metal-organic papers

Poly[[[(2,2′-bipyridine-κ^2N,N')cobalt(II)]-μ_3-5-hydroxyisophthalato-$\kappa^4O,O':O'':O'''$] dihydrate]

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.005 Å
Disorder in solvent or counterion
R factor = 0.054
wR factor = 0.131
Data-to-parameter ratio = 14.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title compound, $\{[Co(C_8H_4O_5)(C_{10}H_8N_2)]\cdot 2H_2O\}_n$ or $\{[Co(OH\text{-}BDC)(2,2'\text{-}bipy)]\cdot 2H_2O\}_n$ (where OH-H_2BDC is 5-hydroxyisophthalic acid and 2,2′-bipy is 2,2′-bipyridine), the Co atoms are chelated by two N atoms from the 2,2′-bipy ligand and by four O atoms from OH-BDC ligands in a highly distorted octahedral geometry. OH-BDC acts as a tetradentate ligand, with one carboxylate group chelating one Co atom and the other binding in a monodentate fashion to two other Co atoms to form a one-dimensional zigzag chain. In the crystal structure, one of the solvent water molecules lies on a crystallographic twofold axis. The one-dimensional molecular chains are assembled into a two-dimensional network via O—H···O hydrogen-bonding interactions, while π–π stacking interactions generate a three-dimensional open framework between the two-dimensional networks.

Comment

The design and synthesis of supramolecular coordination polymer networks, especially those constructed via hydrogen-bonding and π–π interactions, has been a field of rapid growth because of their fascinating structures and promising applications in functional materials (Barton et al., 1999; Chen et al., 2005; Biradha et al., 2000). The coordination chemistry of aromatic polycarboxylate transition metal complexes has received considerable attention, due to the variety of bridging modes displayed by polycarboxylates leading to the formation of porous frameworks (Mori et al., 1997). Encouraged by our previous success in constructing coordination polymers with 5-hydroxyisophthalic acid (OH-H_2BDC) and 2,2′-bipyridine (2,2′-bipy) as ligands (Zhuo et al., 2006), we report here the synthesis and structure of the title compound, (I) (Fig. 1, Table 1), obtained by the hydrothermal reaction between OH-H_2BDC and cobalt(II) chloride with 2,2′-bipy.

(I)
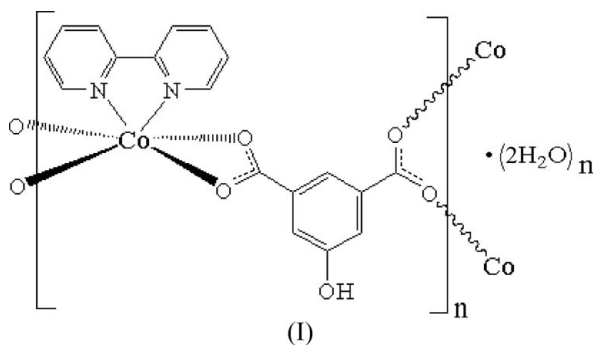
In the structure of (I), each Co^{II} cation has a distorted octahedral environment consisting of four carboxylate O
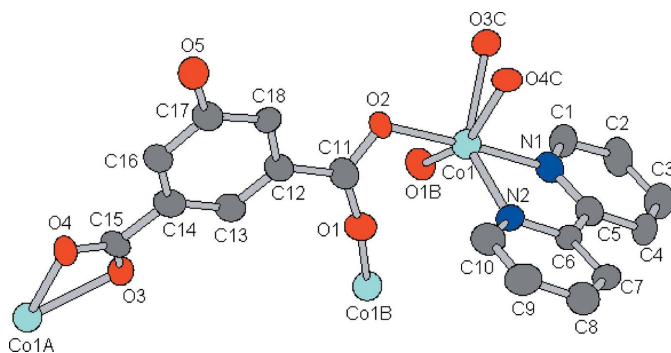
Figure 1
Part of the polymeric structure of the title complex, with 50% probability displacement ellipsoids. H atoms and solvent water molecules have been omitted for clarity. Atoms labelled with the suffixes A, B and C are related to the atoms without suffixes by the symmetry operations $(-\frac{1}{2} + x, 1 - y, -\frac{1}{2} + z)$, $(\frac{1}{2} - x, y, \frac{1}{2} - z)$ and $(\frac{1}{2} + x, 1 - y, \frac{1}{2} + z)$, respectively.
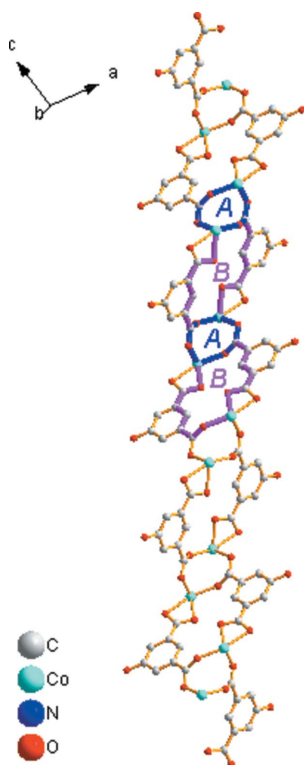

