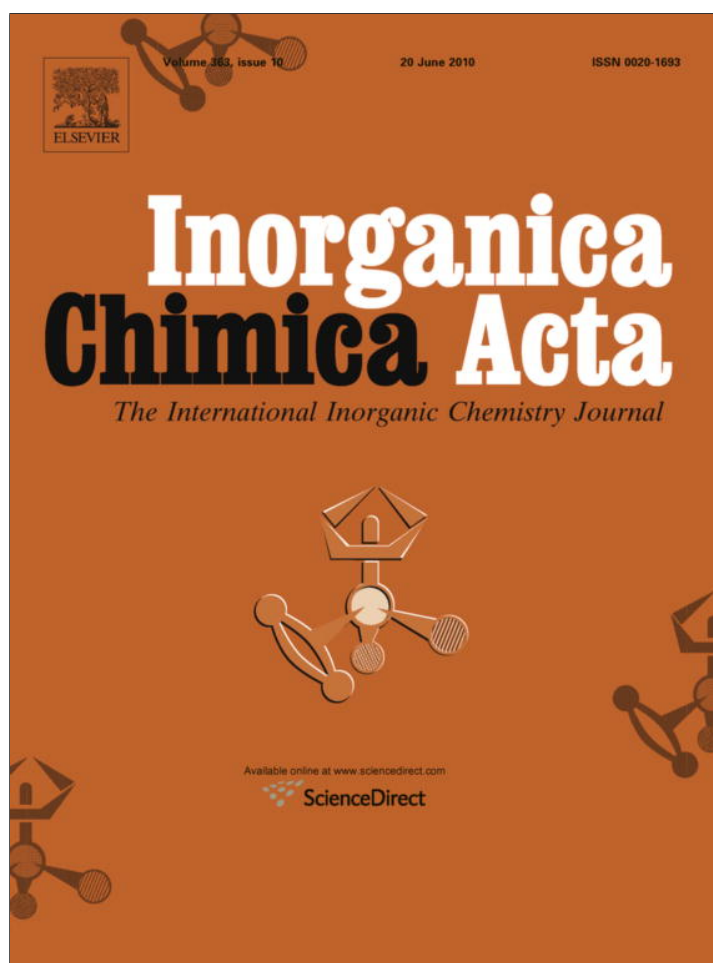


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# A >22 Å long metal-complex anion and a 1D cationic coordination polymer, both based on 4,4'-bipyridine-*N,N'*-dioxide, yielding a 3D and 2-fold interpenetrated fsc net of the hydrogen-bonded metal-organic 1D polymer

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## ABSTRACT

The cationic one-dimensional (1D) coordination polymer chain  $^1_{\infty}\{[\text{Co}(\mu\text{-bpdo})(\text{H}_2\text{O})_4]^{2+}\}$  and the metal-complex anion  $\text{trans-}[\text{Co}(\text{SO}_4)_2(\text{bpdo})_2(\text{H}_2\text{O})_2]^{2-}$ , both based on the 4,4'-bipyridine-*N,N'*-dioxide (bpdo) ligand, form a complementary supramolecular pair  $^1_{\infty}\{[\text{Co}(\mu\text{-bpdo})(\text{H}_2\text{O})_4]^{2+}\}_n \eta[\text{Co}(\text{SO}_4)_2(\text{bpdo})_2(\text{H}_2\text{O})_2]^{2-}$  (**1**) with respect to charge balance and hydrogen bonding. With a length of >22.14 Å along the bpdo-Co-bpdo axis the metal-complex  $\text{trans-}[\text{Co}(\text{SO}_4)_2(\text{bpdo})_2(\text{H}_2\text{O})_2]^{2-}$  is one of the longest and anisotropic counter anions (aspect ratio 22.14:8.11:4.17) observed so far in coordination polymers. Hydrogen-bonding of the anion links the cationic metal-organic 1D polymer into a 2-fold interpenetrated three-dimensional (3D) fsc (or sqc11) 4,6-c 2-nodal net of stoichiometry (4-c)(6-c) with square-planar, 4-connected (Co in anion) and octahedral, 6-connected (Co in cation) nodes in a 1:1 ratio. The 4-c point symbol is (4<sup>4</sup>.6<sup>2</sup>), the 6-c one (4<sup>4</sup>.6<sup>10</sup>.8) yielding a point symbol for the fsc net of (4<sup>4</sup>.6<sup>2</sup>)(4<sup>4</sup>.6<sup>10</sup>.8). The synthesis of **1** requires the presence of a Schiff base. Synthesis under the same conditions in the absence of the Schiff base yields the molecular complex and cocrystal  $[\text{Co}(\text{bpdo})(\text{H}_2\text{O})_5]\text{SO}_4 \cdot 1/2\text{bpdo}$  (**2**) which is related (as pseudo-polymorph) to the known solvate  $[\text{Co}(\text{bpdo})(\text{H}_2\text{O})_5]\text{SO}_4 \cdot 2\text{H}_2\text{O}$  (**3**) (CSD Refcodes RAXMUZ and RAXMUZ01).

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## 1. Introduction

Coordination polymers are of continuous interest because of their various application oriented properties [1–3]. If the coordination polymer chain, net or framework is cationic, as is the case when the metal cations are surrounded by neutral bridging and terminal ligands, the necessary counter ions are typically isolated small anions, such as halides,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{ClO}_4^-$ ,  $\text{BF}_4^-$ ,  $\text{SCN}^-$ , etc. [1,2,4–7]. Examples of rarely used larger anions in coordination polymers include carborane anions  $[\text{CB}_{11}\text{H}_{12}]^-$  [8],  $[\text{PhCB}_9\text{H}_9]^-$ ,  $[\text{BrC}_6\text{H}_4\text{CB}_{11}\text{H}_{11}]^-$ ,  $[\text{PhCB}_9\text{H}_4\text{I}_5]^-$ , and  $[\text{PhCB}_{11}\text{H}_5\text{I}_6]^-$  [9].

