
</tr>
<tr>
<td><img src="image" alt="dca" /></td>
<td><img src="image" alt="enbzpy" /></td>
<td><a href="PF(_6)">Co-(enbzpy)(dca)</a></td>
<td>Very gradual.</td>
<td>124</td>
</tr>
</tbody>
</table>
1.9 Scope of the Present Study.

This thesis presents the synthesis and characterization of polymeric coordination polymers based on Co\textsuperscript{II/III} centers, redox-active dioxolene ligands and N-donor bridging ligands. All synthesized compounds were investigated towards valence tautomeric or spin crossover transitions.

Chapter II describes four one-dimensional coordination polymers based on \{Co(diox)\textsubscript{2}\} units and 4,4'-bipyridyl derivatives. Thermally- and photo-induced valence tautomeric transitions have been monitored by variable temperature magnetic measurements. A solvation effect on the crystal packing and magnetic properties has been observed.

Chapter III presents two one-dimensional coordination polymers employing a divergent 1,2,4,5-tetra(4-pyridyl)benzene (tpb) linker of \{Co(diox)\textsubscript{2}\} units. Structural studies reveal different connecting modes of the ligand. Electronic and magnetic properties of the chain-topology compound are described through spectroscopic and magnetic studies.

Chapter IV focuses on compounds incorporating the flexible 1-hydroxy-1,2,4,5-tetra(4-pyridyl)cyclohexane ligand linking \{Co(diox)\textsubscript{2}\} units. The obtained structures, a two-dimensional sheet and a one-dimensional zig-zag chain, demonstrate the versatility of the linking ligand and the role of steric interactions in molecular materials design.

Chapter V presents three different Co coordination complexes based on 4-pyridyl-2,2′:6′,2″-terpyridine (pterpy). The discrete complex [Co(3,5dbcat)(3,5dbcatH)pterpy] has been investigated on account of unprecedented for VT complexes coordination environment, with three O atoms and 3 N atoms around the cobalt center. Two related one-dimensional chain compounds exhibit Co\textsuperscript{II} SCO phenomenon.

Chapter VI discusses the significance and future directions of the presented work.
1.10 References.


(14) Rotthaus, O.; Jarjayes, O.; Thomas, F.; Philouze, C.; Valle, C. P. Del; Saint-


36, 19.


(67) Slota, M. Faraday Discuss. 2015, 44.


(106) Imaz, I.; MasPOCH, D.; Rodríguez-Blanco, C.; Pérez-Falcón, J. M.; Campo, J.;


CHAPTER II

One dimensional valence tautomeric coordination polymers based on Co-dioxolene units and bipyridyl linking ligands.

2.1 Introduction. ................................................................................................... 57
2.2 Contribution of the candidate. ........................................................................ 58
2.3 Published manuscript and supporting information........................................... 58
2.1 Introduction.

Studies on VT CPs have been, with one exception, focused on one-dimensional compounds and until 2014 only four such compounds had been structurally characterized. In the absence of sufficient number of examples, the aim of the first project within this PhD research was to expand upon a family of 1D VT CPs based on \{Co(3,5-diox)\}_2 VT units and linear N-donor linkers. A target chain is presented in Scheme 2-1. together with selected linking ligands.

![Scheme 2-1](image)

**Scheme 2-1.** Targeted 1D VT CPs and employed N-donor linking ligands (1,2-bpe = 1,2-bis(4-pyridyl)ethane, azpy = trans-4,4'-azopyridine, 1,3-bpp = 1,3-bis(4-pyridyl)propane).

As mentioned in Section 1.2.2., for thermally-induced VT transitions in 1:2 Co:diox VT complexes, one diox ligand stays in the semiquinone state throughout the entire temperature range, while the second one converts from the catecholate to the semiquinone state according to the Equation 2-1.

\[
\text{Co}^{III}(3,5\text{-dbsq})\leftrightarrow\text{Co}^{II}(3,5\text{-dbsq}) (2-1)
\]
Selected ligands, although all based on 4,4’-bipyridyl, differ from each other in the degree of flexibility and ability to form additional short-range interactions with crystallization solvent or neighboring chains. This chapter is focused on the synthesis and characterization of novel 1D VT CPs, as well examining the impact of packing and solvation on the VT properties.

2.2 Contribution of the candidate.

Listed below are contributions of the candidate:

- Planning of the project
- Synthesis of the azpy ligand
- Synthesis of presented coordination polymers
- Characterization of the compounds, except for the techniques mentioned in the preface
- Planning and writing the manuscript

2.3 Published manuscript and supporting information.
Valence Tautomerism in One-Dimensional Coordination Polymers

Olga Drath,‡ Robert W. Gable,‡ Boujemaa Moubarakı,‡ Keith S. Murray,‡ Giordano Poneti,§ Lorenzo Sorace,*§ and Colette Boskovic*‡

INTRODUCTION

With a view toward the miniaturization of electronic devices, the last two decades have seen the development of molecular materials that can be switched between distinguishable electronic states upon application of an appropriate external stimulus, including spin crossover (SCO) and valence tautomeric (VT) compounds.1,2 Due to significant changes in optical and/or magnetic properties associated with the intramolecular electron transfer and/or spin transitions, these materials are of interest for data storage, sensors, display devices, and molecular electronics. Valence tautomerism involves electron transfer between a redox-active metal cation and a redox-active ligand.3–6 Since the first report in 1980,7 a number of octahedral cobalt complexes with redox-active 3,5-di-tert-butylidioxolene (3,5-dbdiox) ligands and N-donor ancillary ligands have been found to undergo both heat- and light-induced VT transitions. For these complexes, electron transfer between the cobalt cation and 3,5-dbdiox ligand is accompanied by a metal-based spin transition such that the complexes switch between low-spin Co(III)–catecholate \( \text{[L-Co}^\text{II}(3,5\text{-dbcat})] \) and high-spin Co(II)–semiquinonate \( \text{[hfs-Co}^\text{III}(3,5\text{-dbsq})] \) forms.

In addition to exhibiting a reversible electronic transition, molecular materials for use in devices should ideally also display abrupt transitions and hysteresis that gives rise to bistability. These characteristics can be accessed in cooperative systems, in which the electronic state changes are propagated throughout the crystal lattice. Already observed for SCO materials8,9 higher cooperativity has been realized by a combination of short-range10–12 and long-range interactions.13 In particular, considerable progress has been achieved with spin crossover coordination polymers (SCO CPs),14–18 which can inform the design of analogous VT coordination polymers (VT CPs). Of most relevance to the design of new VT CPs are 1,2,4-triazole-based 1D SCO CPs, which have been the subject of intensive studies oriented toward transferring the SCO properties to technologically convenient platforms such as composites and gels,19 liquid-crystalline materials,20 dendrimers,21 Langmuir–Blodgett films,22 and nanoparticles.23–25 In some cases, these materials display abrupt and hysteretic thermally induced transitions near room temperature, making them attractive

ABSTRACT: The combination of the divergent bis-pyridyl linking ligands 1,2-bis(4-pyridyl)ethane (1,2-bpe), 4,4'-trans-azopyridine (azpy), and 1,3-bis(4-pyridyl)propane (1,3-bpp) with cobalt and 3,5-di-tert-butylidioxolene (3,5-dbdiox) ligands has afforded the complexes \( \text{[Co}^{\text{III}}(3,5\text{-dbdiox})_{2} (1,2\text{-bpe})]_{\infty} \) (1), \( \text{[Co}^{\text{II}}(3,5\text{-dbdiox})(\text{azpy})]_{\infty} \) (2), \( \text{[trans-Co}(3,5\text{-dbdiox})_{2} (1,3\text{-bpp})]_{\infty} \) (3a), and \( \text{[cis-Co}^{\text{II}}(3,5\text{-dbdiox})_{2} (1,3\text{-bpp})]_{\infty} \) (3b). All species are 1D coordination polymers that crystallize as solvated forms; the geometric isomers 3a,b cocrystallize. Complexes 1, 2, and 3a exhibit around the Co centers a trans disposition of the N-donor atoms from the pyridyl linkers, while an unusual cis disposition is evident in 3b. Single-crystal X-ray structural analysis at 100 or 130 K of solvated forms of these complexes indicates that all complexes possess the \( \text{[Co}^{\text{III}}(3,5\text{-dbcat})(3,5\text{-dbsq})] \) (3,5-dbdiox = 3,5-di-tert-butylcatecholate; 3,5-dbsq = 3,5-di-tert-butylsemiquinonate) charge distribution at the temperature of data collection. Variable-temperature magnetic susceptibility studies reveal that 1, 1·1.5MeCN·2H2O, 2·2EtOH, and 3·MeCN·H2O \( (3 = 3a-3b) \) all exhibit thermally induced valence tautomeric (VT) transitions above 200 K. Multiple heating and cooling cycles indicate that in some cases the behavior is strongly dependent on desolvation processes. Most notably, further desolvation of 1·1.5MeCN·2H2O above 340 K affords \( \chi_{m}T \) values that suggest unusual ferromagnetic coupling in the \( \text{[hfs-Co}^{\text{III}}(3,5\text{-dbsq})] \) valence tautomer. Compound 3·MeCN·H2O exhibits a two-step VT transition that may be ascribed to the presence of the cis and trans geometric isomers. Compounds 1, 1·1.5MeCN·2H2O, 2·2EtOH, and 3·MeCN·H2O all also exhibit a single photoinduced VT transition, comparable to those generally observed for nonpolymeric cobalt–dioxolene complexes.

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candidates for memory and sensor applications. Extending the synthetic approach to divergent bi- and polydentate pyridine-like bridges has afforded 2D and 3D SCO CPs. While most VT complexes are mononuclear, some 1D VT CPs have been reported. The first of these was [Co(pyz)(3,6-dbdiox)2]2 (pyz = pyrazine, 3,6-dbdiox = 3,6-di-tert-butyl-dioxolene), which undergoes a thermally induced VT transition but does not show a photoinduced transition at low temperature. Following a different strategy, Dei and co-workers subsequently reported the formation of a 1D CP constructed from [Co(1,10-phenanthroline)] units linked via a dative bridging dioxolene CP with 4,4-dioxolene units with chiral dioxolene ligands. Another N-donor linking ligand—meso-α,β-bis(4-pyridyl)glycol (dpg)—was used by Tao et al. to synthesize a 1D zigzag chain, which undergoes heat-, pressure-, and light-induced VT intraconversion. The same group reported three 1D VT CPs have been reported. The synthetic approach to divergent bi- and polydentate pyridine-like bridges has a dimensionality of the CP was not established. Another N-donor linking ligand—meso-α,β-bis(4-pyridyl)glycol (dpg)—was used by Tao et al. to synthesize a 1D zigzag chain, which undergoes heat-, pressure-, and light-induced VT intraconversion. The same group reported three 1D VT CPs have been reported. The synthetic approach to divergent bi- and polydentate pyridine-like bridges has a dimensionality of the CP was not established. Another N-donor linking ligand—meso-α,β-bis(4-pyridyl)glycol (dpg)—was used by Tao et al. to synthesize a 1D zigzag chain, which undergoes heat-, pressure-, and light-induced VT intraconversion. The same group reported three 1D VT CPs have been reported. The synthetic approach to divergent bi- and polydentate pyridine-like bridges has a dimensionality of the CP was not established. Another N-donor linking ligand—meso-α,β-bis(4-pyridyl)glycol (dpg)—was used by Tao et al. to synthesize a 1D zigzag chain, which undergoes heat-, pressure-, and light-induced VT intraconversion. 

**Chart 1. Bis-Pyridyl Ligands Used in This Study**

![Chart 1](image)

Inorganic Chemistry

Article

1.3-bpp

1,2-bpe

azpy

pyridyl)ethane (1,2-bpe), trans-4,4'-azopyridine (azpy), and 1,3-bis(4-pyridyl)propane (1,3-bpp) to link {Co(3,5-dbdiox)2} units. Herein we report the synthesis and structural, electronic, and (photo)magnetic properties of the systems obtained using this strategy.

**EXPERIMENTAL SECTION**

**General Considerations.** All of the reagents, excluding azpy, were obtained from commercial sources and were used as received. The azpy ligand was synthesized according to the literature procedure. A method 1. An ethanol solution (3.75 mL) of 3,5-dbc H2 (33 mg, 0.15 mmol) and 1,2-bpe (14 mg, 0.075 mmol) was layered over an aqueous solution (3 mL) of Co(OAc)2·4H2O (19 mg, 0.075 mmol). The ethanol and water layers were separated by a buffer layer of ethyl acetate (1 mL). After 5 days blue rectangular plate-shaped crystals were formed. A sample for single-crystal X-ray diffraction was maintained in contact with the mother liquor to avoid solvent loss and was identified as 1·2H2O. The product was isolated by filtration, washed with cold ethanol, and air-dried, giving a desolvated sample of 1 in 30% yield. Anal. Calc. for C30H44O4CoN2 (1): C, 70.3; H, 7.8; N, 4.1. Found: C, 70.1; H, 7.7; N, 4.2. Selected IR (cm⁻¹): 2952 (vs), 1615 (s), 1580 (m), 1503 (vs), 1464 (vs), 1387 (m), 1356 (s), 1284 (m), 1245 (m), 1209 (m), 1095 (m), 1070 (m), 1035 (m), 986 (s), 827 (m), 551 (w). Thermogravimetric analysis confirmed the absence of solvation for 1.

**Method 2.** Complex 1 was synthesized by adapting the method reported previously by Tao et al. with other ligands. An acetonitrile solution (6.7 mL) of 3,5-dbc H2 (15 mg, 0.067 mmol) and 1,2-bpe (12 mg, 0.067 mmol) was layered over an aqueous solution (1.3 mL) of Co(OAc)2·4H2O (17 mg, 0.067 mmol). Green rectangular plate-shaped crystals were obtained after several weeks. A crystal suitable for single-crystal X-ray diffraction was maintained in the mother liquor and identified as 1·2MeCN·2H2O. The product was isolated by filtration, washed with acetonitrile, and air-dried, affording partially desolvated 1·1.5MeCN·2H2O in 20% yield. Anal. Calc. for C30H46N2O4Co (1·1.5MeCN·2H2O): C, 66.1; H, 7.8; N, 6.3. Found: C, 65.7; H, 7.6; N, 6.3. Selected IR (cm⁻¹): 2953 (vs), 1616 (s), 1578 (m), 1463 (vs), 1387 (m), 1357 (s), 1287 (m), 1243 (m), 1206 (m), 1095 (m), 1067 (m), 1027 (m), 984 (s), 838 (m), 555 (s). Applying the method Tao et al. employed to desolvate related compounds, vacuum drying 1·1.5MeCN·2H2O at 90 °C afforded samples that were very hygroscopic, with elemental and thermogravimetric analysis suggesting adsorption of several water molecules per formula unit upon exposure of the vacuum-dried sample to air.

Complex [Co(3,5-dbdiox)(azpy)]∞ (2). This complex was synthesized according to method 1 used for complex 1, with replacement of 1,2-bpe with azpy (14 mg, 0.075 mmol) to afford green rectangular plate-shaped crystals. A sample for single-crystal X-ray diffraction was maintained in the mother liquor to avoid solvent loss and identified as 2·2EtOH. The product was isolated by filtration, washed with cold ethanol, and air-dried, giving a sample of 2·2EtOH in 18% yield. Anal. Calc. for C30H42N2O4Co (2·2EtOH): C, 65.0; H, 7.8; N, 7.2. Found: C, 64.9; H, 7.2; N, 7.1. Selected IR (cm⁻¹): 2956 (vs), 1600 (s), 1582 (m), 1459 (vs), 1387 (m), 1356 (s), 1288 (m), 1246 (m), 1201 (m), 1097 (m), 1052 (m), 1027 (m), 986 (s), 855 (m), 574 (m). Vacuum drying 2·2EtOH at 90 °C appears to cause decomposition, affording material for which even an approximately good fit of the elemental analysis could not be found.

Complex [trans-Co(3,5-dbdiox)(1,3-bpp)]∞ (3). This compound was synthesized according to method 2 used for complex 1, with replacement of the 1,2-bpe ligand with 1,3-bpp (15 mg, 0.067 mmol). Blue rectangular plate-shaped crystals were obtained after several weeks. A crystal for single-crystal X-ray diffraction was maintained in the mother liquor and identified as 3·2MeCN·H2O. The product was isolated by filtration, washed with acetonitrile and air-dried, giving a partially desolvated sample of 3·MeCN·H2O in 30% yield. Anal. Calc. for C30H42N2O4Co (3·MeCN·H2O): C, 69.4; H, 7.8; N, 4.8. Found: C, 69.1; H, 7.9; N, 4.7. Selected IR (cm⁻¹): 2953 (vs), 1616 (s), 1580 (m), 1503 (w), 1477 (vs), 1445 (vs) 1387 (m), 1356 (s), 1284 (m), 1246 (m), 1208 (m), 1095 (m), 1069 (m), 1018 (m), 986 (s), 856 (s), 490 (w).

**Single-Crystal X-ray Data Collection and Structure Solution.** The crystallographic data (Table 1) for compounds 1·2EtOH and 1·2MeCN·2H2O were collected at 130 K on an Agilent Technologies SuperNova diffractometer using Cu Kα radiation. Data for compounds 2·2EtOH and 3·2MeCN·H2O were collected at 100 K using Mo Kα radiation, on the MX1 and MX2 beamlines, respectively, at the Australian Synchrotron, Victoria, Australia. Using OLEX2, all of the structures were solved with the ShelXT refinement solution program using direct methods and refined with the ShelXL refinement package using least-squares minimization. Compounds 1·2H2O, 2·2EtOH, and 3·2MeCN·H2O contained disordered solvent. A satisfactory disorder model of the solvent could not be found, and therefore the OLEX2 Solvent Mask routine was used to mask out the disordered electron density. The molecular formulas proposed are based on the
Table 1. Crystallographic Data for 1·2H2O, 1·2MeCN·2H2O, 2·2EtOH, and 3·2MeCN·H2O

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<th></th>
<th>1·2H2O</th>
<th>1·2MeCN·2H2O</th>
<th>2·2EtOH</th>
<th>3·2MeCN·H2O</th>
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<tr>
<td>formula</td>
<td>C6H5N2O2Co</td>
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calculated solvent-accessible voids and the electron count, as well as the elemental and thermogravimetric analyses for the dried samples. All attempts to collect data for 3·2MeCN·H2O suggested minor twinning of the crystals; a twin refinement was successfully carried out using the collected data.

**Magnetic Measurements.** Magnetization measurements were carried out using a Quantum Design MPMS SQUID magnetometer equipped with a 5 T magnet. The temperature dependence of the magnetic moment on that of a polycrystalline heavier compound; a twin refinement was successfully carried out using the collected data.

**Photomagnetic Measurements.** Photomagnetic measurements were carried out on pelletized samples obtained by mixing ~0.5 mg of microcrystalline powder (the actual cobalt content being evaluated by scaling the magnetic moment on that of a polycrystalline heavier sample) with KBr powder and pressing into a pellet to facilitate light penetration. Irradiation experiments have been performed using a 532 nm laser beam with the continuous wave laser diode coupled to an optical fiber inserted in the sample space through a hollow sample rod and collimated on the sample by means of an aspheric lens, yielding a radiant power on the sample of about 2 mW cm⁻². Measurement of the effective T_LIESST value (LIESST = light induced excited spin state trapping) consisted of monitoring the temperature featuring a minimum in the d(J_M/T)/dT curve, after reaching the photostationary limit, having switched the laser off at 10 K and warming the sample at a rate of 0.3 K min⁻¹. Magnetic moments were corrected for the diamagnetic contribution of the KBr and the sample holder, independently measured in the same range of field and temperature, as well as for the intrinsic diamagnetism of the sample by using appropriate Pascal constants.

**RESULTS AND DISCUSSION**

**Syntheses.** Crystalline samples of all compounds were obtained at room temperature by solvent diffusion in 10 mL sealed test tubes, using water/ethyl acetate/ethanol for 1 and 2·2EtOH and water/acetonitrile for 1·2MeCN·2H2O and 3·2MeCN·H2O. In all cases, both ligands were dissolved in an organic solvent and carefully layered over an aqueous solution of cobalt(II) acetate, affording rectangular blue or green plate-shaped crystals of the neutral compounds after several weeks. This reaction involves aerial oxidation of the 3,5-dbcat²⁻ ligand and cobalt(II) metal center, which most likely follows ligand coordination to the relatively labile cobalt(II) ion. All compounds crystallize cleanly and can be isolated in moderate to good yield. Once formed, the crystals are completely insoluble in all common solvents. A differently solvated form of
complex 2, 2-2MeCN-2H₂O, has been reported previously by Tao et al.40

**Structure Description.** Selected single-crystal X-ray data for the compounds are reported in Table 1, structural representations of complexes 1, 2 and the two independent molecules of complex 3 are available in Figure 1, and crystal packing diagrams for 1-2H₂O, 1-2MeCN-2H₂O, 2-2EtOH, and 3-2MeCN-H₂O are reported in Figures 2 and 3. Asymmetric units of the compounds are presented in Figure S2 in the Supporting Information. Compound 1-2H₂O crystallizes in the monoclinic space group I2/a. The asymmetric unit contains half of each of two independent cobalt atoms with one of two coordinated dioxolene ligands per metal center, half of each of two independent 1,2-bpe linkers, and disordered solvent. Uniquely among this set of compounds, 1-2MeCN-2H₂O crystallizes in the triclinic space group P1̅. The asymmetric unit contains half of the cobalt atom located on the inversion center, one dioxolene ligand, half of the linking bis-pyridyl ligand, and solvent molecules. Compound 2-2EtOH crystallizes in the monoclinic space group P2₁/n with the asymmetric unit composed of half of each of two independent Co–dioxolene units, the linking azpy ligand, and disordered solvent. In comparison, the previously reported compound 2-2MeCN-2H₂O crystallizes in the triclinic space group P1 with the asymmetric unit comprised of half of one Co–dioxolene unit, half of the linking ligand, and one of each of the solvent molecules.40 In all of these compounds, complexes 1 and 2 form 1D chains with the pyridine linking moieties arranged with a trans disposition with respect to the Co(II) (Figure 2). The differing packing arrangements give rise to a different arrangement of cavities between the chains in which the solvent molecules reside. Compound 3-2MeCN-H₂O, incorporating the flexible linking ligand 1,3-bpp, crystallizes in the monoclinic space group P2₁/n as two independent interweaving chains, one of which (3a) exhibits a trans disposition of the N-donor ligands in each {Co(3,5-dbdiox)₂} unit, while the other possesses the N-donor ligands arranged in a cis manner (3b). The mixture of two geometric isomeric forms of such 1D chains within the one compound is unprecedented. Only one previously reported chain has exhibited the cis disposition of the N-donor linking ligands,39 while the trans disposition has been observed in all other cases.34,37,40 In addition to partially disordered solvent molecules, the asymmetric unit consists of two independent molecules, one for each type of chain, each containing two dioxolene ligands and one 1,3-bpp ligand, coordinated to a cobalt center. The zigzag cis chains pass alternately above and below each of the trans chains (Figure 3). The cavities between the chains are filled with highly disordered solvent: two water molecules and two acetonitrile molecules per two independent cobalt centers. The cobalt centers in all compounds exhibit very slightly distorted octahedral coordination geometries, with SHAPE indices in the range 0.057–0.15 (Table 2 and Chart 2),47 where the SHAPE indices are based on continuous shape measures.
such that the closer the index is to 0, the closer the coordination geometry is to the ideal polyhedron. The Co–O and Co–N bond distances for all complexes (Table 2) are in the ranges 1.855(3)–1.911(3) and 1.926(3)–1.992(4) Å, respectively, which are consistent with Co(III) centers at the temperature of data collection.\textsuperscript{11,40} The calculated MOS values for 1·2H$_2$O, 1·MeCN·2H$_2$O, and 2·2EtOH lie in the range 1.40–1.68 (Table 2). Thus, all of the structural data for the 3,5-dbdiox ligands for complexes 1 and 2 in compounds 1·2H$_2$O, 1·MeCN·2H$_2$O, and 2·2EtOH are consistent with crystallographic disorder of an equal mixture of the catecholate and semiquinonate forms. For comparison purposes, the Co–O and Co–N bond distances reported by Tao et al.\textsuperscript{40} at 100 K for 2·2MeCN·2H$_2$O are very similar to those of 2·2EtOH, while we calculate the MOS value to be −1.61, which is also intermediate between the values characteristic for catecholate and semiquinonate states. It should be noted that for compounds 1·2H$_2$O, 1·MeCN·2H$_2$O, and 2·2EtOH both dioxolene ligands bound to each cobalt center are related by symmetry, while for both trans and cis chain complexes 3a,b in compound 3·2MeCN·H$_2$O, the 3,5-dbdiox ligands on each cobalt center are not symmetry related and exhibit different bond lengths (Table 2). Although there is still disorder of the catecholate and semiquinonate ligands, the MOS pairs of −1.38, −1.72 and −1.13, −1.91 for 3a,b, respectively, suggest that one ligand has more catecholate character and the other more semiquinonate, particularly for 3b. In summary, at the measured temperatures of 130 and 100 K complexes 1, 2, and 3a,b in 1·2H$_2$O, 1·MeCN·2H$_2$O, 2·2EtOH, and 3·2MeCN·H$_2$O can all be formulated as comprised of \{Co$^{III}$(3,5-dbcat)(3,5-dbsq)\} moieties linked by bis-pyridyl ligands.

