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

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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*-butyldioxolene (3,5-dbdiox) ligands has afforded the complexes $[\text{Co}(\text{3,5-dbdiox})_2(\text{tpb})]_\infty$ (**1**) and $[\text{Co}(\text{3,5-dbdiox})_2(\text{tpb})_{0.5}]_\infty$ (**2**). 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 $1 \cdot 3\text{H}_2\text{O}$ and $2 \cdot 9\text{H}_2\text{O}$ both possess the $\{\text{Co}^{\text{III}}(3,5\text{-dbcat})(3,5\text{-dbsq})\}$ ($3,5\text{-dbcat}$ = 3,5-di-*tert*-butylcatecholate; $3,5\text{-dbsq}$ = 3,5-di-*tert*-butyl-semiquinonate) charge distribution at 100 or 130 K, respectively. Variable temperature magnetic susceptibility studies of partially dehydrated $1 \cdot \text{H}_2\text{O}$ 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.¹⁻⁴ 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.⁵ These involve a stimulated intramolecular electron transfer between metal and ligand, affording redox isomers that differ in their charge distribution.⁶ 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.^{7,8} 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 $\{\text{ls-Co}^{\text{III}}(3,5\text{-dbcat})\}$ and high spin Co(II)-semiquinonate $\{\text{hs-}$

$\text{Co}^{\text{II}}(3,5\text{-dbsq})\}$ forms. The VT transitions are most commonly triggered thermally or optically, although pressure,⁹ soft X-ray¹⁰ and magnetic field¹¹ 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.^{12–14} 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 nitrogen-donor ligands forming long chains.^{15–20} To date only two examples of higher dimensional (2D) VT coordination polymers have been reported. One of these employs tetrakis(4-pyridyloxymethylene)methane as a pseudo-tetrahedral 4-connecting node that links $\{\text{Co}(3,5\text{-dbdiox})_2\}$ (3,5-dbdiox= 3,5-di-tert-butyldioxolene) units into a 2D net.²¹ The other very recent example is an unusual manganese-nitronyl-nitroxide two dimensional coordination polymer, which exhibits 20 K hysteresis at room temperature.²²

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 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.^{22–28} In 2012 Wang et al. reported the first facile synthesis and isolation of tpb that did not involve demetallization of a

previously synthesized organo-metallophosphate or coordination polymer.²⁹ This opened a synthetic route to tpb-based coordination polymers in non-acidic environment and with more control of the reaction stoichiometry.²⁹ In the literature compounds tpb acts predominantly as a 4-connecting planar node^{24–28,30,31} or, less commonly, as a 3-connecting t-shaped node, where the fourth pyridyl group does not coordinate.^{30,32} All but one of the reported compounds contain group 11 and 12 metals (Cu, Ag, Zn, Cd), with one only example incorporating Co centers.²⁶ The co-ligands employed in the literature in tpb coordination polymers included cyanide anions,^{30,32} other organic molecules,^{25–27} polyoxometalates,^{25,28} halogen anions,³⁰ sulphides²⁴ and sulphates.³⁰ Given its propensity to form higher dimensional coordination polymers, we decided to investigate tpb for cobalt-dioxolene 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)₂} units.

Chart 1. Linking ligand: 1,2,4,5-tetra(4-pyridyl)benzene (tpb).

2. EXPERIMENTAL

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.²⁹

[Co(3,5-dbdiox)₂tpb]_∞ (1). An ethanol solution (6 ml) of 3,5-dbcath₂ (33 mg, 0.15 mmol) and tpb (14 mg, 0.075 mmol) was layered over an aqueous solution (1 ml) of Co(OAc)₂·4H₂O (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 black-greenish needle-shaped crystals were formed. A sample for single crystal X-ray diffraction was maintained in contact with mother liquor to avoid solvent loss and identified as **1**·3H₂O. The product was isolated by filtration, washed with cold ethanol and air-dried, giving a partially dehydrated bulk sample of **1**·H₂O in 40% yield. Anal. Calcd (%) for C₅₄H₆₀N₄O₅Co (**1**·H₂O): C, 71.7; H, 6.7; N, 6.2. Found: C, 71.7; H, 6.8; N, 6.2. Selected IR (cm⁻¹): 2950 (vs), 1615 (vs), 1592 (m), 1459 (s), 1385 (m), 1357 (m), 1283 (m), 1208 (m), 1097 (m), 1081 (s), 1067 (m), 988 (vs).