The use of a metal-complex anion as a counter ion in coordination networks is very unusual [10] with only few known examples, such as linear cationic coordination polymers with the counter anionic sandwich complex cobalt(III) bis(dicarbollide),  $[\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$  [8], and coordination nets which feature the Keggin-type anions  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$  [11] or  $[\text{SiW}_{12}\text{O}_{40}]^{4-}$  [12] or the complex anion  $[\text{Cu}(4\text{-pySO}_3)_4(\text{H}_2\text{O})_2]^{2-}$  [10]. In these aforementioned cases the complex anions have, however, been added as preformed building blocks into the coordination network synthesis.

Here we report a coordination polymer with an infinite cationic chain and an in-situ formed large metal-complex anion, both containing the 4,4'-bipyridine-*N,N'*-dioxide (bpdo) ligand [4–7,11,13]. The bpdo-ligand displays rich and various hydrogen-bonding modes. Even when it is coordinated to metal ions, its remaining lone pair of electrons may form hydrogen bonds, leading to an extended structure. These hydrogen-bonding interactions are considerably strong, like charge-assisted hydrogen bonds [14], due to the participation of the strongly polarized  $\text{N}^+-\text{O}^-$  group. Most of them fall in the  $\text{O} \cdots \text{O}$  range 2.65–2.75 Å (cf. Table 3) [15].

## 2. Experimental

Commercially available solvents,  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  and the enantiopure amine (from BASF AG, Ludwigshafen, Germany) (*R*)-1-(4-bromophenyl)ethylamine were used as received. Elemental analyses were performed on a VarioEL from Elementaranalysesysteme GmbH. Infrared spectra of **1** and **2** were recorded in the range 400–4000  $\text{cm}^{-1}$  on a Nicolet Magna-IR 760 Fourier-transform spectrometer using a diamond orbit ATR (ATR = attenuated total reflection) unit. NMR spectra were measured on a Bruker Avance 200 MHz spectrometer.

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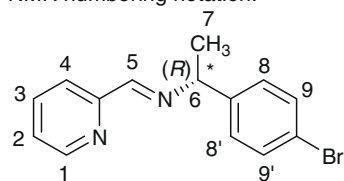
### 2.1. Synthesis of 4,4'-bipyridine-*N,N'*-dioxide dihydrate (bpdo)

4,4'-Bipyridine (4.002 g, 0.026 mol), glacial acetic acid (30 mL), and 30% hydrogen peroxide (5.5 mL) was heated together at 70–80° for 15 h. An additional 3.6 mL of 30% hydrogen peroxide was added and the temperature maintained at 70–80° for another 24 h. On addition of acetone (220 mL) a precipitate occurred which was separated by filtration [16]. The material was recrystallized from hot water (80 mL) by the addition of a large excess of acetone (140 mL), yielding fine yellow needles, m.p. 220°. Yield: 3.28 g, 68%. *Anal. Calc.* for C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>·2H<sub>2</sub>O (208.12): C, 53.57; H, 5.39; N, 12.49. Found: C, 53.95; H, 5.28; N, 12.68%.

### 2.2. Synthesis of (*R,E*)-1-(4-bromophenyl)-*N*-((pyridin-2-yl)methylene)ethanamine

A solution of 2-pyridine carboxaldehyde (20 mmol, 2 mL) in methanol (10 mL) was stirred with two drops of conc. H<sub>2</sub>SO<sub>4</sub> at room temperature for 10 min. After an equimolar amount of *R*-1-(4-bromophenyl)ethanamine (20 mmol, 3 mL) was added the color changed to yellow and the solution was refluxed for 5–6 h at 80 °C to give a dark green solution. The solvent was evaporated to half its volume in vacuo, then, the solution was allowed to evaporate slowly at room temperature. After 2–3 days, a brown solid was obtained, yield: 6.13 g, 94%. *Anal. Calc.* for C<sub>14</sub>H<sub>13</sub>N<sub>2</sub>Br (289.17): C, 58.15; H, 4.53; N, 9.69. Found: C, 57.08; H, 4.54; N, 9.45%. IR (KBr, Bruker IFS25 spectrometer, cm<sup>-1</sup>): 3077.6 (w), 3047.3 (w), 3008.5 (w), 2977.4 (w), 2963.4 (m), 2918.4 (w), 2855.8 (m), 1909.2 (w), 1648.6 (vs), 1585.0 (s), 1566.0 (s), 1479.8 (m), 1467.1 (s), 1437.6 (s), 1403.5 (m), 1365.8 (s), 1323.1 (w), 1287.4 (w), 1226.4 (w), 1198.4 (vw), 1115.7 (m), 1088.3 (m), 1069.8 (m), 1042.4 (w), 1008.3 (vs), 993.5 (s), 975.7 (m), 960.5 (w), 906.1 (w), 871.3 (w), 826.6 (vs), 781.0 (vs), 743.2 (m), 714.9 (w), 667.9 (w), 651.7 (vw), 612.1 (m), 540.6 (s), 502.3 (s), 429.5 (w), 412.6 (m). <sup>1</sup>H NMR (CD<sub>3</sub>OD, 200 MHz), δ/ppm (J/Hz) = 8.581 (d, 1H, H4 or H1, *J* = 4.8 Hz), 8.447 (s, 1H, H5), 8.054 (d, 1H, H1 or H4, *J* = 7.9), 7.813 (t, 1H, H3 or H2, *J* = 7.65), 7.446 (d, 2H, H9/9' or H8/8', *J* = 8.5), 7.39 (not resolved, H2 or H3), 7.324 (d, 2H, H8/8' or H9/9', *J* = 8.3), 4.589 (m, 1H, H6, *J* = 6.6), 1.532 (d, 1H, H7, *J* = 6.7) (see following formula for the NMR assignment)

