

Poly[[aqua(4,4'-diazenediyldibenzoato- κ^4 O,O':O'',O''')cadmium(II)]: a twofold interpenetrated three-dimensional coordination polymer of PtS topology

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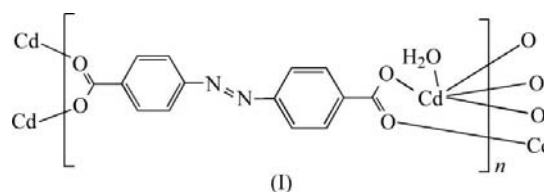
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In the title coordination compound, $[\text{Cd}(\text{C}_{14}\text{H}_8\text{N}_2\text{O}_4)(\text{H}_2\text{O})]_n$, the Cd^{II} cation and the coordinated water molecule lie on a twofold axis, whereas the ligand lies on an inversion center. The Cd^{II} center is five-coordinated in a distorted square-pyramidal geometry by four carboxylate O atoms from four different 4,4'-diazenediyldibenzoate (ddb) anions and one water O atom. The three-dimensional frameworks thus formed by the bridging ddb anions interpenetrate to generate a three-dimensional PtS-type network. Additionally, the coordination water molecule and the carboxylate O atom form a hydrogen-bonding interaction, stabilizing the three-dimensional framework structure.

Comment

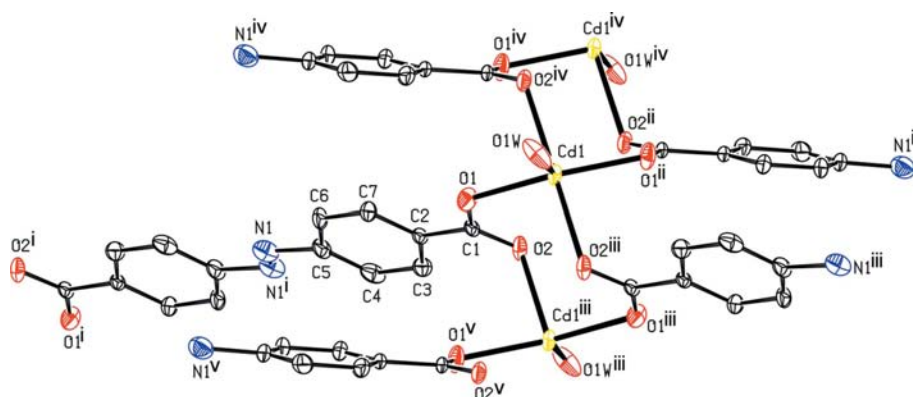
The design and synthesis of metal-organic coordination polymers are of great interest, not only because of the tremendous potential applications of these compounds in nonlinear optics, catalysis, gas absorption, luminescence, magnetism and medicine, but also because of their intriguing variety of architectures and topologies (Batten & Robson, 1998; Eddaoudi *et al.*, 2001; Yang *et al.*, 2008). These coordination polymers can be specially designed by the careful selection of metal cations with preferred coordination geometries, the nature of the anions, the structure of the connecting ligands, and the reaction conditions (Hagman *et al.*, 1999; Hsu *et al.*, 2008). The selection of the ligand is extremely important because changing its geometry can control the topology of the resulting coordination framework (Hu *et al.*, 2006). In this regard, carboxylate-based ligands have been successfully employed in the generation of many interesting systems. The work of Yaghi and co-workers has succeeded in highlighting the value of carboxylate-based systems in the generation of stable highly porous functiona-

lized open networks (Ockwig *et al.*, 2005). In the last decade, aromatic polycarboxylate ligands, such as benzene-1,4-dicarboxylate, benzene-1,3-dicarboxylate, benzene-1,3,5-carboxylate and benzene-1,2,4,5-tetracarboxylate, have been employed extensively in the construction of a variety of high-dimensional structures (Ockwig *et al.*, 2005). Diazenediyldibenzoate-based systems, as one new type of bridging aromatic carboxylate ligand, have rarely been employed in the generation of coordination networks (Chen *et al.*, 2008). In this work, we chose 4,4'-diazenediyldibenzoic acid (H_2ddb) as the carboxylate-containing ligand, yielding the title twofold interpenetrated three-dimensional coordination polymer of PtS topology, $[\text{Cd}(\text{ddb})(\text{H}_2\text{O})]_n$ (I).