{Co(3,5-dbdiox)₂tpb_{0.5}}_∞ (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-dbcath₂ (33 mg, 0.15 mmol) and tpb (8.0 mg, 0.038 mmol) was layered over an aqueous solution (1 ml) of Co(OAc)₂·4H₂O (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**·9 H₂O. 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 CuK α radiation ($\lambda = 1.54184$ 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**·3H₂O were collected at 100 K, using synchrotron MoK α radiation on the MX1 beamline,³³ at the Australian Synchrotron, Victoria, Australia. Data for **2**·9H₂O were collected at 130 K on an Agilent Technologies SuperNova diffractometer using CuK α radiation. Using OLEX2,³⁴ both structures were solved with the ShelXT³⁵ structure solution program using direct methods and refined with the ShelXL 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 OLEX2 Solvent Mask routine³⁶ 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.

Table 1. Selected crystallographic data for **1**·3H₂O and **2**·9H₂O.

Parameter	1 ·3H ₂ O	2 ·9H ₂ O
Formula	C ₅₄ H ₆₄ N ₄ O ₇ Co	C ₄₁ H ₆₇ N ₂ O ₁₃ Co

Formula weight (g/mol)	940.04	854.91
Crystal system	triclinic	monoclinic
Space group	<i>P</i> -1	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	9.935(2)	18.088(2)
<i>b</i> (Å)	10.675(2)	12.0291(16)
<i>c</i> (Å)	12.011(2)	42.985(4)
α (°)	79.73(3)	90
β (°)	75.45(3)	93.856(9)
γ (°)	85.13(3)	90
<i>V</i> (Å ³)	1212.2(5)	9331.7(19)
<i>Z</i>	1	8
<i>T</i> (K)	100	130
ρ_{calc} (gcm ⁻³)	1.222	0.986
μ (mm)	0.403	3.145
Reflections measured	20556	8987
Unique reflections	5225	3695
<i>R</i> _{int}	0.0787	0.0823
<i>R</i> ₁ <i>w</i> ^a	0.0624	0.0628
<i>wR</i> ₂ ^b	0.1781	0.1583
Goodness-of-fit on <i>F</i> ²	1.090	0.953

^a $I > 2\sigma(I)$, ^b F^2 , all data

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 $\chi_M = M_M/H$, where M_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.³⁷ 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⁻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⁻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 *in situ* formation of tpb. Thus, tpb was synthesized and isolated according to the method of Wang *et al.*²⁹ prior to reaction with the cobalt and dioxolene co-ligands. A crystalline sample of compound **1**·3H₂O 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-dbcac²⁻ ligand and cobalt(II) metal center, which most likely follows ligand coordination to the relatively labile cobalt(II) ion. Compound **1**·3H₂O crystallizes cleanly and a pure bulk sample can be isolated in moderate yield. The dried compound undergoes partial dehydration to give **1**·H₂O 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**·H₂O is in good agreement with the pattern calculated from the single crystal data measured for **1**·3H₂O, 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) and thereby favor the tpb acting as a 4-connecting node, dark green plate-shaped crystals of complex **2** co-crystallize as a minor product with **1**. The crystals of both compounds are very small and difficult to distinguish by eye. Efforts to obtain a pure bulk sample of complex **2** involved controlled variation of crystallization temperature and reactant stoichiometry, as well as employing different crystallization solvents. However, it was not possible to obtain a pure bulk sample of **2** for physical measurements and therefore we report only the crystallographic data for this compound.

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**·3H₂O and **2** in **2**·9H₂O are presented in Figure 1. The asymmetric units of the compounds are available in Figure S2. Compound **1**·3H₂O crystallizes in the triclinic space group P $\bar{1}$. The asymmetric unit consists of

half of the cobalt atom located on the inversion center, one 3,5-dbdiox ligand and half of the tpb ligand and one and a half solvent water molecules. The coordination complex **1** is a 1D chain coordination polymer with $\{\text{Co}(3,5\text{-dbdiox})_2\}$ units linked through *trans*-disposed tpb nitrogen atoms, with tpb acting as a 2-connecting linker. Compound **2**·9H₂O crystallizes in the monoclinic *C2/c* space group and the asymmetric unit contains a complete $\{\text{Co}(3,5\text{-dbdiox})_2\}$ moiety and half of a tpb ligand. The Co centers in **2** are linked through *cis*-disposed nitrogen atoms of 4-connecting tpb linkers to give a 1D ribbon coordination polymer.