NMR numbering notation:



### 2.3. Synthesis of catena-{trans-[tetraaqua-(μ-4,4'-bipyridine-*N,N'*-dioxide-κO:O')-cobalt(II)]-trans-[diaqua-bis(4,4'-bipyridine-*N,N'*-dioxide-κO)-di(sulfato)-cobaltate(II)]}, **1**

A solution of CoSO<sub>4</sub>·7H<sub>2</sub>O (0.50 mmol, 0.141 g) in methanol (5 mL) is mixed with a solution of (*R,E*)-1-(4-bromophenyl)-*N*-((pyridin-2-yl)methylene)ethanamine (0.50 mmol, 0.145 g) in methanol (5 mL) and a solution of bpdo (0.50 mmol, 0.113 g) in methanol (10 mL). The combined solution was stirred at room temperature, the resulting dark brown–red solution was filtered and the filtrate set aside for slow solvent evaporation. After a few days, dark purple to red crystals appeared. The same product was obtained when the combined solution was refluxed for 1 h. Yield: 0.13 g; 26%. *Anal. Calc.* for C<sub>30</sub>H<sub>36</sub>Co<sub>2</sub>N<sub>6</sub>O<sub>20</sub>S<sub>2</sub> (982.63): C, 36.67; H, 3.69; N, 8.55; S, 6.53. Found: C, 36.11; H, 3.90; N, 8.35; S, 6.50%. IR (ATR, cm<sup>-1</sup>): 3114.2 (w), 2907.9 (w), 2405.8 (vw),

1926.0 (vw), 1609.7 (vw), 1550.3 (vw), 1465.2 (m), 1422.4 (w), 1330.9 (vw), 1218.5 (m), 1174.2 (s), 1032.1 (s), 964.8 (m), 826.8 (s), 749.8 (w), 698.0 (w), 605.7 (s), 545.4 (s), 471.2 (m), 412.0 (w) (Fig. S8 in Supporting Information).

### 2.4. Synthesis of [pentaqua-(4,4'-bipyridine-*N,N'*-dioxide-κO)-cobalt(II)]sulfate-hemi(4,4'-bipyridine-*N,N'*-dioxide), **2**

A solution of CoSO<sub>4</sub>·7H<sub>2</sub>O (0.50 mmol, 0.141 g) in methanol (5 mL) is mixed with a solution of bpdo (0.50 mmol, 0.112 g) in methanol (10 mL) and the combined solution stirred under reflux (90 °C) for 1 h. The resulting dark red solution was filtered and the filtrate set aside for slow solvent evaporation. After one day, dark red crystals appeared. Yield: 0.14 g; 52%. IR (ATR, cm<sup>-1</sup>): 3111.0 (w), 2359.0 (vw), 1635.9 (w), 1541.7 (w), 1473.0 (m), 1428.4 (w), 1332.3 (vw), 1227.8 (m), 1184.3 (m), 1057.4 (s), 826.7 (s), 607.6 (m), 546.3 (m), 498.1 (m) (Fig. S9 in Supporting Information).

### 2.5. X-ray crystallography

Crystals were carefully selected under a polarizing microscope. *Data collection*: Bruker Apex2 AXS CCD, Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å), graphite monochromator, temperature 203(2) K,  $\omega$ -scans, absorption correction with SADABS [17]. *Structural Analysis and Refinement*: The structure was solved by direct methods (SHELXS), refinement was done by full-matrix least squares on  $F^2$  using the SHELXL program suite [18]; all non-hydrogen positions refined with anisotropic temperature factors; hydrogen atoms for aromatic CH groups were positioned geometrically (C–H = 0.94 Å)

**Table 1**  
Crystal data and structure refinement for **1** and **2**.

Compounds	<b>1</b>	<b>2</b>
Empirical formula	C <sub>30</sub> H <sub>36</sub> Co <sub>2</sub> N <sub>6</sub> O <sub>20</sub> S <sub>2</sub>	C <sub>15</sub> H <sub>22</sub> CoN <sub>3</sub> O <sub>12</sub> S
<i>M</i> (g mol <sup>-1</sup> )	982.63	527.35
Crystal size (mm)	0.14 × 0.14 × 0.05	0.34 × 0.16 × 0.04
Crystal appearance	Needle, red	Plate, red
2 $\theta$ range (°)	4.30–52.88	4.10–51.70
<i>h</i> ; <i>k</i> ; <i>l</i> range	±11; ±13; ±13	–12, 11; –23, 24; ±15
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> 1̄	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> (Å)	9.2199(3)	9.8018(7)
<i>b</i> (Å)	10.4012(3)	19.9150(13)
<i>c</i> (Å)	10.7677(3)	13.0115(8)
$\alpha$ (°)	74.379(2)	90
$\beta$ (°)	76.648(2)	129.653(4)
$\gamma$ (°)	68.213(2)	90
<i>V</i> (Å <sup>3</sup> )	913.47(5)	1955.5(2)
<i>Z</i>	1	4
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.786	1.791
<i>F</i> (0 0 0)	504	1088
$\mu$ (mm <sup>-1</sup> )	1.119	1.059
Maximum/minimum transmission	0.9441/0.8573	0.9639/0.7167
Reflections collected	18 429	18 011
Independent reflections ( <i>R</i> <sub>int</sub> )	3747 (0.0501)	3774 (0.0482)
Observed reflect [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	2954	3161
Parameters refined	292	319
Maximum/minimum $\Delta\rho$ <sup>a</sup> (e Å <sup>-3</sup> )	0.623/–0.397	0.943/–0.673
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>b</sup>	0.0349/0.0805	0.0455/0.1089
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> (all reflections) <sup>b</sup>	0.0498/0.0869	0.0557/0.1147
Goodness-of-fit on <i>F</i> <sup>2</sup> <sup>c</sup>	1.082	1.046
Weight. scheme <i>w</i> ; <i>a</i> / <i>b</i> <sup>d</sup>	0.0393/0.2820	0.0495/3.8756