**Thermogravimetric Analysis.** The thermogravimetric data for compounds 1, 1·1.5MeCN·2H$_2$O, 2·2EtOH, and 3·MeCN·H$_2$O were measured between 298 and 700 K under constant N$_2$ flow (Figure S3 in the Supporting Information). Compound 1 exhibits no mass loss up to the onset of decomposition around 440 K, which is consistent with a solvent-free composition. In contrast, 1·1.5MeCN·2H$_2$O loses mass immediately upon exposure to the N$_2$ flow, due to rapid desolvation. For 1·1.5MeCN·2H$_2$O, the initial mass loss of 7.0% up to 360 K is in agreement with the 7.9% required to lose 1.5 MeCN solvate molecules, with the rapid rate of catecholates and semiquinonates, respectively. A more detailed method proposed by Brown in 2012 to determine the oxidation state of dioxolene ligands utilizes the C–O and all of the ring C=C bonds to calculate a "metrical oxidation state" (MOS), which correlates with the valence of the dioxolene ligand.\textsuperscript{49} The calculated MOS values for 1·2H$_2$O, 1·MeCN·2H$_2$O, and 2·2EtOH lie in the range 1.40–1.68 (Table 2). Thus, all of the structural data for the 3,5-dbdiox ligands for complexes 1 and 2 in compounds 1·2H$_2$O, 1·MeCN·2H$_2$O, and 2·2EtOH are consistent with crystallographic disorder of an equal mixture of the catecholate and semiquinonate forms. For comparison purposes, the Co–O and Co–N bond distances reported by Tao et al.\textsuperscript{40} at 100 K for 2·2MeCN·2H$_2$O are very similar to those of 2·2EtOH, while we calculate the MOS value to be −1.61, which is also intermediate between the values characteristic for catecholate and semiquinonate states. It should be noted that for compounds 1·2H$_2$O, 1·MeCN·2H$_2$O, and 2·2EtOH both dioxolene ligands bound to each cobalt center are related by symmetry, while for both trans and cis chain complexes 3a,b in compound 3·2MeCN·H$_2$O, the 3,5-dbdiox ligands on each cobalt center are not symmetry related and exhibit different bond lengths (Table 2). Although there is still disorder of the catecholate and semiquinonate ligands, the MOS pairs of −1.38, −1.72 and −1.13, −1.91 for 3a,b, respectively, suggest that one ligand has more catecholate character and the other more semiquinonate, particularly for 3b. In summary, at the measured temperatures of 130 and 100 K complexes 1, 2, and 3a,b in 1·2H$_2$O, 1·MeCN·2H$_2$O, 2·2EtOH, and 3·2MeCN·H$_2$O can all be formulated as comprised of \{Co$^{III}$(3,5-dbcat)(3,5-dbsq)\} moieties linked by bis-pyridyl ligands.
desolvation suggesting that some MeCN is lost immediately as the sample is exposed to a nitrogen flow before the heating commences. A plateau between 370 and 420 K may correspond to a putative "1·2H₂O" species, before decomposition at higher temperatures. Compound 2·2EtOH exhibits no mass loss up to 420 K in nitrogen flux, indicating no desolvation in the temperature range of the magnetic measurements (see later). A mass loss of around 8% between 420 and 470 K may be attributed to partial loss of the EtOH solvate molecules (loss of two EtOH molecules would correspond to 12%), before decomposition above 510 K. For compound 3·MeCN·H₂O desolvation is gradual and the initial mass loss of 2.8% up to 450 K is in good agreement with the loss of a single MeCN molecule, before decomposition at higher temperatures.

**Infrared Spectroscopy.** Infrared spectra were obtained for compounds 1, 1·1.5MeCN·2H₂O, 2·2EtOH, and 3·MeCN·H₂O.
H$_2$O as pressed KBr disks (Figure S4 in the Supporting Information). Bands characteristic of the $\nu$(CN) stretching mode for the bis-pyridyl linking ligands are evident between 1600 and 1614 cm$^{-1}$. The slight shift from the frequency observed for the free ligand (1597 cm$^{-1}$ for 1,2-bpe, 1587 cm$^{-1}$ for azpy, 1605 cm$^{-1}$ for 1,3-bpp) confirms the coordination to the metal ion. Other bands in the spectra of the cobalt complexes that are also observed in the spectra of the free ligands are in the ranges 826–837 and 548–576 cm$^{-1}$. Dioxolenes typically display two groups of medium to strong bands between 1250 and 1650 cm$^{-1}$ associated with C–O stretching modes. The spectra of compounds 1, 1-1.5MeCN-2H$_2$O, 2-2EtOH, and 3-MeCN-H$_2$O all exhibit bands in the ranges 1442–1446 and 1284–1288 cm$^{-1}$, associated with 3,5-dbsq, as well as bands in the ranges 1461–1465 and 1357–1356 cm$^{-1}$ due to 3,5-dbsq, suggesting that the dioxolene ligands are present in both oxidation states in all compounds at room temperature.

**Electronic Spectroscopy.** Ultraviolet–visible diffuse reflectance spectra were obtained on ground samples of 1, 1-1.5MeCN-2H$_2$O, 2-2EtOH, and 3-MeCN-H$_2$O at room temperature (Figure S5 in the Supporting Information). All compounds exhibit bands for both chromophores present at room temperature. A broad band centered at 730 nm in all four spectra is assigned to a ligand to metal charge transfer (LMCT) transition of a Co(III)–catecholato chromophore. Shoulders between 400 and 450 nm can be attributed to $\pi\pi^*$ transitions of the azpy ligand. In contrast, the spectrum for compound 1-1.5MeCN-2H$_2$O is suggestive of Co(II)–semiquinonato chromophores and $d\rightarrow \pi^*$ metal to ligand charge transfer (MLCT) transitions. In contrast, the spectrum for compound 2-2EtOH does not clearly show the band characteristic of Co(II), which is due to overlap with the band centered at 480 nm, assigned to $n\rightarrow \pi^*$ transitions of the azpy ligand.

**Magnetic Measurements.** Magnetic susceptibility data (Figure 4) were obtained for compounds 1, 1-1.5MeCN-2H$_2$O, 2-2EtOH, and 3-MeCN-H$_2$O between 2 and 370 K. Multiple heating–cooling cycles were measured in each case. For reference, the expected low-temperature $\chi_mT$ value for a $[\text{ls-Co}^{II}(3,5$-dbcat)(3,5-dbsq)] moiety is 0.38 cm$^3$ mol$^{-1}$ K, while high-temperature values up to 3.75 cm$^3$ mol$^{-1}$ K are typically observed for uncoupled $\text{hs-Co}^{II}$ ion and two semiquinonato radicals belonging to the $[\text{hs-Co}^{II}(3,5$-dbcat)$_2]_2$ species.

Magnetic susceptibility data for 1 were measured in five heating–cooling cycles: from 10 to 300 K and from 190 to 320, 340, 360, and 370 K (Figure 4). In the first cycle the value of $\chi_mT$ increases gradually from 0.43 cm$^3$ mol$^{-1}$ K up to 0.48 cm$^3$ mol$^{-1}$ K at 200 K, before rapidly increasing to 1.49 cm$^3$ mol$^{-1}$ K at 300 K, indicating the onset of the VT transition. The following cooling restores the same curve. Throughout the next three heating cycles (heating to 320, 340, and 360 K, respectively) the $\chi_mT$ profile follows the previously measured curve up to 300 K and then continues increasing, to eventually reach a value of 2.47 cm$^3$ mol$^{-1}$ K in 360 K. When it is cooled from 360 K, the compound unusually exhibits a decrease in the $\chi_mT$ product after heating, which is in contrast to all the other previously reported Co–dioxolene based VT systems. Since polymorph 1 is completely solvent free and no mass loss is observed in the thermogravimetric profile below 430 K, we attribute this behavior to a thermally driven structural rearrangement. Temperature-dependent powder X-ray diffraction confirms that structural rearrangement is taking place at this temperature, with the positions of two major peaks varying following a thermal hysteresis cycle and an extra peak appearing above 393 K (Figure S6 in the Supporting Information).

Magnetic susceptibility data were also obtained for partially desolvated 1-1.5MeCN-2H$_2$O. In the first heating–cooling cycle the $\chi_mT$ value increases from ca. 0.61 cm$^3$ mol$^{-1}$ K, first gradually to 0.93 cm$^3$ mol$^{-1}$ K at 200 K and then more abruptly to 1.53 cm$^3$ mol$^{-1}$ K at 300 K, which indicates the beginning of the VT transition. The cooling process does not restore the curve, suggesting that the process of losing solvent molecules starts below 300 K, consistent with the thermogravimetric analysis (Figure S3 in the Supporting Information). Subsequent heating to 320 K leads to further desolvation. The $\chi_mT$ product follows the previous profile up to 200 K and then rises sharply to finally reach a value of 4.72 cm$^3$ mol$^{-1}$ K at 320 K. Additional cooling–heating cycles (Figure S7 in the Supporting Information) afford $\chi_mT$ reaching a plateau at ca. 5.1 cm$^3$ mol$^{-1}$ K after heating the sample to 360 K, with no change in the curve upon further cooling or heating. This is consistent with the thermogravimetric analysis (Figure S3) and indicates no further desolvation up to 300 K beyond the putative partially desolvated “1-2H$_2$O” species suggested by thermogravimetric analysis. The shift of the VT transition toward the $[\text{ls-Co}^{II}(3,5$-dbsq)$_2]$ species after desolvation has been further demonstrated by comparing room-temperature X-band EPR spectra (Figure S8 in the Supporting Information) of solvated 1-1.5MeCN-2H$_2$O before and after heating at 360 K to partially desolvate the sample. Both species exhibit a sharp signal at $g = 2.007$, originating from the $S = 1/2$ semiquinonate radical of the $[\text{ls-Co}^{II}(3,5$-dbcat)(3,5-dbsq)] tautomer. However, the signal is much more intense (ca. 20 times after double integration of the EPR line and sample mass rescaling) for the solvated sample, the observed intensity difference being consistent with a higher degree of VT interconversion for the heated sample than for the as-synthesized one. Indeed, as the VT conversion proceeds, the radical signal decreases in intensity due to a decreasing fraction of the $[\text{ls-Co}^{III}(3,5$-dbcat)]$[\text{3,5$\cdot$dbsq}]$_2$ tautomer and the concurrent formation of the $[\text{ls-Co}^{III}(3,5$-dbcat)$_2]$ tautomer, which is EPR silent at room temperature because of the fast relaxation induced by $\text{hs-Co}^{II}$. This behavior is likely due to the larger volume available for the expansion accompanying the VT transition following partial solvent loss.

The unusually high $\chi_mT$ values following partial desolvation of 1-1.5MeCN-2H$_2$O at 340 K and above require some further comments. These can only be justified assuming a complete VT transition to a $[\text{hs-Co}^{II}(3,5$-dbsq)$_2]$ charge distribution, involving a relatively strong ferromagnetic coupling between the $\text{hs-Co}^{II}$ center and the two radical semiquinonate ligands. It has indeed been suggested on the basis of DFT calculations that, for a trans disposition of the pyridyl ligands around the cobalt centers, ferromagnetic coupling might be observed. Recently, a high $\chi_mT$ value of around 4.8 cm$^3$ mol$^{-1}$ K at 200 K has been reported for the high-temperature valence tautomer of the mononuclear complex $[\text{trans-Co}(3,5$-dbdiox)$_2$(4-Br-Py)$_2]$ ($4\text{-Br-Py} = 4$-bromopyridine), which might be due to such ferromagnetic coupling. The trans disposition of the pyridyl ligands results in a local D$_{2h}$ symmetry at the Co(II) centers, providing only one possible antiferromagnetic path through the $d_e$ magnetic orbital (transforming as $b_{2g}$ in D$_{2h}$), and two ferromagnetic paths, involving...
heating at 340 K for a SHAPE index determined at 130 K for the cobalt(III) ion in heating and desolvation. However, prior to desolvation, the angles and lengths associated with the cobalt center after 1 complex with structural and chemical features similar to those functional used, have been recently calculated by DFT for a ferromagnetically coupled system can thus be considered as a rare example of a line with the values observed for 1 after desolvation. This system can thus be considered as a rare example of a ferromagnetically coupled {hs-Co\(^{III}\)(3,5-dbsq)\(_2\)} species. Unfortunately, the crystallinity of the sample is not maintained upon heating, and so it is impossible to determine the bond angles and lengths associated with the cobalt center after heating and desolvation. However, prior to desolvation, the SHAPE index determined at 130 K for the cobalt(III) ion in 1-2MeCN-2H\(_2\)O is 0.065 (Table 2), which indicates only very slight deviation from the ideal octahedral coordination geometry that would be required for ferromagnetic coupling in the high-temperature valence tautomer.

The low-temperature \(\chi_mT\) value of 0.98 cm\(^3\) mol\(^{-1}\) K for 2-2EtOH at 10 K suggests the existence of a nonconverting hs-Co(II)-containing phase, as has been observed previously for other VT complexes.\(^{11,40,54,59}\) This is consistent with MOS parameters that are slightly closer to the value characteristic of semiquinonate rather than catecholate states (Table 2). Three parameters that are slightly closer to the value characteristic of other VT complexes.\(^{11,40,54,59}\) This is consistent with MOS parameters that are slightly closer to the value characteristic of semiquinonate rather than catecholate states (Table 2). Three parameters that are slightly closer to the value characteristic of other VT complexes.\(^{11,40,54,59}\) This is consistent with MOS parameters that are slightly closer to the value characteristic of semiquinonate rather than catecholate states (Table 2). Three parameters that are slightly closer to the value characteristic of other VT complexes.\(^{11,40,54,59}\) This is consistent with MOS parameters that are slightly closer to the value characteristic of semiquinonate rather than catecholate states (Table 2). Three parameters that are slightly closer to the value characteristic of other VT complexes.

To date, photoinduced VT interconversions have been reported for three VT CPs based on Co(II)-dioxolene units and pyridyl linkers.\(^{39,40,64}\) As all four compounds in the present work exhibit thermally induced VT transitions, all were also investigated for light-induced transitions. Following irradiation with the 532 nm wavelength light at 10 K, an immediate increase of the \(\chi_mT\) product is evident for 1, 1.5MeCN-2H\(_2\)O, 2-2EtOH, and 3-MeCN-H\(_2\)O, which indicates a photoinduced VT transition (Figure 6). The initial conversion rates are in the range 10−17%, which is comparable with many literature values for cobalt bis-dioxolene VT complexes.\(^{65}\) This behavior can be attributed to sample opacity and incomplete penetration of the laser light or to the significant energy difference between the ground state \{hs-Co\(^{III}\)(3,5-dbsq)(3,5-dbsq)\} and photoinduced metastable state \{hs-Co\(^{III}\)(3,5-dbsq)\} as suggested by the high temperature of thermal VT transition of the chains.\(^{66}\) After the laser was switched off and the samples warmed at a rate of 0.3 K min\(^{-1}\), the \(\chi_mT\) values increase further, due to the non-Curie nature of the photoinduced hs-Co(II) ion, to finally decrease and meet the nonirradiated profiles. The temperatures at which the minimum in the \(d(\chi_mT)/dT\) plots is observed, reported in Table 3 as effective \(T_{LIESST}\) values (LIESST = light induced excited spin state trapping), are in the range 55−65 K, consistent with values reported for other VT complexes (38−80 K).\(^{67}\) For 3-MeCN-H\(_2\)O only one distinct photoinduced transition is observed, in contrast to the thermal data, because either irradiation at low temperature does not activate the second interconversion entirely or the relaxation parameters of the two chains are similar and cannot be resolved on the time scale of the magnetic measurements.

**CONCLUDING REMARKS**

Four new polymeric VT compounds have been synthesized and characterized by single-crystal X-ray diffraction TGA, IR, UV−vis, and magnetic studies; one of these is a differently solvated form of a previously reported complex. All compounds undergo a thermally driven VT transition, the characteristics of which are affected by the choice of linking bis-pyridyl ancillary ligand and the degree of solvation. The role of solvation is particularly evident from a comparison of the behavior of two differently solvated forms of Co\((3,5$-dioxo)\)\(_2(1,2$-bpe)\)\(_\infty\) (1). Com-

![Figure 5. Plot of \(\chi_mT\) vs T (scatter points) for the heating cycles for 3-MeCN-H\(_2\)O as per Figure 4d and first derivative of the final heating cycle (line, arbitrary units).](image-url)
compound 1, crystallizing from an ethanol/water mixture, contains highly disordered and readily lost hydrate molecules. Upon heating, crystallites of 1 undergo a thermally induced structural rearrangement, which, unusually, shifts the VT transition to higher temperatures. Crystallization from acetonitrile instead affords 1·2MeCN·2H₂O, which exhibits a strongly solvent dependent VT conversion with a remarkably high final magnetic susceptibility value, which we attribute to a relatively strong ferromagnetic coupling between the h₅-Co(II) center and the two semiquinonate radicals formed after the VT transition. On the other hand, compound 2·2EtOH exhibits a gradual increase in the χ_mT versus T curve and no desolvation in the measured temperature range. Finally, compound 3·2MeCN·H₂O is, to the best of our knowledge, the first example of a VT coordination polymer containing two individual 1D chains in the structure, which are geometric isomers of each other; one exhibiting a cis and the other a trans disposition of the N-donor ligands with respect to the {Co(3,5-dbdiox)₂} unit, resulting in a two-step temperature-driven VT tautomeric transition in the complex, previously unreported in a VT coordination polymer. Moreover, all four compounds also exhibit the possibility of photoinduction of the VT conversion in the solid state, even if the observed conversion rates of 10−17% indicate only a partial conversion. Overall, this work illustrates the potential of cobalt bis-dioxolene units as robust building blocks for the construction of polymeric systems with thermally and optically controllable electronic states. Ultimately strong intramolecular ferromagnetic interactions and the presence of inequivalent molecular chains in the solid state may give rise to multistable high-spin systems. Furthermore, the synthetic procedure established in this work should be equally applicable to divergent polydentate ligands of denticity greater than two, opening a route to 2D and 3D VT CPs. This is particularly interesting, since only a single VT CP of dimensionality higher than one has been reported to date, and higher dimensional VT CPs are particularly promising for achieving enhanced cooperativity of the VT transition, as well as for transferring the VT properties to more technologically convenient platforms such as gels, films, and nanoparticles for future applications in devices.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b02812.

Additional structural figures, thermogravimetric analysis data, ultraviolet–visible diffuse reflectance spectra, powder X-ray diffraction data, and EPR spectra (PDF) X-ray crystallographic data for 1·2H₂O, 1·2MeCN·2H₂O, 2·2EtOH, and 3·2MeCN·H₂O (CIF)

### AUTHOR INFORMATION

#### Corresponding Authors

* E-mail for L.S.: lorenzo.sorace@unifi.it.
* E-mail for C.B.: c.boskovic@unimelb.edu.au.

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**Figure 6.** Plot of χ_mT versus T for the photoinduced VT transitions for (a) 1, (b) 1·1.5MeCN·2H₂O, (c) 2·2EtOH, and (d) 3·MeCN·H₂O. Insets: Plot of d(χ_mT)/dT versus T for the LIESST branch, the minimum used to evaluate the effective T_LIESST.

**Table 3. Conversion Rates and T_LIESST Parameters for Photoinduced VT Transitions in 1, 1·1.5MeCN·2H₂O, 2·2EtOH, and 3·MeCN·H₂O**

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Notes

The authors declare no competing financial interest.

