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catena-Poly[bis[aqua(2,2-bipyridine-κ^2N,N')cobalt(II)]-μ-1,2,4,5-benzene-tetracarboxylato-κ^4O^1:O^2:O^3:O^4]

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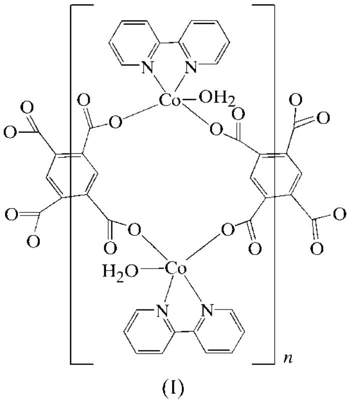
In the title complex, $[Co_2(C_{10}H_2O_8)(C_{10}H_8N_2)_2(H_2O)_2]$, the four carboxylate groups are fully deprotonated and coordinate to four Co^{II} cations in a monodentate fashion, forming a one-dimensional ribbon-like double-chain structure, with centrosymmetric $[Co_2(C_{10}H_2O_8)(C_{10}H_8N_2)_2(H_2O)_2]$ repeating units and a cavity of approximately 6.8 × 6.6 Å. Moreover, a three-dimensional supramolecular structure is formed by face-to-face π–π interactions between the aromatic rings of the 2,2′-bipyridine moieties of two adjacent chains, and by hydrogen-bonding interactions between the coordinated aqua O atom and the coordinated carboxyl O atom from different chains.

Comment

Coordinate polymer solids with a variety of cavities or channels are currently under intense study because of the scope they offer for the generation of new materials with a range of potentially useful properties (Yaghi *et al.*, 1998; Stein *et al.*, 1993). Popular bridging ligands in this field are 1,2,4,5-benzenetetracarboxylic acid (H_4TCB) and 4,4′-bipyridine, and their derivatives (Eddaoudi *et al.*, 2001). We have studied some transition metal complexes bridged by TCB^{4-} or H_2TCB^{2-} anions, such as those with Co^{II} (Wang *et al.*, 2000), Ni^{II} (Cheng *et al.*, 2001) and Cu^{II} (Hu *et al.*, 2003). In the course of our studies, the title novel infinite one-dimensional coordination polymer, $[Co_2(TCB)(2,2'\text{-bipy})_2(H_2O)_2]_n$ (2,2′-bipy is 2,2′-bipyridine), (I), was prepared and its structure is reported here. It should be noted that the synthetic conditions, such as H-atom receptors, temperature and solvents, *etc.*, play an imporant role in determining the compositions of these complexes.



(I)

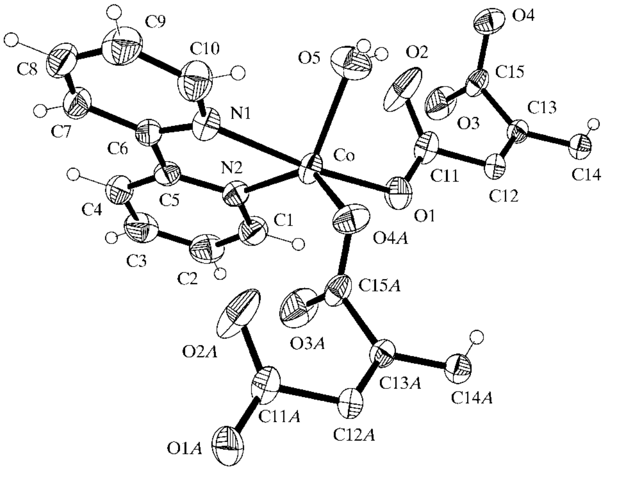


Figure 1
The coordination environment of the Co^{II} ion in (I), with the atom-numbering scheme, showing displacement ellipsoids at the 50% probability level.

In (I), each Co^{II} cation has a five-coordination environment, completed by two carboxyl O atoms belonging to two TCB^{4-} anions, one aqua O atom and two N atoms from one 2,2′-bipy ligand (Fig. 1). The Co—O bond lengths are all about 2.05 Å, while the Co—N1 bond [2.1590 (17) Å] is longer than the Co—N2 bond [2.0640 (17) Å]. An infinite one-dimensional polymer with a double-chain structure is formed by the Co^{II} cations, the μ_4-bridging TCB^{4-} anions, the aqua molecules and the terminal 2,2′-bipy ligands (Fig. 2).

