

catena-Poly[[[triaquasulfato-cobalt(II)]- μ -4,4'-bipyridine] ethane-1,2-diol solvate]

Wen-Jie Lu,* Yi-Min Zhu and Kai-Long Zhong

 Department of Chemical and Environmental Engineering, Wuyi University, Jiangmen, Guangdong Province, People's Republic of China
 Correspondence e-mail: wjlu_56@yahoo.com.cn

Received 3 July 2006

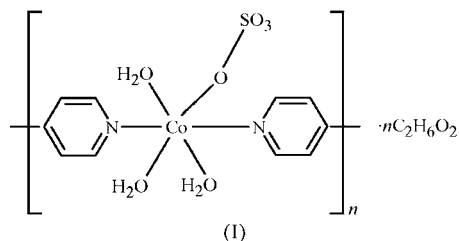
Accepted 10 August 2006

Online 31 August 2006

In the title compound, $[[\text{Co}(\text{SO}_4)(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_3] \cdot \text{C}_2\text{H}_6\text{O}_2]_n$, each Co^{II} center is octahedrally coordinated by two N atoms from two bridging 4,4'-bipyridine (bipy) ligands and four O atoms, one from a monodentate sulfate ligand and three from aqua ligands. The bipy ligands occupy special positions of site symmetry $\bar{1}$ and bridge adjacent cobalt(II) centers to form one-dimensional linear coordination chains. Adjacent chains are arranged in a cross-like fashion around the mid-point of the bipy ligands, resulting in a three-dimensional supramolecular array.

Comment

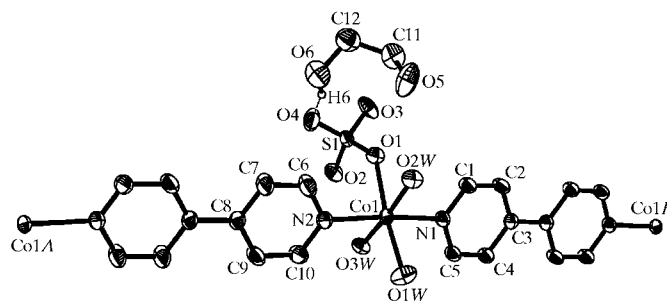
Supramolecular assembly and crystal engineering of metal-organic coordination frames have recently attracted great interest, owing to their interesting structural topologies and potential application as functional materials (Batten & Robson, 1998; Eddaoudi *et al.*, 2001). It is well established that two main weak interactions, *viz.* hydrogen bonds (Aakeröy & Beatty, 1998) and π - π interactions (Ning *et al.*, 1999), play vital roles in molecular recognition and supramolecular chemistry. Some interesting coordination polymers assembled with 4,4'-bipyridine (bipy) have been reported, showing



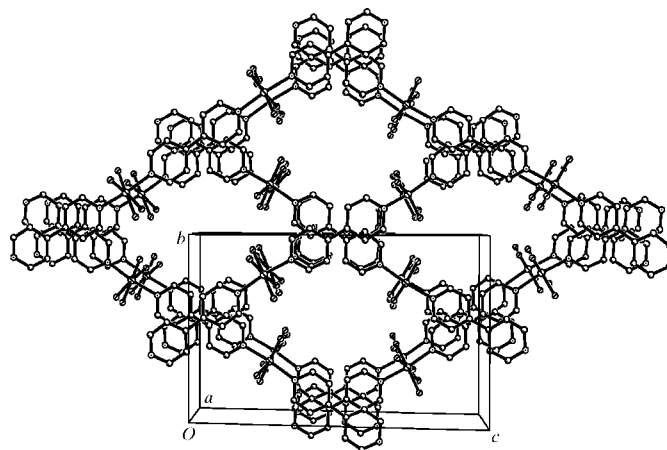
various structural motifs, including two-dimensional layers (Carlucci *et al.*, 1997; Tong *et al.*, 1998) and three-dimensional nets (Lu *et al.*, 1998; Hagrman, *et al.*, 1998; Kondo, *et al.*, 1999; Greve *et al.* 2003; Zhang *et al.*, 1999). We have carried out solvothermal reactions using $\text{Co}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$ and bipy in the