<sup>a</sup> Largest difference peak and hole.

<sup>b</sup>  $R_1 = [\sum(|F_o| - |F_c|)] / \sum|F_o|$ ;  $wR_2 = [\sum(w(F_o^2 - F_c^2)^2) / \sum(w(F_o^2)^2)]^{1/2}$ .

<sup>c</sup> Goodness-of-fit =  $[\sum(w(F_o^2 - F_c^2)^2) / (n - p)]^{1/2}$ .

<sup>d</sup>  $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$  where  $P = (\max(F_o^2 \text{ or } 0) + 2F_c^2) / 3$ .

and refined using a riding model, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ ; H atoms on the aqua ligands were found and refined with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ . The representative nature of the single crystals investigated was verified by positively matching the measured X-ray powder diffractogram of a larger crystal selection with the diffractogram simulated from the data of the single-crystal X-ray refinement (see Fig. S1 in Supporting Information). Graphics were obtained with DIAMOND [19]. Computations on the supramolecular  $\pi$ -interactions were carried out with PLATON for Windows [20]. Crystal data and details on the structure refinement are given in Table 1.

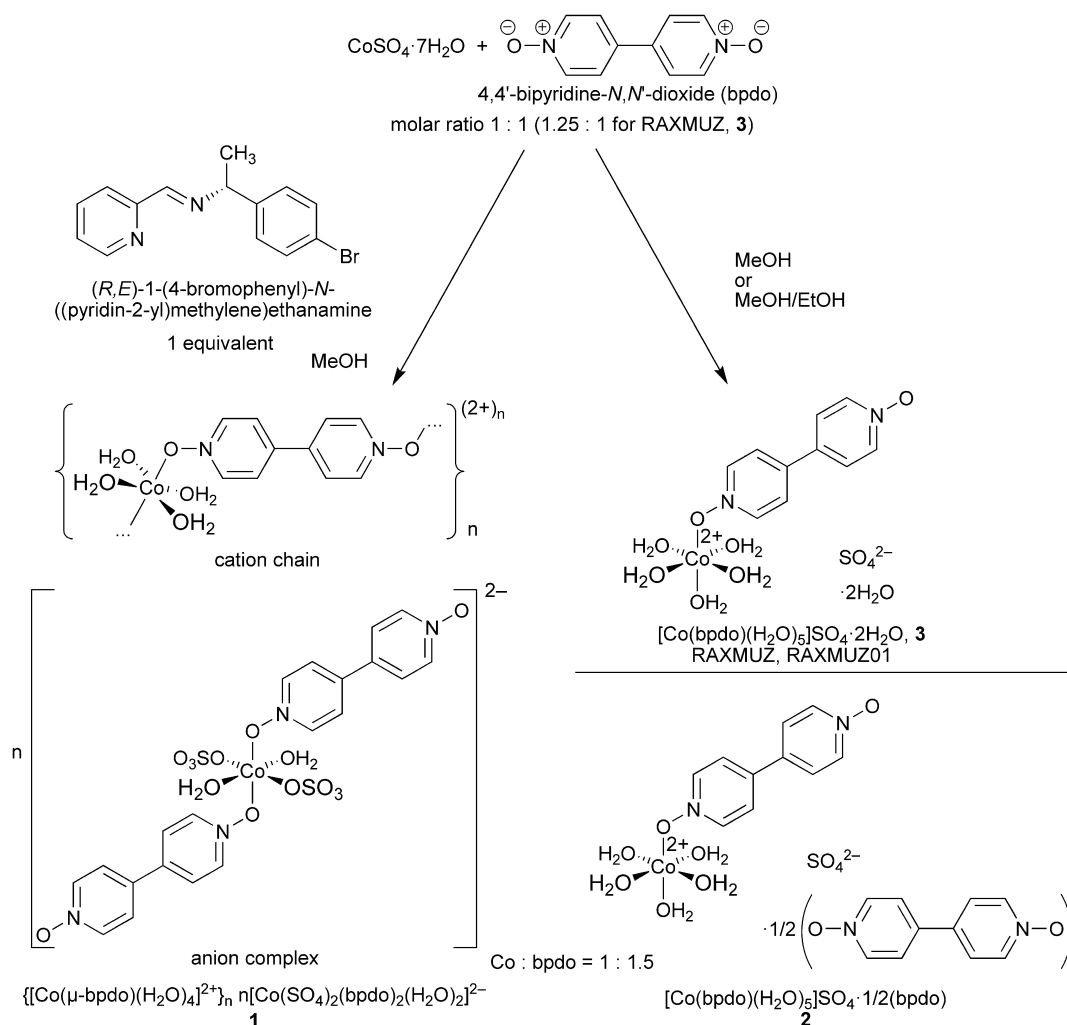
### 3. Results and discussion

The reaction of  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  with bpdo in methanol at room temperature or under reflux in the presence of the Schiff base (*R,E*)-1-(4-bromophenyl)-*N*-((pyridin-2-yl)methylene)ethanamine results in the formation of catena- $\{trans\text{-}[tetraaqua-(\mu\text{-}4,4'\text{-bipyridine-}N,N'\text{-dioxide-}\kappa\text{O:}O')\text{-cobalt(II)}]\text{-}trans\text{-}[\text{diaqua-bis}(4,4'\text{-bipyridine-}N,N'\text{-dioxide-}\kappa\text{O})\text{-di(sulfato)-cobaltate(II)}]\}$  **1**,  $1_\infty\{[\text{Co}(\mu\text{-bpdo})(\text{H}_2\text{O})_4]^{2+}\}_n n[\text{Co}(\text{SO}_4)_2(\text{bpdo})_2(\text{H}_2\text{O})_2]^{2-}$  (Scheme 1).

Previously, crystals of the molecular complex  $[\text{Co}(\text{bpdo})(\text{H}_2\text{O})_5]\text{SO}_4 \cdot 2\text{H}_2\text{O}$ , **3** (CSD Refcodes RAXMUZ and RAXMUZ01) were prepared by slow evaporation of a EtOH or MeOH or EtOH/H<sub>2</sub>O solution containing bpdo and  $\text{CoSO}_4$  [4]. Without the presence of

