STRUCTURAL
CHEMISTRY

ISSN 2053-2296

Structural investigation of one- and two-dimensional coordination polymers based on cobalt–bis(dioxolene) units and 1-hydroxy-1,2,4,5-tetrakis(pyridin-4-yl)cyclohexane

Olga Drath, Robert W. Gable and Colette Boskovic*

Received 12 February 2018

Accepted 2 May 2018

Edited by F. A. Almeida Paz, University of Aveiro, Portugal

Keywords: two-dimensional coordination polymer; one-dimensional zigzag chain; crystal structure; valence tautomerism; cobalt; polypyridyl ligands; redox-active ligands; metal-organic frameworks.

CCDC references: 1840985; 1840984; 1840983; 1840982

Supporting information: this article has supporting information at journals.iucr.org/c

School of Chemistry, The University of Melbourne, Parkville, Victoria 3010, Australia. *Correspondence e-mail: c.boskovic@unimelb.edu.au

The combination of cobalt, 3,5-di-*tert*-butyldioxolene (3,5-dbdiox) and 1-hydroxy-1,2,4,5-tetrakis(pyridin-4-yl)cyclohexane (tpch) yields two coordination polymers with different connectivities, *i.e.* a one-dimensional zigzag chain and a two-dimensional sheet. Poly[[bis(3,5-di-*tert*-butylbenzene-1,2-diolato)bis(1,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dien-1-yl-3-olato)[μ_4 -1-hydroxy-1,2,4,5-tetrakis(pyridin-4-yl)cyclohexane]cobalt(III)]–ethanol–water 1/7/5], $\{[\text{Co}_2(\text{C}_{14}\text{H}_{20}\text{O}_2)_4(\text{C}_{26}\text{H}_{24}\text{N}_4\text{O})] \cdot 7\text{C}_2\text{H}_5\text{OH} \cdot 5\text{H}_2\text{O}\}_n$ or $\{[\text{Co}_2(3,5\text{-dbdiox})_4(\text{tpch})] \cdot 7\text{EtOH} \cdot 5\text{H}_2\text{O}\}_n$, is the second structurally characterized example of a two-dimensional coordination polymer based on linked $\{\text{Co}(3,5\text{-dbdiox})_2\}$ units. Variable-temperature single-crystal X-ray diffraction studies suggest that *catena*-poly[[[(3,5-di-*tert*-butylbenzene-1,2-diolato)(1,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dien-1-yl-3-olato)-cobalt(III)]- μ -1-hydroxy-1,2,4,5-tetrakis(pyridin-4-yl)cyclohexane]–ethanol–water (1/1/5)], $\{[\text{Co}(\text{C}_{14}\text{H}_{20}\text{O}_2)_2(\text{C}_{26}\text{H}_{24}\text{N}_4\text{O})] \cdot \text{C}_2\text{H}_5\text{OH} \cdot 5\text{H}_2\text{O}\}_n$ or $\{[\text{Co}(3,5\text{-dbdiox})_2(\text{tpch})] \cdot \text{EtOH} \cdot 5\text{H}_2\text{O}\}_n$, undergoes a temperature-induced valence tautomeric interconversion.

1. Introduction

Electronically labile coordination polymers (CPs) represent the intersection between stimuli-responsive coordination complexes and crystalline molecule-based materials (Kahn, 1998; Sato, 2016). The possibility of converting between two or more electronically distinguishable states by applying an external stimulus makes electronically labile CPs potential candidates for new types of switches, sensors or data storage devices. Valence tautomerism involves an electron transfer between a redox-active metal centre and a non-innocent ligand, stimulated by the application of an external perturbation, such as a change of temperature or light irradiation (Dei *et al.*, 2004; Tezgerevska *et al.*, 2014). Most valence tautomeric (VT) CPs are based on Co–dioxolene systems, where the electron transfer is accompanied by a spin transition at the cobalt centre, involving a transition from $\{ls\text{-Co}^{\text{III}}(\text{cat})\}$ at low temperature to $\{hs\text{-Co}^{\text{II}}(3,5\text{-sq})\}$ at high temperature (ls = low spin, hs = high spin, cat = catecholate and sq = semiquinonate). All but one of the previously structurally characterized Co VT CPs exhibit a one-dimensional (1D) chain topology (Drath *et al.*, 2016, 2017; Imaz *et al.*, 2008; Jung & Pierpont, 1994; Chen *et al.*, 2014; Drath & Boskovic, 2018; Li *et al.*, 2011). There is a single literature example of a two-dimensional (2D) Co–dioxolene VT CP (Li *et al.*, 2011), as well as a 2D VT CP based on Mn and nitronyl–nitroxide ligands (Lannes *et al.*, 2016).