The coordination mode of the TCB^{4-} anion in (I) is similar to that in $[Cu_2(TCB)(phen)_2]_n{\cdot}nH_2O$ (phen is 1,10-phenanthroline; Shi *et al.*, 2001). The four carboxylate groups are fully deprotonated and coordinate to four Co^{II} cations in a monodentate fashion, forming a one-dimensional ribbon-like

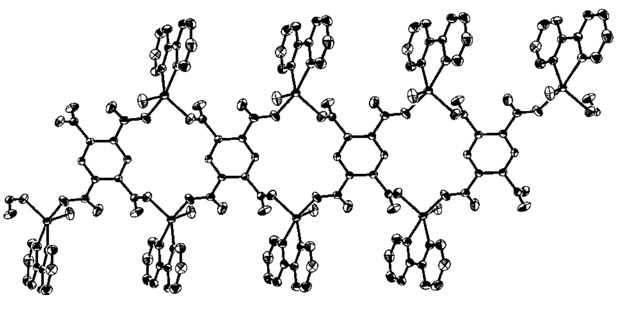


Figure 2
The double-chain structure of (I), showing the cavities.

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double-chain structure with cavities of approximately 6.8 × 6.6 Å. Intermolecular hydrogen-bonding interactions of 2.623 (2) Å are found between the coordinated aqua O atom and the coordinated carboxyl O atom from different chains, resulting in a two-dimensional supramolecular structure.

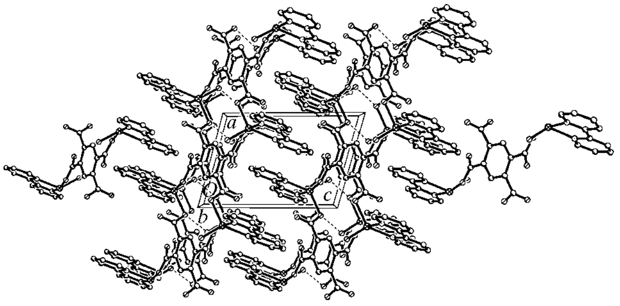

Figure 3
The three-dimensional network structure of (I).

Furthermore, a three-dimensional network structure is formed by face-to-face π–π interactions of approximately 3.78 Å between the aromatic rings of the 2,2′-bipy ligands of two adjacent chains (Fig. 3).

Experimental

A solution of dimethylformamide (10 ml) containing $CoCl_2\cdot6H_2O$ (0.5 mmol, 0.119 g) and H_4TCB (0.5 mmol, 0.127 g) was added slowly to a solution of dimethylformamide (10 ml) containing 2,2′-bipyridine (0.5 mmol, 0.078 g). The mixture was stirred for 30 min and left to stand at room temperature for about three weeks. Deep-red prism-shaped crystals of (I) were obtained.

Crystal data

$[Co_2(C_{10}H_2O_8)(C_{10}H_8N_2)_2(H_2O)_2]$
$M_r = 716.38$
Triclinic, $P\overline{1}$
$a = 7.5859$ (8) Å
$b = 8.9838$ (10) Å
$c = 10.6729$ (11) Å
$\alpha = 80.441$ (2)°
$\beta = 72.913$ (2)°
$\gamma = 77.096$ (2)°
$V = 673.75$ (12) Å^3

$Z = 1$
$D_x = 1.766$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 534 reflections
$\theta = 2.4$–23.0°
$\mu = 1.30$ mm^{-1}
$T = 273$ (2) K
Prism, red
0.31 × 0.21 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min} = 0.727$, $T_{max} = 0.855$
4962 measured reflections

2406 independent reflections
2273 reflections with $I > 2\sigma(I)$
$R_{int} = 0.015$
$\theta_{max} = 25.2$°
$h = -9 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.071$
$S = 1.08$
2406 reflections
217 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0362P)^2 + 0.3213P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.023$
$\Delta\rho_{max} = 0.31$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O5—H12···O4^{i}	0.854 (9)	1.770 (10)	2.623 (2)	177 (3)
O5—H13···O2	0.855 (10)	2.010 (17)	2.715 (2)	139 (2)

Symmetry code: (i) $1 - x, 1 - y, -z$.

The positions and isotropic displacement parameters of the water H atoms, H12 and H13, were refined subject to O—H = 0.85 (1) Å. The other H atoms were positioned geometrically and allowed to ride on their parent atoms at distances of 0.93 Å, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1428). Services for accessing these data are described at the back of the journal.

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