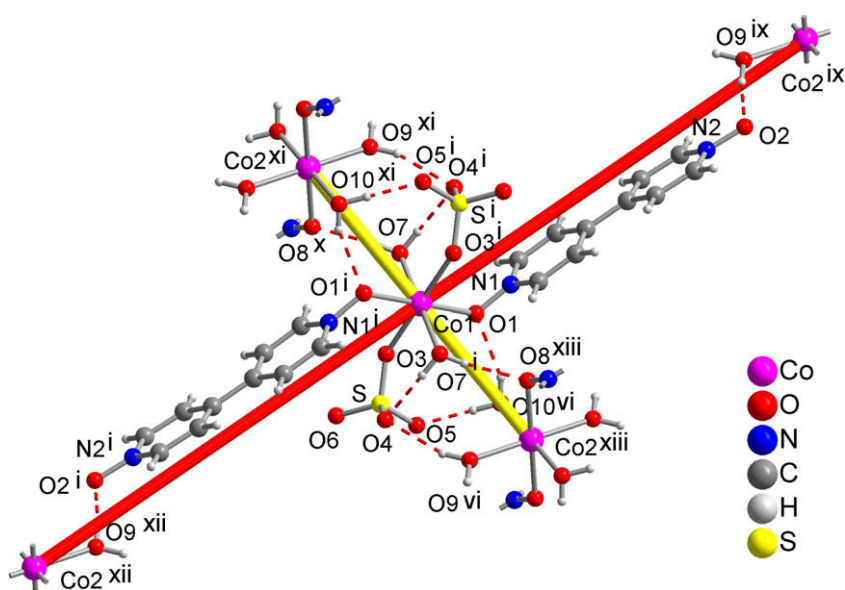
the auxiliary Schiff base, albeit under otherwise identical (concentration, crystallization) conditions, we obtained a cocrystal with the same molecular complex  $[\text{Co}(\text{bpdo})(\text{H}_2\text{O})_5]\text{SO}_4 \cdot 1/2(\text{bpdo})$ , **2** but with half a molecule of bpdo instead of two molecules of water embedded in the crystal lattice (Scheme 1). From X-ray powder diffractometry compound **1** is phase pure (Figs. S1 and S2 in Supporting Information). Compound **2** crystallizes together with **3** and  $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$ , both of which can be identified in the X-ray powder diffractogram (Fig. S3). We see the role of the Schiff base (SB) in the synthesis of **1** in an initial lowering of the available  $\text{Co}^{2+}$  ions through SB complexation, so that building blocks with two bpdo ligands  $\{\text{Co}(\text{bpdo})_2\}$  will form in solution despite the Co:bpdo ratio of 1:1. These  $\{\text{Co}(\text{bpdo})_2\}$  building blocks then assemble into cation chains (with additional  $\text{Co}^{2+}$  ions) and crystallize with the  $[\text{Co}(\text{SO}_4)_2(\text{bpdo})_2(\text{H}_2\text{O})_2]^{2-}$  anions. For compound **2** and **3** the building blocks in solution would be more like 1:1 Co:bpdo species from which crystallization starts.

The one-dimensional coordination polymeric cation in **1** is a kinked zigzag chain with the cobalt atom and the central C–C bond of bpdo situated on an inversion center. Four aqua ligands complete the octahedral cobalt coordination sphere with the two *trans*-configured bridging bpdo ligands (Fig. 1a). In the complex anion the cobalt atom also sits on an inversion center leading to the *trans*-configuration of the two aqua, sulfato and bpdo ligands (Fig. 1b). Bond lengths and angles of the two  $\text{CoO}_6$  chromophores