Figure 1. Structural representation of the coordination polymers **1** (top) and **2** (bottom) emphasizing the chain motif of **1** in **1**·3H₂O and the ribbon motif of **2** in **2**·9H₂O. Color code: Co, cyan; O, red; N, blue and C, black. Hydrogen atoms and solvent molecules omitted for clarity.

Selected interatomic distances and angles for **1**·3H₂O and **2**·9H₂O 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**·3H₂O and **2**·9H₂O lie within the range 1.871(5)-1.905(5) Å and the Co-O distances are between 1.921(3) and 1.947(7) Å, which is indicative of low spin cobalt(III) at the temperature of data collection.³⁸ The dioxolene C-O bond lengths are in 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.^{39,40} 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.^{41,42} This parameter correlates the bond distances with the valence of the dioxolene ligand. The values obtained are all are 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 2.1⁴³ 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-dbcate)(3,5-dbsq)] units connected by tpb linker into 1D chains.

Table 2. Selected interatomic distances, angles and other parameters for **1**·3H₂O and **2**·9H₂O.

Distance (Å) / Parameter	1 ·3H ₂ O	2 ·9H ₂ O
Co···Co ^a	9.935(2)	9.297(2) ^c , 12.029(3) ^d
Co···Co ^b	12.011(2)	13.479(2)
Co–O	1.887(2), 1.882(2)	1.905(5), 1.874(5), 1.871(5), 1.901(5)
Co–N	1.921(3)	1.935(7), 1.947(7)
O–C	1.324(4), 1.328(4)	1.316(9), 1.314(9), 1.312(9), 1.348(9)

C _a –C _b ^e	1.429(4)	1.400(1),
C _b –C _c , C _a –C _f ^e	1.398(5), 1.412(4)	1.416(1), 1.417(1)
C _c –C _d , C _e –C _f ^e	1.395(4), 1.384(5)	1.374(1), 1.404(1)
C _d –C _e ^e	1.418(5)	1.411(1)
MOS ^f	-1.51	-1.57, -1.59
SHAPE Index (<i>O_h</i>) ^g	0.055	0.146

^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 labelling of dioxolene positions. ^f Metrical Oxidation State.^{41,42} ^g The closer the index to zero, the less distortion from *O_h* symmetry.⁴³

Chart 2. Co···Co distances in 2·9H₂O.

Chart 3. Atom labelling for dioxolene ligands.

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.^{24–32} 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 {Co(3,5-dbdiox)₂} 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 opposite 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°. ³² 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.

Figure 2. Eclipsed (top) and staggered (bottom) conformations of the tpb ligand evident in **1** and **2**.

The co-synthesis of two distinctive compounds differing in the conformation of the tpb ligand has been reported twice previously. Han *et al.* described two co-crystallizing supramolecular isomers, presenting 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 co-crystallized 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.³² 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 towards 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 towards 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.

Figure 3. Crystal packing diagram for $1 \cdot 3\text{H}_2\text{O}$ (left) and $2 \cdot 9\text{H}_2\text{O}$ (right).

3.3. Thermogravimetric Analysis. The thermogravimetric analysis data for partially dehydrated $1 \cdot \text{H}_2\text{O}$ were measured between 298 K and 800 K under constant N_2 flow (Figure S4). The compound rapidly loses 2% of the mass upon exposure to the N_2 flow, which corresponds to complete dehydration of $1 \cdot \text{H}_2\text{O}$. 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 part component.

3.4. Infrared Spectroscopy. An infrared spectrum for compound $1 \cdot \text{H}_2\text{O}$ was obtained as a pressed KBr disc (Figure S5). A band characteristic of the $\nu(\text{CN})$ 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.⁴⁴ Another characteristic

band associated with the tpb ligand is very strong band at 823 cm^{-1} (819 cm^{-1} for the free ligand) related to the arene $\nu(\text{CH})$ 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-dbcate²⁻ can be observed at 1358 cm^{-1} and 1283 cm^{-1} , while the band at 1474 cm^{-1} corresponds to the $\nu(\text{CO})$ of the 3,5-dbsq.⁴⁰

3.5. Electronic Spectroscopy. An ultra violet-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 ($^1A_{1g} \rightarrow ^1T_{1g}$) associated with low spin octahedral Co(III).⁴⁵ A broad band centered at 750 nm corresponds to a ligand to metal charge transfer (LMCT) transition of a Co(III)-catecholato chromophore.⁴⁶ Moreover the spectral pattern between 470 and 670 nm is suggestive of a Co(II)-semiquinone chromophores and d $\rightarrow$ π^* metal to ligand charge transfer (MLCT) transitions. Overall, the room temperature ultra violet-visible spectrum is consistent with **1**·H₂O being comprised of a mixture of [Co^{III}(3,5-dbcate)(3,5-dbsq)] and [Co^{II}(3,5-dbsq)₂] valence tautomers.^{47,48}

Figure 4. Normalized diffuse reflectance spectrum for **1**·H₂O plotted as the Kubelka-Munk function.