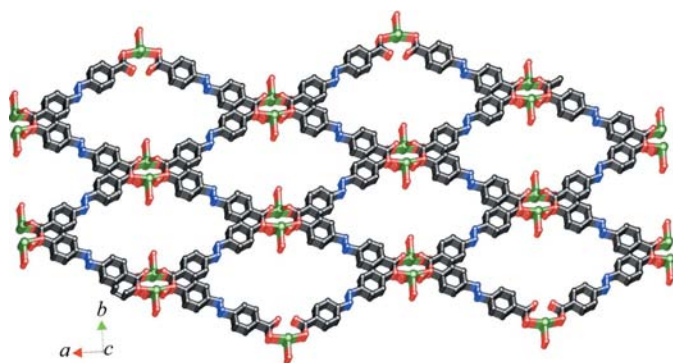


Selected bond distances and angles for (I) are listed in Table 1. As shown in Fig. 1, the asymmetric unit of (I) contains one-half of a Cd^{II} cation, one-half of a ddb anion and one-half of a water molecule. The Cd^{II} cation and the water molecule lie on a twofold axis, whereas the ddb ligand is located around an inversion center. The Cd^{II} center is five-coordinated in a distorted square-pyramidal geometry by four carboxylate O atoms from four different ddb anions and one water O atom. Four O atoms from four ddb anions [O1, O1ⁱⁱ, O2ⁱⁱⁱ and O2^{iv}; symmetry codes are as given in Fig. 1] make up the basal plane, while the apical site is occupied by one water O atom (O1W). The average Cd—O distances in (I) (Table 1) are comparable with those observed for $[\text{Cd}(1,4\text{-ndc})(L)]_n$ (1,4-ndc is naphthalene-1,4-dicarboxylate and L is pyrazino[2,3-*f*][1,10]-phenanthroline) (Qiao *et al.*, 2008). In (I), each ddb anion coordinates to four Cd^{II} centers in a tetramonodentate mode (see scheme), forming a three-dimensional framework structure (Fig. 2). Interestingly, the two symmetry-related three-dimensional frameworks interpenetrate to generate a three-dimensional PtS-type network (Fig. 3). Additionally, the coordinated water molecule and the carboxylate O atom form a hydrogen-bonding interaction, stabilizing the three-dimensional framework structure of (I) (Table 2).

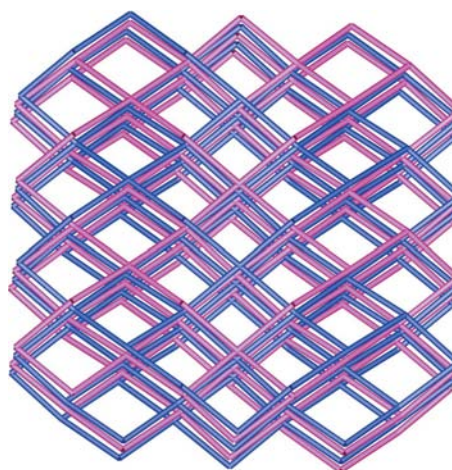
The topological structure of (I) can be achieved by reducing the three-dimensional structure to a simple node-and-linker net. As discussed above, each Cd^{II} center can be defined as a 4-connected node. Each carboxylate O atom of ddb connects one Cd^{II} center, and each ddb ligand bridges four adjacent Cd^{II} atoms through its carboxylate O atoms. Therefore, the ddb ligand can also be considered as a 4-connected node. Both the Cd^{II} and ddb nodes are equivalent. Therefore, the framework topology of (I) can be regarded as a three-dimensional 4-connected PtS-type net ($4^2.8^4$) (Carlucci *et al.*, 2003). Furthermore, two such nets interpenetrate (Fig. 4), and there are some earlier examples of interpenetrated PtS nets (Abrahams *et al.*, 1994; Nattinen & Rissanen, 2003; Du *et al.*, 2005; Grosshans *et al.*, 2003; Blatov *et al.*, 2004).


Figure 1

A view of the coordination mode of compound (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity. [Symmetry codes: (i) $-x, -y, 1-z$; (ii) $1-x, y, \frac{1}{2}-z$; (iii) $1-x, 1-y, 1-z$; (iv) $x, 1-y, z-\frac{1}{2}$; (v) $x, 1-y, \frac{1}{2}+z$.]


Figure 2

A view of the three-dimensional framework of (I).


Figure 4

Schematic representation of the twofold interpenetrated PtS nets.