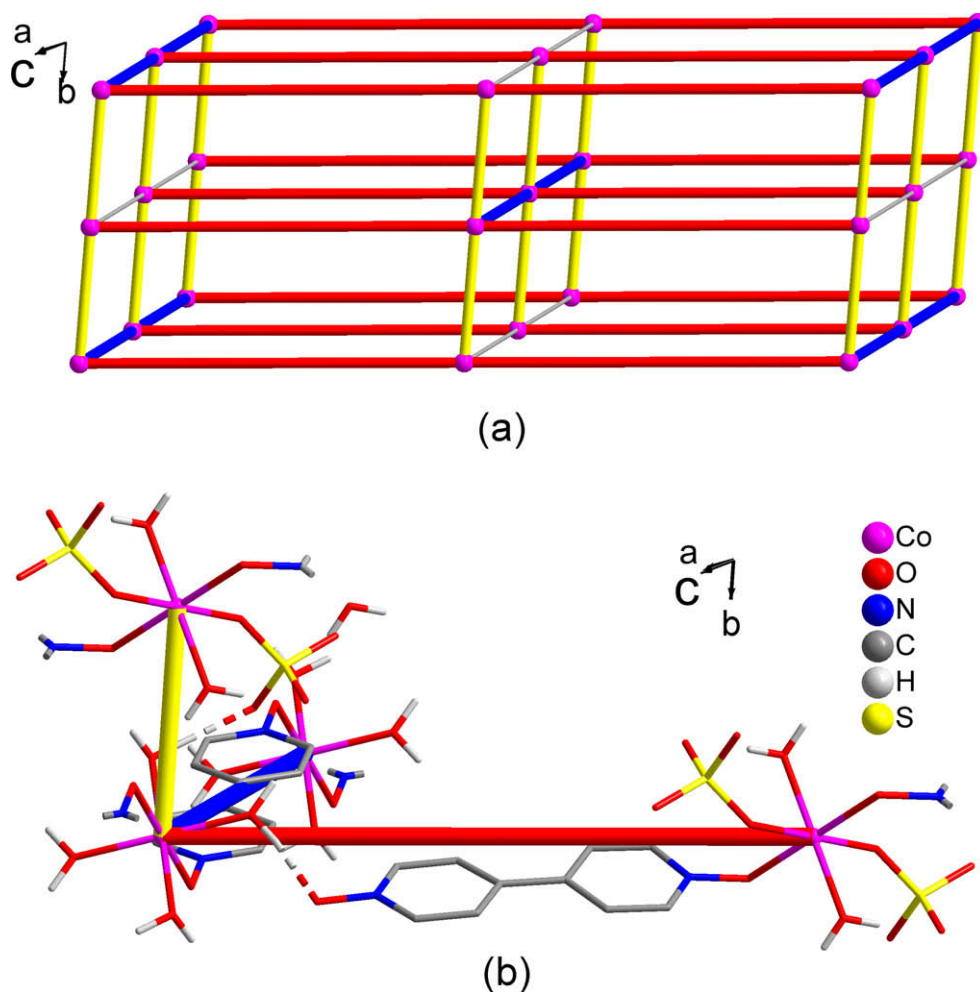


**Scheme 1.** Synthetic scheme and schematic drawings of the products **1–3** from the reaction of  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  with bpdo with (left) and without (right) the presence of an auxiliary Schiff base reagent.

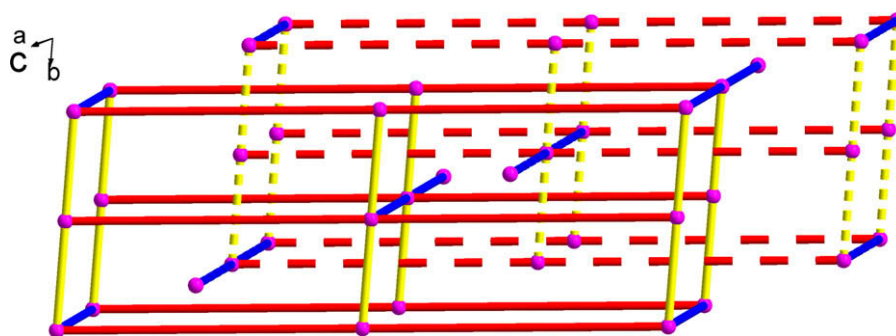




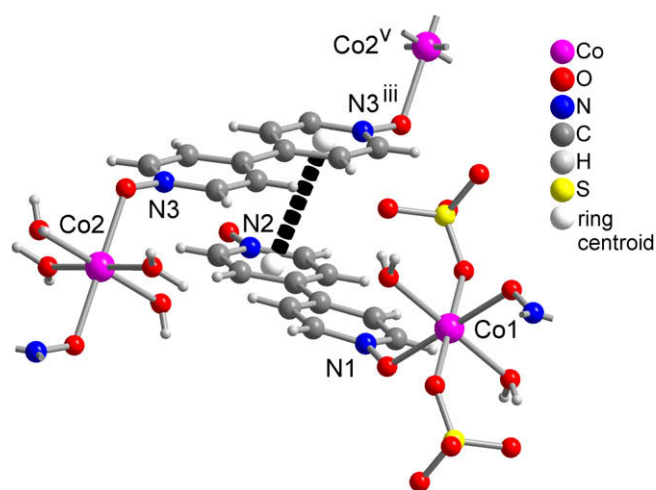
**Fig. 2.** Hydrogen bonding interactions of a Co1-anion between four Co2-cationic chains in **1**; H-bond lengths, angles and symmetry relations in Table 3. Colored bars connect the Co nodes; red bars depict the Co2-OH<sub>2</sub>···bpdo-Co1 connection, yellow bars the Co2-OH<sub>2</sub>···O-SO<sub>3</sub>-Co1 connectivity (cf. Figs. 3 and 4). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