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references

**Figure S1.** Calculated (dotted lines) and experimental (solid lines) powder X-ray diffraction patterns for 1·2MeCN·2H₂O (black dotted line), 1·1.5MeCN·2H₂O (black solid line), 1·2H₂O (purple dotted line) and unsolvated 1 (red solid line), obtained by air-drying 1·2H₂O. The theoretical patterns were calculated using the single crystal data obtained at 130 K and the experimental patterns were collected at room temperature. The minor differences between calculated and experimental pattern for each pair of compounds can be attributed to temperature effects, partial desolvation and the onset of the VT transition. The patterns for 1·2MeCN·2H₂O and 1·1.5MeCN·2H₂O are very different from those of 1·2H₂O and 1, reflecting structural differences evident from the single crystal diffraction studies of the solvated compounds.
Figure S2. Asymmetric units of the 1D chain complexes (a) I in 1·2H$_2$O, (b) I in 1·2MeCN·2H$_2$O, (c) 2 in 2·2EtOH, (d) cis-disposed 3b in 3·2MeCN·H$_2$O and (e) trans-disposed 3a in 3·2MeCN·H$_2$O. Color code: Co, cyan; O, red; N, blue and C, black.
Figure S3. Thermogravimetric analysis profiles for 1 (red), 1·1.5MeCN·2H2O (black), 2·2EtOH (blue) and 3·MeCN·H2O (green).

Figure S4. Infrared spectra (KBr disk) of compounds 1 (red), 1·1.5MeCN·2H2O (black), 2·2EtOH (blue) and 3·MeCN·H2O (green).
**Figure S5.** Ultra-violet-visible diffuse reflectance spectra for 1 (red), 1·1.5MeCN·2H$_2$O (black), 2·2EtOH (blue) and 3·MeCN·H$_2$O (green).

**Figure S6.** Temperature-dependent powder X-ray diffraction data for 1: (a) Evolution of the 13-18 ° region upon heating from 291 K to 393 K; (b) evolution of the same region after cooling down from 393 K to 373 K and subsequent heating. The arrow evidences the onset of a new peak possibly due to a different phase upon heating; (c),(d): hysteretic behaviour of the two major peak positions upon heating (full squares) and cooling (empty triangles).
Figure S7. Plots of $\chi_m T$ vs $T$ for 1·1.5MeCN·2H$_2$O showing additional cooling-heating cycles following those presented in Figure 4b, indicating no further desolvation in this temperature range.

Figure S8. X-band EPR spectra measured for powder sample of 1·1.5MeCN·2H$_2$O at 298 K before (black) and after (red) heating to 370 K to partially desolvate the sample. Signals are rescaled per mole of measured sample.
CHAPTER III

Valence tautomeric coordination polymers based on Co-dioxolene units and tetrapyridyl linking ligands.

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3.1 Introduction

Formerly, only one example of a 2D CP based on \{\text{Co}(3,5\text{-diox})_2\} VT units has been reported, when a 4-connecting linker (tetrakis(4-pyridyloxymethylene)methane) was used to connect cobalt centers into two-dimensional sheet (Section 1.7.3). Expanding polymeric structures from 1D to 2D is usually associated with increased porosity of the CP and the compound synthesized by Tao et al. was a good candidate to study solvation and pressure effects on VT transitions\(^2\). Following studies on 1D VT CPs, discussed in the previous chapter of this dissertation, the focus of the research presented in this chapter was to employ tetrapyridyl-type ligands into synthesis of novel 2D VT CPs (Scheme 3-1).

Scheme 3-1. Schematic representation of a target 2D VT CP based on \{\text{Co}(3,5\text{-diox})_2\} units.
The selected ligand 1,2,4,5-tetra(4-pyridyl)benzene (tpb), has been reported previously as 4-connecting and 3-connecting linker in several porous 2D and 3D coordination polymers, which makes it a promising candidate for the synthesis of higher-dimensional VT CPs.

### 3.2 Contribution of the candidate.

Listed below are contributions of the candidate:

◇ Planning of the project
◇ Synthesis of the ligands and coordination polymers
◇ Characterization of the compounds, except for the techniques mentioned in the preface
◇ Writing the manuscript

### 3.3 Published manuscript and supplementary information.
One Dimensional Chain and Ribbon Cobalt-Dioxolene Coordination Polymers: A New Valence Tautomeric Compound

Olga Drath,† Robert William Gable,‡ Giordano Poneti,§ Lorenzo Sorace,§ and Colette Boskovic*†§

†School of Chemistry, University of Melbourne, Melbourne, Victoria 3010, Australia
‡Instituto de Química, Universidade Federal do Rio de Janeiro, Rio de Janeiro 21941-901, Brazil
§UdR INSTM and Department of Chemistry “U. Schiff”, University of Florence, 50019 Sesto Fiorentino, Italy

Supporting Information

ABSTRACT: The combination of the divergent tetrakis-pyridyl linking ligand 1,2,4,5-tetra(4-pyridyl)benzene (tpb) with cobalt and 3,5-di-tert-butylidioxolene (3,5-db dioxy) ligands has afforded the complexes [Co(3,5-dbdiox)2(tpb)] · 3H2O and [Co(3,5-dbdiox)2(tpb)] · 9H2O. Both species are 1D coordination polymers that crystallize as the hydrated compounds 1·3H2O and 2·9H2O. While the tpb in complex 1 is a 2-connecting linker, affording a conventional 1D chain, the tpb in 2 is a 4-connecting linker, giving rise to a ribbon topology. Single crystal X-ray structural analysis indicates that 1·3H2O and 2·9H2O both possess the {CoIII(3,5-dbcat)(3,5-dbsq)} (3,5-dbcat = 3,5-di-tert-butylcatecholate; 3,5-dbsq = 3,5-di-tert-butyl-semiquinonate) charge distribution at 100 or 130 K, respectively. Variable temperature magnetic susceptibility studies of partially dehydrated 1·H2O indicate a thermally induced valence tautomeric (VT) transition above 300 K.

1. INTRODUCTION

Materials that can be reversibly switched between distinguishable states have potential for applications in many areas including display devices and smart windows, memory applications, spintronics, energy conversion, and catalysis. Molecular systems that can be switched in this way offer advantages over comparable-sized nanoscale bulk materials in terms of their synthesis, tunability, and facility of characterization. One class of molecules that can be switched between forms with different electronic states are those that undergo intramolecular electron transfer. Coordination complexes comprised of redox-active metal centers bound to redox-active ligands can in some cases be induced to undergo so-called valence tautomeric (VT) transitions. These involve a stimulated intramolecular electron transfer between metal and ligand, affording redox isomers that differ in their charge distribution. Octahedral cobalt complexes with dioxolene ligands comprise by far the largest chemical family of VT complexes, particularly those that incorporate 3,5-di-tert-butyldioxolene (3,5-dbdiox) and nitrogen-donor ancillary ligands. For these complexes, electron transfer between the cobalt cation and 3,5-dbdiox ligand is accompanied by a metal-based spin transition such that the complexes switch between low spin Co(III)-catecholate {ls-CoIII(3,5-dbcat)} and high spin Co(II)-semiquinonate {hs-CoII(3,5-dbsq)} forms. The VT transitions are most commonly triggered thermally or optically, although pressure, soft X-ray, and magnetic field stimulated VT transitions have also been reported.

Cooperative interactions between the chemical moieties that switch electronic state can modulate the characteristics of the electronic transition, inducing the abruptness and bistability/hysteresis that will facilitate application in devices. As observed previously for SCO materials, higher cooperativity can be realized by a combination of short-range and long-range interactions. Expanding long-range contacts involves employing covalent linkages to build polymeric structures. The simplest such polymeric VT species are one-dimensional (1D) coordination polymers, which predominantly consist of Co-bis(dioxolene) units linked by divergent 2-connecting ligands forming long chains. The other very recent example is an unusual manganese-nitronyl-nitroxide two-dimensional coordination polymer, which exhibits 20 K hysteresis at room temperature.

With a view to synthesizing new 2D cobalt-dioxolene VT coordination polymers, we turned our attention to 1,2,4,5-tetra(4-pyridyl)benzene (tpb; Chart 1) as a linking ancillary ligand. The ligand tpb has served as a useful linker in several other examples of higher dimensional (2D) VT coordination polymers have been reported. One of these employs tetrakis(4-pyridyloxy)methylene methane as a pseudo-tetrahedral 4-connecting node that links {Co(3,5-dbdiox)} (3,5-dbdiox = 3,5-di-tert-butylidioxolene) units into a 2D net. The other very recent example is an unusual manganese-nitronyl-nitroxide two-dimensional coordination polymer, which exhibits 20 K hysteresis at room temperature.

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previously reported 2D and 3D coordination polymers. Since tpb can be formed by dehydrogenative coupling of 1,3-bis(4-pyridyl) propane in acidic conditions, most previously reported compounds have been obtained from solvothermal reactions involving in situ formation of the tpb ligand.\textsuperscript{22–28} In 2012, Chang and Wang reported the first facile synthesis and isolation of tpb that did not involve demetalization of a previously synthesized organo-metallophosphate or coordination polymer.\textsuperscript{29} This opened a synthetic route to tpb-based coordination polymers in nonacidic environment and with more control of the reaction stoichiometry.\textsuperscript{29} In literature compounds tpb acts predominately as a 4-connecting planar node,\textsuperscript{23–28,30} or, less commonly, as a 3-connecting t-shaped node, where the fourth pyridyl group does not coordinate.\textsuperscript{23,31} All but one of the reported compounds contain group 11 and 12 metals (Cu, Ag, Zn, Cd), with only one example incorporating Co centers.\textsuperscript{26} The coligands employed in the literature in tpb coordination polymers included cyanide anions,\textsuperscript{3,33} other organic molecules,\textsuperscript{25–27} polynuclear anions,\textsuperscript{34} sulfides,\textsuperscript{24} and sulfates.\textsuperscript{23} Given its propensity to form higher dimensional compounds have been obtained from solvothermal reactions involving in situ formation of the tpb ligand.\textsuperscript{22–28} In literature compounds tpb acts predominantly as a 4-connecting planar node,\textsuperscript{23–28,30} or, less commonly, as a 3-connecting t-shaped node, where the fourth pyridyl group does not coordinate.\textsuperscript{23,31} All but one of the reported compounds contain group 11 and 12 metals (Cu, Ag, Zn, Cd), with only one example incorporating Co centers.\textsuperscript{26} The coligands employed in the literature in tpb coordination polymers included cyanide anions,\textsuperscript{3,33} other organic molecules,\textsuperscript{25–27} polynuclear anions,\textsuperscript{34} sulfides,\textsuperscript{24} and sulfates.\textsuperscript{23} Given its propensity to form higher dimensional coordination polymers, we decided to investigate tpb for cobalt-doped VT coordination polymers and report herein the results of our exploration of 1,2,4,5-tetra(4-pyridyl)benzene as a linker of \{Co(3,5-dbdiox)\}_n units.

2. EXPERIMENTAL SECTION

2.1. Synthesis. All reagents, excluding the tpb linking ligand, were obtained from commercial sources and used as received. The tpb ligand was synthesized according to the literature procedure.\textsuperscript{29}

2.1.1. [Co(3,5-dbdiox)tpb]_m (1). An ethanol solution (6 mL) of 3,5-dbcatH_3 (33 mg, 0.15 mmol) and tpb (14 mg, 0.075 mmol) was layered upon an aqueous solution (1 mL) of Co(OAc)_2·4H_2O (17 mg, 0.075 mmol). The ethanol and water layers were separated by a buffer layer of ethanol/water (1 mL). After 5 days dark greenish needle-shaped crystals were formed. A sample for single crystal X-ray diffraction was maintained in contact with the mother liquor to avoid solvent loss and identified by single crystal X-ray diffraction as 2-9H_2O. A pure bulk sample of 2 could not be obtained.

2.1.2. [Co(3,5-dbdiox)tpb]_m(2). In an effort to favor the 4-connecting mode of tpb, modification of the above method for 1 involved changing the tpb and Co-bis(3,5-dbdiox) ratio to 1:2. An ethanol solution (6 mL) of 3,5-dbcatH_3 (33 mg, 0.15 mmol) and tpb (80 mg, 0.038 mmol) was layered upon an aqueous solution (1 mL) of Co(OAc)_2·4H_2O (17 mg, 0.075 mmol). The ethanol and water layers were separated by a buffer layer of ethanol/water (1 mL). When the reaction mixture was kept at 35 °C for several weeks, a small quantity of plate-shaped crystals of complex 2 formed alongside the needles of 1. A single crystal containing complex 2 was hand-picked from the reaction mixture, maintained in contact with the mother liquor to avoid solvent loss, and identified by single crystal X-ray diffraction as 2-9H_2O. A pure bulk sample of 2 could not be obtained.

2.2. General and Physical Measurements. Elemental analyses were performed by the Campbell Microanalytical Laboratory, Department of Chemistry, University of Otago, New Zealand. Thermogravimetric analyses were performed on a Mettler Toledo thermal analyzer. Infrared spectra (KBr disk) were recorded on a Bruker TENSOR 27 FTIR spectrometer. Ultraviolet–visible absorption diffuse reflectance spectra were measured on a Thermo Scientific Evolution 220 UV–visible spectrophotometer. The powder X-ray diffraction pattern was acquired at 293 K on an Agilent Technologies SuperNova diffractometer using Cu Kα radiation (λ = 1.54184 Å), operated at 40 kV and 35 mA; data were collected with 2θ angles in the range 5–50°.

2.3. Single Crystal X-ray Diffraction Studies. The crystallographic data (Table 1) for compound 1-3H_2O were collected at 100 K, using synchrotron Mo Kα radiation on the MX1 beamline,\textsuperscript{22} at the Australian Synchrotron, Victoria, Australia. Data for 2-9H_2O were collected at 130 K on an Agilent Technologies SuperNova diffractometer using Cu Kα radiation. Using OLEX2,\textsuperscript{35} both structures were solved with the ShelXT\textsuperscript{33} structure solution program using direct methods and refined with the ShelXL\textsuperscript{36} refinement package using least-squares minimization. Solvent voids are apparent in both structures, and several electron density peaks indicate the existence of disordered solvent. For complex 1, the Solvent Mask routine\textsuperscript{35} suggested the presence of 3 molecules of water per formula unit; however, the refinement was carried out without the use of the Solvent Mask routine and a site for a partially occupied water molecule was found. For complex 2, the Solvent Mask indicates 9 molecules of water per formula unit, and the refinement was carried out applying the Solvent Mask procedure.

2.4. Magnetic and Photomagnetic Measurements. Magnetic susceptibility measurements were carried out using a Quantum Design MPMS SQUID magnetometer equipped with a 5 T magnet. The temperature dependence of the magnetization (M) was followed from 2 to 360 K by applying a 1 kOe field (H) below 40 K to reduce saturation effects and 10 kOe field from 40 to 360 K. Magnetic susceptibility per mole (χ_m) was then evaluated as χ_m = M/H, where M is the molar magnetization, evaluated on the basis of sample mass and molecular weight, taking into account the contribution of the sample holder and the intrinsic diamagnetic contribution of the sample.
sample.\textsuperscript{30} Thermal hysteresis effects were checked by measuring different cycles allowing thermal equilibration of the samples by waiting 120 s after stabilization at each temperature, resulting in an average 1.6 K min\textsuperscript{−1} sweep rate in heating and cooling cycles.

Photomagnetic measurements were carried out on pelletized samples obtained by mixing \~0.5 mg of microcrystalline powder (the actual cobalt content being evaluated by scaling the magnetic moment to that of a polycrystalline heavier sample) with KBr powder and pressing into a pellet to facilitate light penetration. Irradiation experiments were performed at 10 K using laser diodes of different wavelengths (532, 648, 805, and 904 nm). Each source was coupled to an optical fiber inserted in the sample space through a hollow sample rod and collimated on the sample by means of an aspheric lens, yielding a radiant power on the sample of about 2 mW cm\textsuperscript{−2}.

3. RESULTS AND DISCUSSION

3.1. Syntheses. Since the catechol ligand must be deprotonated prior to coordination to the Co center, the commonly employed one-pot solvothermal synthesis of the target coordination polymers was unviable in the present case as it requires acidic conditions for the \textit{in situ} formation of tpb. Thus, tpb was synthesized and isolated according to the method of Chang and Wang\textsuperscript{29} prior to reaction with the cobalt and dioxolene coligands. A crystalline sample of compound 1·3H\textsubscript{2}O was obtained by solvent diffusion in 10 mL sealed test tubes, using water/ethanol layers. Both organic ligands were dissolved in ethanol, and the resulting solution was carefully layered over an aqueous solution of cobalt(II) acetate, with an intervening buffer layer containing ethanol and water in 1:1 ratio. All three components were present in a ratio close to that of product 1. Dark green needles of the neutral product were evident after 5 days. This reaction involves aerial oxidation of both the 3,5-dbdcat\textsuperscript{2−} ligand and cobalt(II) metal center, which most likely follows ligand coordination to the relatively labile cobalt(II) ion. Compound 1·3H\textsubscript{2}O crystallizes cleanly and a pure bulk sample can be isolated in moderate yield. The dried compound undergoes partial dehydration to give 1·H\textsubscript{2}O, and all physical measurements reported below for the bulk sample were performed on the partially dehydrated form. The powder X-ray diffraction pattern measured for 1·H\textsubscript{2}O is in good agreement with the pattern calculated from the single crystal data measured for 1·3H\textsubscript{2}O, indicating retention of crystallinity and structure upon partial dehydration (Figure S1).

Under slightly warmer conditions, and with modification of the reaction stoichiometry to reduce the amount of tpb relative to \{Co(3,5-dbdiox)\}\textsubscript{3} and thereby favor the tpb acting as a 4-connecting node, dark green plate-shaped crystals of complex \textit{C} crystallize as a minor product with \{Co(3,5-dbdiox)\}\textsubscript{3} acting as a 2-connecting linker. Compound 2·9H\textsubscript{2}O crystallizes in the monoclinic \textit{C}2/c space group, and the asymmetric unit contains a complete \{Co(3,5-dbdiox)\}\textsubscript{3} moiety and half of a tpb ligand. The cobalt centers in 2 are linked through \textit{c}-disposed nitrogen atoms of 4-connecting tpb linkers to give a 1D ribbon coordination polymer.

Selected interatomic distances and angles for 1·3H\textsubscript{2}O and 2·9H\textsubscript{2}O are presented in Table 2. The Co–O/N bond distances are informative about the cobalt oxidation and spin state, while the dioxolene-based distances indicate the ligand oxidation state. The Co–N distances in 1·3H\textsubscript{2}O and 2·9H\textsubscript{2}O lie within the range 1.871(5)−1.905(5) Å, and the Co–O distances in 1·3H\textsubscript{2}O and 2·9H\textsubscript{2}O lie within the range 1.165(5)−1.207(5) Å. The Co–N distances in 1·3H\textsubscript{2}O and 2·9H\textsubscript{2}O lie within the range 1.871(5)−1.905(5) Å, and the Co–O distances in 1·3H\textsubscript{2}O and 2·9H\textsubscript{2}O lie within the range 1.165(5)−1.207(5) Å.

3.2. Description of Structures. Selected single crystal X-ray data for the two compounds are reported in Table 1, and structural representations of complexes 1 in 1·3H\textsubscript{2}O and 2 in 2·9H\textsubscript{2}O are presented in Figure 1. The asymmetric units of the compounds are available in Figure S2. Compound 1·3H\textsubscript{2}O crystallizes in the triclinic space group \textit{P}\textit{T}. The asymmetric unit consists of half of the cobalt atom located on the inversion center, one 3,5-dbdiox ligand, half of the tpb ligand, and one and a half solvent water molecules. The coordination complex 1 is a 1D chain coordination polymer with \{Co(3,5-dbdiox)\}\textsubscript{3} units linked through \textit{trans}-disposed tpb nitrogen atoms, with tpb acting as a 2-connecting linker. Compound 2·9H\textsubscript{2}O crystallizes in the monoclinic \textit{C}2/c space group, and the asymmetric unit contains a complete \{Co(3,5-dbdiox)\}\textsubscript{3} moiety and half of a tpb ligand. The cobalt centers in 2 are linked though \textit{c}-disposed nitrogen atoms of 4-connecting tpb linkers to give a 1D ribbon coordination polymer.

Isomorphic, cleavage, and Other Structural Parameters for 1·3H\textsubscript{2}O and 2·9H\textsubscript{2}O

<table>
<thead>
<tr>
<th>parameter</th>
<th>1·3H\textsubscript{2}O</th>
<th>2·9H\textsubscript{2}O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co–Co$^{\text{c}}$</td>
<td>9.935(2)</td>
<td>9.297(2), 12.028(3)$^{d}$</td>
</tr>
<tr>
<td>Co–Co$^{b}$</td>
<td>12.011(2)</td>
<td>13.479(2)</td>
</tr>
<tr>
<td>Co–O</td>
<td>1.887(2), 1.882(2)</td>
<td>1.905(5), 1.874(5), 1.871(5), 1.901(5)</td>
</tr>
<tr>
<td>Co–N</td>
<td>1.921(3)</td>
<td>1.935(7), 1.947(7)</td>
</tr>
<tr>
<td>O–C</td>
<td>1.324(4), 1.328(4)</td>
<td>1.316(9), 1.314(9), 1.312(9), 1.346(9)</td>
</tr>
<tr>
<td>C$^{\text{c}}$–C$^{\text{c}}$</td>
<td>1.429(4)</td>
<td>1.400(1)</td>
</tr>
<tr>
<td>C$^{\text{e}}$–C$^{\text{e}}$, C$^{\text{f}}$–C$^{\text{f}}$, C$^{\text{g}}$–C$^{\text{g}}$</td>
<td>1.398(5), 1.412(4)</td>
<td>1.416(1), 1.417(1)</td>
</tr>
<tr>
<td>C$^{\text{e}}$–C$^{\text{e}}$, C$^{\text{f}}$–C$^{\text{f}}$, C$^{\text{g}}$–C$^{\text{g}}$</td>
<td>1.395(4), 1.384(5)</td>
<td>1.374(1), 1.404(1)</td>
</tr>
<tr>
<td>C$^{\text{e}}$–C$^{\text{e}}$, C$^{\text{f}}$–C$^{\text{f}}$, C$^{\text{g}}$–C$^{\text{g}}$</td>
<td>1.418(5)</td>
<td>1.411(1)</td>
</tr>
<tr>
<td>MOS$^{g}$</td>
<td>−1.51</td>
<td>−1.57, −1.59</td>
</tr>
<tr>
<td>SHAPE index ($O_{2}$)$^{f}$</td>
<td>0.055</td>
<td>0.146</td>
</tr>
</tbody>
</table>

$^{a}$Intrachain distance. $^{b}$Closest interchain distance. $^{c}$Closest distance “across the ribbon”, see Chart 2. $^{d}$Closest distance “along the ribbon”, see Chart 2. $^{e}$See Chart 3 for labeling of dioxolene positions. $^{f}$Metrical oxidation state. $^{g}$The closer the index to zero, the less distortion from $O_{2}$ symmetry. $^{h}$The closer the index to zero, the less distortion from $O_{2}$ symmetry.
between 1.921(3) and 1.947(7) Å, which is indicative of low spin cobalt(III) at the temperature of data collection.\(^{37}\) The dioxolene C−O bond lengths are in the range 1.312(9)−1.348(9) Å, which are intermediate between values reported for catecholate (1.33−1.39 Å) and semiquinonate (1.27−1.31 Å) ligands.\(^{38,39}\) The "metrical oxidation state" (MOS) was also calculated for both structures based on all C−O and C−C ring distances in the dioxolene ligand.\(^{40,41}\) This parameter correlates the bond distances with the valence of the dioxolene ligand.\(^{40}\) The values obtained are all close to \(-1.5\) (Table 2), corresponding to a crystallographic averaging of distinct catecholate and semiquinonate ligands. Continuous shape measurements carried out with the software SHAPE 2.1\(^{42}\) confirm that the cobalt centers in both compounds exhibit only very small distortions from ideal octahedral coordination geometry, with SHAPE indices of 0.055 and 0.146 for 1 and 2, respectively (the closer the index is to zero, the less distortion). In summary, at the temperature of structural data collection, both complexes can be formulated as \([ls-Co^{III}(3,5-dbcat)(3,5-dbsq)]\) units connected by tpb linker into 1D chains.