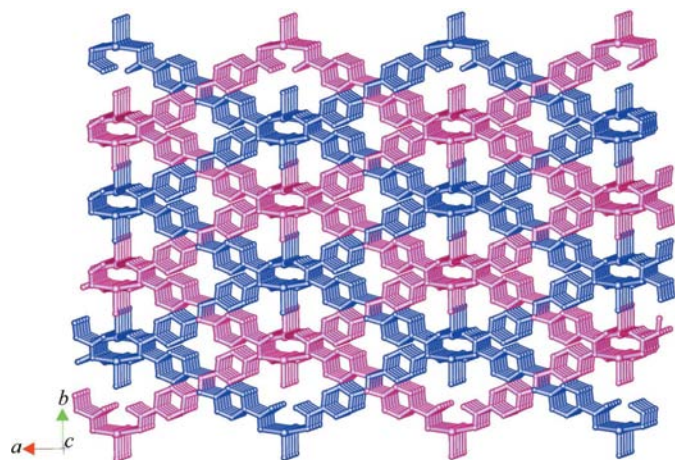
two-dimensional sheet structure, with the phen molecules attached on both sides of the sheet.

Experimental

A mixture of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ (0.114 g, 0.5 mmol) and H_2ddb (0.135 g, 0.5 mmol) was dissolved in distilled water (12 ml), followed by the addition of triethylamine until the pH of the system was about 5.5. The resulting solution was stirred for about 1 h at room temperature, sealed in a 23 ml Teflon-lined stainless steel autoclave and heated at 423 K for 5 d under autogenous pressure. The reaction system was then cooled slowly to room temperature. Pale-yellow block-shaped crystals of (I) suitable for single-crystal X-ray diffraction analysis were collected from the final reaction system by filtration, washed several times with distilled water and dried in air at ambient temperature (yield 45% based on Cd^{II}).

Crystal data

$[\text{Cd}(\text{C}_{14}\text{H}_8\text{N}_2\text{O}_4)(\text{H}_2\text{O})]$	$V = 667.56 (12) \text{ \AA}^3$
$M_r = 398.64$	$Z = 2$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 14.8094 (11) \text{ \AA}$	$\mu = 1.66 \text{ mm}^{-1}$
$b = 6.4226 (7) \text{ \AA}$	$T = 293 \text{ K}$
$c = 7.0194 (8) \text{ \AA}$	$0.30 \times 0.27 \times 0.20 \text{ mm}$
$\beta = 90.949 (9)^\circ$	


Figure 3

A view of the twofold interpenetrated three-dimensional framework of (I).

It is noteworthy that the structure of (I) is entirely different from that of the related structure $[\text{Cd}(\text{ddb})(\text{H}_2\text{O})_2]_n$ (Chen *et al.*, 2008). In that reported complex, each carboxylate group of the ddb anion chelates one Cd^{II} atom to form a simple zigzag chain structure. The structure of (I) is also entirely different from that of the related polymer $[\text{Cd}(\text{ddb})(\text{phen})(\text{H}_2\text{O})]_n$ (phen is 1,10-phenanthroline; Chen *et al.*, 2008). In that structure, each ddb anion bridges three Cd^{II} atoms to yield a

Data collection

Bruker APEX diffractometer	3196 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	1572 independent reflections
$T_{\min} = 0.597$, $T_{\max} = 0.715$	1243 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.031$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.072$	
$S = 0.96$	$\Delta\rho_{\text{max}} = 1.14 \text{ e } \text{\AA}^{-3}$
1572 reflections	$\Delta\rho_{\text{min}} = -0.80 \text{ e } \text{\AA}^{-3}$
104 parameters	
1 restraint	

Table 1

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

Cd1—O1	2.208 (2)	Cd1—O2 ⁱ	2.374 (3)
Cd1—O1W	2.215 (5)		
O1—Cd1—O1 ⁱⁱ	163.32 (16)	O1W—Cd1—O2 ⁱⁱⁱ	87.46 (7)
O1—Cd1—O1W	98.34 (8)	O1—Cd1—O2 ⁱ	96.48 (10)
O1—Cd1—O2 ⁱⁱⁱ	84.26 (9)	O2 ⁱ —Cd1—O2 ⁱⁱⁱ	174.92 (14)

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

Table 2

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H1W \cdots O2 ^{iv}	0.85 (5)	1.89 (3)	2.670 (4)	152 (6)

Symmetry code: (iv) $-x + 1, y + 1, -z + \frac{1}{2}$.

Carbon-bound H atoms were positioned geometrically, with $C-H = 0.93 \text{ \AA}$, and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The water H atom was located in a difference Fourier map and refined with a distance restraint of $O-H = 0.82 (3) \text{ \AA}$ and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. The maximum residual electron-density peak was located 0.86 \AA from N1.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINTE* (Bruker, 1999); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine

structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* and *PLATON* (Spek, 2009); software used to prepare material for publication: *publCIF* (Westrip, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3124). Services for accessing these data are described at the back of the journal.

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