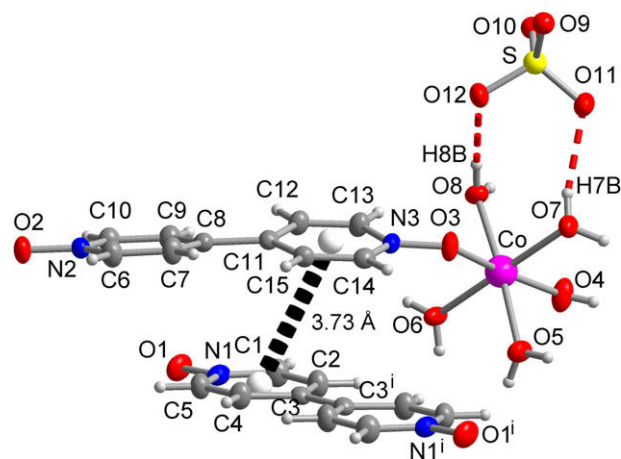
**Fig. 3.** (a) Primitive cubic, pcu-type net from which the fsc net of **1** is obtained upon omission of each second connectivity (grey bars) along one direction. Square-planar, 4-connected (Co1 in anion) and octahedral, 6-connected nodes (Co2 in cation) alternate along *b* and the *ac* diagonal. Colored bars connect the (pink) Co nodes (see Fig. S4 for a different view). (b) Blue bars depict the 1D [-Co2-bpdo-]<sub>n</sub> cation chains, red bars the Co2-OH<sub>2</sub>···bpdo-Co1 connection, yellow bars the Co2-OH<sub>2</sub>···O-SO<sub>3</sub>-Co1 connectivity (cf. Fig. 2). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 4.** Interpenetration of two mixed-covalent and -supramolecular fsc nets of **1**. The two symmetry-related nets are differentiated by solid and dashed bars which connect the (pink) Co nodes (see Fig. S5 for a different view). Blue bars depict the 1D  $\{-\text{Co2-bpdo-}\}_n$  cation chains, red bars the  $\text{Co2-OH}_2 \cdots \text{bpdo-Co1}$  connection, yellow bars the  $\text{Co2-OH}_2 \cdots \text{O-SO}_3\text{-Co1}$  connectivity (cf. Figs. 2 and 3). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 5.**  $\pi$ -Stacking interaction (dashed line) in **1** of the near-parallel pyridyl rings (dihedral angle  $5.6(1)^\circ$ ) which belong to the symmetry-related interpenetrating nets. Centroid-centroid distance  $3.603(2)$  Å, interplanar separation as normal from ringN2 to ringN3  $3.427(1)$  Å, slip-angle  $14.6^\circ$  (angle between the centroid vector of ringN2  $\cdots$  ringN3<sup>iii</sup> and the normal to the plane of ringN2) (cf. Table S1 in Supporting Information); symmetry transformations iii =  $1-x, 1-y, 1-z$ ; v =  $1+x, y, -1+z$ .



**Fig. 6.** Ellipsoid plot (50% probability) of a molecule of **2** with part of the overall  $\pi$ -stacking and hydrogen-bonding scheme (see Figs. S6 and S7 for additional  $\pi$ -stacking and hydrogen-bonding interactions); symmetry transformation i =  $-x, 1-y, 1-z$ ; bond lengths and angles in Table 4.

The length of the bpdo ligands creates large voids in a single net, so that two symmetry related nets interpenetrate (Fig. 4) [29]. Such interpenetrating mixed metal-organic and supramolecular networks have recently been analyzed [30].

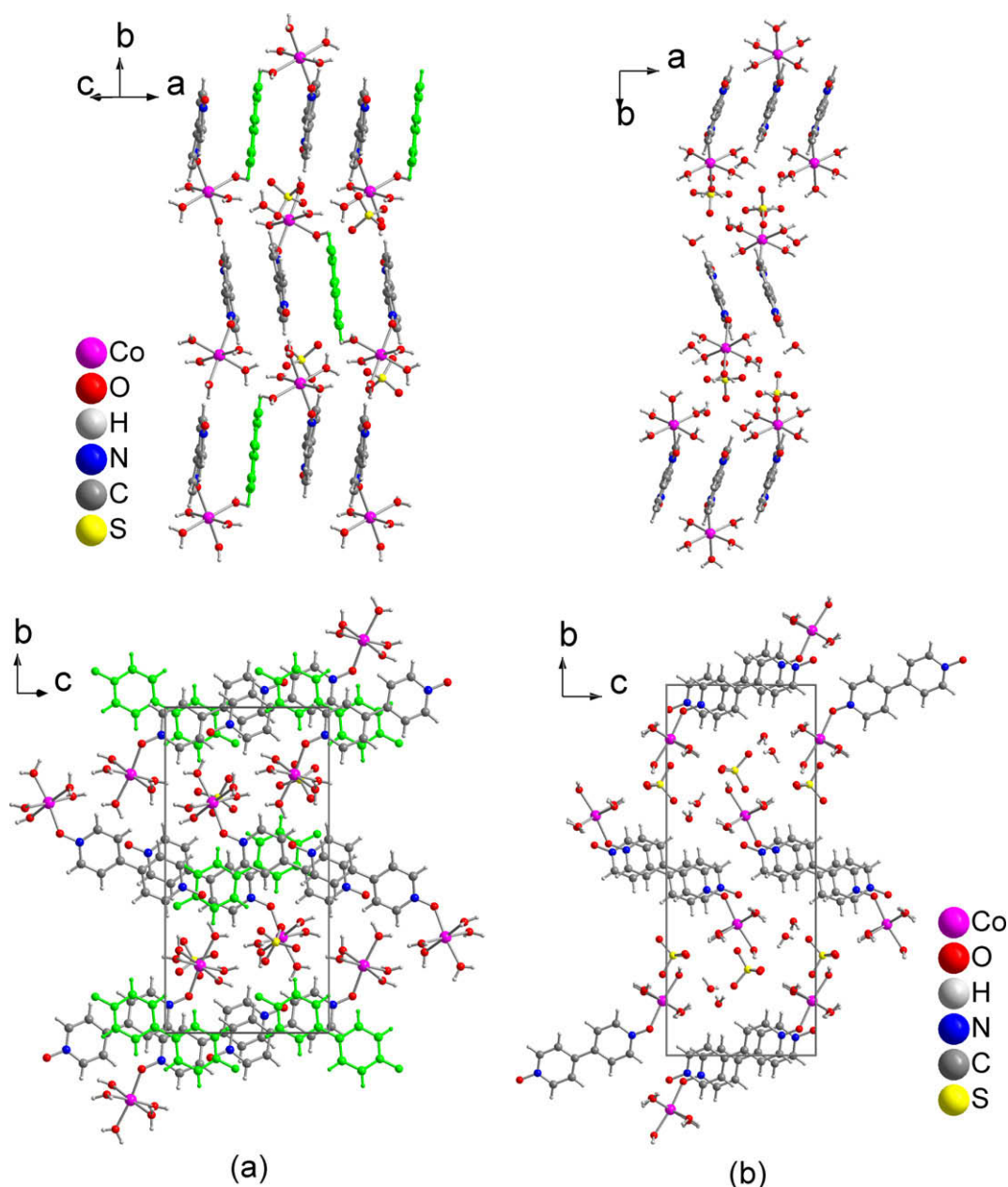
The bpdo ligands are involved in  $\pi$ - $\pi$  stacking interactions [31] (Fig. 5) and thereby direct the interpenetration of independent, albeit symmetry related, nets as  $\pi$ -stacking is one of the primary weak intermolecular forces to control the intergrowth of interpenetrating networks [32].