Previously reported coordination polymers with tpb exhibit 3- or 4-connecting linking modes for the tpb ligands, with the 2-connecting mode observed here for 1 previously unreported.\(^{33−35}\) While the 4-connecting mode for tpb is possible in 2 where the nitrogen donor ligands are cis-disposed, steric clashes between the tert-butyl groups of the dioxolene ligands (Figure S3) will likely inhibit close approach of four \([ls-Co^{III}(3,5-dbcat)(3,5-dbsq)]\) moieties when the N-donor ligands are trans-disposed as in 1, preventing the tpb acting as a 4-connector. While the tpb ligand in 1 adopts the commonly observed eclipsed conformation (Figure 2), a rarer staggered conformation is evident for the 4-connecting tpb in 2. In the eclipsed form, the two diagonally opposite (i.e., 1,4-disposed or 2,5-disposed) pyridyl rings are completely eclipsed and the four nitrogen atoms are coplanar. The staggered conformation involves a dihedral angle of the two opposite pyridyl rings close to 90°.\(^{31}\) The ensuing coordination polymer 2 has a ribbon rather than a chain 1D topology, most likely due to the bulkiness of the tert-butyl groups of the dioxolene ligands and relative rigidity of the tpb ligand.

The cosynthesis of two distinctive compounds differing in the conformation of the tpb ligand has been reported twice previously. Han et al. described two cocrystallizing supracoordination polymers with tpb exhibiting statically identical hexa-coordinate environments of Cd(II) centers. In both structures, tpb acts as 4-connecting node; however the variation of the ligand conformation from staggered to eclipsed leads to the change of the net topology from 2D to 3D.\(^{24}\) Tong et al. described two cocrystallized coordination polymers with one compound incorporating 4-connecting tpb in the eclipsed conformation, while a t-shaped 3-connecting staggered mode was evident in the second compound.\(^{31}\) In this case, conversion between the two compounds can be partially controlled by the stoichiometry and time of the reaction. These literature reports and the present work reveal the coordinative flexibility of the tpb ligand arising from rotation of the C−C bond between the benzene and pyridine rings.

In the structure of 1·3H₂O, the chains run along the [1,1,0] axis, so that tert-butyl groups point toward the central benzene ring of a tpb ligand from a neighboring chain. This creates three types of relatively hydrophobic cavities, limiting the incorporation of hydrate molecules (Figure 3 left). Ribbons of 2·9H₂O run along the b axis with tert-butyl groups of neighboring chains pointing toward each other. The 3D packing evident for 2-
9H₂O affords two types of voids (Figure 3, right). Smaller hydrophobic cavities are lined by tert-butyl groups, while much larger (16.3 Å across) hydrophilic cavities can accommodate the hydrate molecules.

3.3. Thermogravimetric Analysis. The thermogravimetric analysis data for partially dehydrated 1·H₂O were measured between 298 and 800 K under constant N₂ flow (Figure S4). The compound rapidly loses 2% of the mass upon exposure to the N₂ flow, which corresponds to complete dehydration of 1·H₂O. The resulting compound then appears to be stable up to around 500 K, with a subsequent rapid loss above 550 K of more than 50% associated with decomposition of the organic component.

3.4. Infrared Spectroscopy. An infrared spectrum for compound 1·H₂O was obtained as a pressed KBr disc (Figure S5). A band characteristic of the ν(CN) stretching mode for the tpb linking ligand is evident at 1615 cm⁻¹. The band is slightly shifted from the frequency observed for the free ligand (1596 cm⁻¹), due to the coordination to the metal ion. Another characteristic band associated with the tpb ligand is a very strong band at 823 cm⁻¹ (819 cm⁻¹ for the free ligand) related to the arene ν(CH) bending and ring-puckering vibrations. The infrared spectrum is consistent with the presence of the dioxolene ligand in two redox states at room temperature. Bands characteristic of the C–O stretching mode of the 3,5-dbcat⁻² can be observed at 1358 and 1283 cm⁻¹, while the band at 1474 cm⁻¹ corresponds to the ν(CO) of the 3,5-dbsq⁻.

3.5. Electronic Spectroscopy. An ultraviolet–visible diffuse reflectance spectrum was obtained on a 2% KBr solid solution of a ground sample of 1·H₂O (Figure 4). A shoulder between 400 and 450 nm can be assigned to d–d transitions (¹Aᵣₑ → ¹T₁ₑ) associated with low spin octahedral Co(III). A broad band centered at 750 nm corresponds to a ligand to metal charge transfer (LMCT) transition of a Co(III)-catecholate chromophore. Moreover the spectral pattern between 470 and 670 nm is suggestive of a Co(II)-semiquinone chromophores and d → π* metal to ligand charge transfer (MLCT) transitions. Overall, the room temperature ultraviolet–visible spectrum is consistent with 1·H₂O being comprised of a mixture of [Co(III)(3,5-dbcat)(3,5-dbsq)] and [Co(II)(3,5-dbsq)] valence tautomers.

3.6. Magnetic and Photomagnetic Measurements. Magnetic susceptibility data (Figure 5) were measured for 1·H₂O in multiple cycles between 2 and 360 K, progressively increasing the higher temperature end of the cycle and cooling the sample back to 180 K, to check for irreversible processes.

The predicted low temperature value of χₘT for a {ls-CoIII(3,5-dbcat)(3,5-dbsq)} moiety is 0.38 cm³ mol⁻¹ K⁻¹, the slightly higher experimental value observed in the low temperature region (T < 200 K) for 1·H₂O is then suggestive of a small trapped fraction of hs-CoIII fraction, which has been previously observed for a number of VT cobalt-dioxolene compounds. The very gradual increase from 0.56 cm³ mol⁻¹ K to 0.64 cm³ mol⁻¹ K observed in the 7–270 K range is also consistent with the presence of a small amount of hs-CoIII, which does not obey Curie law. Above 280 K, a more rapid increase ensues, reaching a value of 0.76 cm³ mol⁻¹ K at the maximum measured temperature of 360 K. We assign this increase to the beginning of an incomplete thermally induced VT transition to a {hs-CoIII(3,5-dbsq)} species. Considering that the high temperature χₘT values typically observed for {hs-CoIII(3,5-dbsq)} valence tautomers are up to 3.75 cm³ mol⁻¹ K⁻¹, the observed transition is far from complete at 360 K. The relatively high VT transition temperature is not uncommon for VT coordination polymers and may be due to partial collapse of the 3D structure upon dehydration sterically hindering the expansion in cobalt coordination sphere associated with a VT transition. Multiple heating–cooling cycles show no changes in the magnetic measurement curve, which is consistent with the limited solvent loss evident in the thermogravimetric analysis. Complete dehydration does not occur until 500 K. In principle, if it was possible to dehydrate 1 without it decomposing, the VT transition might shift to lower temperatures.

The possibility of photoinduction of the metastable phase at low temperature was investigated at different wavelengths (see Experimental Section). However, only a marginal degree of photoconversion was observed, estimated at less than 1%. This prevented the characterization of the metastable state relaxation properties, either via T_LIESST determination or by measuring the decay of the metastable state at fixed temperature. The extremely low extent of photoconversion is consistent with the outcome of the characterization of the thermal transition and in accordance with the inverse gap energy law, which quantitatively describes the inverse proportionality between the transition temperature and the T_LIESST temperature in spin crossover systems.

4. CONCLUDING REMARKS

The combination of the tpb ligand and {Co(3,5-dbdiox)} units has afforded two coordination polymers, although the initial target of a 2D net has proved elusive. The compounds obtained are instead 1D coordination polymers with chain (1) and ribbon (2) topologies. To our knowledge complex 1 is the first example of a cooperative 1,3-diolato system.
example of tpb acting as 2-connecting ligand, while complex 2 is a rare example of a 4-connecting tnp with a staggered conformation of the pyridyl groups. Magnetochemical, structural, and spectroscopic studies suggest that compound 1·H₂O can be formulated as \( \{ls-Co^{III}(3,5-dbcat)(3,5-dbsq)\} \) below 300 K, with an incomplete thermally induced VT transition to a \( \{ls-Co^{III}(3,5-dbsq)\} \) species commencing above 300 K.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.cgd.7b00110.

Additional structural figures, thermogravimetric analysis data, and infrared spectra (PDF)

#### Accession Codes

CCDC 1522817–1522818 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

### AUTHOR INFORMATION

#### Corresponding Author

*E-mail: c.boskovic@unimelb.edu.au.

**ORCID**

Robert William Gable: 0000-0002-4626-0217

Lorenzo Sorace: 0000-0003-4785-1331

Colette Boskovic: 0000-0002-1882-2139

#### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

#### Notes

The authors declare no competing financial interest.

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#### REFERENCES


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One dimensional chain and ribbon cobalt-dioxolene coordination polymers: a new valence tautomeric compound

Olga Drath, † Robert William Gable, † Giordano Poneti, ‡ Lorenzo Sorace, § Colette Boskovic* †

† School of Chemistry, University of Melbourne, Victoria, 3010, Australia.

‡ Instituto de Química, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil

§ UdR INSTM and Department of Chemistry “U. Schiff”, University of Florence, 50019 Sesto Fiorentino, Italy
Figure S1. Comparison of experimental X-ray powder diffraction pattern measured for 1·H₂O (top) with the pattern simulated from the single crystal data collected for 3·H₂O (bottom).
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CHAPTER IV
Synthesis and investigation of one- and two-dimensional valence tautomeric coordination polymers based on Co-bis(dioxolene) units and 1-hydroxy-1,2,4,5-tetra(4-pyridyl)cyclohexane.

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4.1 Introduction

In the pursuit of two-dimensional VT CPs, an important issue is to find a ligand suitable for connecting the \( \{\text{Co(diox)}_2\} \) (diox = dioxolene) units into a polymeric net. Polymers with a 1,2,4,5-tetra(4-pyridyl) benzene (tbt) (Chapter III) have shown that linkers chosen to connect more than two metal centers should be flexible enough to accommodate the bulky tert-butyl groups of the dioxolene ligand.

The oxidative coupling of 1,3-bipyridylpropane (1,3-bpp) described in Chapter III can lead to different products, depending on the reaction pH. In their 2012 publication, Wang and Chang present a detailed synthetic procedure for obtaining different forms of the 1,3-bpp dimer: three hydrates of tpb and, a previously unreported, 1-hydroxy-1,2,4,5-tetra(4-pyridyl) cyclohexane (tpch).\(^1\) Compared to synthesis of the tbt, tpch can be formed without the addition of phosphoric acid at a higher pH. Chart 4-1 presents the redox reactions involved in the synthesis of the 1,3-bpp ligand dimers.

Since the tpch ligand contains a flexible cyclohexane ring, it is a potential candidate for linking \( \{\text{Co(3,5-diox)}_2\} \) into an infinite array. To date, there have been only two reports of polymeric structures involving the tpch ligand. In each case, the ligand was synthesized through \textit{in situ} metal/ligand reactions without isolating the ligand. Meng \textit{et al.} obtained a (3,4)-connected network based on 1,3,5-benzenetricarboxylate (btc), Zn\(^{2+}\) and tpch (Figure 4-1). Interestingly, the solvothermal synthesis was conducted in the presence of a polyoxometalate (K\(_{12}\)[\(\alpha\)-H\(_2\)P\(_2\)W\(_{12}\)O\(_{48}\)]\(\cdot\)~24H\(_2\)O), which is believed to act as reaction mediator. However, the study does not explain the exact role of the polyoxometalate in the process of the synthesis.\(^2\) The tpch ligand acts as a 4-connecting node for the Zn centers and, together with 3-connecting btc, creates a self-penetrating net of unprecedented topology.
Chart 4.1. Oxidation and reduction processes involved in the synthesis of tpb and tpch ligands.

Fe$^{3+}$ + e$^{-}$ → Fe$^{2+}$

NO$_3$ + 10 H$^+$ + 8 e$^{-}$ → NH$_4^+$ + 3H$_2$O

Figure 4.1. [Zn$_3$(btc)$_2$(tpch)(H$_2$O)$_2$]·2H$_2$O ball and stick representation showing: (a) Single unit of the btc-linked grid part along the c axis. (b) Unit of the complex along the c axis. (c) Zig-zag chain part of the complex, linked by the tpch ligand. (d) Btc-linked grid part of the complex along the b axis. (e) Unit of the complex along the b axis. (f) Zig-zag chain part of the complex, linked by the tpch ligand, along the b axis$^2$. 
Subsequently, the same group published a coordination polymer based on CuCl$_2$ and tpch obtained *in situ*. Polyoxometalate reagents are not incorporated in the product. Later studies suggest that the compound can be also obtained without the presence of polyoxometalate units. In [Cu$_2$Cl$_2$(tpch)]$_x$, each Cu$^+$ center is three-coordinate and surrounded by two pyridyl N atoms of different tpch ligands and one Cl$^-$ anion. The tpch acts as a 4-connecting node for Cu atoms, giving a rise to a 2D (4,4) sheet. The sheets along different directions interpenetrate, creating a 3D supramolecular arrangement (Figure 4-2).

![Figure 4-2](image)

**Figure 4-2.** (a) The 2D (4,4) coordination polymer sheet of [Cu$_2$Cl$_2$(tpch)]$_x$. (b) The two-fold diagonal/diagonal inclined interpenetration in the structure of [Cu$_2$Cl$_2$(tpch)]$_x$.

In the present work, the tpch ligand was selected due to its greater flexibility than the previously employed tpb. In order to gain more control over the stoichiometry, the ligand was synthesized according to the Chang and Wang method and isolated prior to synthesis of the coordination polymer. The aim was to achieve 2D sheet topology in a valence tautomeric coordination polymer where tpch links four different {Co(3,5-diox)$_2$} units.
4.2 Experimental.

4.2.1 Synthesis of the ligand and the coordination complex

All manipulations were performed under aerobic conditions. All the reagents were obtained from commercial sources and were used as received.

1-hydroxy-1,2,4,5-tetra(4-pyridyl)cyclohexane (tpch). The tpch ligand was synthesized according to the literature procedure.\(^1\) A solvothermal reaction of Fe(NO\(_3\))\(_3\)·9H\(_2\)O (0.16 g, 0.41 mmol), 1,3-bpp (1.3 g, 6.4 mmol), oxalic acid dihydrate (0.15 g, 1.2 mmol) and water (12 ml) was conducted at 180 °C for 48 h. The obtained product was recrystallized from EtOH to give tpch as colorless crystals in 20% yield. The experimental powder X-ray diffraction (PXRD) pattern of tpch is in perfect agreement with the one calculated from a literature reported single-crystal XRD data (Figure 4-3).\(^1\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(8.3 (6H, m), 8.2 (2H, m), 7.5 (4H, dd), 7.2 (2H, dd), 7.1 (2H, m), 3.6 (1H, m), 3.4 (2H, m), 1.9 (3H, m), 1.8 (1H, m).

\{[Co(3,5-dbcat)\(_2\)]\(_2\)tpch\} (1). An ethanol solution (6.7 ml) of 3,5-dbcatH\(_2\) (33 mg, 0.13 mmol) and tpch (6 mg, 0.01 mmol) was layered over an aqueous solution (1.3 ml) of Co(OAc)\(_2\)·4H\(_2\)O (17 mg, 0.067 mmol). After 3 weeks blue rectangular plate-shaped crystals were formed along with an amorphous precipitate. A sample for single crystal X-ray diffraction was maintained in contact with the mother liquor to avoid solvent loss. A single crystal was handpicked from the solution and identified as \{[Co(3,5-dbcat)\(_2\)]\(_2\)tpch\}·2EtOH·15H\(_2\)O (1·2EtOH·15H\(_2\)O). Despite efforts, a bulk sample of the complex 1 could not be obtained.

\{Co(3,5-dbcat)\(_2\)tpch\} (2). An ethanol solution (5 ml) of 3,5-dbcatH\(_2\) (33 mg, 0.13 mmol) and tpch (13 mg, 0.026 mmol) was layered over an aqueous solution (2 ml) of Co(OAc)\(_2\)·4H\(_2\)O (17 mg, 0.067 mmol). The ethanol and water layers were separated by a buffer layer of ethanol and water in 1:1 ratio (1 ml). After 2 weeks blue rectangular plate-
shaped crystals were formed. A sample for single crystal X-ray diffraction was maintained in contact with the mother liquor to avoid solvent loss and identified as \{\text{Co}(3,5\text{-dbcat})\cdot\text{tpch}\}\cdot\text{EtOH}\cdot5\text{H}_2\text{O} (2\cdot\text{EtOH}\cdot5\text{H}_2\text{O}). The bulk sample was isolated by filtration, washed with cold ethanol and air dried, giving a partially desolvated sample of \text{2}\cdot\text{EtOH}\cdot2\text{H}_2\text{O} in 30 \% yield. Anal. Calcd (\%) for C_{56}H_{74}N_{4}CoO_{10}: C, 67.9; H, 7.5; N, 5.7. Found: C, 67.7; H, 7.6; N, 4.6. Selected IR (cm\textsuperscript{-1}): 2965 (vs), 1613 (s), 1580 (m), 1481 (w), 1458 (vs), 1387 (m), 1357 (s), 1222 (w), 1209 (m), 1096 (m), 1071 (w), 985 (s), 827 (m), 557 (w).

4.2.2 Magnetic measurements

Magnetic susceptibility measurements were carried out using a Quantum Design MPMS SQUID magnetometer equipped with a 5 T magnet. The temperature dependence of the magnetization (M) was measured from 2 to 360 K by applying a 1 kOe field (H) below 40 K to reduce saturation effects and 10 kOe field from 40 to 360 K. Magnetic susceptibility per mole (\chi_M) was then evaluated as \chi_M = M_M/H, where M_M is the molar magnetization per mole, evaluated on the basis of sample mass and molecular weight, taking into account the contribution of the sample holder and the intrinsic diamagnetic contribution calculated using Pascal’s constants.\textsuperscript{4}

4.2.3 Other physical measurements

Elemental analyses were performed by the Campbell Microanalytical Laboratory, Department of Chemistry, University of Otago, New Zealand. Thermogravimetric analyses were performed on a Mettler Toledo thermal analyser. Infrared spectra (KBr disk) were recorded on a Bruker Tensor 27 FTIR spectrometer. Ultraviolet-visible absorption diffuse reflectance spectra were measured on a Thermo Scientific-Evolution 220 UV-Visible spectrophotometer. Powder diffraction data were acquired at 25°C on a Bruker D4 ENDEAVOR X-ray diffractometer, fitted with a LynxEye Position Sensitive
Detector, and using a copper tube source (CuKα, λ = 1.5406 Å), operated at 40 kV and 35 mA. Data was collected with 5-70 degree 2 theta angle range with a 0.02 degree step size and a 0.1 s per step dwell time. EPR studies under photo-irradiation were performed using a Bruker Elexsys E500 spectrometer equipped with a ⁴He continuous flow cryostat (ESR900, Oxford Instruments).

4.2.4  X-ray crystallography

X-ray diffraction data for 1·2 EtOH·15H₂O was collected at 100 K and for the 2·EtOH·5H₂O at 100 K, 275 K and 315 K. Data were collected using synchrotron radiation on the MX1 beamline at the Australian Synchrotron, Victoria, Australia. All the structures were solved in OLEX² with the ShelXT structure solution program using intrinsic phasing and refined with the ShelXL refinement package using least squares minimization. The compounds contained disordered water molecules. A satisfactory disorder model of the solvent was not found, and therefore the OLEX² Solvent Mask routine was used to mask out the disorder electron density. The molecular formulas are proposed based on the calculated solvent accessible voids and the electron count (364 e per unit cell for 1 and 81.8 e per unit cell for 2).
Table 4-1. Crystallographic data for 1·2EtOH·15H₂O, 2·EtOH·5 H₂O and 2·EtOH·3 H₂O.

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<th>2·EtOH·5H₂O</th>
<th>2·EtOH·3H₂O</th>
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<td>100</td>
<td>275</td>
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<td>Empirical formula</td>
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<td>C₅₆H₆₆N₄CoO₁₃</td>
<td>C₅₆H₆₆N₄CoO₁₁</td>
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<tr>
<td>Formula weight / g mol⁻¹</td>
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<td>1076.19</td>
<td>1076.19</td>
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<tr>
<td>Crystal system</td>
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<td></td>
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<tr>
<td>Space group</td>
<td>P2₁/c</td>
<td>P1</td>
<td>P1</td>
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<td>10.072(2)</td>
<td>10.066(2)</td>
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<tr>
<td>b / Å</td>
<td>11.679(2)</td>
<td>16.135(3)</td>
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<tr>
<td>c / Å</td>
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<td>18.192(4)</td>
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<tr>
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<td>17020/51/684</td>
<td>17440/45/683</td>
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<td>0.0797</td>
<td>0.0733</td>
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<td>0.0939</td>
<td>0.0847</td>
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<td>wR² (all data)</td>
<td>0.3147</td>
<td>0.2782</td>
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<tr>
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<td>2.54/-0.85</td>
<td>1.47/-0.80</td>
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</table>
4.3 Results and Discussion.

