

Poly[aqua[μ_2 -1,4-bis(imidazol-1-ylmethyl)benzene- $\kappa^2 N^3:N^3'$](μ_2 -5-hydroxybenzene-1,3-dicarboxylato- $\kappa^4 O^1,O^1':O^3,O^3'$)cadmium(II)], a twofold interpenetrated CdSO₄-like metal-organic polymer

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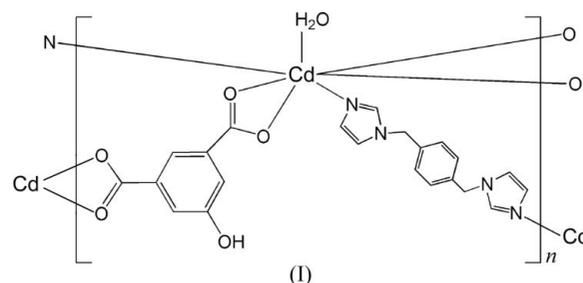
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In the title cadmium(II) complex, [Cd(C₈H₄O₅)(C₁₄H₁₄N₄)(H₂O)]_n, the 5-hydroxybenzene-1,3-dicarboxylate (5-OH-1,3-bdc) and 1,4-bis(imidazol-1-ylmethyl)benzene (1,4-bix) ligands bridge water-coordinated Cd^{II} atoms to generate a three-dimensional network. Two carboxylate groups from different ligands function as *O,O'*-chelates, while two imidazole N atoms from different ligands coordinate in a monodentate fashion, and one water molecule completes the seven-coordinate pentagonal bipyramid around the Cd^{II} atom, in which the N atoms occupy the axial sites and the O atoms occupy the equatorial sites. The overall architecture is a twofold interpenetrated CdSO₄-type framework. The two crystallographically equivalent frameworks are linked by O—H...O hydrogen bonds between the water, hydroxy and carboxylate groups.

Comment

The design and synthesis of metal-organic frameworks (MOFs) has been an area of rapid growth in recent years owing to the potential applications of MOFs in nonlinear optics, luminescence, magnetism, catalysis, gas absorption, ion exchange and as zeolite-like materials for molecular selection (O'Keeffe *et al.*, 2008). Structural diversity in MOFs can occur as a result of various processes, including supramolecular isomerism, interpenetration or interweaving (Batten & Robson, 1998; Batten, 2001). Ideally, the topologies of MOFs can be controlled and modified by the coordination geometry preferred by the metal ion and the chemical structure of the organic ligand chosen (Abrahams *et al.*, 1999; Yang *et al.*, 2008). In this regard, rigid N-donor 4,4'-bipyridine (bipy) and

its derivatives have been studied in the construction of MOFs (Qiao *et al.*, 2008). So far, a number of MOFs based on bipy and its derivatives have been reported, including one-dimensional chains, two-dimensional layers and three-dimensional frameworks (Carlucci *et al.*, 2003). However, reports of MOFs constructed by flexible N-donor ligands are relatively rare (Wang *et al.*, 2006). Among such ligands, bis(imidazole) derivatives are a good choice (Yang *et al.*, 2008), leading to some intriguing interpenetrating architectures and topologies (Wang *et al.*, 2006). In this work, we chose 5-hydroxybenzene-1,3-dicarboxylic acid (5-OH-1,3-H₂bdc) as a dicarboxylate ligand and 1,4-bis(imidazol-1-ylmethyl)benzene (1,4-bix) as a flexible N-donor ligand, yielding a new coordination polymer, [Cd(5-OH-1,3-bdc)(1,4-bix)(H₂O)]_n (I), with a fascinating twofold interpenetrated three-dimensional CdSO₄-like framework. After the acceptance of this paper, we noticed that the structure of (I) has recently been described by Xia *et al.* (2011). However, the interpenetrated topology and hydrogen-bonding interactions were not well discussed in that report.