© 2018 International Union of Crystallography

With the goal of obtaining a 2D VT CP, we employed a divergent polypyridyl ligand, namely 1-hydroxy-1,2,4,5-tetrakis(pyridin-4-yl)cyclohexane (tpch), to connect $\{\text{Co}(\text{3,5-dbdiox})_2\}$ (3,5-dbdiox is 3,5-di-*tert*-butyldioxolene) units into an infinite 2D array. The oxidative coupling of 1,3-bipyridylpropane (1,3-bpp) (Chang & Wang, 2012) can lead to different products, depending on the pH of the reaction (Scheme 1). The forms of the 1,3-bpp dimer that can be obtained in the

Scheme 1

solvothermal reaction are three hydrates of 1,2,4,5-tetrakis(pyridin-4-yl)benzene (tpb) and 1-hydroxy-1,2,4,5-tetrakis(pyridin-4-yl)cyclohexane (tpch). The combination of tpb and cobalt with 3,5-di-*tert*-butylcatechol (3,5-dbcath₂) has previously led to the formation of two CPs, although only 1D

Scheme 2

chain and ribbon topologies could be achieved (Drath *et al.*, 2017). The benzene ring of the tpb ligand introduces additional rigidity into the structure, which appears to prevent the formation of the desired 2D net. As the tpch ligand has

previously been reported as a 4-connecting linker in 2D zinc and copper CPs (Meng *et al.*, 2011, 2008), it was anticipated to be able to accommodate the bulky *tert*-butyl groups of the 3,5-dbdiox ligand.

In the present article, we report the structures of a two-dimensional sheet, *i.e.* $\{[\text{Co}_2(\text{3,5-dbdiox})_4(\text{tpch})]\cdot 7\text{EtOH}\cdot 5\text{H}_2\text{O}\}_n$, denoted **1**·7EtOH·5H₂O (see Scheme 2), and a one-dimensional zigzag chain, *i.e.* $\{[\text{Co}(\text{3,5-dbdiox})_2(\text{tpch})]\cdot \text{EtOH}\cdot 5\text{H}_2\text{O}\}_n$, denoted **2**·EtOH·5H₂O (see Scheme 3).

2·EtOH·5H₂O
Scheme 3

2. Experimental

All manipulations were performed under aerobic conditions. All reagents were obtained from commercial sources and were used as received. The tpch ligand was synthesized according to the literature procedure of Chang & Wang (2012) in 15% yield.

2.1. Synthesis and crystallization

2.1.1. Preparation of 1·7EtOH·5H₂O. An ethanol solution (6.7 ml) of 3,5-di-*tert*-butylcatechol (3,5-dbcath₂) (33 mg, 0.13 mmol) and tpch (6 mg, 0.01 mmol) was layered over an aqueous solution (1.3 ml) of $\text{Co}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$ (17 mg, 0.067 mmol). After three weeks, blue rectangular plate-shaped crystals formed, along with an amorphous precipitate. A sample suitable 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 $\{[\text{Co}_2(\text{3,5-dbdiox})_4(\text{tpch})]\cdot 7\text{EtOH}\cdot 5\text{H}_2\text{O}\}_n$ (**1**·7EtOH·5H₂O).

2.1.2. Preparation of 2·EtOH·5H₂O. An ethanol solution (5 ml) of 3,5-dbcath₂ (33 mg, 0.13 mmol) and tpch (13 mg, 0.026 mmol) was layered over an aqueous solution (2 ml) of $\text{Co}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$ (17 mg, 0.067 mmol). The ethanol and water layers were separated by an intermediate layer of ethanol and water in a 1:1 ratio (1 ml). After two 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 was identified as $\{[\text{Co}(\text{3,5-dbdiox})_2(\text{tpch})]\cdot \text{EtOH}\cdot 5\text{H}_2\text{O}\}_n$ (**2**·EtOH·5H₂O).

Table 1
Experimental details.