hope of obtaining complexes retaining some of the solvent molecules capable of hydrogen bonding. We report here the crystal structure of the title new polymeric compound containing ethane-1,2-diol solvent molecules, $[[\text{Co}(\text{SO}_4)(\text{bipy})(\text{H}_2\text{O})_3] \cdot \text{C}_2\text{H}_6\text{O}_2]_n$ (I).

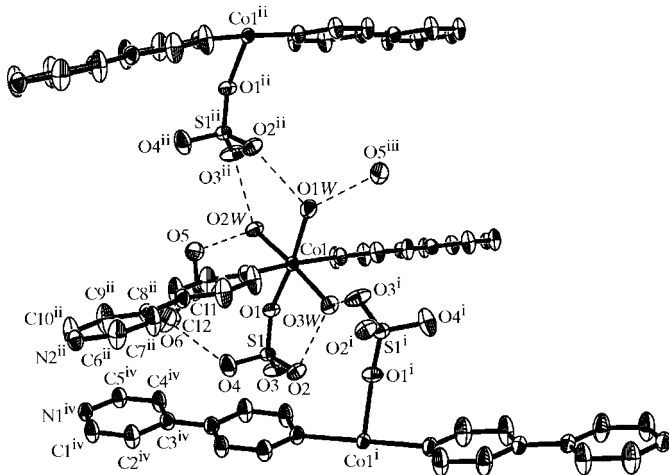
Part of the structure of (I) is shown in Fig. 1. Each Co^{II} center is situated on an inversion center with an octahedral geometry (Table 1). The bipy ligand functions as a bridging ligand to adjacent Co^{II} centers, leading to the formation of linear $-\text{Co}-\text{bipy}-\text{Co}-$ chains in which the separation of neighboring Co^{II} centers connected by one bipy ligand is 11.4045 (15) Å, and the nearest $\text{Co} \cdots \text{Co}(x-1, y, z)$ inter-chain separation is 7.5232 (12) Å. The geometry of the bipy, aqua and sulfate ligands is in very good agreement with those observed in other cobalt complexes, *e.g.* $[\text{Co}(\text{SO}_4)(\text{bipy})(\text{H}_2\text{O})_3] \cdot 2\text{H}_2\text{O}$ (Lu *et al.*, 1998).


Figure 1

Part of the chain structure of the title compound, showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level. The dashed line represents an $\text{O}-\text{H} \cdots \text{O}$ interaction. H atoms not involved in hydrogen bonds have been omitted for clarity. Unlabeled atoms are related to labeled atoms by $(-x+1, -y+1, -z+1)$ and $(-x+1, -y+2, -z+2)$.


Figure 2

The crystal structure of the title compound, viewed along the *a* axis. Sulfate anions, ethane-1,2-diol solvent molecules and H atoms have been omitted for clarity.


Figure 3

Hydrogen-bonding interactions (dashed lines) and π - π stacking interactions between adjacent chains. H atoms have been omitted for clarity. The symmetry codes are as in Table 2, with the addition of (iv) $x + \frac{1}{2}$, $-y + \frac{3}{2}$, $z + \frac{1}{2}$.