The asymmetric unit of (I) contains one Cd^{II} atom, one 5-OH-1,3-bdc anion, one 1,4-bix ligand and one coordination water molecule (Fig. 1). Each Cd^{II} atom is seven-coordinated in a pentagonal bipyramid by four carboxylate O atoms from two different 5-OH-1,3-bdc anions, one water O atom and two N atoms from two distinct 1,4-bix ligands. The N atoms occupy the axial sites and the O atoms occupy the equatorial sites of the bipyramid. The Cd—O_{carboxylate} distances (Table 1) are comparable to those observed in [Cd(1,4-bdc)(bpdo)(H₂O)]_n (1,4-bdc is benzene-1,4-dicarboxylate and bpdo is 4,4'-bipyridine *N,N'*-dioxide; Xu & Xie, 2010).

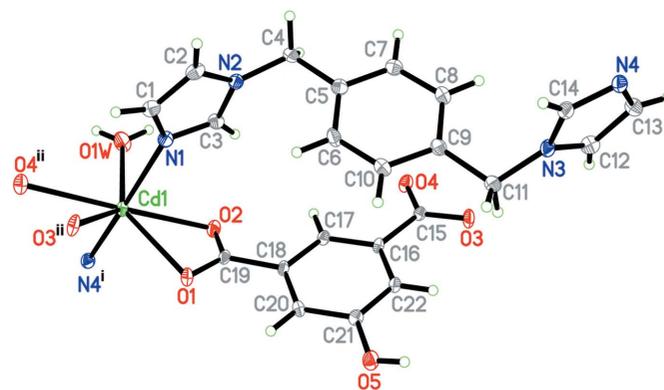


Figure 1
A view of the local coordination of the Cd^{II} atom in (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i) $x, y + 1, z - 1$; (ii) $x + \frac{1}{2}, -y + 1, z - \frac{1}{2}$.]

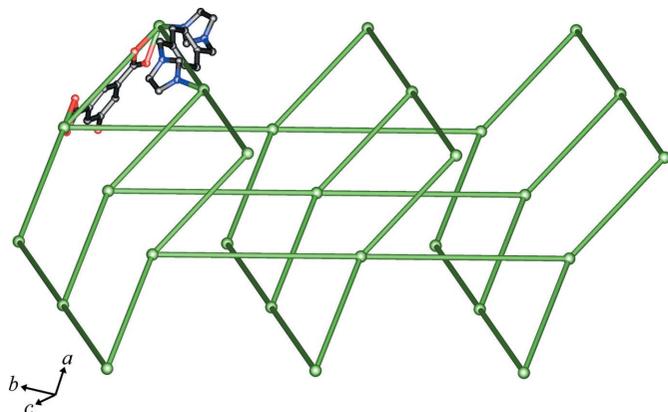


Figure 2
A view of a single CdSO₄ net of (I), showing bridging by 1,4-bix and 5-OH-1,3-bdc ligands.

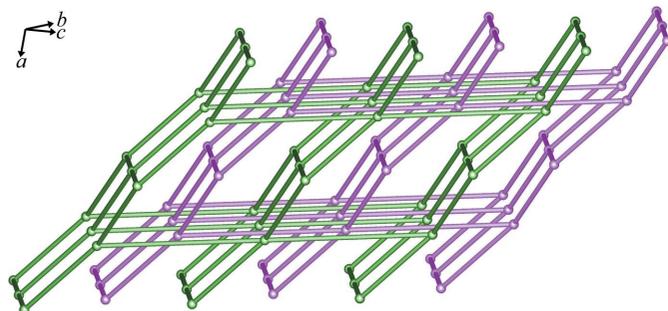


Figure 3
A view of the twofold interpenetrating three-dimensional CdSO₄ net of (I).