3.6. Magnetic and photomagnetic measurements. Magnetic susceptibility data (Figure 5) were measured for **1**·H₂O in multiple cycles between 2 K 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 $\chi_m T$ for a {*ls*-Co^{III}(3,5-dbcac)(3,5-dbsq)} moiety is 0.38 cm³mol⁻¹K; 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*-Co^{II} fraction, which has been previously observed for a number of VT cobalt-dioxolene compounds.^{49,50} The very gradual increase from 0.56 cm³mol⁻¹K to 0.64 cm³mol⁻¹K observed in the 7-270 K range is also consistent with the presence of a small amount of *hs*-Co^{II}, which does not obey Curie law.⁵¹ Above 280 K a more rapid increase ensues, reaching a value of 0.76 cm³mol⁻¹K 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*-Co^{II}(3,5-dbsq)₂} species. Considering that the high temperature $\chi_m T$ values typically observed for {*hs*-Co^{II}(3,5-dbsq)₂} valence tautomers are up to 3.75 cm³mol⁻¹K,^{2,47} the observed transition is far from complete at 360 K. The relatively high VT transition temperature is not uncommon for VT coordination polymers⁵² and may be due to partial collapse of the 3D structure upon dehydration sterically hindering the expansion in molecular volume associated with a VT transition.⁴⁰ 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.

Figure 5. Plot of $\chi_m T$ versus T for $1 \cdot \text{H}_2\text{O}$.

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*⁵³ or by measuring the decay of the metastable state at fixed temperature.⁵⁴ 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.⁵⁵

4. CONCLUDING REMARKS

The combination of the tpb ligand and $\{\text{Co}(\text{3,5-dbdiox})_2\}$ 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 tpb acting as 2-connecting ligand, while complex **2** is a rare example of a 4-connecting tpb with a staggered conformation of the pyridyl groups. Magnetochemical, structural and spectroscopic studies suggest that compound **1**·H₂O can be formulated as $\{ls\text{-Co}^{\text{III}}(3,5\text{-dbcat})(3,5\text{-dbsq})\}$ below 300 K, with an incomplete thermally-induced VT transition to a $\{hs\text{-Co}^{\text{II}}(3,5\text{-dbsq})_2\}$ species commencing above 300 K.

ASSOCIATED CONTENT

Supporting information. The Supporting Information is available free of charge on the ACS Publication website.

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

Accession Codes

CCDC 1522817 and 1522818 contain the supplementary crystallographic data for **1**·3H₂O and **2**·9H₂O, respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Notes

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REFERENCES

- (1) Sato, O. *Nat. Chem.* **2016**, 8, 644.
- (2) Sato, O.; Tao, J.; Zhang, Y.-Z. *Angew. Chem. Int. Ed. Engl.* **2007**, 46, 2152.
- (3) *Spin-Crossover Materials*; Halcrow, M. A., Ed.; John Wiley & Sons Ltd: Chichester, 2013.
- (4) Chorazy, S.; Stanek, J. J.; Nogaś, W.; Majcher, A. M.; Rams, M.; Koziel, M.; Juszyńska-Gałązka, E.; Nakabayashi, K.; Ohkoshi, S.; Sieklucka, B.; Podgajny, R. *J. Am. Chem. Soc.* **2016**, 138, 1635.
- (5) Evangelio, E.; Ruiz-Molina, D. *Eur. J. Inorg. Chem.* **2005**, 2005, 2957.
- (6) Tezgerevska, T.; Alley, K. G.; Boskovic, C. *Coord. Chem. Rev.* **2014**, 268, 23.
- (7) Boskovic, C. In *Spin-Crossover Materials*; Halcrow, M. A., Ed.; John Wiley & Sons Ltd:

Chichester, 2013; pp. 203–224.