Compound **2** consists of the molecular complex  $[\text{Co}(\text{bpdo})(\text{H}_2\text{O})_5]^{2+}$  which crystallizes with the  $\text{SO}_4^{2-}$  counterion and half a molecule of bpdo (per formula unit) (Fig. 6). There are medium  $\pi$ -stacking interactions [31] between pyridyl rings of coordinated and free bpdo units (Fig. 6 and Fig. S6, Table S2). All H atoms of the aqua ligands in **2** enter in hydrogen bonds to sulfate or bpdo-O atoms (Fig. S7, Table S3).

Compound **2** is a pseudo-polymorph [33] (although this term is a matter of dispute [34]) of  $[\text{Co}(\text{bpdo})(\text{H}_2\text{O})_5]\text{SO}_4 \cdot 2\text{H}_2\text{O}$ , **3** [4] in that it differs in the guest molecule of crystallization, namely  $1/2\text{bpdo}$  instead of  $2\text{H}_2\text{O}$ . The packing of both forms is similar in the sense that hydrophobic layers of  $\pi$ -stacked bpdo-planes and hydrophilic layers of  $\{\text{Co}(\text{H}_2\text{O})_5\}\text{-SO}_4 (+2\text{H}_2\text{O})$  alternate along the  $b$ -direction (Fig. 7) [35]. The uncoordinated bpdo guest molecules are part of the hydrophobic layer in **2** and are stacked after each second coordinated bpdo moieties along  $a$  (Fig. 7a). The additional  $\pi$ -stacking between the coordinated and free bpdo weakens the  $\pi$ -stacking between the coordinated bpdo so that these molecules are moved apart in the  $c$ -direction when compared to **3** (Fig. 7). The water of crystallization is part of the hydrophilic layer in **3** and widens this layer in the  $b$ -direction (Fig. 7b). The different solvates and their packing are reflected in the relative cell constants:  $a$  and  $c$  being larger for **2**,  $b$  being larger for **3** (see Fig. 7).

#### 4. Conclusions

Cobalt sulfate,  $\text{CoSO}_4$  reacts with bpdo in the presence of a Schiff base to the compound  $1_\infty\{[\text{Co}(\mu\text{-bpdo})(\text{H}_2\text{O})_4]^{2+}\}_n n[\text{Co}(\text{SO}_4)_2(\text{bpdo})_2(\text{H}_2\text{O})_2]^{2-}$  (**1**) with a cationic coordination polymeric chain and a  $>22$  Å long complex anion. Compound **1** forms a doubly-interpenetrated fsc net from the covalent cation chain and hydrogen-bonding bridging action between the cation chain and complex anion. In the absence of the Schiff base under otherwise identical conditions the molecular pseudo-polymorphic complexes  $[\text{Co}(\text{bpdo})(\text{H}_2\text{O})_5]\text{SO}_4 \cdot 1/2\text{bpdo}$  (**2**) and  $[\text{Co}(\text{bpdo})(\text{H}_2\text{O})_5]\text{SO}_4 \cdot 2\text{H}_2\text{O}$  (**3**) are obtained.



**Fig. 7.** Packing diagram (two views each) of the different solvates (pseudo-polymorphs) (a)  $[\text{Co}(\text{bpdo})(\text{H}_2\text{O})_5]\text{SO}_4 \cdot 1/2(\text{bpdo})$ , **2** and (b)  $[\text{Co}(\text{bpdo})(\text{H}_2\text{O})_5]\text{SO}_4 \cdot 2\text{H}_2\text{O}$ , **3** (space group  $P2_1/n$ ). The uncoordinated bpdo guest molecules in **2** are shown in green in (a). Cell constants for **3** from RAXMUZ [4a]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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### Appendix A. Supplementary material

CCDC 768484 and 768485 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.03.025.

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