	1 ·7EtOH·5H ₂ O	2 ·EtOH·5H ₂ O
Crystal data		
Chemical formula	[Co ₂ (C ₁₄ H ₂₀ O ₂) ₄ (C ₂₆ H ₂₄ N ₄ O)]·7C ₂ H ₆ O·5H ₂ O	[Co(C ₁₄ H ₂₀ O ₂) ₂ (C ₂₆ H ₂₄ N ₄ O)]·C ₂ H ₆ O·5H ₂ O
<i>M_r</i>	1820.10	1044.17
Crystal system, space group	Monoclinic, <i>P</i> ₂ ₁ / <i>c</i>	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	100	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	23.849 (5), 11.679 (2), 18.319 (4)	10.072 (2), 16.135 (3), 18.192 (4)
α , β , γ (°)	90, 95.28 (3), 90	75.34 (3), 83.15 (3), 78.70 (3)
<i>V</i> (Å ³)	5080.8 (18)	2797.1 (11)
<i>Z</i>	2	2
Radiation type	Synchrotron	Mo <i>K</i> α
μ (mm ⁻¹)	0.39	0.37
Crystal size (mm)	0.10 × 0.07 × 0.02	0.10 × 0.04 × 0.02
Data collection		
Diffractometer		ADSC Quantum 210r
Absorption correction		Multi-scan (<i>SADABS</i> ; Bruker, 2012)
<i>T</i> _{min} , <i>T</i> _{max}	0.583, 0.745	0.963, 0.993
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	73724, 10426, 7436	107853, 17013, 12047
<i>R</i> _{int}	0.093	0.080
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.629	0.746
Refinement		
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.081, 0.231, 1.05	0.094, 0.276, 1.04
No. of reflections	10426	17013
No. of parameters	526	682
No. of restraints	21	88
H-atom treatment	H-atom parameters constrained	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	1.09, -0.73	2.65, -0.85

Computer programs: *Bluice* (McPhillips *et al.*, 2002), *XDS* (Kabsch, 1993), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *SHELXL2018* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

2.2. Refinement

Single-crystal X-ray diffraction data for **1** were collected at 100 K, while data for **2** were collected at 100, 275 and 315 K. Due to crystal decomposition, variable-temperature studies could not be performed on **1**. All data collections employed synchrotron radiation on the MX1 beamline at the Australian Synchrotron, Victoria, Australia (McPhillips *et al.*, 2002). Data collection and structure refinement details are summarized in Table 1 for **1** and for **2** at 100 K; data for **2** at 275 and 315 K are summarized in Tables S1 and S2 of the supporting information. For all the structures, the hydroxy group of the tpch ligand is disordered over four positions on the cyclohexane ring; refinement was carried out with these atoms restrained to ideal geometry. For all structures, one of the *tert*-butyl groups also displays disorder; refinement was carried out with these groups disordered over two components, both being restrained to ideal geometry. The structures of both complexes contain voids filled with solvent molecules, which, apart from the molecules of ethanol, appeared to be highly disordered. A satisfactory disorder model of this solvent could not be found, and therefore the *OLEX2* (Dolomanov *et al.*, 2009) 'solvent mask' routine was used to mask out the disordered electron density. For **1**, the voids are comprised of rhombic-shaped channels, situated along the *b* axis, and smaller triangular-shaped channels lying along the *c* axis. The larger channels are bounded mostly by aromatic rings, while the latter channels are bounded, on two sides, by OH groups with only the third

side bounded by hydrophobic alkyl groups. With the possibility of O—H...O and O—H... π hydrogen bonds (Ostojić *et al.*, 2008), these channels could be filled by either water or ethanol. Although a definite solvent composition could not be reliably determined, solvent compositions that fit with the *OLEX2* solvent-mask data are fifteen molecules of water or a mixture of five molecules of water and five molecules of ethanol. As the voids are not strongly hydrophilic, the latter composition is more likely. For compound **2**, the solvent voids are channels lying along the *a* axis. The proposed molecular formulas, *i.e.* **1**·7EtOH·5H₂O, **2**·EtOH·5H₂O at 100 and 275 K, and **2**·EtOH·3H₂O at 315 K, are based on the calculated solvent-accessible voids and the electron count. For **2**, solvent loss occurred between the data collections at 275 and 315 K. The final *R* and *wR2* values are relatively high, a consequence of the disorder of the crystals and the relatively weak data.

