

**μ -1,2-Bis(4-pyridyl)ethene- $\kappa^2N:N'$ -
 bis(tetraqua[4-[2-(4-pyridinio)-
 ethenyl]pyridine- κN]cobalt(II))
 hexaaquacobalt(II) tetrakis(sulfate)
 octahydrate**

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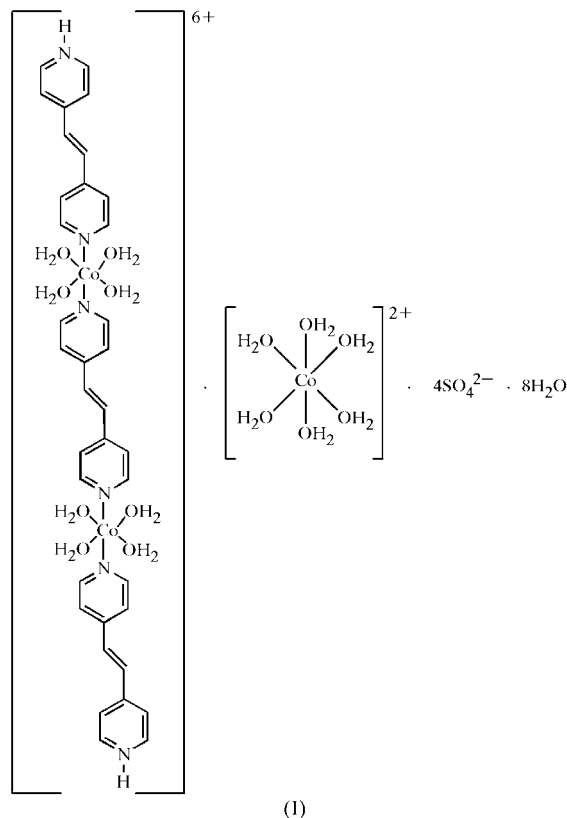
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The title compound, $[\text{Co}_2(\text{C}_{12}\text{H}_{11}\text{N}_2)_2(\text{C}_{12}\text{H}_{10}\text{N}_2)(\text{H}_2\text{O})_8] \cdot [\text{Co}(\text{H}_2\text{O})_6](\text{SO}_4)_4 \cdot 8\text{H}_2\text{O}$, consists of bis(4-pyridyl)ethenedicobalt(II) cations, hexaaquacobalt cations, sulfate anions and water solvent molecules that are linked by hydrogen bonds into a network structure. In the hexaaquacobalt cation, the six water molecules are coordinated in an octahedral geometry to the Co atom, which lies on an inversion centre. The other cation is a 1,2-bis(4-pyridyl)ethene-bridged centrosymmetric dimer, consisting of protonated 1,2-bis(4-pyridyl)ethene cations, a bridging 1,2-bis(4-pyridyl)ethene ligand and tetraaquacobalt cations. Each Co atom is six-coordinated by four water molecules and two N atoms from a protonated 1,2-bis(4-pyridyl)ethene cation and the bridging 1,2-bis(4-pyridyl)ethene ligand, and the geometry around each Co atom is octahedral.

Comment

Much interest at present is focused on the deliberate construction of coordination polymers (Carlucci *et al.*, 1994; Munakata *et al.*, 1999; Hirsch *et al.*, 1997; Hoskins & Robson, 1990), and a large amount of this interest has involved linear



pyridyl-donor ligands. These include pyrazine (Carlucci *et al.*, 1995), 4,4'-bipyridine (bipy; Yaghi & Li, 1996) and longer bridges (Soma & Iwamoto, 1997). Bipy has been used extensively before (Huang & Xiong, 1997); however, few coordination polymers are known for the other ligands (Batten *et al.*, 1999). Against this background, we report here the structure