4.3.1 Synthesis of complexes.

The ligand tpch was synthesized and isolated by a literature method prior to the synthesis of the target coordination polymer. Due to the fact that the formation of \(\text{Co}^{\text{III}}(\text{cat})(\text{sq})\) requires deprotonating the 3,5-dbcatH2, a one pot \textit{in situ} method in acidic conditions is not a suitable procedure. Polymeric coordination compounds \(1 \cdot 2\text{EtOH} \cdot 15\text{H}_2\text{O}\) and \(2 \cdot \text{EtOH} \cdot 2\text{H}_2\text{O}\) were obtained at room temperature under aerobic conditions via slow diffusion. In both cases the cobalt(II) salt was dissolved in water and the ethanolic solution of both ligands was carefully layered over the aqueous layer. In case of the synthesis of compound \(2 \cdot \text{EtOH} \cdot 2\text{H}_2\text{O}\), the layers were additionally separated by a buffer layer of a 1:1 H2O:EtOH mixture. Single crystals of compound \(1 \cdot 2\text{EtOH} \cdot 15\text{H}_2\text{O}\) grew out of the cloudy solution when the Co\textsuperscript{II} cation and catecholate were in 4-fold and 8-fold excess, respectively, in relation to the concentration of the linking ligand. Despite several attempts, it was not possible to obtain a sufficient yield of \(1 \cdot 2\text{EtOH} \cdot 15\text{H}_2\text{O}\) for physical measurements. Moreover, any increase of the tpch:Co ratio seems to favor the formation of the 1D chain-type complex \(2\). A possible explanation for the low yield of complex \(1\) and complex \(2\) being favored in the slow diffusion reaction may be the bulkiness of the \textit{tert}-butyl group on the dioxolene ligand, inhibiting the formation of the 2D structure, identified previously in this research (Chapter III). Hence, bulk measurements were only pursued \(2 \cdot \text{EtOH} \cdot 2\text{H}_2\text{O}\). The elemental analysis, confirmed by the X-ray powder diffraction and TGA studies indicate that \(2\) contains unknown impurities, which could not be removed despite considerable effort. The X-ray powder diffraction does not contain main peaks corresponding to the compound \(1\). The sample of \(2\) appears homogenous under a standard laboratory microscope. Based on the elemental analysis simulations it is unlikely that the sample contains any of the starting material. The tpch ligand was
synthesized in a low yield purified by recrystallization from EtOH. The obtained tpch batch was highly crystalline, the collected powder diffraction pattern matched the generated theoretical powder pattern (Figure 4-3.), and the measured unit cell matched data found in literature.¹ The lack of previously reported experimental data on tpch prevented comparison of the ¹H NMR spectrum with published data. The signals can be assigned based on the predicted spectrum, however the signal at 5.87 ppm, integrating to ~0.3 H, remains unaccounted for, and is most likely related to impurities in the ligand.⁵

Figure 4-3. Comparison of experimental X-ray powder diffraction pattern measured for tpch (red) with the pattern simulated from the single crystal data collected for tpch·2H₂O (black).¹
4.3.2 Structural studies

4.3.2.1 Structure of \{[\text{Co(3,5-diox)}_2]\text{tpch}\} \cdot 2\text{EtOH} \cdot 15\text{H}_2\text{O} (1 \cdot 2\text{EtOH} \cdot 15\text{H}_2\text{O})

The crystal structure of $1 \cdot 2\text{EtOH} \cdot 15\text{H}_2\text{O}$ was measured at 100 K. The asymmetric unit is presented in Figure 4-4 and coordination sphere around the Co center in Figure 4-5. Figure 4-6 presents the 2D polymer’s structure and packing arrangements. Table 4-2 presents selected interatomic distances. Compound $1 \cdot 2\text{EtOH} \cdot 15\text{H}_2\text{O}$ crystallizes in the monoclinic space group $P2_1/c$. The asymmetric unit consist of one cobalt atom, two 3,5-dbdox ligands, half of the tpch ligand. The unit cell also contains solvent, two ethanol and fifteen water molecules per formula unit. The cobalt coordination sphere adopts a slightly disordered octahedral shape (Figure 4-5) and consist of four oxygen atoms from two 3,5-dbdox ligands, and two nitrogen atoms in a cis disposition, each from a different tpch ligand. The SHAPE Index, which describes how close the coordination geometry is to an ideal polyhedron, was calculated to be 0.212 for octahedral geometry.\(^6\) Each tpch ligand connects four different Co atoms into a 2D sheet, which is, to the best of our knowledge, the second literature example of a two-dimensional CP based on Co-dioxolene units (Figure 4-6). When comparing the connectivity of 1 with the previously reported Co-based 2D VT CP (see Chapter I, section 1.7.3)\(^7\), it becomes evident that relative flexibilities of the ligand give rise to different geometries. In the compound synthesized by Tao et al, each tetrakis(4-pyridyloxymethylene)methane (tpom) ligand links Co centers in a way that the corresponding pyridyl rings are always parallel to each other. In other words, if the 2D sheet was rotated around the $b$ axis, at any given moment, each tpom ligand would appear to be in the exact same position. In contrast, in compound $1 \cdot 2\text{EtOH} \cdot 15\text{H}_2\text{O}$ each second row of linking ligands is twisted perpendicularly in respect to the previous row, which results in the cross-section through the 2D sheet along the $ab$ plane having a zig-zag like character (Figure 4-6c). For both structures, the tert-butyl groups of the 3,5-diox ligands are pointing above and below the sheet, which creates a
hydrophobic space between sheets. Tao et al. described this structure as a “sandwiched” layer of the bridging ligand between two layers of Co atoms.\(^7\)

At 100 K, the Co-O distances are 1.854(3)-1.907(3) Å and Co-N distances equal 1.953(4) and 1.964(3) Å. These bond lengths are indicative of the +3 oxidation state of the cobalt cation.\(^8\) The interatomic distances within the dioxolene ligand have been also analyzed. In 2011, Brown examined 259 structures based on dioxolene, reporting an unambiguous ligand oxidation.\(^9\) When the two different dioxolene ligands in the asymmetric unit of 1·2 EtOH·15 H\(_2\)O are compared, the differences in the C-C and C-O distances become evident. Table 4-2 compares selected interatomic distances in 1·2EtOH·15H\(_2\)O with the average literature values calculated by Brown. The bond lengths in the first dioxolene (named ‘Dioxolene 1’) are much closer to the values characteristic for the semiquinone, while the bond lengths in the second ligand (‘Dioxolene 2’) match better with the average catecholate state. Moreover, Brown proposed an empirical parameter, the Metrical Oxidation State (MOS), as a good measure of the apparent oxidation state of the ligand. The theoretical value of the MOS parameter for a semiquinone is -1, while the catecholate ligand should have an MOS value equal to -2. The calculated parameter for the two 3,5-dbdiox in the 1·2EtOH·15H\(_2\)O structure gives a value for the Dioxolene 1 closer to -1, whereas Dioxolene 2 has MOS near -2, which is consistent with the intramolecular distances.
Figure 4-4. The asymmetric unit of the complex 1 in $1 \cdot 2\text{EtOH} \cdot 15\text{H}_2\text{O}$ (hydrogen atoms and solvent molecules omitted for clarity).

Figure 4-5. Coordination sphere around the Co centre in $1 \cdot 2\text{EtOH} \cdot 15\text{H}_2\text{O}$. 
Figure 4-6. a) View of the 2D layered structure of 1·2EtOH·15H₂O. b) Packing of the sheets of 1·2EtOH·15H₂O. c) Cross-section of the sheet. Solvent molecule, hydrogen atoms and dioxolene ligands (in a) and c)) omitted for clarity. The OH group on the hexane group of the tpch ligand is disordered over four positions.
**Chart 4-2.** Atom labelling for dioxolene ligands.

**Table 4-2.** Selected interatomic distances for 1·2 EtOH·15 H₂O.

<table>
<thead>
<tr>
<th>Distance (Å) / Parameter</th>
<th>1·2 EtOH·15 H₂O</th>
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</thead>
<tbody>
<tr>
<td>Co···Co&lt;sup&gt;a&lt;/sup&gt;</td>
<td>9.219</td>
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<tr>
<td>Co–O</td>
<td>1.854(3) – 1.907(3)</td>
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<tr>
<td>Co–N</td>
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<table>
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<tr>
<th>Distance (Å)</th>
<th>Dioxolene 1</th>
<th>Dioxolene 2</th>
<th>Avg. values for semiquinone&lt;sup&gt;(11)&lt;/sup&gt;</th>
<th>Avg. values for catecholate&lt;sup&gt;(11)&lt;/sup&gt;</th>
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<td>O–C&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>1.348</td>
<td>1.285(13)</td>
<td>1.355(15)</td>
</tr>
<tr>
<td>C&lt;sub&gt;a&lt;/sub&gt;–C&lt;sub&gt;b&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt;</td>
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<td>1.408(5)</td>
<td>1.459(19)</td>
<td>1.406(17)</td>
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<tr>
<td>C&lt;sub&gt;b&lt;/sub&gt;–C&lt;sub&gt;c&lt;/sub&gt;, C&lt;sub&gt;a&lt;/sub&gt;–C&lt;sub&gt;f&lt;/sub&gt;&lt;sup&gt;b,c&lt;/sup&gt;</td>
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<td>1.425(10)</td>
<td>1.391(13)</td>
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<td>C&lt;sub&gt;c&lt;/sub&gt;–C&lt;sub&gt;d&lt;/sub&gt;, C&lt;sub&gt;e&lt;/sub&gt;–C&lt;sub&gt;f&lt;/sub&gt;&lt;sup&gt;b,c&lt;/sup&gt;</td>
<td>1.371</td>
<td>1.406</td>
<td>1.364(14)</td>
<td>1.394(13)</td>
</tr>
<tr>
<td>C&lt;sub&gt;d&lt;/sub&gt;–C&lt;sub&gt;e&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.432(5)</td>
<td>1.398(6)</td>
<td>1.429(15)</td>
<td>1.383(17)</td>
</tr>
<tr>
<td>MOS&lt;sup&gt;d&lt;/sup&gt;</td>
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<td>-1.86</td>
<td>-1&lt;sup&gt;e&lt;/sup&gt;</td>
<td>-2&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Closest Co···Co distance. <sup>b</sup> Averaged distances. <sup>c</sup> See Chart 2 for labelling of dioxolene positions. <sup>d</sup> Metrical Oxidation State. <sup>e</sup> Theoretical oxidation state values.
4.3.2.2 Structure of [Co(3,5-diox)₂tpch]·EtOH·5H₂O (2·EtOH·5H₂O)

The X-ray diffraction data of 2·EtOH·nH₂O were measured at 100 K, 275 K (n = 5) and 315 K (n = 3) to monitor changes in the Co-O, Co-N and 3,5-db-diox ligand bond lengths associated with a thermally-driven valence tautomeric transition.

The asymmetric unit of 2·EtOH·5H₂O structure is presented in Figure 4-7, the chain motif of the 1D polymeric structure is shown in Figure 4-8 and the packing diagram is shown in Figure 4-9. Table 4-3 presents selected interatomic distances. The compound crystallizes in the triclinic P̅1 group throughout the measured temperature range. The asymmetric unit of 2·EtOH·5H₂O consists of a cobalt center, two 3,5-db-diox ligands, two halves of tpch ligands, a molecule of solvent ethanol and highly disordered solvent. At every temperature, the ethanol molecule is ordered by hydrogen bonding to the non-coordinating pyridyl group of the tpch ligand, while the disordered solvent was identified as five water molecules per formula unit at 100 K and 275 K, and three water molecules at 315 K. The OH group of the tpch ligand is disordered over four positions on the cyclohexane ring.

The Co center is surrounded by four oxygen atoms and two nitrogen atoms in cis arrangement. At 100 K the SHAPE index is close to zero, which indicates a low level of distortion from the octahedral coordination sphere. However, the level of distortion increases with the temperature of collection (Table 4-3). Each tpch ligand connects two cis-[Co(3,5-db-diox)₂] units, creating a zig-zag chain. The 2-linking mode of the tpch has not been hitherto reported. The chains run parallel to each other creating predominantly hydrophobic zig-zag shaped cavities (Figure 4-9).
Figure 4-7. Left: The asymmetric unit of the complex 2 in 2·EtOH·5H₂O collected at 100 K. (hydrogen atoms and solvent molecules omitted for clarity). Right: Coordination sphere around the Co centre in complex 2 at 100 K.

Figure 4-8. The chain motif of the 2·EtOH·5H₂O collected at 100 K. (hydrogen atoms and solvent molecules omitted for clarity).
Temperature-dependent Co-ligand bond lengths are indicative of the VT transition and reported in Table 4-3. At 100 K Co-O bonds are in the range 1.862(3)-1.918(3) Å and Co-N bonds in the range 1.939(3)-1.955(3) Å, which is in good agreement with previously reported values for octahedral $\theta$-Co$^{III}$ complexes. No significant changes in the Co-N distances can be observed when the crystal is heated to 275 K, which suggests that below this temperature, the majority of the Co centers stay in the +3 oxidation state. Interestingly, there is a small decrease in one of the Co-O bonds, suggesting that the compound needs to go through some slight rearrangement in order to accommodate the changes in the oxidation state of 3.5-dbdiox ligands. This type of change has been observed in previously reported Co-diox complexes. At 315 K the Co-O distances increase to 1.911(3)-1.966(3) Å, while Co-N distances lie between 2.009(4) and 2.013(3) Å.
Å. These changes indicate the VT transition occurs around room temperature and there is a significant fraction of $hs$-Co$^{II}$ centers at 315 K. Figure 4-10 shows the measured Co-ligand distances as a function of the collection temperature. On average, Co-N and Co-O distances increase by 0.06 Å and, based on the graph, the VT transition begins above 275 K. Assuming that a completed VT transition is associated with a mean increase in Co-ligand bond lengths of $c.a. 0.15$ Å, a % rate of VT conversion at 315 K for $2\cdot$EtOH$\cdot$5H$_2$O can be estimated as 40%.$^{11}$

The dioxolene interatomic distances and MOS parameters are also reported in Table 4-3. At 100 K the bond lengths of Dioxolene 1 are closer to the values characteristic for semiquinone, while the values for the Dioxolene 2 seem to stay slightly above those reported for catechol. The dioxolene oxidation states can be confirmed by the MOS parameters calculated to be -1.68 and -1.21. The values of the MOS at 315 K show a small shift towards semiquinone-only values for Dioxolene 1 and 2; however the change is not significant enough to confirm the VT transition. Moreover, the values at 275 K suggest a transitional phase before the start of the VT conversion, when the compound has to first undergo a structural rearrangement. Finally, the generally small temperature-triggered differences in the C-C and C-O bond distances and MOS parameters for the dioxolene ligand suggest that the method presented by Brown may not be sensitive enough to probe small changes in the oxidation states within Co-diox complexes.
Table 4-3. Selected interatomic distances for 2·EtOH·5H₂O.

<table>
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<tr>
<th>Distance Parameter</th>
<th>100 K</th>
<th>275 K</th>
<th>315 K</th>
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<tr>
<td>Co···Co</td>
<td>15.230, 15.240</td>
<td>15.138, 15.170</td>
<td>15.361, 15.364</td>
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<tr>
<td>Co–O_{min}</td>
<td>1.862(3)</td>
<td>1.866(3)</td>
<td>1.911(3)</td>
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<tr>
<td>Co–O_{max}</td>
<td>1.918(3)</td>
<td>1.914(3)</td>
<td>1.966(3)</td>
</tr>
<tr>
<td>Co–N_{min}</td>
<td>1.939(3)</td>
<td>1.955(2)</td>
<td>2.009(4)</td>
</tr>
<tr>
<td>Co–N_{max}</td>
<td>1.955(3)</td>
<td>1.959(3)</td>
<td>2.013(3)</td>
</tr>
<tr>
<td>O–C (^b)</td>
<td>1.343</td>
<td>1.307</td>
<td>1.332</td>
</tr>
<tr>
<td>C(_a)–C(_b) (^c)</td>
<td>1.422(5)</td>
<td>1.448(5)</td>
<td>1.398(5)</td>
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<tr>
<td>C(_b)–C(_c), C(_a)–C(_e) (^b,c)</td>
<td>1.400</td>
<td>1.415</td>
<td>1.381</td>
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<tr>
<td>MOS (^d)</td>
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<tr>
<td>SHAPE (^e)</td>
<td>0.103</td>
<td>0.159</td>
<td>0.258</td>
</tr>
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</table>

\(^a\) Closest Co···Co distance. \(^b\) Averaged distances. \(^c\) See Chart 2 for labelling of dioxolene positions. \(^d\) Metrical Oxidation State. \(^e\) The closer the index to zero, the less distortion from \(O_h\) symmetry. \(^6\)
4.3.3 X-ray powder diffraction studies

As discussed above, the elemental analysis of $2 \cdot \text{EtOH} \cdot 2\text{H}_2\text{O}$ indicated a small impurity in the sample. X-ray powder diffraction (XPRD) measurements were undertaken to identify the nature of the impurities. XPRD studies were performed on $2 \cdot \text{EtOH} \cdot 2\text{H}_2\text{O}$ (Figure 4-11) and compared with theoretical XRPD patterns generated from the single crystal X-ray diffraction studies for $1 \cdot 2\text{EtOH} \cdot 15\text{H}_2\text{O}$ and $2 \cdot \text{EtOH} \cdot 2\text{H}_2\text{O}$. Although compound $2 \cdot \text{EtOH} \cdot 2\text{H}_2\text{O}$ was found to be a predominant phase in the collected sample, a number of peaks of uncertain origin are present. The main peaks of the theoretical XRPD pattern corresponding to $1 \cdot 2\text{EtOH} \cdot 15\text{H}_2\text{O}$ are not apparent, therefore it has been concluded that the synthesized compound does not contain the 2D CP. The low sample
yield and time constraints prevented quantitative XPRD analysis to identify the nature of the impurities.

Figure 4-11. Powder diffraction pattern collected on the bulk sample of 2·EtOH·2 H₂O (red) compared with theoretical patterns generated for 1·2 EtOH·15 H₂ (blue) and 2·EtOH·2 H₂O (green).
4.3.4 Thermogravimetric analysis

The thermogravimetric analysis of 2·EtOH·2H₂O measured between 298 K and 900 K under N₂ gas stream is presented in the Figure 4-12. The curve shows a first mass loss from 298 K to 405 K, followed by a further gradual loss up to 505 K, totally 8%. The weight percentage of 2·EtOH·2H₂O calculated for one ethanol and two water molecules equals ~8.4% which is within reasonable agreement of the mass loss up to 505 K. However, due to the fact that the sample was not pure, the solvent percentage in the sample can only be estimated. Above 505 K the mass loss curve becomes much sharper and the organic part of the compound undergoes thermal decomposition.

![Thermogravimetric analysis of 2·EtOH·2H₂O.](image)

**Figure 4-12.** Thermogravimetric analysis of 2·EtOH·2H₂O.
4.3.5 Infrared spectroscopy

The infrared spectrum of 2·EtOH·2H₂O was collected at room temperature as a pressed KBr pellet and is presented in Figure 4-13. A band characteristic of the \( \nu(C=N) \) stretching mode for the tpch ligand is evident at 1612 cm\(^{-1}\). Aromatic ring C-H stretch at 2965 cm\(^{-1}\) confirms the 3,5-dbdiox presence, while the information of the oxidation state of the ligand can be found in the 1500 cm\(^{-1}\) - 1200 cm\(^{-1}\) range. The C-O bond and C-C bond stretches for catecholate can be observed at 1245 cm\(^{-1}\) and 1481 cm\(^{-1}\), respectively. The C-O stretching mode for semiquinone is evident at 1458 cm\(^{-1}\). The infrared spectrum of 2·EtOH·2 H₂O is consistent with both catecholate and semiquinonate, which are the ligands coordinated to the Co center at room temperature.

Figure 4-13. Infrared spectrum of 2·EtOH·2 H₂O.
4.3.6 Electronic spectroscopy

The UV-Vis diffuse reflectance spectrum was collected at room temperature as a KBr solid solution (~3%). The normalized diffuse reflectance function is presented in Figure 4-14. The sharp band at 310 nm can be assigned to intermolecular transitions within the dioxolene ligand.\(^\text{13}\) The shoulder at 350 nm corresponds to the ligand-to-metal-charge-transfer (LMCT) from the catecholate \(\pi^*\) orbital.\(^\text{14}\) The band at 400 nm can be assigned to the d-d transitions in octahedral Co\(^{\text{III}}\) complexes\(^\text{14}\) or, most likely to the semiquinone \(\pi-\pi^*\) transitions.\(^\text{15}\) The broad absorption with a center around 750 nm corresponds to the semiquinone centered transition.\(^\text{13}\)

The band suggesting presence of the Co\(^{\text{II}}\)-semiquinone chromophore fraction can be identified between 500 nm and 700 nm and assigned as metal-to-ligand charge transfer (MLCT) band. The room temperature spectrum shows bands corresponding to both redox states of Co-dioxolene couple, which is consistent with the onset of a VT transition.\(^\text{16}\)

![Normalized diffuse reflectance spectrum](image_url)

**Figure 4-14.** Normalized diffuse reflectance spectrum for 2·EtOH·2 H\(_2\)O plotted as the Kubelka-Munk function.
4.3.7 Magnetic measurements.

Magnetic susceptibility data for 2·EtOH·2H₂O were measured in multiple cycles between 2 K and 340 K to check for the reversibility of the apparent VT process (Figure 4-15). The high value (2.0 cm³mol⁻¹K) of the $\chi_mT$ at low temperature (50 K) suggests a trapped fraction of $hs$-Co$^{II}$-sq species.¹⁷ The abrupt decrease upon cooling from 50 K to 2 K corresponds to the depopulation of the spin-orbit states due to the zero-field splitting (ZFS) in $hs$-Co$^{II}$ ion. The ZFS arises through coupling of the ground state with excited states via spin–orbit coupling.¹⁸ The gradual increase of the $\chi_mT$ value (from 2.0 cm³mol⁻¹K to 3.2 cm³mol⁻¹K) between 50 K and 270 K may also be attributed to the $hs$-Co$^{II}$ fraction with a non-Curie behavior, i.e. with a magnetic moment being temperature-dependent. Above 270 K the $\chi_mT$ starts increasing more sharply, reaching the final value of 4.34 cm³mol⁻¹K. The abrupt increase suggests a VT transition of the remaining $ls$-Co$^{III}$-cat fraction into $hs$-Co$^{II}$-sq. The transition is not completed in the measured temperature range. Subsequent heating-cooling cycles show solvent-dependent nature of the VT transition. Solvent loss shifts the $T_{1/2}$ towards lower temperatures and makes it slightly sharper. A similar phenomenon, of ‘unlocking’ VT transitions by the removal of the solvent has been previously reported for VT coordination complexes, as well as observed in the course of the research for this dissertation (see Chapter 1, Magnetic studies).¹¹
Figure 4-15. Plot of the $\chi T$ versus $T$ for $2\cdot$EtOH$\cdot$2 H$_2$O in cooling (black) and heating-cooling cycles (red).