3. Results and discussion

3.1. Synthesis

Polymeric coordination compounds **1**·7EtOH·5H₂O and **2**·EtOH·5H₂O were obtained at room temperature under aerobic conditions *via* slow diffusion. In both cases, the cobalt(II) salt was dissolved in water and the ethanol solution of both ligands was carefully layered over the aqueous layer. In the case of the synthesis of compound **2**·EtOH·5H₂O, the layers were additionally separated by an intermediate layer of

Figure 1

The coordination environment of the Co atom in the asymmetric unit of complex **1**. All H atoms and solvent molecules have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

a 1:1 H₂O–EtOH mixture. Single crystals of compound **1**·7EtOH·5H₂O grew out of the cloudy solution when the cobalt(II) cation and catechol ligand were in fourfold and eightfold excess, respectively, in relation to the concentration of the linking ligand. Despite several attempts, it was not possible to obtain a sufficient quantity of **1**·7EtOH·5H₂O for

physical measurements. Moreover, any increase of the tpch–Co ratio seems to favour the formation of the 1D chain-type complex **2**. A possible explanation for the low yield of complex **1**, and complex **2** being favoured in the slow diffusion reaction, may be the bulkiness of the *tert*-butyl group on the dioxolene ligand, inhibiting the formation of the 2D structure. Although crystals of **2**·EtOH·5H₂O grow in sufficient quantity, they are always contaminated with an unknown by-product and it was not possible to obtain an analytically pure bulk sample of this compound, despite attempting synthesis with different reagent ratios and at different temperatures. Based on elemental analysis and additional PXRD measurements, the contamination is not from either uncoordinated ligands or compound **1**. It was not possible to distinguish the unknown additional phase from compound **2** using a standard microscope.

3.2. Structural description

3.2.1. Structure of 1·7EtOH·5H₂O. The crystal structure of **1**·7EtOH·5H₂O was measured at 100 K. The coordination environment around the Co^{III} atom is presented in Fig. 1 and the 2D polymer structure and packing in Fig. 2. Tables 2 and 3 present selected interatomic distances.

Compound **1**·7EtOH·5H₂O crystallizes in the monoclinic space group *P*2₁/*c*. The asymmetric unit consists of one Co^{III} atom, two 3,5-dbdiox ligands, half of the tpch ligand and solvent, which was identified as five molecules of ethanol and four molecules of water per formula unit. The unit cell also contains additional highly disordered solvent, *i.e.* two ethanol and fifteen water molecules per formula unit. The cobalt coordination sphere adopts a slightly disordered octahedral shape and consists of four O atoms from two 3,5-dbdiox ligands and two N atoms in a *cis* disposition, each from a different tpch ligand. The SHAPE Index (see Table S3 in the supporting information), the deviation from zero of which indicates how close the coordination geometry is to an ideal polyhedron, is calculated as 0.212 for octahedral geometry (Alvarez *et al.*, 2002). Each tpch ligand connects four different Co^{III} atoms in a square-planar arrangement (Fig. 2*a*) and, with each Co^{III} atom connecting to two different tpch ligands, the result is a 2D sheet lying in the *bc* plane. The *tert*-butyl groups of the 3,5-dbdiox ligands are oriented such that they lie on the outside of the sheet, while the Co^{III} atoms and tpch ligands are on the inside (Fig. 2*b*); the tpch ligands lie in the centre of the sheet between rows of Co^{III} atoms. The orientation of the tpch ligands are such that they lie parallel to the *c* axis, while also linking the Co^{III} atoms into a zigzag arrangement along the *b* axis (Fig. 2*c*). These sheets stack along the *a* axis. Within each sheet, there are channels, lying along the *b* axis (Fig. 2*b*), in which the solvent molecules reside. This complex is, to the best of our knowledge, only the

Table 2

Selected geometric parameters (Å, °) for the Co coordination sphere in **1**·7EtOH·5H₂O and **2**·EtOH·*n*H₂O.