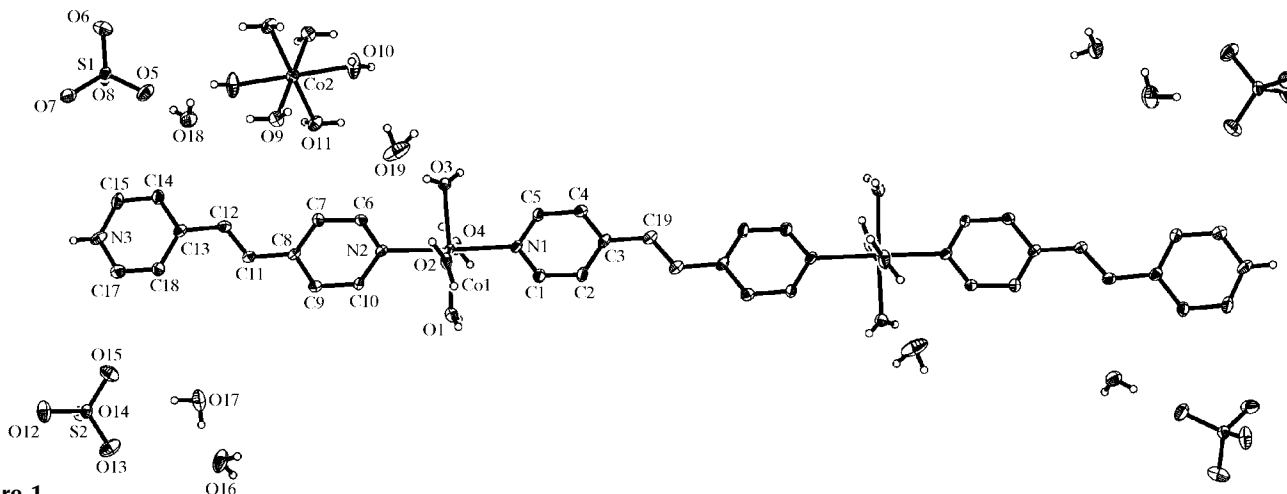
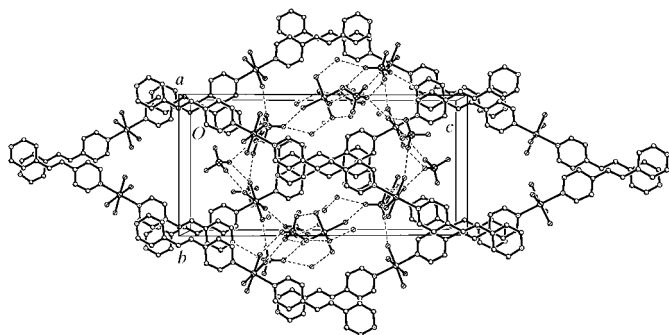


Figure 1

ORTEP (Johnson, 1976) plot of the title compound, showing 50% probability displacement ellipsoids. Only the contents of the asymmetric unit are labelled. H atoms of aromatic rings have been omitted for clarity.


Figure 2

The three-dimensional network formed by hydrogen-bonding interactions (dashed lines) in the title compound.

of the title compound, (I), to outline further studies on coordination polymers constructed through the interaction of metal ions with pyridyl-donor ligands with two-connecting geometry.

The title compound consists of $[\text{C}_{36}\text{H}_{48}\text{Co}_2\text{N}_6\text{O}_8]^{6+}$ cations, hexaaquacobalt cations, sulfate anions and water solvent molecules (Fig. 1 and Table 1). In the $[\text{C}_{36}\text{H}_{48}\text{Co}_2\text{N}_6\text{O}_8]^{6+}$ cation, the Co^{2+} ion coordinates to four O atoms from four water molecules and two N atoms from a protonated 1,2-bis(4-pyridyl)ethene cation and a 1,2-bis(4-pyridyl)ethene ligand, and the geometry around the Co^{2+} ion is a distorted octahedral. The bridging 1,2-bis(4-pyridyl)ethene ligand links two Co^{2+} ions, forming a centrosymmetric dimer. In this dimeric cation, the two terminal 1,2-bis(4-pyridyl)ethene ligands are protonated at one end, and the bridging ligands act in a monodentate mode. This coordination mode is quite different from that reported by Batten *et al.* (1999) for $[\text{Cu}\{1,2\text{-bis}(4\text{-pyridyl)ethene}\}_2\text{BF}_4\cdot\text{CH}_3\text{CN}]$, in which the 1,2-bis(4-pyridyl)ethene ligand coordinates in a bridging fashion. In (I), there is a six-coordinate hexaaquacobalt cation to balance the charge and complex hydrogen bonds are present (Table 2).

