

Poly[[*trans*-diaquabis(μ_2 -biphenyl-2,2'-dicarboxylato)bis(μ_2 -4,4'-bipyridine)dicobalt(II)] biphenyl-2,2'-dicarboxylic acid disolvate]

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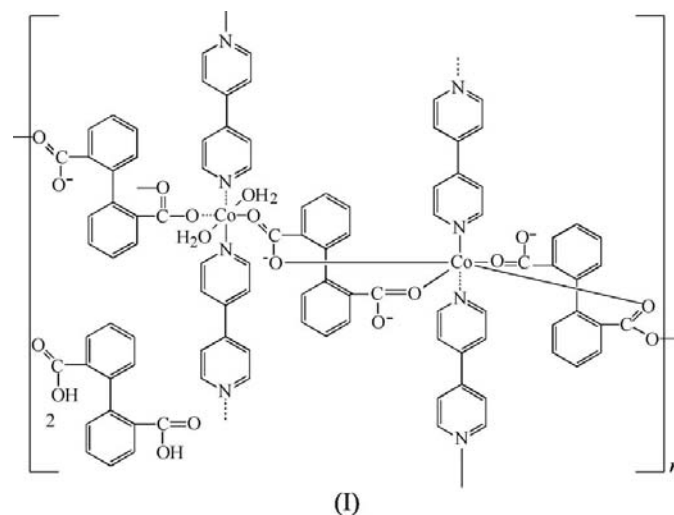
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In the title compound, $\{[\text{Co}_2(\text{C}_{14}\text{H}_8\text{O}_4)_2(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2] \cdot 2\text{C}_{14}\text{H}_{10}\text{O}_4\}_n$, each Co^{II} ion is six-coordinate in a slightly distorted octahedral geometry. Both Co^{II} ions are located on twofold axes. One is surrounded by two O atoms from two biphenyl-2,2'-dicarboxylate (dpa) dianions, two N atoms from two 4,4'-bipyridine (bpy) ligands and two water molecules, while the second is surrounded by four O atoms from two dpa dianions and two N atoms from two bpy ligands. The coordinated dpa dianion functions as a κ^3 -bridge between the two Co^{II} ions. One carboxylate group of a dpa dianion bridges two adjacent Co^{II} ions, and one O atom of the other carboxylate group also chelates to a Co^{II} ion. The Co^{II} ions are bridged by dpa dianions and bpy ligands to form a chiral sheet. There are several strong intermolecular hydrogen bonds between the H_2dpa solvent molecule and the chiral sheet, which result in a sandwich structure.

Comment

Biphenyl-2,2'-dicarboxylate (dpa) has the capability of affording new coordination polymers (Xu *et al.*, 2006) for several reasons. Firstly, the freedom of rotation about the biphenyl central bond enables dpa to link metal ions or clusters into macrocycles or helical chains (Wang *et al.*, 2002, 2005; Wang, Hong *et al.*, 2003). Secondly, the dpa ligand contains two bridging moieties, which can lead to a variety of coordination modes with metals and provides abundant structural motifs (Wang, Zheng *et al.*, 2003; Lu & Schauss, 2003; Rueff *et al.*, 2002). Finally, dpa can act not only as a hydrogen-bond donor but also as an acceptor, which makes it a candidate for the construction of supramolecular networks. Some metal-organic frameworks based on the dpa ligand have been reported (Hu *et al.*, 2007; Rueff *et al.*, 2003; Wang *et al.*, 2004; Yin *et al.*, 2007). However, it is interesting that in all these dpa-containing structures, only a few simple coordination modes are known, although a variety are anticipated in metal-organic

frameworks under appropriate conditions. Here, the title compound, $\{[\text{Co}_2(\text{dpa})_2(\text{bpy})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{dpa}\}_n$ (bpy is 4,4'-bipyridine), (I), represents a novel example.



As shown in Fig. 1, the asymmetric unit of (I) consists of two crystallographically independent Co^{II} atoms located on