1·7EtOH·5H ₂ O		2·EtOH· <i>n</i> H ₂ O			
		100 K (<i>n</i> = 5)		275 K (<i>n</i> = 5)	315 K (<i>n</i> = 3)
Co1—O1	1.907 (3)	Co1—O1	1.863 (3)	1.860 (2)	1.924 (3)
Co1—O2	1.891 (3)	Co1—O2	1.880 (3)	1.865 (2)	1.906 (3)
Co1—O3	1.854 (3)	Co1—O3	1.905 (2)	1.893 (2)	1.934 (3)
Co1—O4	1.884 (3)	Co1—O4	1.917 (2)	1.912 (2)	1.967 (3)
Co1—N1	1.954 (4)	Co1—N1	1.941 (3)	1.953 (2)	2.012 (3)
Co1—N2 ⁱ	1.964 (3)	Co1—N3	1.955 (3)	1.960 (3)	2.010 (4)
O3—Co1—O2	87.65 (11)	O1—Co1—O2	88.39 (11)	87.35 (10)	87.26 (13)
O3—Co1—O1	87.03 (12)	O1—Co1—O3	88.19 (11)	88.02 (10)	92.27 (14)
O3—Co1—O4	87.95 (12)	O1—Co1—O4	91.63 (12)	91.56 (11)	87.97 (13)
O3—Co1—N1	87.73 (13)	O1—Co1—N1	88.40 (11)	88.70 (10)	178.91 (13)
O3—Co1—N2 ⁱ	178.92 (15)	O1—Co1—N3	178.52 (11)	178.52 (11)	85.85 (13)
O2—Co1—O1	85.28 (12)	O2—Co1—O3	175.44 (11)	174.26 (10)	171.87 (13)
O2—Co1—N1	174.63 (12)	O2—Co1—O4	90.99 (11)	91.60 (10)	91.89 (13)
O2—Co1—N2 ⁱ	92.63 (13)	O2—Co1—N1	90.96 (11)	91.02 (11)	91.58 (13)
O1—Co1—N1	91.75 (14)	O2—Co1—N3	92.99 (11)	94.11 (11)	95.19 (13)
O1—Co1—N2 ⁱ	94.03 (14)	O3—Co1—O4	86.09 (10)	85.13 (10)	84.08 (11)
O4—Co1—O2	89.57 (12)	O3—Co1—N1	91.96 (11)	92.27 (10)	92.48 (12)
O4—Co1—O1	172.94 (12)	O3—Co1—N3	90.46 (11)	90.54 (11)	91.74 (13)
O4—Co1—N1	93.00 (15)	O4—Co1—N1	178.05 (11)	177.37 (10)	176.53 (11)
O4—Co1—N2 ⁱ	91.01 (14)	O4—Co1—N3	88.89 (12)	88.62 (11)	88.04 (14)
N1—Co1—N2 ⁱ	92.04 (14)	N1—Co1—N3	91.04 (12)	91.06 (11)	91.66 (13)

Symmetry code: (i) $x, -y + \frac{1}{2}, z - \frac{1}{2}$.

second literature example of a 2D CP comprised of linked Co-dioxolene units. Comparison of **1** with the previously reported Co-based 2D VT CP, which incorporates the tetrakis(pyridin-4-yloxymethylidene)methane (tpom) ligand (Li *et al.*, 2011), reveals that the central cyclohexane ring in tpch and the central tetrahedral C atom in tpom have given both ligands the

geometry to form 2D structures. The differing connectivity of the ligands, however, gives rise to different topologies. In the compound synthesized by Li *et al.*, each tpom ligand links four Co^{III} centres into a tetrahedral arrangement, with the orientation of all ligands being identical throughout the sheet, in contrast to the tpch ligands in **1**·7EtOH·5H₂O, where the

Figure 2

(a) View of the linking between the ligands and the Co atoms of **1**·7EtOH·5H₂O. (b) Packing of the sheets of **1**·7EtOH·5H₂O. (c) Cross-section of the sheet of **1**·7EtOH·5H₂O. Solvent molecules, H atoms and dioxolene ligands in parts (a) and (c) have been omitted for clarity.

ligands adopt differing zigzag orientations (Fig. 2c). For both structures, the *tert*-butyl groups of the 3,5-diox ligands are on the outside of the sheets containing the Co^{III} atoms and linking ligands, creating a hydrophobic region between the sheets, while both structures can be described as having a 'sandwiched' layer of the bridging ligand between two layers of Co^{III} atoms.