- (8) Dei, A.; Sorace, L. *Appl. Magn. Reson.* **2010**, *38*, 139.
- (9) Roux, C.; Adams, D. M.; Itie, J. P.; Polian, A.; Hendrickson, D. N.; Verdaguer, M. *Inorg. Chem.* **1996**, *35*, 2846.
- (10) Poneti, G.; Mannini, M.; Sorace, L.; Saintavit, P.; Arrio, M.; Otero, E.; Cezar, J. C.; Dei, A. *Angew. Chem. Int. Ed. Engl.* **2010**, *49*, 1954.
- (11) Zvezdin, A. K.; Mischenko, A. S. *Los Alamos Natl. Lab. Prepr. Arch. Condens. Matter* **2002**, 1.
- (12) Sciortino, N. F.; Scherl-Gruenwald, K. R.; Chastanet, G.; Halder, G. J.; Chapman, K. W.; Létard, J.-F.; Kepert, C. J. *Angew. Chem. Int. Ed. Engl.* **2012**, *51*, 10154.
- (13) Valverde-Muñoz, F. J.; Seredyuk, M.; Muñoz, M. C.; Znovjyak, K.; Fritsky, I. O.; Real, J. A. *Inorg. Chem.* **2016**, *55*.
- (14) Muñoz, M. C.; Real, J. A. *Coord. Chem. Rev.* **2011**, *255*, 2068.
- (15) Chen, X.; Wei, R.; Zheng, L.; Tao, J. *Inorg. Chem.* **2014**, *53*, 13212.
- (16) Chen, L.; Wei, R.; Tao, J.; Huang, R.; Zheng, L. *Sci. China Chem.* **2012**, *55*, 1037.
- (17) Drath, O.; Gable, R. W.; Moubaraki, B.; Murray, K. S.; Poneti, G.; Sorace, L.; Boskovic, C. *Inorg. Chem.* **2016**, *55*, 4141.
- (18) Bodnar, S. H.; Caneschi, A.; Dei, A.; Shultz, A.; Sorace, L. *Chem. Commun.* **2001**, 2150.
- (19) Imaz, I.; Maspoch, D.; Rodríguez-Blanco, C.; Pérez-Falcón, J. M.; Campo, J.; Ruiz-Molina, D. *Angew. Chem. Int. Ed. Engl.* **2008**, *47*, 1857.
- (20) Jung, O.; Pierpont, C. G. *J. Am. Chem. Soc.* **1994**, *116*, 2229.
- (21) Li, B.; Chen, L.-Q.; Wei, R.-J.; Tao, J.; Huang, R.-B.; Zheng, L.-S.; Zheng, Z. *Inorg. Chem.* **2011**, *50*, 424.

- (22) Lannes, A.; Suffren, Y.; Tommasino, J. B.; Chiriac, R.; Toche, F.; Khrouz, L.; Molton, F.; Duboc, C.; Kieffer, I.; Hazemann, J.; Reber, C.; Hauser, A.; Luneau, D. *J. Am. Chem. Soc.* **2016**, *138*, 6838
- (23) Hu, S.; Zhang, Z.-M.; Meng, Z.-S.; Lin, Z.-J.; Tong, M.-L. *CrystEngComm* **2010**, *12*, 4378.
- (24) Han, L.; Zhao, W.; Zhou, Y.; Li, X.; Pan, J. *Cryst. Growth Des.* **2008**, *8*, 3504.
- (25) Meng, J.-X.; Li, Y.; Fu, H.; Wang, X.-L.; Wang, E.-B. *CrystEngComm* **2011**, *13*, 649.
- (26) Sun, L. X.; Qi, Y.; Che, Y. X.; Batten, S. R.; Zheng, J. M. *Cryst. Growth Des.* **2009**, *9*, 2995.
- (27) Zhang, J.; Wu, T.; Feng, P.; Bu, X. *Chem. Matter.* **2008**, *20*, 5457.
- (28) Zheng, N.; Bu, X.; Feng, P. *J. Am. Chem. Soc.* **2002**, *124*, 9688.
- (29) Chang, Y.; Wang, S.; Chang, Y.; Wang, S. *J. Am. Chem. Soc.* **2012**, *134*, 9848.
- (30) Hu, S.; Zhang, Z.-M.; Meng, Z.-S.; Lin, Z.-J.; Tong, M.-L. *CrystEngComm* **2010**, *12*, 4378.
- (31) Wang, X. L.; Cao, J. J.; Hou, J. L.; Liu, G. C.; Zhao, D.; Liu, X. J.; Li, N.; Tian, A. X. *Chinese Chem. Lett.* **2013**, *24*, 877.
- (32) Mao, L.; Liu, W.; Li, Q.; Jia, J.; Tong, M. *Cryst. Growth Des.* **2014**, *14*.
- (33) Cowieson, N. P.; Aragao, D.; Clift, M.; Ericsson, D. J.; Gee, C.; Harrop, S. J.; Mudie, N.; Panjikar, S.; Price, J. R.; Riboldi-Tunnicliffe, A.; Williamson, R.; Caradoc-Davies, T. *J. Synchrotron Radiat.* **2015**, *22*, 187.
- (34) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. a K.; Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339.
- (35) Sheldrick, G. M. *Acta Cryst.* **2007**, *A64*, 112