The relatively high values of the $\chi_m T$ product obtained for $2\cdot$EtOH$\cdot$2H$_2$O require some additional remarks. The $\chi_m T$ values for the high temperature valence tautomers of Co-diox based VT CPs do not usually exceed 3.5 cm$^3$mol$^{-1}$K$^{-1}$. Higher values have previously been observed for only two VT coordination complexes, $[\text{trans-Co}(3,5$-dbdiox)$_2(4$-Br-Py)$_2]$ (4-Br-Py = 4-bromopyridine) reported by Schmidt et al.$^{23}$ and $[\text{trans-Co}(3,5$-dbdiox)$_2(1,2$-bpe)]$·$2\text{MeCN}$·$2\text{H}_2\text{O}$ obtained within this PhD project (see Chapter II). However, the cause of such high values is likely due to the ferromagnetic coupling, which according to DFT calculations performed by Khusniyarow et al. may occur in $[\text{hs-Co}^{II}(\text{sq})_2(\text{NL})_2]$ (NL is a N donor ligand) homologues.$^{24}$ In the case of $2\cdot$EtOH$\cdot$2H$_2$O, the ligands are arranged in a cis manner around the Co center, which most
likely forms antiferromagnetic coupling between $hs$-Co$^{II}$ and two 3,5-dbsq radicals. The unusually high value of the $\chi_m T$ product is likely due to the underestimated molecular weight of the sample and unknown nature of the impurities in the measured material. Therefore, to fully elucidate the magnetic behavior of the $2 \cdot$ EtOH$ \cdot$ 2H$_2$O, the sample should be prepared at the satisfactory level of purity. Nevertheless the shape of the $\chi_m T$ vs $T$ curve can be explained by a predicted magnetic behavior of the $2 \cdot$ EtOH$ \cdot$ 2 H$_2$O compound. Furthermore, the onset of the temperature-induced VT transition found through magnetic measurements on the bulk sample is consistent with the temperature-dependent changes in Co-ligand interatomic distances for a single crystal of $2 \cdot$ EtOH$ \cdot$ 2H$_2$O.

4.3.8 Electron paramagnetic resonance spectroscopy.

The possibility of the photoinduced VT transition in the sample was also investigated by electron paramagnetic resonance (EPR) spectroscopy under light irradiation. EPR studies predict only one signal for ligand organic radical ($S = 1/2$) with g value close to 2.0 for the \{Co$^{III}$(cat)(sq)\} complex. During the VT transition, the complex is converted into \{hs-Co$^{II}$(sq)$_2$\}, where both the semiquinone radical and the $hs$-Co$^{II}$ ion have unpaired electrons. However, \{hs-Co$^{II}$(sq)$_2$\} is EPR silent due to a fast relaxation of $hs$-Co$^{II}$. When a VT complex is being irradiated at low temperatures, the gradual time-dependent decrease of EPR signal intensity indicates a photo-induced transition. $2 \cdot$ EtOH$ \cdot$ 2H$_2$O was investigated by EPR at 5 K, but no changes in the signal size could be seen when the sample was irradiated with wavelengths of 532 nm or 645 nm (Figure 4-16). The results suggested that the system is not undergoing photoinduced VT intraconversion, which is in good agreement with the inverse-energy-gap law proposed by Hauser (see section 1.4.2). Due to the fact that temperature-dependent single-crystal X-ray crystallography
and magnetic studies suggest the beginning of the VT transition above 275 K, the expected degree of photoconversion for the $2\cdot$EtOH$\cdot$2H$_2$O is low.

![EPR spectra](image)

**Figure 4-16.** X-band EPR spectra measured for powder sample of $2\cdot$EtOH$\cdot$2H$_2$O at 5 K before (black) and after irradiation with 532 nm wavelength laser beam (multi-color, following the black line). The after irradiation spectra were measured in 40 intervals (10 sec each).

### 4.4 Concluding remarks.

Two novel CPs have been obtained from employing the flexible tetrapyridyl ligand tpch to connect $\{\text{Co}(3,5\text{-dbdiox})_2\}$ units. Compound 1·2EtOH·15H$_2$O is the second reported 2D Co-dioxolene based coordination polymer, while $2\cdot$EtOH·5H$_2$O demonstrates a rare 1D zig-zag chain topology. Magnetic studies of the compound
2·EtOH·2H₂O suggest a temperature-induced VT transition starting above 250 K, which can be corroborated by electronic spectroscopy and variable-temperature X-ray crystallography. The transition is marginally solvent-dependent. The results of the study show the importance of the linking ligand choice in the pursuit of 2D VT CPs based on \{Co(3,5-dbdiox)₂\} units. The features that should be taken into account are the flexibility of the ligand and the geometry, enabling the accommodation of large Co-diox units. Moreover the twofold role of the tert-butyl groups of the 3,5-dbdiox ligands has been shown. Although the electron-donating nature of these groups provides an appropriate redox potential and causes the VT transition to occur near room temperature, the bulky constitution hinders the formation of higher-dimensional polymeric structures. Although the obtained sample of 2·EtOH·2H₂O was found to not be pure, physical measurements demonstrate a clear evidence of a temperature-induced VT transition between \{[ls-Co^{III}(3,5-dbcat)(3,5-dbsq)]\} and \{[hs-Co^{II}(3,5-dbsq)]₂\} in 2. Complex 1 may potentially be a second 2D VT CP based on Co. Due to time constraints, it was not possible to obtain pure bulk samples of either 1 or 2 within the scope of this PhD, however the promise of these compounds from preliminary characterization is sufficient, and synthesis and full characterization of bulk samples of both compounds should be pursued vigorously as a direct follow-up to this thesis. Additionally, the possibility of employing non-substituted dioxolene ligands to avoid steric hindrance arising from the bulky tert-butyl groups (preventing formation of a 2D CP) could be explored in the future.
4.5 References.


CHAPTER V

Valence tautomeric and spin crossover coordination complexes linked by 4-pyridyl-2,2’:6’,2”-terpyridine.

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### 5.1 Introduction.

As mentioned previously (Chapter 1, section 1.3), 2,2':6',2''-terpyridine (terpy) is a ligand widely used in coordination chemistry, often forming SCO complexes with Fe$^{2+}$ and Co$^{2+}$. The attachment of a pyridyl ring in the 4’ position of the terpy makes it an interesting linker for CPs, in which it can act as a tridentate or monodentate ligand, creating an appropriate coordination environment for both Co$^{II}$ SCO and Co-diox based VT coordination complexes. The aim of this project was to explore possibilities of employing 4-pyridyl-2,2':6',2''-terpyridine (pterpy) in Co-based CPs, with the ultimate goal of combining VT and SCO properties in one compound. The synthetic strategies employed were based on compounds previously reported in the literature.

Two linking modes of the pterpy ligand can be distinguished. In the first mode, the coordination sphere of every cobalt center includes three N atoms from the terpy moiety of the pterpy ligand and one N atom from the 4-pyridyl ring of the second pterpy, leaving two coordination positions for other ligands (Scheme 5-1 a). The second mode assumes two different coordination environments for alternating octahedral metal centers. The first one is surrounded by six N atoms from terpy groups of two different pterpy ligands, the second one is coordinated by N atoms of 4-pyridyl groups of two different pterpy ligands and four other positions are available for other ligands (Scheme 5-1 b).
The previously described (Section 1.8) Co SCO CPs reported by Hayami et al. correspond to the network type presented in the Scheme 5-1a. In \{[Co(pyterpy)Cl]_{\infty} \cdot \text{MeOH}\} the coordination sphere of the cobalt center is completed by two Cl\(^{-}\) anions in a \textit{trans} position (Figure 1-13). This type of geometry does not allow synthesis of a Co-diox based 1D VT CP. Since dioxolene is a bidentate ligand, in order to connect 1:1 Co:diox units pterpy needs to coordinate to Co with a \textit{cis} disposition. In the literature, there has been one crystal structure of a Co CP incorporating pterpy in this way. Hayami \textit{et al.} reported \([\text{Co(pyterpy)(SO}_4] \cdot \text{MeOH} \cdot \text{EtOH} \cdot \text{H}_2\text{O}\) which can be obtained by a reaction of pterpy and CoSO\(_4\) in a mixture of MeOH and EtOH (Figure 5-1). The compound forms a 1D zig-zag chain, where SO\(_4^{2-}\) coordinates to Co\(^{2+}\) with two oxygen atoms in \textit{cis} positions. The chains run along \textit{c} axis creating zig-zag channels filled by crystallization solvent.
Figure 5-1. Packing of [Co(pyterpy)(SO$_4$)]·MeOH·EtOH·H$_2$O. Hydrogen atoms and solvent molecules omitted for clarity.\(^{6}\)

The supramolecular packing of [Co(pyterpy)(SO$_4$)]·MeOH·EtOH·H$_2$O determines its host-guest exchange properties. Crystallization solvent molecules can be removed from the compound by heating, and consequently water molecules from the air are being incorporated in the structure resulting in [Co(pyterpy)(SO$_4$)]·5H$_2$O. The temperature dependence of the $\chi mT$ product was obtained between 2 K and 300 K revealing that both compounds stay in $hs$-Co$^{II}$ in the whole measured temperature range. The room temperature $\chi mT$ values (2.70 and 2.50 cm$^3$mol$^{-1}$K, respectively) are higher than spin-
only values for $hs$-$Co^{II}$, which can be accounted for the spin-orbit coupling in the octahedral $hs$-$Co^{II}$. The Curie-Weiss law was applied to the range of 100-300 K and Curie constants were calculated as 2.74 cm$^3$ K mol$^{-1}$ and 2.75 cm$^3$ K mol$^{-1}$, which stays in agreement with values previously reported for octahedral $hs$-$Co^{II}$.

The second synthetic strategy assumes two types of a coordination sphere around the metal centers. If 3,5-dbdiox were to be incorporated into available coordination positions (Scheme 5-1b), the resulting complex would be a combination of two types of complexes: [Co(pterpy)$_2$]$^{2+}$ and [Co(NL)$_2$(sq)(diox)]. Several complexes with a general formula of [Co(NL)$_2$(sq)(diox)] have been previously found to exhibit VT interconversions and examples have been presented in Chapter I of this dissertation (section 1.2.2). Furthermore, a series of complexes based on [Co(pterpy)$_2$]$^{2+}$ has been recently reported by Dunbar et al. as exhibiting SCO transitions. Change of the counteranion affects packing and short-range interactions within the compound, hence altering its magnetic properties. The compound [Co(pterpy)$_2$][PF$_6$] shows very gradual SCO transition with the $\chi_M T$ curve not reaching a plateau at 390 K (Figure 5-2). The room temperature value of $\chi_M T$ of 1.421(1) cm$^3$ K mol$^{-1}$ corresponds to ca. 56% of $hs$-$Co^{2+}$ fraction ($g = 2.16$). Likewise, the low temperature value of the $\chi_M T$ product suggests incomplete relaxation into $ls$-$Co^{2+}$. When PF$_6^-$ is replaced by a radical TCNQ$^-$ (7,7,8,8-tetracyanoquinodimethane), the SCO transition becomes slightly sharper, and upon cooling to 150 K the complex converts almost completely from $hs$-$Co^{2+}$ into $ls$-$Co^{2+}$ state. The study suggests that $\pi-\pi$ stacking interactions between TCNQ and pyridyl rings of the pterpy distort the Co$^{2+}$ coordination geometry and help to stabilize the $ls$ state (Figure 5-3). A difference between the magnetic behavior could also be seen for two different solvates of [Co(pterpy)$_2$][TCNQ]$_2$. For [Co(pterpy)$_2$][TCNQ]$_2$:DMF·MeOH the SCO starts at lower temperatures and is more gradual than for [Co(pterpy)$_2$][TCNQ]$_2$:MeCN·MeOH (Figure 5-3). As a result, at 390 K, these two
compounds show \( \chi M T \) values equivalent to \( \sim 27\% \) and \( \sim 67\% \) of full \( \text{hs-Co}^{\text{II}} \) population, respectively.

**Figure 5-2.** \( \chi M T \) versus \( T \) for [Co(pterpy)₂][PF₆] (green), [Co(pterpy)₂][TCNQ]₂·DMF·MeOH (blue) and [Co(pterpy)₂][TCNQ]₂·MeCN·MeOH (red).\(^8\)
Two 1 D polymeric compounds constructed according to Scheme 5-1b were previously obtained by Nishikori et al by employing derivatives of acetylacetonate. Acetylacetonate in its anionic keto-form can act as a bidentate O-donor ligand analogous to dioxolene and as such is incorporated in the polymeric structure in a similar manner. [{Co(hfac)$_2$} {Ni(pyterpy)$_2$}]$_2$ and [Co(CNacac)$_2$][Ni(pyterpy)$_2$]SO$_4$.S (hfac = hexafluoroacetyloacetonate, CNacac = 3-cyanocetyloacetonate, S = MeOH and H$_2$O in an unknown ratio) are products of a self-assembly of component complexes in solution. In the first compound, the twisted linkage of the two complexes introduces additional axial chirality, which is enhanced by a chiral network of the incorporated [Co(hfac)$_3$]$^-$ counterions. In [Co(CNacac)$_2$][Ni(pyterpy)$_2$]SO$_4$.S such an effect is not observed since the twisting is smaller and the disorder of solvent molecules results in the racemic
compound. Nishikori presents a detailed crystallographic study using achiral building blocks to create chiral and achiral CPs. An emphasis is put on the fact that while the choice of metal ions and ligands is essential for crystal engineering, guest molecules such as counterions and solvent may have a crucial impact on packing and supramolecular structure of the compound. In the context of this thesis, the paper presents a way to use pterpy as a 1D linker in a manner that opens a possibility to incorporate 1:2 Co:dioxolene complexes. What is more, the authors do not mention any magnetic studies conducted on the compounds, which leaves this area for a further exploration.

5.2 Experimental.

5.2.1 Synthesis of the ligand and the coordination complexes.
All manipulations were performed under aerobic conditions. All the reagents were obtained from commercial sources and were used as received.

4’-(4-pyridyl)-2,2’:6’,2’’-terpyridine (pterpy). The ligand was synthesized according to the literature procedure. A quantity of 2-acetylpyridine (3.0 g, 25 mmol) was added into a solution of 4-pyridylcarboxyaldehyde (1.33 g, 12.5 mmol) in 60 mL of EtOH. Next, KOH pellets (1.9 g, 25 mmol) and NH₃(aq) (36 mL, 30%, 31 mmol) were added to the solution. The mixture was stirred for 4 h at room temperature. Brown powder was collected and washed with EtOH. The product was recrystallized from CHCl₃/MeOH (3:1) to give block-shaped colorless crystals in 52% yield. IR (KBr) (υmax, cm⁻¹): 3051(C–H, arom); 1476–1593(C=C, arom); 1395(C=N).¹H NMR ([CD₃]₂SO): 9.11 (3H, m), 9.07 (2H, dd), 9.03 (2H, dd), 8.24 (2H, tt), 8.15 (2H, dd), 7.72 (2H, td), 7.64 (1H, s).

[Co(3,5-dbcat)(3,5-dbcath)pterpy] (3). An aqueous solution (1 ml) of Co(OAc)₂·4H₂O (17 mg, 0.067 mmol) was layered over a DMSO (DMSO = dimethylsulfoxide) solution (6 ml) of 3,5-dbcat (15 mg, 0.067 mmol) and pterpy (21 mg, 0.067 mmol). The DMSO and water layers were separated by a buffer layer of DMSO/water (1 ml). After 10 days
dark brownish-orange plate-shaped crystals were formed. A sample for single crystal X-ray diffraction was maintained in contact with the mother liquor to avoid solvent loss and identified as 3·2DMSO·H₂O. The product was isolated by filtration, washed with cold water and air dried, giving a sample of 3·2DMSO·H₂O in 50% yield. Anal. Calcd (%) for C₅₂H₆₉N₄O₇S₂Co (3·2DMSO·H₂O): C, 63.4; H, 7.1; N, 5.7. Found: C, 63.1; H, 6.7; N, 5.9. ESI-MS (CH₃CN) m/z: 221 [catH⁻], 966 [{Co(3,5-dbcat)(3,5-dbcat)terpy}·2DMSO]⁻.

[CoCl₂pterpy]⁺ (4) A MeOH (1 ml) solution of CoCl₂·6H₂O (17 mg, 0.067 mmol) was layered over a DMSO solution (6 ml) of pterpy (21 mg, 0.067 mmol). The methanol and DMSO layers were separated by a buffer layer of DMSO/water (1 ml). A sample for single crystal X-ray diffraction was maintained in contact with the mother liquor to avoid solvent loss and identified as 4·2DMSO. Despite the efforts a clean bulk sample of the compound could not be obtained.

[Co(hfac)₂(H₂O)₂]. The ligand was synthesized according to a literature procedure.¹⁰ A solution of Co(OAc)₂·4H₂O (2.10 g, 8.42 mmol) in H₂O (4 ml) was added to a solution of protonated hfac (2.28 g, 16.08 mmol) in MeOH (20 ml). The solution was heated at 60°C for 30 min with stirring until it turned dark red. The solution was left for a slow evaporation for 5 days to yield an orange microcrystalline product in 65% yield. IR (KBr) (v_max, cm⁻¹): 3405(O-H, water), 1644, 1565, 1538(C=O/C=C), 1486(C-H), 1257(C-C), 1227 (C-F₃).

[Zn(hfac)₂(H₂O)₂]. The ligand was synthesized according to a literature procedure.¹⁰ A solution of ZnOAc·4H₂O (0.91 g, 4.2 mmol) in H₂O (4 ml) was added to a solution of protonated hfac (1.1 g, 8.0 mmol) in MeOH (10 ml). The solution was heated to 60°C for 60 min with stirring. The solution was left for a slow evaporation for 7 days to yield
colorless plate-like crystals in 47% yield. IR (KBr) (υ\text{max}, \text{cm}^{-1}): 3500(O-H, water), 1647,1566, 1540(C=O/C=C), 1488(C-H), 1253(C-C), 1233(C-F). 

\{[\text{Co(pyterpy)}_2\text{Co(hfac)}_2]\} \cdot \text{[Co(hfac)]}_2 \ (5). \text{ The compound was synthesized by a slightly adapted literature procedure.}^{11} \text{ Pterpy (0.12 g, 0.40 mmol) was added to a suspension of the CoSO}_4\cdot\text{H}_2\text{O (0.035 g, 0.20 mmol) in MeOH/H}_2\text{O (50 ml, 4:1) and heated under reflux for 2 h. A resulting dark red solution was filtered and a solution of [Co(hfac)]_2(H_2O)_2 \ (0.40 mmol, 0.20 g) in MeOH (5 ml) was added. The mixture was heated under reflux for another hour and left for a slow evaporation. After 10 days the resulting dark-red crystalline product was obtained. A single crystal of 5 was hand-picked and identified as } \{[\text{Co(pyterpy)}_2\text{Co(hfac)}_2]\} \cdot \text{[Co(hfac)]}_2. \text{ A bulk sample of 5 was collected by filtration, washed with cold methanol and air dried, giving 53% yield. Anal. Calcd (\%) for C_{80}H_{36}N_{8}O_{16}F_{48}Co_4 (5): C, 38.2; H, 1.4; N, 4.5. Found: C, 38.5; H, 1.5; N, 4.2.}

\{[\text{Co(pyterpy)}_2][\text{Zn(hfac)}_2]\} \cdot \text{[Zn(hfac)]}_2 \ (6). \text{ The compound was synthesized by the same procedure as 5. Pterpy (0.12 g, 0.40 mmol) was added to a suspension of the CoSO}_4\cdot\text{H}_2\text{O (0.035 g, 0.20 mmol) in MeOH/H}_2\text{O (50 ml, 4:1) and heated under reflux for 2 h. A resulting dark red solution was filtered and a solution of [Zn(hfac)]_2(H_2O)_2 \ (0.40 mmol, 0.20 g) in MeOH (5 ml) was added. After 10 days the resulting dark-red crystalline product was obtained. A single crystal of 6 was hand-picked and identified as } \{[\text{Co(pyterpy)}_2][\text{Zn(hfac)}_2]\} \cdot \text{[Zn(hfac)]}_2. \text{ A bulk sample of 6 was collected by filtration, washed with cold methanol and air dried, giving 41% yield. Anal. Calcd (\%) for C_{80}H_{36}N_{8}O_{16}F_{48}CoZn_3 (6): C, 38.0; H, 1.4; N, 4.4. Found: C, 38.2; H, 1.5; N, 4.3.}

5.2.2 **Magnetic measurement**

Variable temperature magnetic susceptibility measurements were performed with a Quantum Design MPMS-5 susceptometer, equipped with a 5 T magnet. Data were
collected on powdered, dry crystals with eicosane restraint. Susceptibility data was collected with the magnetic field of 0.1 T. Pascal’s constants were used to estimate the diamagnetic correction for each complex.

5.2.3 Other physical measurements

Elemental analyses were performed by the Campbell Microanalytical Laboratory, Department of Chemistry, University of Otago, New Zealand. Thermogravimetric analyses were performed on a Mettler Toledo thermal analyzer. Infrared spectra (KBr disk) were recorded on a Bruker Tensor 27 FTIR spectrometer. Ultraviolet-visible absorption spectra were measured on a Varian Cary50 Bio UV-visible spectrometer and diffuse reflectance spectra were measured on a Thermo Scientific-Evolution 220 UV-Visible spectrophotometer. The powder X-ray diffraction pattern was acquired at 130 K on an Agilent Technologies SuperNova diffractometer using CuKα radiation (λ = 1.54184 Å), operated at 40 kV and 35 mA; data were collected with 20 angles in the range 5-50°.

5.2.4 X-ray crystallography

X-ray diffraction data for compound 3·2DMSO·2H2O and 6 were collected using synchrotron radiation on the MX1 beamline,12 at the Australian Synchrotron, Victoria, Australia. Datasets for 3·2DMSO·2H2O were collected at 100 K and for 6 were collected at 100 K, 150 K, 200 K, 250 K and 300 K. Data for 4·2DMSO and 5 were collected at 130 K on an Agilent Technologies SuperNova diffractometer using CuKα radiation. All structures were solved using OLEX213 software with the ShelXT14 structure solution program using intrinsic phasing and refined with the ShelXL refinement package using least squares minimization. For 3·2DMSO·2H2O the resulting data suggested twinning, but the Olex2 software was not able to find the twinning law. The relation between the Co centers in the asymmetric unit and the presence of strong unresolved electron density peaks suggested higher symmetry, but the poor quality of the data prevented identification of the correct space group. Moreover, the compound contained disordered solvent. A
satisfactory disorder model of the solvent was not found and therefore the Olex2 Solvent Mask routine was used to mask out disordered electron density. The molecular formula proposed is based on the electron count (325 e⁻ per unit cell). For 5 and 6 the crystals were found to be twinned by merohedry with a BASF (relative batch scale factor) equal to 0.108 and 0.353, respectively.
Table 5-1. Crystallographic data for 3·2DMSO·2H₂O, 4·2DMSO and 5.