The $[\text{C}_{36}\text{H}_{48}\text{Co}_2\text{N}_6\text{O}_8]^{6+}$ cations are arranged in a parallel fashion, but only the terminal protonated 1,2-bis(4-pyridyl)ethene ligands of each cation are overlapped. The sulfate anions, water molecules and hexaaquacobalt cations are distributed regularly between the overlap area. There are two kinds of parallel arrangement directions of $[\text{C}_{36}\text{H}_{48}\text{Co}_2\text{N}_6\text{O}_8]^{6+}$ cations, which cross one another. The angle between the crossing molecules is $57.75(3)^\circ$ and there are also significant face-to-face π - π interactions of the pyridyl rings between the molecules; the average distance is about 3.329 Å. The crossing $[\text{C}_{36}\text{H}_{48}\text{Co}_2\text{N}_6\text{O}_8]^{6+}$ cations form a regular grid structure, and interact with π - π interactions, forming alternate layers. There are channels between the layer grids, and the sulfate anions, the hexaaquacobalt cations and the water molecules reside in channels through the structure, interacting *via* numerous hydrogen bonds (Table 2 and Fig. 2).

Experimental

Cobalt sulfate heptahydrate (0.6 g, 2 mmol) was dissolved in water (10 ml) and the solution was mixed with a dimethylformamide solu-

tion (10 ml) of 1,2-bis(4-pyridyl)ethene (0.4 g, 2 mmol), trimesic acid (0.4 g, 2 mmol) and 2,2'-dithiosalicic acid (0.6 g, 2 mmol) at 298 K. The reaction mixture was filtered and brown block-shaped crystals separated from the solution after about three months.

Crystal data

$[\text{Co}_2(\text{C}_{12}\text{H}_{11}\text{N}_2)_2(\text{C}_{12}\text{H}_{10}\text{N}_2)(\text{H}_2\text{O})_8][\text{Co}(\text{H}_2\text{O})_6](\text{SO}_4)_4\cdot 8\text{H}_2\text{O}$
 $M_r = 1506.06$
 Monoclinic, $P2_1/c$
 $a = 10.2353(8) \text{ \AA}$
 $b = 12.1885(9) \text{ \AA}$
 $c = 24.9647(19) \text{ \AA}$
 $\beta = 93.895(2)^\circ$
 $V = 3107.2(4) \text{ \AA}^3$
 $Z = 2$
 $D_x = 1.610 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 Cell parameters from 5517 reflections
 $\theta = 1.9\text{--}25.1^\circ$
 $\mu = 1.03 \text{ mm}^{-1}$
 $T = 298(2) \text{ K}$
 Block, brown
 $0.31 \times 0.18 \times 0.15 \text{ mm}$

Data collection

Bruker SMART CCD area detector diffractometer
 ω scans
 Absorption correction: numerical (*SADABS*; Sheldrick, 1996)
 $T_{\text{min}} = 0.81$, $T_{\text{max}} = 0.85$
 16 014 measured reflections
 5517 independent reflections

4657 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.057$
 $\theta_{\text{max}} = 25.1^\circ$
 $h = -12 \rightarrow 12$
 $k = -14 \rightarrow 14$
 $l = -21 \rightarrow 29$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.068$
 $wR(F^2) = 0.144$
 $S = 1.20$
 5517 reflections
 425 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0549P)^2 + 2.9068P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.016$
 $\Delta\rho_{\text{max}} = 0.72 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.47 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Co1—O4	2.095 (3)	Co1—N1	2.153 (4)
Co1—O3	2.096 (3)	Co2—O11	2.065 (3)
Co1—O1	2.106 (3)	Co2—O9	2.094 (3)
Co1—O2	2.107 (3)	Co2—O10	2.127 (4)
Co1—N2	2.151 (4)		
O4—Co1—O3	95.94 (13)	O2—Co1—N2	90.27 (14)
O4—Co1—O1	85.40 (13)	O4—Co1—N1	87.90 (14)
O3—Co1—O1	177.59 (13)	O3—Co1—N1	90.98 (14)
O4—Co1—O2	172.56 (13)	O1—Co1—N1	91.08 (14)
O3—Co1—O2	91.00 (13)	O2—Co1—N1	89.29 (14)
O1—Co1—O2	87.77 (12)	N2—Co1—N1	178.45 (15)
O4—Co1—N2	92.72 (14)	O11—Co2—O9	90.17 (13)
O3—Co1—N2	87.54 (14)	O11—Co2—O10	91.36 (15)
O1—Co1—N2	90.39 (14)	O9—Co2—O10	91.40 (15)