Figure 2
A view of the title complex, showing the formation of eight-atom (A) and 16-atom (B) subrings by coordination of the OH-BDC ligands to Co. The 2,2′-bipy ligands have been omitted for clarity.

atoms from three different OH-BDC anions and two N atoms from the 2,2′-bipy molecule (Fig. 1). The 2,2′-bipy ligand acts as a chelating ligand to individual Co^{II} atoms, while the OH-BDC anion functions as a tetradentate bridging ligand, with one carboxylate group chelating one Co atom and the other binding in a monodentate fashion to two other Co atoms.

Two Co atoms are bridged by chelation of a pair of OH-BDC ligands into a dinuclear cobalt unit, generating an eight-membered ring, A (Fig. 2). The Co···Co distance is 3.781 (5) Å. The one-dimensional zigzag chain extends through the OH-BDC ligands, forming a second 16-atom
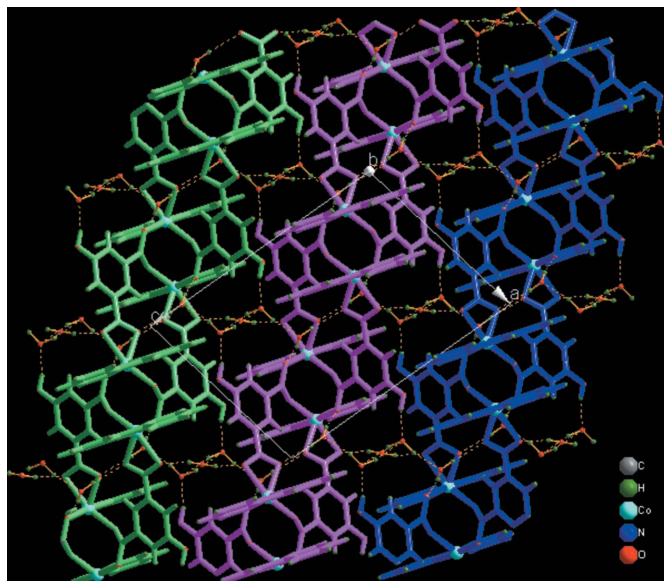

Figure 3
The two-dimensional network formed by O—H···O hydrogen-bonding interactions (dashed lines), viewed along the b axis.

subring, B. The aromatic rings of two adjacent 2,2′-bipy units are arranged in a parallel fashion, with a face-to-face separation of 3.601 (5) Å (Fig. 3). These π–π stacking interactions stabilize the whole chain.

In the crystal structure of (I), one of the solvent water molecules (O6) lies on a crystallographic twofold axis. The one-dimensional $\{4[Co(C_8H_4O_5)(C_{10}H_8N_2)]\cdot8[H_2O]\}_n$ chains are assembled into a two-dimensional network *via* O—H···O hydrogen-bonding interactions, involving both the carboxylate and hydroxy O atoms of the OH-BDC ligands and water molecules, and between the water molecules themselves (Table 2, Fig. 3). Additional π–π stacking interactions occur between adjacent two-dimensional layers, stabilizing the supramolecular network (Fig. 4). Here, the centroid-to-centroid distances between adjacent six-membered rings of 2,2′-bipy molecules are 3.661 (5) Å, typical of π–π stacking.

Experimental

A mixture of CoCl$_2$·4H$_2$O (0.048 g, 0.2 mmol), 5-hydroxyisophthalic acid (99%, 0.2 mmol), 2,2′-bipyridine (0.016 g, 0.1 mmol) and NaOH (0.018 g, 0.45 mmol) in H$_2$O (10 ml) was introduced into a Parr Teflon-lined stainless-steel vessel (23 ml), after which the vessel was sealed and heated to 393 K. The temperature was held for 3 d and then the mixture was slowly cooled to room temperature, giving red crystals of (I) (yield 0.062 g, 60%; m.p. 504–505 K).