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Table 5-2. Crystallographic data for 6 collected at 100 K, 150 K, 200 K, 250 K, 300 K and 350 K.

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5.3 Results and discussion.

5.3.1 Synthesis.

The aim of the project was to synthesize new VT and/or SCO coordination compounds based on Co centers and pterpy aiming at two different connectivities represented by Scheme 5-1a and Scheme 5-1b. The first approach involves a self-assembly reaction of a Co$^{2+}$, 3,5-dbcat$^{2-}$ and pterpy in a 1:1:1 ratio followed by an oxidation of a cobalt center. The main obstacle seems to be associated with the chelating nature of pterpy ligand, which can easily displace other weaklier bound ligands. One way to solve this problem could be to use an excess of the ligand competing with pterpy, in this case 3,5-dbcat$^{2-}$, which has not yielded the target compound [Co(pyterpy)(3,5-dbdiox)]$_\infty$. Similarly, binding one 3,5-dbcat$^{2-}$ to the cobalt center prior to addition of pterpy could also help to obtain the target complex. Since Co$^{III}$-cat complexes tend to undergo rapid oxidation in air, leading to inert Co$^{III}$-cat complexes we tried anaerobic synthesis, in which firstly 3,5-dbcat$^{2-}$ was introduced to the Co$^{2+}$ solution and then followed by the addition of pterpy. A color change of the Co$^{2+}$ solution from pink to blue may indicate either a formation of the 1:1 Co-diox complex or a change from the octahedral to tetrahedral geometry. In each attempt, pterpy added to the reaction mixture in the following step manages to displace 3,5-cat$^{2-}$ and form a [Co(pterpy)$_2$]$^{2+}$ species and, despite several attempts, the target chain could not be obtained. Unfortunately, due to time constraints, a full survey of solvents and concentrations could not be conducted. Instead, two novel compounds based on Co$^{2+}$ and pterpy were obtained and studied. Crystals of mononuclear 3·2DMSO·2H$_2$O grow when Co(OAc)$_2$·4H$_2$O is dissolved in water and the resulting solution is carefully layered over a DMSO solution of both ligands. The compound is not stable in solution and recrystallization attempts from various solvents have been unsuccessful. Nevertheless, a bulk solid sample of 3·2DMSO·2H$_2$O was obtained and characterized by various methods. When the aqueous solution of Co(OAc)$_2$·4H$_2$O is replaced by methanol solution
of CoCl$_2$·4H$_2$O, a new polymorph of the previously reported Co$^{II}$ SCO CP is obtained.$^6$

A pure bulk batch of 4·2DMSO could not be obtained, even after adjusting the synthetic procedure to the compound stoichiometry and removing 3,5-dbcat$^{2-}$ from the reaction mixture. These difficulties partially arise due to the relatively fast solvent exchange occurring in the compound exposed to other organic solvents or moisture in the air. Moreover, the solution also yields crystals of poorly soluble pterpy and, despite many attempts, a full separation of these two types of crystals could not be achieved. Therefore, only the crystal structure of 4·2DMSO is reported herein.

Within the second synthetic approach (Scheme 5-1b), an opportunity to investigate different Co coordination environments within the same 1D CP was explored. Yet again, due to problems with pterpy displacing 3,5-diox in the Co coordination sphere, the target complex $\{[\text{Co}(\text{pyterpy})_2][\text{Co}(3,5\text{-dbdiox})_2]\}$ has not been obtained, either under aerobic or anaerobic conditions. Despite the synthetic setbacks, the polymeric compounds based on [Co(pterpy)$_2$]$^{2+}$ were investigated for possible SCO behavior. Continuing Nishikori’s research$^{11}$ two compounds were obtained $\{[\text{Co}(\text{pyterpy})_2][\text{Co}(\text{hfac})_2]\}$,[Co(hfac)$_3$]$_2$ (5) and $\{[\text{Co}(\text{pyterpy})_2][\text{Zn}(\text{hfac})_2]\}$,[Zn(hfac)$_3$]$_2$ (6). Crystals of both compounds form when MeOH/H$_2$O solutions of [Co(pterpy)$_2$]SO$_4$ and Co(hfac)$_2$·2H$_2$O (or Zn(hfac)$_2$·2H$_2$O) are slowly evaporated over 10 days.

The purity and isostructurality of bulk samples of 5 and 6 were additionally confirmed by collecting their X-ray powder diffraction patterns and comparing them to theoretical patterns generated from X-ray data collected for a single crystal of 5 (Figure 5-4).
5.3.2 Structural studies.

5.3.2.1 [Co(3,5-dbcat)(3,5-dbcatH)terpy·2DMSO·2H₂O (3·2DMSO·2H₂O)]

A crystal structure of 3·2DMSO·2H₂O was collected at 100 K. Compound 3·2DMSO·2H₂O crystallizes in the triclinic P̅1 space group. The asymmetric unit contains two molecules of complex 3, two DMSO molecules and two water molecules (one of which is disordered). The unique feature of 3 is the Co center coordination sphere consisting of three O atoms and three N atoms (Figure 5-5). Typically VT complexes contain either 1:2 or 1:4 Co:O ratio. In 3 one dioxolene ligand coordinates with both oxygen atoms and the other with just one. The non-coordinating oxygen atom is protonated and forms a hydrogen bond with the oxygen of the other dioxolene. The N atoms come from terpy part of the pterpy. Molecules of 3 form layers perpendicular to

![Figure 5.4](image.png)

**Figure 5-4.** Powder diffraction patterns collected for samples of 5 (red) and 6 (orange) in comparison to theoretical powder pattern generated from X-ray data collected for a single crystal of 5 (black).
the $bc$ plane and separated by DMSO molecules (Figure 5-6). The reliability ($R$) factor of the crystallographic data collected for $3\cdot2$DMSO$\cdot2$H$_2$O (Table 5-1) equals 0.14 and is relatively high; nevertheless general trends in the bond distances in the compound will be discussed. The Co-N bond distances stay in range of $1.888(4)$-$1.931(5)$ Å and Co-O bonds in the range $1.865(6)$-$1.942(5)$ Å, which is indicative of $3^+$ oxidation state of cobalt (Table 5-3.).$^{15}$ Intermolecular distances of both dioxolene ligands suggest a catecholate state at 100 K.$^{16}$ Subsequently the MOS values are in range between $-1.89$ and $-2.13$, indicative of the -2 oxidation state of the ligand. SHAPE indices for both Co$^{2+}$ ions in the asymmetric unit equal 0.809-0.868, which indicates minimal distortion from ideal $O_h$ geometry.

![Figure 5-5](image.png)

**Figure 5-5.** The structural representation of 3 in $3\cdot2$DMSO$\cdot2$H$_2$O. Hydrogen atoms omitted for clarity.
Figure 5-6. Packing of 3·2DMSO·2H₂O. Blue color represents layers of 3 and DMSO molecules are represented by an orange color.

Chart 5-1. Atom labelling for dioxolene ligands.
Table 5-3. Selected interatomic distances for 3·2DMSO·2H₂O.

<table>
<thead>
<tr>
<th>Distance (Å) / Parameter</th>
<th>3·2DMSO·2H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co···Co&lt;sup&gt;a&lt;/sup&gt;</td>
<td>7.577</td>
</tr>
<tr>
<td>Co–O</td>
<td>1.888(4)-1.926(4)</td>
</tr>
<tr>
<td>Co–N</td>
<td>1.865(6)-1.936(5)</td>
</tr>
<tr>
<td>O–C&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.363</td>
</tr>
<tr>
<td>C&lt;sub&gt;a&lt;/sub&gt;–C&lt;sub&gt;b&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1.416(8)</td>
</tr>
<tr>
<td>C&lt;sub&gt;b&lt;/sub&gt;–C&lt;sub&gt;c&lt;/sub&gt;, C&lt;sub&gt;a&lt;/sub&gt;–C&lt;sub&gt;f&lt;/sub&gt;&lt;sup&gt;b,c&lt;/sup&gt;</td>
<td>1.398</td>
</tr>
<tr>
<td>C&lt;sub&gt;c&lt;/sub&gt;–C&lt;sub&gt;d&lt;/sub&gt;, C&lt;sub&gt;e&lt;/sub&gt;–C&lt;sub&gt;f&lt;/sub&gt;&lt;sup&gt;b,c&lt;/sup&gt;</td>
<td>1.407</td>
</tr>
<tr>
<td>C&lt;sub&gt;d&lt;/sub&gt;–C&lt;sub&gt;e&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1.396(8)</td>
</tr>
<tr>
<td>MOS&lt;sup&gt;d&lt;/sup&gt;</td>
<td>-1.97</td>
</tr>
<tr>
<td>SHAPE&lt;sup&gt;e&lt;/sup&gt;</td>
<td>0.809, 0.868</td>
</tr>
</tbody>
</table>

<sup>a</sup> Closest Co···Co distance. <sup>b</sup> Averaged distances. <sup>c</sup> See Chart 5-1 for labeling of dioxolene positions. <sup>d</sup> Metrical Oxidation State.<sup>17</sup>

5.3.2.2  [CoCl₂pterpy]ₜₘ₂DMSO (4·2DMSO)

Compound 4·2DMSO crystallizes in the orthorhombic Pccn space group. The equatorial positions in the octahedral Co coordination sphere are filled by three nitrogen atoms of the terpy moiety and one nitrogen atom of the pyridyl moiety from the pterpy ligand,
which creates a 1D chain aligned along the $c$ axis (Figure 5-7). The two axial positions are taken by Cl$^-$ anions. Neighboring [CoCl$_2$pterpy] moieties are twisted with respect to each other, with a torsion angle of approximately 71°. This distinguishes 4·2DMSO from the previously reported [Co(pyterpy)Cl$_2$]·MeOH where all pterpy ligands in a chain are parallel to each other.$^5$ The neighboring chains form π–π stacking interactions between pyridyl rings of pterpy, subsequently forming quasi-2D supramolecular structures (Figure 5-8a). Layers of polymeric [CoCl$_2$pterpy]$_\infty$ chains are separated by layers of DMSO crystallization solvent (Figure 5-8b, Figure 5-8c). At 130 K Co-Cl distances stay in the range 2.4854(5)-2.4737(5) Å and Co-N in the range 2.069(3)-2.165(2) 2.069(3) Å, which are similar values to those reported by Hayami et al.$^5$ This suggests a $hs$-Co$^{2+}$ state of the Co center and does not allow a possibility of SCO transition at higher temperatures. The SHAPE index calculated for the Co$^{2+}$ indicates a high level of distortion from ideal octahedral geometry (Table 5-4).

Figure 5-7. The chain motif of 4 in 4·2DMSO.
Figure 5-8. a) Two neighboring chains of 4 in 4·2DMSO. b), c) Packing scheme of 4·2DMSO.
Table 5-4. Selected interatomic distances for 4·2DMSO.

<table>
<thead>
<tr>
<th>Distance (Å) / Parameter</th>
<th>4·2DMSO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co···Co$^a$</td>
<td>11.307</td>
</tr>
<tr>
<td>Co···Co$^b$</td>
<td>7.834</td>
</tr>
<tr>
<td>Co–Cl</td>
<td>2.4854(5), 2.4737(5)</td>
</tr>
<tr>
<td>Co–N$^c$</td>
<td>2.150, 2.166</td>
</tr>
<tr>
<td>Co–N$^d$</td>
<td>2.069(3), 2.075(3)</td>
</tr>
<tr>
<td>Co–N$^e$</td>
<td>2.165(2), 2.149(2)</td>
</tr>
<tr>
<td>SHAPE$^e$</td>
<td>15.425</td>
</tr>
</tbody>
</table>

$^a$ Closest Co···Co distance in the chain. $^b$ Closest Co···Co distance between different chains. $^c$ For the 4-pyridyl moiety. $^d$ For the central N atom of the terpy moiety. $^e$ For other two N atoms of the terpy moiety.

5.3.2.3 [Co(pyterpy)$_2$Co(hfac)$_2$]$_2$[Co(hfac)$_3$]$_2$ (5)

The structure of 5 was collected at 130 K. Complex 5 crystallizes in the chiral tetragonal $P4_2$ space group and is isostructural with previously reported [Ni(pyterpy)$_2$Co(hfac)$_2$]$_2$[Co(hfac)$_3$]$_2$. The main component consists of a cationic 1D chain comprised of alternating [Co(hfac)$_2$] and [Co(pyterpy)$_2$]$^{2+}$ units, which are positioned with respect to each other in such a way that the torsion angle between the hfac$^-$ plane in [Co(hfac)$_2$] and the terpy plane of [Co(pyterpy)$_2$]$^{2+}$ is approximately 45° (Figure 5-9). The asymmetric unit comprises one {Co(hfac)$_2$} unit, one {Co(pyterpy)$_2$}$^{2+}$ unit and four halves of the [Co(hfac)$_3$] complex. Each unit cell contains four different [Co(pyterpy)$_2$Co(hfac)$_2$] units. Two pairs of molecules related to each other by the 4$_2$
screw axes can be distinguished. One 1D chain pair runs along \(a\) axis, while the other along \(b\) axis. For each pair the chains are related to each other by 2-fold axes parallel to the \(c\) axis, which means they run in the opposite directions to each other (Figure 5-10). The charge of the polymeric network is balanced by \(\text{Co(hfac)}_3^-\) anions, which reside in channels between the chains. The presence of three identical bidentate ligands confers optical isomerism, in every four \(\text{Co(hfac)}_3^-\) units one has a \(\Delta\) and three have \(\Lambda\) configuration (Figure 5-11). One of the hfac chelate rings lies flat on the 2-fold axis, while the other two are related to each other by that axis. The anionic complex moieties fill the channels in such a way that every second channel is filled only with \(\Lambda\) units and the other with 1:1 \(\Delta/\Lambda\) units (in contrast to one channel filled with only \(\Delta\) and the other with 1:1 \(\Delta/\Lambda\), reported by Nishikori et al., which may suggest that this effect is random and dependent on the crystal chosen for the measurement) (Figure 5-12). This anionic network is also chiral.

**Figure 5-9.** The chain motif in 5. Hydrogen atoms omitted for clarity.
Figure 5-10. Packing schemes of 1D in 5.

Figure 5-11. Structural representations of counterions in 5, Δ-[Co(hfac)$_3$] (left) and Λ-[Co(hfac)$_3$] (right). Hydrogen atoms omitted for clarity.
Figure 5-12. Packing scheme of 5. Moeities of [Co(pyterpy)$_2$Co(hfac)$_2$]$_\infty$ chains (black), Λ-[Co(hfac)$_3$] - green and Δ-[Co(hfac)$_3$] (red).

Both Co$^{II}$ cations in the 1D chain have octahedral coordination, however, the geometry of the pterpy ligand enforces significant distortion on the [Co(pyterpy)$_2$]$^{2+}$ unit. The SHAPE parameters, describing how close complex geometry reflects the ideal polyhedron, were calculated for all Co centers. For [Co(pyterpy)$_2$Co(hfac)$_2$] the parameter equals 2.163 and for all units with hfac the values range between 0.027 and 0.209. The other difference caused by the geometry of the ligand is evident from the Co-N and Co-O bond lengths (Table 5-5). The Co-O bond lengths for all Co-hfac complexes are in the 2.032(13)-2.085(11) range, which is consistent with previously reported values for hs-Co$^{II}$ systems. The [Co(pyterpy)$_2$]$^{2+}$ ion shows significant variances in length for
different bonds around the Co center. The equatorial Co-N bond lengths are significantly elongated, while the axial bonds are much shorter. As discussed before for other Co-bis(terpyridine) systems, those changes are not only a consequence of the ligand geometry but also Jahn-Teller effect arising from the remaining $e_g$ electron in the $ls$ state.\(^1\)

**Table 5-5.** Selected interatomic distances for 5.

<table>
<thead>
<tr>
<th>Distance (Å) / Parameter</th>
<th>[Co(pyterpy)$_2$Co(hfac)$_2$]$_3$[Co(hfac)$_3$]$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co···Co(^a)</td>
<td>10.943</td>
</tr>
<tr>
<td>Co–O</td>
<td>2.032(13)-2.085(11)</td>
</tr>
<tr>
<td>Co–N(^b)</td>
<td>2.040(9)-2.115(11)</td>
</tr>
<tr>
<td>Co–N(^c)</td>
<td>1.867(9), 1.872(8)</td>
</tr>
<tr>
<td>SHAPE(^d)</td>
<td>2.163(^e), 0.027-0.209(^f)</td>
</tr>
</tbody>
</table>

\(^a\) Closest Co···Co distance in the chain.\(^b\) Equatorial.\(^c\) Axial.\(^d\) The closer the index to zero, the less distortion from $O_h$ symmetry.\(^19\)

5.3.2.4 [Co(pyterpy)$_2$Zn(hfac)$_2$]$_n$[Zn(hfac)$_3$]$_2$ (6)

Compound 6 is isostructural with 5, hence a detailed description of the structure will not be provided in this section. However, the structure of 6 was collected at 100 K, 150 K, 200 K, 250 K, 300 K and 350 K and changes in bond lengths with temperature were analyzed to investigate the possibility of a SCO transition in the [Co(pyterpy)$_2$]$^{2+}$ unit (Table 5-6.). The equatorial Co-N distances in SCO complexes with N-donor chelating ligands usually undergo only small temperature-dependent changes and are much less conclusive for determining the $T_c$ of the SCO transition.\(^20\) In the case of 6 investigated here, the thermally-dependent changes in the equatorial Co-N bond lengths are quite
small, except for a small decrease between 150 and 200 K, larger increase between 250 K and 300 K and then a further decrease at 350 K (Figure 5-13). This type of structural rearrangement with a local decrease of some of the Co-O/N, just before the transition (between 150 K and 200 K) and bigger increase, has been reported previously in other Co-based spin crossover complexes.20 The axial Co-N distances present a more consistent increase above 200 K with a more abrupt change between 300 K and 350 K, suggesting a possible SCO above 300 K, however overall these changes cannot be treated as a definitive evidence of spin changes on the Co center. The data collected at 350 K is much poorer quality, with large thermal expansion and atomic displacement parameters, which suggests that the crystal may be already decomposing. The distances between the metal centers within the chain also increase with the temperature, from 10.969 Å at 100 K to 11.059 Å at 350 K. Finally, unlike the observation for 2·EtOH·5H₂O (Table 4-3, Chapter 4) the SHAPE index for the analyzed Co²⁺ in 6 does not change significantly with the temperature.

Table 5-6. Selected interatomic distances for 6.

<table>
<thead>
<tr>
<th>Distance (Å) / Parameter</th>
<th>[Co(pyterpy)₂Zn(hfac)₃]⁺[Zn(hfac)₃]₂⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (K)</td>
<td>100</td>
</tr>
<tr>
<td>Co···Zn</td>
<td>10.969</td>
</tr>
<tr>
<td>Co–N</td>
<td>2.054(9)-2.121(9)</td>
</tr>
<tr>
<td>Co–N</td>
<td>1.897(6),1.905(6)</td>
</tr>
<tr>
<td>SHAPE</td>
<td>2.375</td>
</tr>
</tbody>
</table>

*Closest Co···Zn distance in the chain. *Equatorial. *Axial. *The closer the index to zero, the less distortion from O₈ symmetry. Values for [Co(pyterpy)₂]²⁺ unit. 19
5.3.3 Thermogravimetric studies.

5.3.3.1 Compound [Co(3,5-dbcat)(3,5-dbcatH)terpy·2DMSO·H₂O (3·2DMSO·H₂O)

The TGA desolvation curve of 3 is in good agreement with elemental analysis. The profile shows a first mass loss of ~2% below 375 K, which can be attributed to the one water molecule. A further decrease between 375 K and 510 K corresponds to two DMSO molecules equivalent to around 15% of the compounds molecular mass. Above 510 K the organic part of the complex starts decomposing.
5.3.3.2 Compounds \([\text{Co(pyterpy)}_2\text{Co(hfac)}_2]_\infty[\text{Co(hfac)}_3]_2 \quad (5)\) and \([\text{Co(pyterpy)}_2\text{Zn(hfac)}_2]_\infty[\text{Zn(hfac)}_3]_2 \quad (6)\)

The TGA profile for 5 (Figure 5-15) shows no significant mass loss below 590 K, which agrees with the solvent-free formula derived from crystallographic studies and elemental analysis. The first significant decrease of about 54% can be attributed to the mass of two [Co(hfac)_3]⁻ counterion complexes. The TGA profile for 6 is very similar to that of 5 with the only change being a first mass loss occurring ca. 583 K.
5.3.4 Infrared spectroscopy

The infrared spectra of 3·2DMSO·H₂O, 5 and 6 were collected at room temperature as pressed KBr pellets.

5.3.4.1 Compound 3·2DMSO·H₂O

The infrared spectrum of 3·2DMSO·H₂O is presented in Figure 5-16. The presence of the 3,5-diox ligand can be immediately confirmed by an aromatic ring C-H stretch at 2952 cm⁻¹. Further, we can find the information on the oxidation state of the ligand in the 1500-1200 cm⁻¹ region. The ring stretching C-C mode for the catecholate form of the ligand can be seen at 1476 cm⁻¹. In addition, the band at 1438 cm⁻¹ stays in a good agreement with values characteristic for the ring stretching C-C mode reported for 3,5-dbsq⁻ species. Finally, a sharp band at 1240 cm⁻¹ can be attributed to the C-O stretching frequency in
3,5-dbcat\(^2\) coordinated to a cobalt ion. Bands corresponding to the presence of pterpy in the complex can be found at 3052 cm\(^{-1}\) (C-H aromatic), between 1594-1547 cm\(^{-1}\) (C=C aromatic) and at 1410 cm\(^{-1}\) (C=N aromatic).\(^5\)

![Infrared spectrum for 3·2DMSO·H\(_2\)O collected at room temperature.](image)

**Figure 5-16.** Infrared spectrum for 3·2DMSO·H\(_2\)O collected at room temperature.

### 5.3.4.2 Compounds

\([\text{Co(pyterpy)}_2\text{Co(hfac)}_2]_\infty[\text{Co(hfac)}_3]_2\) (5) and 

\([\text{Co(pyterpy)}_2\text{Zn(hfac)}_2]_\infty[\text{Zn(hfac)}_3]_2\) (6).