For **1**·7EtOH·5H₂O at 100 K, the Co—O distances are 1.854 (3)–1.907 (3) Å and the Co—N distances are 1.953 (4) and 1.964 (3) Å. These bond lengths are indicative of the +3 oxidation state of the cobalt cation (Brese & O'Keeffe, 1991). The interatomic distances within the dioxolene ligand have been also analysed. In 2011, Brown examined 259 structures based on dioxolene, reporting an unambiguous ligand oxidation (Brown, 2012) and 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 catechololate ligand should have a MOS value equal to −2. The calculated MOS parameters for the 3,5-dbdiox ligands in **1**·7EtOH·5H₂O are −1.25 for the dioxolene ligand with O1 and O2 as the coordinating atoms, and −1.86 for the other dioxolene ligand (see Table S5 in the supporting information). In conclusion, the interatomic distances within complex **1** are consistent with the formation of {Co^{III}(3,5-dbcac)(3,5-dbsq)} (3,5-dbsq is 3,5-di-*tert*-butylsemiquinone) units.

3.2.2. Structure of 2·EtOH·*n*H₂O. The X-ray diffraction data for **2**·EtOH·*n*H₂O were measured at 100 (*n* = 5), 275

Table 3

Selected bond lengths (Å) for the dioxolene ligands in **1**·7EtOH·5H₂O and **2**·EtOH·*n*H₂O.

1·7EtOH·5H ₂ O		2·EtOH· <i>n</i> H ₂ O			
			100 K (<i>n</i> = 5)	275 K (<i>n</i> = 5)	315 K (<i>n</i> = 3)
O1—C1	1.313 (4)	O1—C2	1.343 (4)	1.333 (4)	1.330 (5)
O1—C2	1.316 (5)	O2—C1	1.341 (4)	1.326 (4)	1.328 (5)
O3—C15	1.338 (5)	O3—C16	1.307 (4)	1.294 (3)	1.303 (4)
O4—C16	1.356 (5)	O4—C15	1.305 (4)	1.289 (4)	1.298 (5)
C1—C2	1.440 (5)	C1—C2	1.423 (5)	1.399 (5)	1.434 (6)
C3—C2	1.438 (5)	C1—C6	1.397 (5)	1.379 (5)	1.384 (6)
C4—C3	1.368 (5)	C2—C3	1.408 (5)	1.387 (5)	1.410 (6)
C4—C5	1.432 (5)	C3—C4	1.405 (5)	1.387 (5)	1.387 (6)
C6—C5	1.371 (5)	C4—C5	1.419 (5)	1.386 (5)	1.413 (7)
C1—C6	1.395 (5)	C5—C6	1.391 (5)	1.382 (5)	1.386 (7)
C15—C16	1.408 (5)	C15—C16	1.447 (5)	1.434 (4)	1.443 (5)
C16—C17	1.387 (6)	C15—C20	1.406 (4)	1.391 (4)	1.409 (6)
C17—C18	1.406 (6)	C16—C17	1.427 (4)	1.404 (4)	1.418 (5)
C19—C18	1.397 (6)	C17—C18	1.388 (4)	1.364 (5)	1.375 (6)
C20—C19	1.406 (6)	C18—C19	1.418 (5)	1.403 (5)	1.416 (7)
C15—C20	1.415 (5)	C19—C20	1.380 (5)	1.361 (5)	1.361 (7)

(*n* = 5) and 315 K (*n* = 3) to monitor changes in the Co—O, Co—N and 3,5-dbdiox-ligand bond lengths associated with a thermally-driven valence tautomeric transition.

The coordination environment surrounding the Co^{III} atom is presented in Fig. 3, the chain motif of the 1D polymer is shown in Fig. 4 and the packing diagram is shown in Fig. 5. Tables 3 and 4 present selected interatomic distances.

Compound **2**·EtOH·*n*H₂O crystallizes in the triclinic *P* $\bar{1}$ space group, which persists throughout the measured temperature range; the only apparent physical change is loss of some solvent water at 315 K. The asymmetric unit consists of a cobalt centre, two 3,5-dbdiox ligands, two halves of different tpch ligands, a molecule of solvent ethanol and highly disordered solvent. At every temperature, the ethanol molecule is ordered by hydrogen bonding to the noncoordinating pyridyl group of the tpch ligand, while the disordered solvent was identified as five water molecules per formula unit at 100 and 275 K, and three water molecules at 315 K.