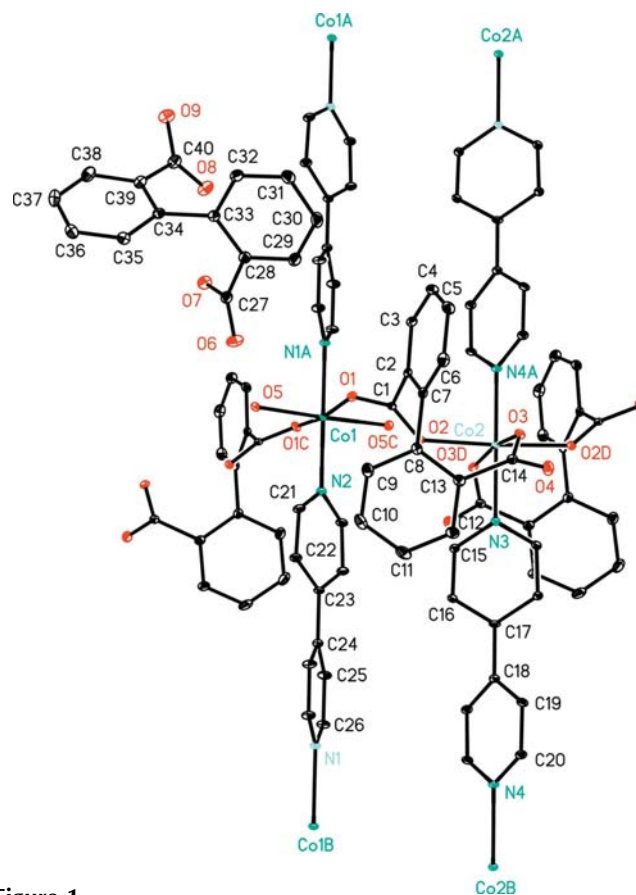


Figure 1

The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 10% probability level. H atoms have been omitted for clarity. [Symmetry codes: (A) $x, y, z - 1$; (B) $x, y, z + 1$; (C) $1 - x, -y, z$; (D) $2 - x, -y, z$.]

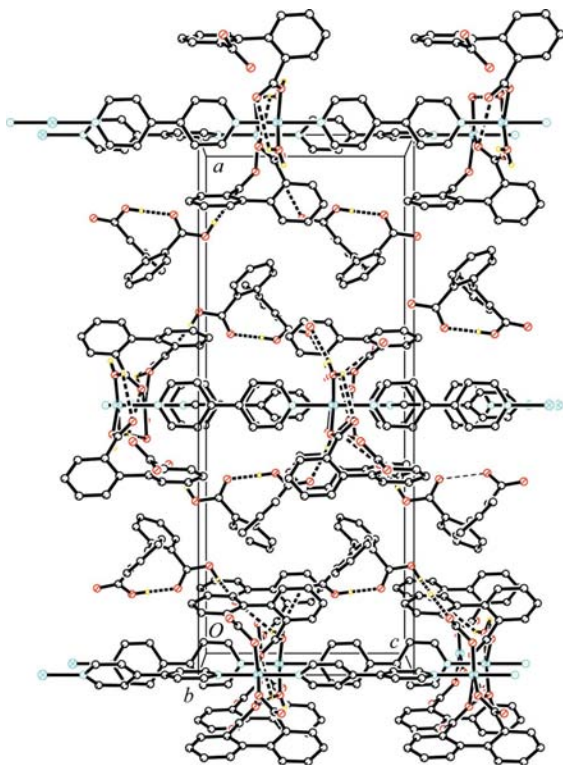


Figure 2
A perspective view of the two-dimensional sheet of (I), along the *b* axis.

twofold axes which run across the Co ions and bpy ligands. Both are six-coordinate in a slightly distorted octahedral geometry, but the environments of the two are different. Co1 is surrounded by two O atoms from two dpa dianions, two N atoms from two *trans* monodentate bpy ligands, and two water molecules (O5) which occupy the axial positions. The Co1–N bond lengths are 2.125 (3) and 2.177 (3) Å, which are typical Co–N distances (Wang *et al.*, 2004), and the Co1–O distances are 2.067 (2) and 2.107 (2) Å, which fall within the typical range of Co–O bond lengths for octahedral coordination (Rueff *et al.*, 2003, 2002; Hu *et al.*, 2007). The O5–Co1–O5(1–*x*, –*y*, *z*) angle is 178.20 (14)°, which is close to being linear, and the N–Co–O angles range from 85.67 (7) to 94.33 (7)°, consistent with the distorted octahedral coordination environment of Co1. Co2 is six-coordinated by two chelating carboxylate groups of two dpa dianions, with Co2–O2 and Co2–O3 distances of 2.0847 (19) and 2.179 (2) Å, respectively, and by two N atoms of two bpy ligands in *trans* positions, with Co2–N distances of 2.129 (3) and 2.161 (3) Å. Atoms O2 and O2ⁱⁱⁱ [symmetry code: (iii) 2–*x*, –*y*, *z*] are located in axial positions, with an O2–Co–O2ⁱⁱⁱ angle of 176.67 (11)°, whereas the N–Co2–O angles around the Co2 centre range from 85.43 (5) to 94.57 (5)°. Just as for Co1, the bond lengths and angles agree with those in a related complex (Wang *et al.*, 2004).