The spectra of isomorphous 5 and 6 are essentially identical and therefore are discussed together. For both complexes the spectra dominated by bands corresponding to the hfac\(^-\)
ion. In particular, a band at 1642 cm\(^{-1}\) can be attributed to C=O stretch and 1267 cm to C-F\(_3\) stretch.\(^{22}\) Bands at 1612 and 1554 cm\(^{-1}\) can correspond to C=C stretches in hfac\(^{-}\) as well as C=C (aromatic) in pterpy. Characteristic peaks for both ligands can be found in the fingerprint region, 792 cm\(^{-1}\) for pterpy and 670 cm\(^{-1}\) for hfac\(^{-}\)\(^{5,22}\).

![Infrared spectra](image-url)

**Figure 5-17.** Infrared spectra collected at room temperature for 5 (red) and 6 (orange).

### 5.3.5 Electronic spectroscopy

#### 5.3.5.1 Compound 3·2DMSO·H\(_2\)O

The UV-Vis diffuse reflectance spectrum for 3·2DMSO·H\(_2\)O was collected at room temperature as a KBr solid solution. The normalized Kubelka-Munk function is presented in Figure 5-18. The bands at 286 nm and 338 nm can be assigned to the intraligand
transitions within pterpy ($\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$), while the band at 310 nm could correspond to $\pi \rightarrow \pi^*$ transition within the dioxolene ligand.\textsuperscript{23,24} We expect three bands characteristic for the Co\textsuperscript{III}-catecholate species.\textsuperscript{25,26} The ligand-to-metal-charge-transfer band (from $\pi^*$catecholate orbital) is supposed to appear $\sim$ 350 nm, but cannot be distinguished in the spectrum collected for 3. The band at 408 nm can be attributed to d-d transitions in octahedral Co\textsuperscript{III} complexes. Finally, the broad shoulder between 700-900 nm could relate to the symmetry forbidden ligand-to-metal-charge-transfer in Co\textsuperscript{III}-cat chromophores. The interesting feature is the presence of a very broad band centered at 518 nm. A band of this wavelength is not expected for a Co\textsuperscript{III}-cat\textsuperscript{26} or Co\textsuperscript{III}-pterpy complex.\textsuperscript{24} The band could be a manifestation of a small Co\textsuperscript{II}-sq fraction in the compound, meaning 3·2DMSO·H\textsubscript{2}O may be undergoing some VT transition at room temperature. The peak could correspond to metal-to-ligand charge transfer band from a $d$ orbital of the Co\textsuperscript{II} center to $\pi^*$ orbital of the dioxolene ligand.\textsuperscript{26} Another interpretation could be that the band corresponds to a charge transfer band on Co\textsuperscript{II}-pterpy complexes.\textsuperscript{27} All interpretations suggest a fraction of Co\textsuperscript{II} present in the complex in room temperature, which suggests at least a partial VT transition occurring in the complex.
Figure 5-18. Normalized diffuse reflectance spectrum for $3\cdot2\text{DMSO}\cdot\text{H}_2\text{O}$ plotted as the Kubelka-Munk function.

UV-Vis solution spectra were collected at room temperature at a concentration of $1.4\cdot10^{-3}$ M in dichloromethane solution (Figure 5-19). The changes in the spectra relate to gradual decomposition of the complex were monitored by re-collecting the spectra after 15, 25, 35, 45 minutes and after 24 h. The concentration of the solution was adjusted to maximize the absorbance between 350-700 nm. The main two bands that can be seen in solution are at 408 nm and 515 nm. The first may correspond to $d-d$ transitions in Co$^{III}$ complexes$^{25}$ or could be a purely ligand centered band characteristic for semiquinonate species.$^{28}$ The second can be attributed to metal to ligand charge transfer band in Co$^{II}$-sq or Co$^{II}$-pterpy complexes.$^{27}$ Over time, the intensity of both bands decreases, however after 24 h the band at 408 nm can be still seen, while the peak at 515 nm can no longer be distinguished. The experiment confirms decomposition of 3 in dichloromethane.
5.3.5.2 Compounds \([\text{Co(pyterpy)}_2\text{Co(hfac)}_2]_\infty[\text{Co(hfac)}_3]_2\) (5) and \([\text{Co(pyterpy)}_2\text{Zn(hfac)}_2]_\infty[\text{Zn(hfac)}_3]_2\) (6).

The UV-Vis diffuse reflectance spectra for 5 and 6 were collected at room temperature as KBr solid solutions (~3%). Both compounds show bands at the same wavelengths. The normalized Kubelka-Munk functions are presented in Figure 5-20. The peaks at 312 and 330 nm correspond to aromatic bands of the pterpy ligand \((\pi \rightarrow \pi^* \text{ and } n \rightarrow \pi^*)\). Further band are corresponding to the presence of 

\(\text{Co}^{II}\) ions and transitions \(4\text{T}_{1\text{g}}\rightarrow 4\text{T}_{1\text{g}} \text{ Co}^{II}\) (482 nm), \(4\text{T}_{1\text{g}}\rightarrow 4\text{A}_{2\text{g}} \text{ Co}^{II}\) (520) and \(4\text{T}_{1\text{g}}\rightarrow 4\text{T}_{2\text{g}} \text{ Co}^{II}\) (570 nm) \(,\) 

The time-dependence of the UV-Vis spectra of the \(3\cdot2\text{DMSO-H}_2\text{O}\) solution in dichloromethane \((1.4\cdot10^{-3}\ \text{M})\).

**Figure 5-19.** The time-dependence of the UV-Vis spectra of the \(3\cdot2\text{DMSO-H}_2\text{O}\) solution in dichloromethane \((1.4\cdot10^{-3}\ \text{M})\).
Figure 5-20. Normalized diffuse reflectance spectrum for 5 (red) and 6 (orange) plotted as the Kubelka-Munk function.

5.3.6 Magnetic measurements

5.3.6.1 Compound 3·2DMSO·2H2O

Magnetic susceptibility data for 3·2DMSO·2H2O were measured between 2 K and 300 K (Figure 5-21) in two cooling and heating cycles. The $\chi_M T$ value at 300 K equals 0.5 cm$^3$mol$^{-1}$K and upon cooling decreases gradually to 0.15 cm$^3$mol$^{-1}$K. Since 3,5-dbcat$^{2-}$ and Co$^{3+}$ are both diamagnetic, low temperature value of magnetic susceptibility for [Co$^{III}$(3,5-dbcat)(3,5-dbcatH)terpy] is expected to be zero. The higher $\chi_M T$ value could be attributed to a temperature independent magnetism observed previously in Co(III) complexes. Another interpretation is associated with a potential VT transition starting above room temperature, with a wide and slightly decreasing plateau, not unusual for VT
complexes. This interpretation is consistent with solution and solid UV-Vis spectra of 3·2DMSO·2H₂O, which manifest bands characteristic for Co²⁺-sq chromophores. Nevertheless, magnetic measurements need to be conducted at higher temperatures order to confirm this hypothesis.

**Figure 5-21.** Plot of the $\chi_T$ versus $T$ for 3·2DMSO·2H₂O.

5.3.6.2 Compound $\text{[Co(pyterpy)₂Co(hfac)₂]}\cdot\text{[Co(hfac)₃]}_2$ (5)

Magnetic susceptibility measurements for 5 were conducted between 2 K and 360 K (Figure 5-22). The $\chi_M T$ value at low temperature (2 K) is reasonably high, which can be accounted for the fact that along with the $ls$-CoII in the $\text{[Co(pyterpy)}₂]^{2+}$, 5 contains also three $hs$-CoII centers, which makes the system complicated to study. The value of 9
cm³mol⁻¹ K is much higher than the sum of spin-only values (assuming g = 2) of $\chi_MT$ for all the paramagnetic components in 5 (Equation 5-1).

$$\chi_MT = \frac{N\beta^2}{3k} g^2S(S + 1) \cong \frac{1}{8} g^2S(S + 1) \quad (5-1)$$

In the case of high spin octahedral Co¹⁺, spin-orbit coupling and magnetic anisotropy must be taken into account. Elucidation of the magnetic behavior of 5 is very complicated and only the potential SCO properties of the [Co(pyterpy)₂]²⁺ component were investigated. The SCO transition was estimated by eliminating the contribution of two [Co(hfac)_3]⁻ anions from the $\chi_MT$ vs $T$ plot for 5. The values were extracted from the temperature-dependent magnetic measurements performed by Palii et al.¹⁸ and subtracted from the curve collected for 5 (Figure 5-22). The obtained curve shows a gradual decrease from 360 K before reaching a plateau c.a. 250 K. From 100 K to 2 K a more abrupt drop can be observed, due to ZFS and depopulation of spin-orbit states. Although the decrease of $\chi_MT$ product while cooling from 360 K stays in agreement with previously reported $T_c$ for SCO Co¹⁺ complexes, the obtained result of subtraction can only be treated as a motivation for further investigation. Furthermore, the contribution of the [Co¹⁺(hfac)₂] unit in the chain is still present in the curve. In order to remove the contribution of additional Co¹⁺ centers, we decided to synthesize a [Zn¹⁺(hfac)₂] based analog of 5.
Figure 5-22. Plot of the measured $\chi_M T$ versus $T$; measured for 5 (black), values reported by Palii et al for Et₄N[Co^II(hfac)₃] (grey),¹⁸ and a difference between the plot measured for 5 and the plot corresponding to two Et₄N[Co^II(hfac)₃] based on Palii measurements (red circles).

5.3.6.3 Compound [Co(pyterpy)₂Zn(hfac)₂]₉[Zn(hfac)₃]₂ (6)

Magnetic susceptibility measurements for 6 were performed between 2 K and 360 K in cooling and heating cycles (Figure 5-23), to elucidate the magnetic behavior of [Co(pyterpy)₂]²⁺ in 6. The $\chi_M T$ versus $T$ curve shows similar features to the one generated by subtracting values reported by Palii et al for Et₄N[Co^II(hfac)₃] from the curve measured for 5. That is a sudden drop at low temperatures, a plateau between 100 K and 250 K and a gradual increase of the $\chi_M T$ product above 250 K.
Figure 5-23. Plot of the $\chi_M T$ versus $T$ for 6.

The increase is sharper than the one seen in the curve simulated for 5 (Figure 5-22) and agrees with the axial Co-N bond lengths increase presented in Figure 5-13. This suggests a SCO transition between $ls$-Co$\text{II}$ and $hs$-Co$\text{II}$ occurring for [Co(pyterpy)$_2$]$^{2+}$. The decrease of $\chi_M T$ on cooling from 100 K to 2 K is characteristic for $hs$-Co$\text{II}$ complexes related to ZFS. This behavior could possibly arise only due to not all of the Co centers in [Co(pyterpy)$_2$]$^{2+}$ relaxing back to $ls$-Co$\text{II}$ state. Secondly, the $\chi_M T$ value of the plateau at 150 K reaches slightly above 3 cm$^3$mol$^{-1}$K, which is much higher than values reported by Dunbar et al. for [Co(pyterpy)$_2$](PF$_6$)$_2$ and [Co(pyterpy)$_2$](TCNQ)$_2$\^{8} (0.41-0.61 cm$^3$mol$^{-1}$K) and most probably arises from additional paramagnetic component in the compound, other than [Co(pyterpy)$_2$]$^{2+}$ unit. A likely explanation for this result can be the fact that although due to chelating nature of the ligand bis-terpy complexes of transitional metals are expected to be stable, exchange in solution is possible. In 1962 Hogg and Wilkins conducted a comprehensive study on exchange in chelate compounds.
in transitional metals. By using radiochemically pure $[^3]$Hterpyridine they investigated the lability of bis-terpy complexes of various $M^{2+}$ metals of d-block. Interestingly the rate of ligand exchange in $Zn^{2+}$ is so rapid, that obtaining detailed kinetic data was not possible. The exchange rate for $[Co(terpy)_2]^{2+}$ was found to be $40 \cdot 10^{-3}$ min$^{-1}$. The synthesis procedure of 6 follows a procedure proposed by Nishikori and assumes an excess of Co[pterpy]$^{2+}$ salt in relation to Zn(hfac)$_2$$ \cdot $2H$_2$O. Furthermore, crystals of 6 grow slowly, upon gradual evaporation of the solvent and for several days stay in contact with solution of Co[pterpy]SO$_4$. That creates conditions favorable for the exchange of $Zn^{2+}$ and Co$^{2+}$ metals in solution. If some of the zinc centers in $[Zn(hfac)_3]$$_2$ were to be replaced by cobalt centers, it would generate an additional contribution to the magnetic susceptibility data of 6. On account of a comparable number of electrons and similar molecular masses of Co$^{2+}$ and Zn$^{2+}$, the partial replacement of Zn centers by Co would not be clearly seen in X-ray crystallographic studies or elemental analysis.

5.4 Concluding remarks.

Four Co-based coordination compounds, one discrete and three polymeric, were synthesized using the N-donor pterpy ligand. Compound 3·2DMSO·2H$_2$O presents an unprecedented coordination environment for Co switchable coordination complexes, with three O and three N atoms coordinating to the metal center. Spectroscopic data and preliminary results of magnetochemistry suggest a potential VT transition occurring above room temperature. However, the magnetic properties of the compound need further investigation, in particular magnetic susceptibility data should be measured above 300 K in order to confirm the hypothesis of valence tautomeric properties of 3·2DMSO·2H$_2$O and to identify the $T_c$ of the transition. Furthermore, better quality crystallographic data is required. Compound 4·2DMSO is a novel solvate of a compound reported previously and based on the interatomic distances measured at low temperature appears to not show any potential for SCO behavior above 130 K. This result endorses conclusions from
Hayami et al. regarding [Co(pyterpy)X₂] (X = Cl, Br). Cobalt(II) based SCO complexes are very sensitive to guest molecules and change of crystallization solvent can significantly affect their magnetic properties. Studies on 5 and 6 reveal that the center in the [Co(pyterpy)₂]²⁺ component of both compounds most likely undergoes a SCO transition. The phenomenon has not been previously reported for a [Co(pyterpy)₂]²⁺ unit in a coordination polymer and only two Co²⁺ SCO CPs have ever been described in the literature. The high value of the χMT product measured for 6 is consistent with a trapped fraction of hs-Co²⁺ centers. The synthetic procedure of 6 could be modified, by removing the heating step and adjusting the ratio of starting materials to the proposed molecular formula of the compound. However, this approach does not guarantee prevention of any Zn²⁺ ↔ Co²⁺ exchange with mother liquor while the compound crystallizes. The magnetic properties of 6 could also be elucidated by using techniques providing detailed information on percentage of Co and Zn centers in the compound, e.g. metal analysis, XAS/EXAFS or neutron diffraction studies.³²

Finally, due to the time restrictions, the target complexes [Co(pyterpy)(3,5-dbdiox)]∞ and {[Co(pyterpy)₂][Co(3,5-dbdiox)₂]}∞ could not be obtained within this Ph.D. project. The example of 3·2DMSO·2H₂O shows that chelating nature of pterpy ligand does not always prevent incorporation of other ligands into a complex. The second anticipated 1D (Scheme 5-1) chain could be an interesting material to study VT and SCO properties and further efforts should be made to achieve the goal of combing two different magnetic behaviors within one compound. Recently, an inspiring research has been published presenting a good way of connecting two different metal complexes using a click-chemistry approach. Rentschler et al. synthesized click-functionalized single-molecule magnets based on Co and linked them with alkyne-functionalized copper metallacrown complexes into the extended supramolecular structure.³³,³⁴
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CHAPTER VI

Concluding remarks and future work.

The research presented in this thesis was aimed to synthesize novel electronically labile coordination polymers (CPs) based on cobalt centers. Compared to discrete complexes, CPs exhibit additional features, such as increased cooperativity via long-range interactions, which can enable exploration of host-guest interactions and provide new ways of incorporating valence tautomeric (VT) and spin crossover (SCO) properties into real-life devices. The compounds obtained within the scope of this PhD research and described in this thesis represent more than one-third of currently published crystal structures of Co VT CPs (Table 1-2), while polymeric compounds 5 and 6 are new additions to the very small family of Co II SCO CPs (Table 1-3).

The main focus of the work was directed at VT CPs based on ({Co(3,5-dbdiox)2}) systems. Six 1D compounds that exhibit thermally-induced VT transitions were obtained and characterized, four of which also undergo light-induced transitions. Multiple cooling-heating cycles indicate a strong dependence on desolvation processes for temperature-driven interconversions. While solvated compounds undergo a more gradual thermally-induced transition, it appears that a solvent-free (yet crystalline) compound is a good candidate for a molecular material that undergoes a well-defined and reversible transition. In order to compete with a conventional magnetic material this sharp transition should be paired with bistability enabling 'molecular switch' properties. As shown in the research from Ghosh and Costa on Co SCO CPs and from the studies
of Sato et al. on dinuclear VT compounds, short-range interactions such as C-H···π bonds not only stabilize the crystal structure, but also enhance cooperativity effects, resulting in magnetic hysteresis.\textsuperscript{1,2} Therefore a new approach to the synthesis of switchable CPs would be to incorporate building blocks that can generate additional supramolecular interactions. This could be implanted by using neutral linkers that incorporate additional functional groups capable of forming intermolecular interactions like hydrogen bonding or π–π stacking (Chart 6-1 a). Since both \{\text{Co}^{III}(3,5\text{-dbcat})(3,5\text{-dbsq})\} and \{\text{Co}^{II}(3,5\text{-dbsq})_{2}\} VT moieties and the N-donor linking ligands employed to data are neutral, all previously reported VT CPs based on these units are uncharged. Instead, the use of charged ligands (Chart 6-1 b) to link \{\text{Co}(3,5\text{-dbdiox})_{2}\} could open new possibilities for studying counter-ion effects on cooperativity, and, ultimately the nature of the VT transition. Both strategies can also be applied for Co SCO CPs. Alongside the polypyridyl linkers, one should also look at ligands with five-member tetrazole rings. The advantage of this approach over using pyridyl-based molecules may eliminate steric hindrance with the α-proton. Due to the variety of binding modes, 1,2,3-triazole-, 1,2,4-triazole- and tetrazole- based ligands have been widely used in 1D, 2D and 3D coordination complexes, achieving a variety of architectures.\textsuperscript{3,4}
The results presented in Chapters II-IV show that while creating new 1D VT materials appears to be an attainable goal, the synthesis of higher dimensional polymeric compounds still poses substantial challenges. A significant obstacle lies in the steric hindrance of tert-butyl groups of the 3,5-dbdiox ligands, and the way to address it may be by using more flexible linking ligands with longer ‘arms’ that can better accommodate the bulky groups. Secondly, the possibility of using two types of linkers, O-donor bis-dioxolenes and N-donor ligands, has not yet been fully explored, but based on separate research from Dei, Sato and Ruiz-Molina, may be a promising approach to the synthesis of two-dimensional Co CPs.5-8

**Chart 6-1.** Proposed pyridyl and tetrazole based ancillary ligands for future VT and VT/SCO coordination polymers.
In the pursuit of novel VT CPs, compounds based on redox pairs other than Co-diox species should also be considered. The 2D VT CPs based on Mn and nitroxide radical ligands has particularly shown very promising magnetic properties, including a sharp transition around room temperature and a hysteresis of 20 K. Syntheses of similar compounds based on imidazole-based radical ligands can be expected to follow. Moreover, since the polymeric net has a positive charge, this type of CPs provides an opportunity to study the anion-effect on magnetic properties of the material.

Expanding Co VT CPs into three dimensions has so far proved elusive and the group of compounds one could look to for inspiration are 3D FeII SCO CPs. Tetracyanometalate $[\text{M}^{II}(\text{CN})_4]^2-$ (M = Ni, Pd, Pt) employed in 2D and 3D FeII SCO Hoffmann networks demand all equatorial positions at the octahedral metal center to be available for coordination, which cannot be achieved for either 1:1 or 1:2 Co:diox complexes. A better approach might be to employ larger linking ligands, e.g. adamantane with N-donor substituents (Chart 6-1 c) or metalloligands (Chart 6-1 d) that can accommodate large $\{\text{Co}(3,5-$dbdiox)$_2\}$ units. Incorporating other metal complexes could also lead to materials combining different functionalities like VT/SCO compounds. Porphyrins complexes with FeIII have been shown to undergo SCO transitions and functionalizing the porphyrin ligand with N-donor groups may enable connecting $\{\text{Co}(3,5-$dbdiox)$_2\}$ units into infinite array (Chart 6-1 d).

In Chapter V, preliminary studies of new CoII SCO CPs are presented. The magnetic behavior of compound 6 needs further elucidation and studies regarding accurate metal content should be conducted. Nevertheless, it is evident from this work that ligands employed in discrete CoII SCO complexes can be also good candidates for novel polymeric SCO compounds. The derivatives of ligands used in complexes showing
magnetic hysteresis e.g. 3-formylsaicylic acid or 4-terpyridone are ideal for preliminary work.\textsuperscript{11}

Finally, the ultimate goal beyond simply synthesizing switchable CPs is the transfer of their properties into real-life devices. Several ways to transfer VT properties into hybrid molecular electronic devices have been presented in literature.\textsuperscript{12,13} Nanoscale metal-organic particles can be produced from coordination polymers by a fast addition of a poor solvent. Similarly, polymeric chains can be functionalized with groups enabling grafting on gold surfaces or synthesis of liquid crystals.\textsuperscript{14} The promising structures which have been elucidated in this work allow a possibility of adapting the VT and SCO compounds into industrially convenient platforms in the future.
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(12) Vázquez-Mera, N. A.; Novio, F.; Roscini, C.; Bellacanzone, C.; Guardingo, M.;


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Appendices
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- The advisory committee has met and agreed to the inclusion of this publication in the student's thesis
- All of the co-authors of the publication have reviewed the above information and have agreed to its veracity
- 'Co-Author Authorisation' forms for each co-author are attached.

Supervisor's name | Colette Boskovic |
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| Student's contribution (%) | 60% |
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| Volume/page numbers | 55(9), 4141-4151 |
| Status | Published |
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Co-author's name: Colette Boskovic
Co-author's signature: [Signature]
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| Authors                                         | Olga Drath, Robert W. Gable, Giordano Poneti, Lorenzo Sorace, and Colette Boskovic |
| Student’s contribution (%)                      | 70%                                                                                          |
| Journal or book name                            | Crystal Growth&Design                                                                        |
| Volume/page numbers                             | 17(6), 3156-3162                                                                            |
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Co-author’s name: Robert W. Gable
Co-author’s signature: [Signature]
Date (dd/mm/yy): 27/06/2017
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| Co-author’s name | Co-author’s signature | Date (dd/mm/yy) |
| Keith S. Murray | Keith S. Murray | 27/06/2017 |
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Author/s:
Drath, Olga Maria

Title:
Valence tautomerism and spin crossover in switchable cobalt coordination polymers

Date:
2017

Persistent Link:
http://hdl.handle.net/11343/208856

File Description:
complete thesis with appendices

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