The Co^{III} centre is surrounded by four O atoms and two N atoms in a *cis* arrangement. At 100 K, the SHAPE index

Figure 3

The coordination environment of the Co atom in the asymmetric unit of complex **2** at 100 K. All H atoms and solvent molecules have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

Figure 4

The chain motif of **2**·EtOH·5H₂O collected at 100 K. H atoms and solvent molecules have been omitted for clarity.

Figure 5
Packing diagram of complex molecule **2** in $2\cdot\text{EtOH}\cdot 5\text{H}_2\text{O}$.

(Alvarez *et al.*, 2002) is 0.103, which indicates a very low level of distortion from a regular octahedral coordination sphere. However, the level of distortion increases with the temperature of collection, reaching 0.258 at 315 K (Table S3 in the supporting information). Each tpch ligand connects two *cis*- $\{\text{Co}(3,5\text{-dbdiox})_2\}$ units, creating a zigzag chain (Fig. 4). The tpch ligand has not been hitherto reported acting as a 2-connecting linker. The chains run parallel to each other, creating predominantly hydrophobic zigzag-shaped interchain cavities (Fig. 5).

Temperature-dependent Co—O, Co—N and 3,5-dbdiox-ligand bond lengths are consistent with the onset of a VT transition (Table 4). At 100 K, the Co—O bonds are in the range 1.863 (3)–1.917 (3) Å and the Co—N bonds in the range 1.941 (3)–1.955 (3) Å, which is in good agreement with previously reported values for octahedral *ls*-Co^{III} complexes (Brese & O’Keeffe, 1991). 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 centres 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 undergo a slight structural rearrangement to accommodate the changes in the oxidation state of the 3,5-dbdiox ligands associated with the VT transition. This type of change has been observed in previously reported Co–dioxolene complexes (Mulyana *et al.*, 2010; Rupp *et al.*, 2017). At 315 K, the Co—O distances increase to 1.906 (3)–1.967 (3) Å, while the Co—N distances lie between 2.010 (4) and 2.012 (3) Å. These changes indicate that the VT transition begins around room temperature and

there is a significant fraction of *hs*-Co^{II} centres at 315 K. Fig. 6 shows the measured Co—O and Co—N distances as a function of the collection temperature. On average, the Co—N and Co—O distances increase by 0.06 Å and 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 *ca* 0.15 Å, the extent of VT conversion at 315 K for $2\cdot\text{EtOH}\cdot 5\text{H}_2\text{O}$ can be estimated as 40% (Mulyana *et al.*, 2010).

The thermally-dependent changes in dioxolene interatomic distances and MOS parameters are also observed (Table S5 in the supporting information). At 100 K, the bond lengths of the

Figure 6
Plot of the Co—O and Co—N bond lengths in $2\cdot\text{EtOH}\cdot 5\text{H}_2\text{O}$ as a function of temperature.

first dioxolene (coordinated to the Co centre by atoms O1 and O2) are closer to the values characteristic for semiquinone, while the values for the second redox-active ligand 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 both ligands. Although this change alone is not sufficient to confirm the VT transition, it is consistent with the changes expected to accompany the observed temperature-dependence of the Co–O/N bond lengths associated with a VT transition.

4. Concluding remarks

Two novel CPs have been obtained by employing the flexible tetrapyridyl ligand tpch to connect $\{\text{Co}(3,5\text{-dbdiox})_2\}$ units. Compound **1**·7EtOH·5H₂O is the second reported 2D coordination polymer based on Co–dioxolene units, while **2**·EtOH·5H₂O demonstrates a rare 1D zigzag chain topology. Variable-temperature X-ray crystallography studies of **2**·EtOH·*n*H₂O (*n* = 5 at 100 and 275 K, and *n* = 3 at 315 K) suggest a temperature-induced VT transition between $\{[s\text{-Co}^{\text{III}}(3,5\text{-dbcat})(3,5\text{-dbsq})]\}$ and $\{[hs\text{-Co}^{\text{III}}(3,5\text{-dbsq})_2]\}$ starting above 250 K. The results of the study show the importance of the choice of linking ligand in the pursuit of 2D VT CPs based on $\{\text{Co}(3,5\text{-dbdiox})_2\}$ units. The features that should be considered are the flexibility and the geometry of the ligand, to enable the accommodation of large Co–dioxolene 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 to facilitate the VT transition near room temperature, the steric bulk potentially hinders the formation of higher-dimensional polymeric structures. The possibility of employing differently-substituted dioxolene ligands to reduce steric hindrance may represent a viable route to future 3D VT coordination polymers.