Co1 and Co2 are bridged by a dpa dianion, which adopts an *anti* conformation and acts as a κ^3 -bridge, forming a one-dimensional chain along the *b* axis, as shown in Fig. 2. The Co···Co separation across the dpa bridge is 5.176 (4) Å. One carboxylate group of a dpa dianion bridges two adjacent Co^{II}

ions, and one of the O atoms of the other carboxylate group also bonds to a Co^{II} ion. Due to steric hindrance, the dihedral angle between the carboxylate group and the linking benzene ring [48.4 (4)°] is larger than that in the related complex [34.58 (3)°; Wang *et al.*, 2004]. The chains are further connected by bpy ligands to form a two-dimensional chiral structure (Fig. 2). The two pyridyl rings in bpy are not coplanar, the C22–C23–C24–C25 torsion angle being –23.2 (3)°. The structure can be regarded as grid sheets with a (4,4) net topology, which is constructed through Co^{II} centres bridged by dpa dianions along the *b* axis and bpy ligands along the *c* axis.

Adjacent two-dimensional sheets are parallel and are linked *via* hydrogen-bonding interactions (see Table 1) through uncoordinated H₂dpa solvent molecules to form a sandwich structure (Fig. 2). The hydrogen bonding does not extend along the *a* axis, but there is interdigitation between adjacent sandwich units.

Experimental

An aqueous solution (10 ml) of cobalt sulfate heptahydrate (0.85 g, 3.02 mmol) was added dropwise to a solution of dimethylformamide (10 ml) containing 4,4'-bipyridine (0.47 g, 3.01 mmol), diphenyl-2,2'-dicarboxylic acid (0.73 g, 3.01 mmol) and 2,2'-dithiosalicylic acid (0.92 g, 3.00 mmol) at room temperature. The reaction mixture was filtered and the filtrate was left to stand for about four weeks until red single crystals were obtained (yield 53%, based on Co). Red block-shaped crystals of (I) suitable for X-ray diffraction were collected by filtration, washed with water and ethanol, and finally dried in air.

Crystal data

$[\text{Co}_2(\text{C}_{14}\text{H}_8\text{O}_4)_2(\text{C}_{10}\text{H}_8\text{N}_2)_2 \cdot 2(\text{H}_2\text{O})_2] \cdot 2\text{C}_{14}\text{H}_{10}\text{O}_4$	$V = 3283.8 (6) \text{ \AA}^3$
$M_r = 1431.11$	$Z = 2$
Orthorhombic, $P2_12_12$	Mo $K\alpha$ radiation
$a = 10.1264 (10) \text{ \AA}$	$\mu = 0.58 \text{ mm}^{-1}$
$b = 28.487 (3) \text{ \AA}$	$T = 298 \text{ K}$
$c = 11.3835 (11) \text{ \AA}$	$0.40 \times 0.17 \times 0.08 \text{ mm}$

Data collection

Bruker APEX CCD area-detector diffractometer	17371 measured reflections
Absorption correction: integration (SADABS; Bruker, 2001)	5840 independent reflections
$T_{\min} = 0.89$, $T_{\max} = 0.95$	5236 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.040$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.100$	$\Delta\rho_{\text{max}} = 0.61 \text{ e \AA}^{-3}$
$S = 1.05$	$\Delta\rho_{\text{min}} = -0.42 \text{ e \AA}^{-3}$
5840 reflections	Absolute structure: Flack (1983), with 1476 Friedel pairs
468 parameters	Flack parameter: 0.013 (15)
4 restraints	

The water and carboxylic acid H atoms were refined subject to the restraint O–H = 0.82 (5) Å. All other H atoms were included in the refinement in calculated positions in the riding-model approximation, with C–H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O5—H5A...O6	0.79 (3)	2.04 (3)	2.821 (4)	167 (5)
O7—H7A...O8	0.87 (3)	1.75 (3)	2.620 (4)	177 (5)
O9—H9A...O4 ⁱ	0.89 (4)	1.59 (4)	2.462 (4)	168 (5)
O5—H5B...O3 ⁱⁱ	0.72 (4)	2.08 (4)	2.775 (3)	164 (5)

Symmetry codes: (i) $x - 1, y, z - 1$; (ii) $x - 1, y, z$.

structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3036). Services for accessing these data are described at the back of the journal.

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