Crystal data

[Co(C$_8$H$_4$O$_5$)(C$_{10}$H$_8$N$_2$)]·2H$_2$O	$Z = 4$
$M_r = 431.26$	$D_x = 1.540$ Mg m^{-3}
Monoclinic, $P2/n$	Mo $K\alpha$ radiation
$a = 10.917$ (3) Å	$\mu = 0.97$ mm^{-1}
$b = 11.530$ (3) Å	$T = 298$ (2) K
$c = 15.079$ (5) Å	Block, red
$\beta = 101.473$ (5)°	$0.32 \times 0.28 \times 0.26$ mm
$V = 1860$ (1) Å^3	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	9780 measured reflections
φ and ω scans	3643 independent reflections
Absorption correction: multi-scan	2931 reflections with $I > 2\sigma(I)$
($SADABS$; Sheldrick, 2000)	$R_{int} = 0.035$
$T_{min} = 0.747$, $T_{max} = 0.787$	$\theta_{max} = 26.0°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0615P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.054$	$+ 2.1186P]$
$wR(F^2) = 0.131$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{max} < 0.001$
3643 reflections	$\Delta\rho_{max} = 0.26$ e Å^{-3}
258 parameters	$\Delta\rho_{min} = -0.41$ e Å^{-3}
H-atom parameters constrained	Extinction correction: $SHELXL97$
	(Sheldrick, 1997)
	Extinction coefficient: 0.003

Table 1
Selected geometric parameters (Å, °).

Co1—O1^i	2.045 (2)	Co1—N1	2.105 (3)
Co1—O2	2.052 (2)	Co1—O3^{ii}	2.165 (3)
Co1—N2	2.102 (3)	Co1—O4^{ii}	2.259 (2)
O1^i—Co1—O2	91.12 (10)	N2—Co1—O3^{ii}	136.06 (10)
O1^i—Co1—N2	120.04 (11)	N1—Co1—O3^{ii}	88.24 (11)
O2—Co1—N2	106.59 (11)	O1^i—Co1—O4^{ii}	155.47 (9)
O1^i—Co1—N1	83.01 (11)	O2—Co1—O4^{ii}	83.68 (9)
O2—Co1—N1	174.06 (11)	N2—Co1—O4^{ii}	84.33 (10)
N2—Co1—N1	75.85 (12)	N1—Co1—O4^{ii}	102.04 (10)
O1^i—Co1—O3^{ii}	97.63 (10)	O3^{ii}—Co1—O4^{ii}	58.97 (9)
O2—Co1—O3^{ii}	93.44 (9)		

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O8—H8$B\cdots$O6^{iii}	0.96	2.41	3.107 (6)	129
O8—H8$A\cdots$O7	0.95	1.91	2.701 (5)	139
O7—H7$B\cdots$O2	0.85	2.18	3.009 (4)	166
O7—H7$A\cdots$O3^i	0.85	2.14	2.951 (4)	159
O6—H6$A\cdots$O4^{iv}	0.85	2.05	2.886 (3)	167
O8—H8$B\cdots$O8^v	0.96	1.91	2.686 (10)	137
O5—H5$\cdots$O8^v	0.82	1.89	2.680 (6)	163

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

The H atoms were positioned geometrically, with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C), and O—H in the range 0.82–0.96 Å and U_{iso}(H) = 1.2 or 1.5U_{eq}(O).

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve
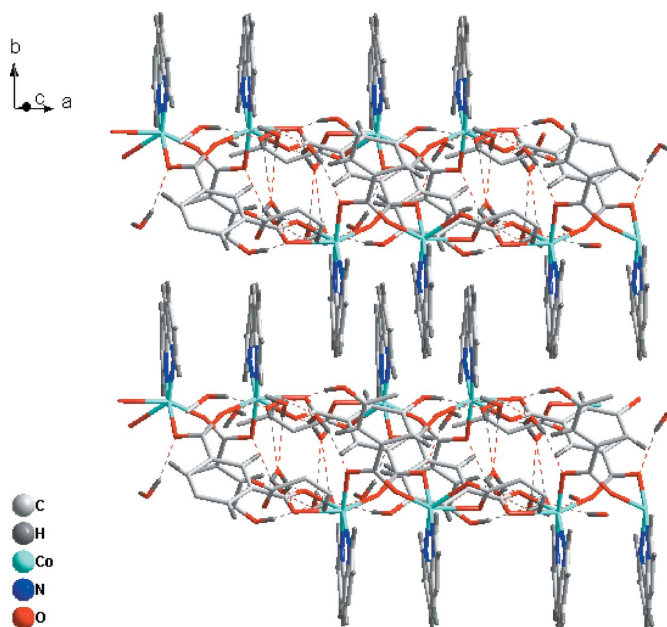

Figure 4
A view of the title complex along the *c* axis, showing the π–π stacking interactions between interleaved bipyridine ligands linking adjacent two-dimensional layers. Dashed lines indicate O—H$\cdots$O hydrogen bonds.

structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2000); software used to prepare material for publication: *SHELXTL*.

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