Acknowledgements

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. Writing of the manuscript was supported by a Postgraduate Writing-Up Award to OD, which was funded by the Albert Shimmins Fund. The authors declare no competing financial interest. Part of this research was undertaken on the MX1 beamline at the Australian Synchrotron, part of ANSTO, Victoria, Australia.

Funding information

Funding for this research was provided by: Australian Research Council (grant No. DP150100353 to CB).

References

- Alvarez, S., Avnir, D., Lluell, M. & Pinsky, M. (2002). *New J. Chem.* **26**, 996–1009.
- Brese, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* **B47**, 192–197.
- Brown, S. N. (2012). *Inorg. Chem.* **51**, 1251–1260.
- Bruker (2012). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Chang, Y. & Wang, S. (2012). *J. Am. Chem. Soc.* **134**, 9848–9851.
- Chen, X., Wei, R., Zheng, L. & Tao, J. (2014). *Inorg. Chem.* **53**, 13212–13219.
- Dei, A., Gatteschi, D., Sangregorio, C. & Sorace, L. (2004). *Acc. Chem. Res.* **37**, 827–835.
- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
- Drath, O. & Boskovic, C. (2018). *Coord. Chem. Rev.* In the press. doi:10.1016/j.ccr.2017.11.025.
- Drath, O., Gable, R. W., Moubaraki, B., Murray, K. S., Poneti, G., Sorace, L. & Boskovic, C. (2016). *Inorg. Chem.* **55**, 4141–4151.
- Drath, O., Gable, R. W., Poneti, G., Sorace, L. & Boskovic, C. (2017). *Cryst. Growth Des.* **17**, 3156–3162.
- Imaz, I., Maspoche, D., Rodríguez-Blanco, C., Pérez-Falcón, J. M., Campo, J. & Ruiz-Molina, D. (2008). *Angew. Chem. Int. Ed.* **47**, 1857–1860.
- Jung, O. & Pierpont, C. G. (1994). *J. Am. Chem. Soc.* **116**, 2229–2230.
- Kabsch, W. (1993). *J. Appl. Cryst.* **26**, 795–800.
- Kahn, O. (1998). *Science*, **279**, 44–48.
- Lannes, A., Suffren, Y., Tommasino, J. B., Chiriac, R., Toche, F., Khrouz, L., Molton, F., Duboc, C., Kieffer, I., Hazemann, J. L., Reber, C., Hauser, A. & Luneau, D. (2016). *J. Am. Chem. Soc.* **138**, 16493–16501.
- Li, B., Chen, L.-Q., Wei, R.-J., Tao, J., Huang, R.-B., Zheng, L.-S. & Zheng, Z. (2011). *Inorg. Chem.* **50**, 424–426.
- McPhillips, T. M., McPhillips, S. E., Chiu, H.-J., Cohen, A. E., Deacon, A. M., Ellis, P. J., Garman, E., Gonzalez, A., Sauter, N. K., Phizackerley, R. P., Soltis, S. M. & Kuhn, P. (2002). *J. Synchrotron Rad.* **9**, 401–406.
- Meng, J.-X., Li, Y., Fu, H., Wang, X.-L. & Wang, E.-B. (2011). *CrystEngComm*, **13**, 649–655.
- Meng, J., Wang, X., Wang, E., Li, Y., Qin, C. & Xu, X. (2008). *Inorg. Chim. Acta*, **361**, 2447–2454.
- Mulyana, Y., Poneti, G., Moubaraki, B., Murray, K. S., Abrahams, B. F., Sorace, L. & Boskovic, C. (2010). *Dalton Trans.* **39**, 4757–4767.
- Ostojić, B. D., Janjić, G. V. & Zarić, S. D. (2008). *Chem. Commun.* pp. 6546–6548.
- Rupp, F., Chevalier, K., Graf, M., Schmitz, M., Kelm, H., Grün, A., Zimmer, M., Gerhards, M., van Wüllen, C., Krüger, H. J. & Diller, R. (2017). *Chem. Eur. J.* **23**, 2119–2132.
- Sato, O. (2016). *Nat. Chem.* **8**, 644–656.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Tezgerevska, T., Alley, K. G. & Boskovic, C. (2014). *Coord. Chem. Rev.* **268**, 23–40.