- (36) van der Sluis, P.; Spek, A. L. *Acta Cryst.* **1990**, *A46*, 194.
- (37) Bain, G. A.; Berry, J. F. *J. Chem. Ed.* **2008**, *85*, 532.
- (38) Brese, N. E.; O'Keeffe, M. *Acta Cryst.* **1991**, *B47*, 192.
- (39) Boone, S. R.; Purser, G. H.; Chang, H.; Lowery, M. D.; Hendrickson, D. N.; Pierpont, C. *G. J. Am. Chem. Soc.* **1989**, *111*, 2292.
- (40) Mulyana, Y.; Poneti, G.; Moubaraki, B.; Murray, K. S.; Abrahams, B. F.; Sorace, L.; Boskovic, C. *Dalton Trans.* **2010**, *39*, 4757.
- (41) Carugo, O.; Castellani, C. B.; Djinic, K.; Rizzi, M. *J. Chem. Soc. Dalton Trans.* **1992**, *10*, 1.
- (42) Brown, S. N. *Inorg. Chem.* **2012**, *51*, 1251.
- (43) Alvarez, S.; Avnir, D.; Llunell, M.; Pinsky, M. *New J. Chem.* **2002**, *26*, 996.
- (44) Garcia, H. C.; De Almeida, F. B.; Diniz, R.; Yoshida, M. I.; De Oliveira, L. F. C. *J. Coord. Chem.* **2011**, *64*, 1125.
- (45) Benelli, C.; Dei, A.; Gatteschi, D.; Pardi, L. *Inorg. Chim. Acta* **1989**, *163*, 99.
- (46) Caneschi, A.; Dei, A.; Gatteschi, D.; Sorace, L.; Vostrikova, K. *Angew. Chem. Int. Ed.* **2000**, *39*, 246.
- (47) Beni, A.; Dei, A.; Laschi, S.; Rizzitano, M.; Sorace, L. *Chem. Eur. J.* **2008**, *14*, 1804.
- (48) Touceda, P. T.; Patricia, T. T.; Vázquez, S. M.; Sandra, M. V.; Lima, M.; Manuela, L.; Lapini, A.; Andrea, L.; Foggi, P.; Paolo, F.; Dei, A.; Andrea, D.; Righini, R.; Roberto, R. *Phys. Chem. Chem. Phys.* **2012**, *14*, 1038.
- (49) Mondal, M. K.; Tiwari, A.; Mukherjee, C. *Chem. Commun.* **2016**, *52*, 11995.
- (50) Alley, K. G.; Poneti, G.; Robinson, P. S. D.; Nafady, A.; Moubaraki, B.; Aitken, J. B.; Drew, S. C.; Ritchie, C.; Abrahams, B. F.; Hocking, R. K.; Murray, K. S.; Bond, A. M.;

- Harris, H. H.; Sorace, L.; Boskovic, C. *J. Am. Chem. Soc.* **2013**, *135*, 8304.
- (51) Lloret, F.; Julve, M.; Cano, J.; Ruiz-García, R.; Pardo, E. *Inorg. Chim. Acta* **2008**, *361*, 3432.
- (52) Chen, X.; Wei, R.; Zheng, L.; Tao, J. *Inorg. Chem* **2014**, *53*, 13212.
- (53) Létard, J.-F. *J. Mater. Chem.* **2006**, *16*, 2550.
- (54) Dapporto, P.; Dei, A.; Poneti, G.; Sorace, L. *Chem. Eur. J.* **2008**, *14*, 10915.
- (55) Hauser, A. In *Spin Crossover in Transition Metal Compounds II*; Gutlich, P.; Goodwin, H. a., Eds.; Springer: Berlin Heidelberg, 2004; pp. 155–198.

SYNOPSIS

Structural characterization of two new 1D coordination polymers with cobalt-bis(dioxolene) units linked by polypyridyl ligands reveals contrasting chain and ribbon topologies. The chain compound exhibits a thermally-induced valence tautomeric transition.