Adjacent chains are each arranged in a cross-like fashion, intersecting at the centers of the bipy ligands, resulting in a three-dimensional supramolecular array. The rhombic channels ($12.016 \times 10.777 \text{ \AA}$) running along the a axis (Fig. 2) are filled with the sulfate anions and ethane-1,2-diol molecules. The structure of the resulting array is predominantly directed by π - π stacking interactions between the bipy bridges and numerous classical hydrogen-bonding interactions, namely O—H...O interactions involving the water molecules, sulfate ligands and ethane-1,2-diol solvent molecules (Fig. 3 and Table 2). The two pyridyl rings of each bipy ligand are coplanar with one another. The close bipy rings N1BC/C1BC—C5BC and N2A/C6A—C10A have a face-to-face distance of 4.042 \AA , showing significant inter-chain π - π stacking interaction (Fig. 3). It is noteworthy that such an arrangement of the title compound is different from those of three recently documented one-dimensional coordination polymers with analogous coordination chain skeletons, in which the chains in adjacent layers are rotated by 60° to provide helical staircase networks (Hagman *et al.*, 1998; Lu *et al.*, 1998; Kondo *et al.*, 1999). It is also different from another arrangement of one-dimensional coordination chains with a similar chain skeleton, *e.g.* in $[\text{Co}(\text{bipy})(\text{O}_2\text{CCH}_3)_2(\text{H}_2\text{O})_2]$ (Zhang *et al.*, 1999) and $[\text{Co}(\text{bipy})(\text{H}_2\text{O})_4](\text{NO}_3)_2 \cdot \text{bipy}$ (Carlucci *et al.*, 1997), in which adjacent chains are only interconnected by hydrogen bonds, resulting in three-dimensional networks.

Experimental

4,4'-Bipyridine (0.1 mmol), trimethylammonioacetate (0.1 mmol), $\text{Co}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$ (0.1 mmol), ethane-1,2-diol (2.0 ml) and water (1.0 ml) were placed in a thick Pyrex tube. The tube was sealed and heated at 353 K for 3 d to give red block-like crystals of the title compound. Analysis found: C 33.76, H 4.80, N 7.96%; calculated for $\text{C}_{12}\text{H}_{20}\text{CoN}_2\text{O}_9\text{S}$: C 33.73, H 4.72, N 6.56%. FT-IR (KBr, cm^{-1}): 3400 (*m*, *b*), 3070 (*w*), 1604 (*m*), 1531 (*w*), 1488 (*w*), 1411 (*m*), 1430 (*w*), 1218 (*m*), 1120 (*s*), 806 (*m*).

Crystal data

$[\text{Co}(\text{SO}_4)(\text{C}_{10}\text{H}_8\text{N}_2) \cdot (\text{H}_2\text{O})_3] \cdot \text{C}_2\text{H}_6\text{O}_2$
 $M_r = 427.29$
 Monoclinic, $P2_1/n$
 $a = 7.5232 (12) \text{ \AA}$
 $b = 11.7458 (18) \text{ \AA}$
 $c = 19.475 (3) \text{ \AA}$
 $\beta = 98.671 (3)^\circ$

$V = 1701.2 (5) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.668 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 1.18 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
 Block, red
 $0.40 \times 0.35 \times 0.23 \text{ mm}$

Data collection

Bruker SMART CCD 1K area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.649$, $T_{\max} = 0.773$

9065 measured reflections
 2989 independent reflections
 2535 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.029$
 $\theta_{\text{max}} = 25.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.083$
 $S = 1.08$
 2989 reflections
 258 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0325P)^2 + 1.9234P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.71 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$

H atoms treated by a mixture of independent and constrained refinement

Table 1

Selected geometric parameters (\AA , $^\circ$).

Co1—O2W	2.090 (2)	O2—S1	1.479 (2)
Co1—O3W	2.094 (2)	O3—S1	1.469 (2)
Co1—O1	2.0954 (19)	O4—S1	1.453 (2)
Co1—O1W	2.099 (2)	O5—C11	1.423 (4)
Co1—N1	2.145 (2)	O6—C12	1.411 (5)
Co1—N2	2.161 (2)	C11—C12	1.489 (5)
O1—S1	1.473 (2)		
O2W—Co1—O3W	173.38 (9)	O1—Co1—O1W	170.56 (9)
O2W—Co1—O1	81.62 (8)	N1—Co1—N2	173.36 (9)
O3W—Co1—O1	91.79 (8)	O5—C11—C12	115.3 (3)
O2W—Co1—O1W	89.05 (10)	O6—C12—C11	113.5 (3)
O3W—Co1—O1W	97.52 (9)		