The H atoms of the solvent water molecules were refined subject to the restraint O—H = 0.82 (5) Å. The other H atoms were positioned geometrically and allowed to ride on their parent atoms at distances of 0.82 (O—H), 0.86 (N—H) and 0.93 Å (C—H), with $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{parent atom})$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

Table 2
Hydrogen-bond geometry (Å, °).

	D—H	H···A	D···A	D—H···A
O1—H1B···O6 ⁱⁱ	0.82	1.92	2.688 (4)	155
O1—H1A···O13 ⁱⁱⁱ	0.82	2.02	2.738 (5)	145
O2—H2B···O12 ⁱⁱⁱ	0.82	1.91	2.699 (5)	160
O2—H2A···O8 ^{iv}	0.82	2.01	2.711 (4)	143
O3—H3B···O19	0.82	1.89	2.686 (6)	162
O3—H3A···O6 ⁱ	0.82	1.97	2.711 (5)	150
O4—H4B···O7 ⁱⁱ	0.82	2.00	2.781 (5)	159
O4—H4A···O13 ^v	0.82	2.02	2.703 (5)	141
O9—H9B···O18	0.82	1.95	2.761 (6)	172
O10—H10B···O5 ⁱ	0.82	2.17	2.813 (5)	136
O10—H10A···O12 ^{vi}	0.82	1.91	2.698 (5)	161
O11—H11B···O16 ^{vii}	0.82	1.86	2.669 (6)	167
O11—H11A···O14 ^{viii}	0.82	1.93	2.739 (5)	169
N3—H3N···O8 ^{viii}	0.86	1.87	2.723 (5)	174
O16—H16A···O13 ^{ix}	0.76 (4)	2.04 (4)	2.797 (6)	174 (6)
O16—H16B···O6 ^{vi}	0.76 (4)	2.30 (4)	3.024 (6)	161 (6)
O17—H17A···O15	0.80 (4)	2.28 (5)	2.987 (7)	147 (5)
O17—H17B···O14 ^{ix}	0.82 (4)	2.28 (5)	2.936 (7)	138 (6)
O18—H18A···O17 ^{vi}	0.79 (4)	2.07 (4)	2.855 (8)	170 (6)
O18—H18B···O5	0.77 (4)	2.09 (4)	2.844 (6)	166 (6)
O19—H19B···O12 ^{vi}	0.80 (4)	2.20 (5)	2.939 (7)	155 (6)

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

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ1033). Services for accessing these data are described at the back of the journal.

References

- Batten, S. R., Jeffery, J. C. & Ward, M. D. (1999). *Inorg. Chim. Acta*, **292**, 231–237.
- Bruker (2000). *SMART, SAINT, SADABS and SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Carlucci, L., Ciani, G. & Proserpio, D. M. (1994). *Chem. Commun.* pp. 2755–2757.
- Carlucci, L., Ciani, G. & Proserpio, D. M. (1995). *Chem. Int. Ed. Engl.* **34**, 1895–1899.
- Hirsch, K. A., Wilson, S. C. & Moore, J. S. (1997). *Chem. Eur. J.* **3**, 765–771.
- Hoskins, B. F. & Robson, R. (1990). *J. Am. Chem. Soc.* **112**, 1546–1551.
- Huang, S. D. & Xiong, R.-G. (1997). *Polyhedron*, **16**, 3929–3932.
- Johnson, C. K. (1976). *ORTEP II*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Munakata, M., Wu, L. P. & Kuroda-Sowa, T. (1999). *Adv. Inorg. Chem.* **46**, 173–178.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXL97 and SHELXS97*. Release 97-2. University of Göttingen, Germany.
- Soma, T. & Iwamoto, T. (1997). *Acta Cryst.* **C53**, 1819–1821.
- Yaghi, O. M. & Li, H. (1996). *J. Am. Chem. Soc.* **118**, 295–298.