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
O3W—H3WA...O3 ⁱ	0.86 (2)	1.83 (2)	2.683 (3)	171 (3)
O3W—H3WB...O2	0.86 (2)	1.89 (2)	2.721 (3)	163 (4)
O2W—H2WA...O3 ⁱⁱ	0.81 (2)	1.81 (3)	2.625 (3)	176 (4)
O2W—H2WB...O5	0.81 (2)	2.18 (3)	2.983 (4)	169 (4)
O1W—H1WA...O5 ⁱⁱⁱ	0.77 (3)	2.03 (3)	2.790 (4)	166 (4)
O1W—H1WB...O2 ⁱⁱ	0.77 (3)	1.95 (3)	2.714 (3)	170 (5)
O6—H6...O4	0.91 (4)	1.87 (5)	2.749 (4)	164 (7)

Symmetry codes: (i) $-x + \frac{3}{2}$, $y + \frac{1}{2}$, $-z + \frac{3}{2}$; (ii) $x - 1$, y , z ; (iii) $-x + \frac{1}{2}$, $y + \frac{1}{2}$, $-z + \frac{3}{2}$.

The H atoms of CH and CH_2 groups were positioned geometrically and allowed to ride on their parent atoms [$C\text{—}H = 0.93$ and 0.97 \AA , respectively, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$]. The H atoms of OH groups and water molecules were located in a difference Fourier map and refined with restraints on the O—H bond lengths.

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 1998); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1998); software used to prepare material for publication: SHELXTL.

X-ray data were collected at the Chinese University of Hong Kong.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ3018). Services for accessing these data are described at the back of the journal.

References

- Aakeröy, C. B. & Beatty, A. M. (1998). *Chem. Commun.* pp. 1067–1068.
- Batten, S. R. & Robson, R. (1998). *Angew. Chem. Int. Ed.* **37**, 1460–1494.
- Bruker (1998). *SMART, SAINT and SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Carlucci, L., Ciani, G., Proserpio, D. M. & Sironi, A. (1997). *J. Chem. Soc. Dalton Trans.* pp. 1801–1803.
- Eddaoudi, M., Moler, D. B., Li, H. L., Chen, B. L., Reineke, T. M., O’Keeffe, M. & Yaghi, O. M. (2001). *Acc. Chem. Res.* **34**, 319–330.
- Greve, J., Jess, I. & Näther, C. (2003). *J. Solid State Chem.* **175**, 328–340.
- Hagrman, D., Hammond, R. P., Haushalter, R. & Zubieta, J. (1998). *Chem. Mater.* **10**, 2091–2094.
- Kondo, M., Shimamura, M., Noro, S. I., Yoshitomi, T., Minakoshi, S. & Kitagawa, S. (1999). *Chem. Lett.* pp. 285–286.
- Lu, J., Yu, C., Niu, T. Y., Paliwala, T., Crisci, G., Somosa, F. & Jacobson, A. J. (1998). *Inorg. Chem.* **37**, 4637–4640.
- Ning, G. L., Wu, L. P., Sugimoto, K., Munakata, M., Kuroda-Sowa, T. & Maekawa, M. (1999). *J. Chem. Soc. Dalton Trans.* pp. 2529–2536.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXS97 and SHELXL97*. University of Göttingen, Germany.
- Tong, M. L., Cai, J. W., Yu, X. L., Che, X. M., Ng, S. W. & Mak, T. C. W. (1998). *Aust. J. Chem.* **51**, 637–641.
- Zhang, Y. S., Enright, G. D., Breeze, S. R. & Wang, S. (1999). *New J. Chem.* **23**, 625–628.