Each crystallographically unique Cd^{II} atom is bridged by the 1,4-bix ligands and 5-OH-1,3-bdc anions to generate a novel three-dimensional framework (Fig. 2). The Cd^{II}–Cd distances bridged by 1,4-bix and 5-OH-1,3-bdc are 14.3668 (12) and 9.8433 (8) Å, respectively. Topologically, the Cd^{II} centre is defined as a four-connected node, and 1,4-bix and the 5-OH-1,3-bdc serve as linkers. Therefore, on the basis of the concept of chemical topology, the overall structure of (I) is a four-connected framework with the Schläfli symbol of 6⁵8. Topological analysis reveals that this three-dimensional framework is a typical CdSO₄ net. Interestingly, the large spaces in the single three-dimensional framework allow another identical framework to interpenetrate it, providing a twofold interpenetrating CdSO₄ framework (Fig. 3). Each CdSO₄ net is hydrogen bonded to its neighbour through O–H⁺···O hydrogen bonds among the water molecules, hydroxy group and carboxylate O atoms (Table 2).

So far, some related interpenetrated CdSO₄-like MOFs based on both dicarboxylate and flexible N-donor bridging ligands have been reported. The structure of [Zn₂(1,4-bdc)Cl₂(bpp)]_n [1,4-bdc is benzene-1,4-dicarboxylate and bpp is 1,3-bis(4-pyridyl)propane; Zhang *et al.*, 2006] also contains two crystallographically equivalent nets, but differs from (I) in that the four-connected nodes are based on Zn^{II} dimers rather than mononuclear complexes. [Zn(mip)(bpa)]_n [mip is 5-methylisophthalate and bpa is 1,2-bis(4-pyridyl)ethane; Ma

et al., 2009] shows an unusual threefold interpenetrated CdSO₄ topology. [Ni(oba)(bbi)]₂·H₂O [oba is 4,4'-oxybis(benzoate) and bbi is 1,1'-(1,4-butanediyl)bis(imidazole); Yang *et al.*, 2009] also shows twofold interpenetrated nets as in (I); however, the nets are crystallographically distinct.

Experimental

A mixture of CdCl₂·2.5H₂O (0.5 mmol), 1,4-bis(imidazol-1-ylmethyl)benzene (0.5 mmol), 5-hydroxybenzene-1,3-dicarboxylic acid (0.5 mmol) and water (12 ml) was sealed in a 23 ml Teflon-lined stainless steel Parr bomb. The bomb was heated at 413 K for 3 d and then cooled to room temperature. Colourless block-shaped crystals were collected and washed with water; the yield based on Cd was about 40%.

Crystal data

| | |
|--|---|
| [Cd(C ₈ H ₄ O ₅)(C ₁₄ H ₁₄ N ₄)(H ₂ O)] | $V = 1042.16 (14) \text{ \AA}^3$ |
| $M_r = 548.82$ | $Z = 2$ |
| Monoclinic, Pn | Mo $K\alpha$ radiation |
| $a = 11.5800 (9) \text{ \AA}$ | $\mu = 1.10 \text{ mm}^{-1}$ |
| $b = 8.4221 (6) \text{ \AA}$ | $T = 293 \text{ K}$ |
| $c = 11.6393 (9) \text{ \AA}$ | $0.18 \times 0.16 \times 0.11 \text{ mm}$ |
| $\beta = 113.354 (1)^\circ$ | |

Data collection

| | |
|---|--|
| Bruker APEX diffractometer | 3693 independent reflections |
| Absorption correction: multi-scan (SADABS; Sheldrick, 1996) | 3404 reflections with $I > 2\sigma(I)$ |
| $T_{\min} = 0.39$, $T_{\max} = 0.57$ | $R_{\text{int}} = 0.031$ |
| 6155 measured reflections | Standard reflections: 0 |

Refinement

| | |
|---------------------------------|--|
| $R[F^2 > 2\sigma(F^2)] = 0.028$ | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.054$ | $\Delta\rho_{\text{max}} = 0.38 \text{ e \AA}^{-3}$ |
| $S = 1.02$ | $\Delta\rho_{\text{min}} = -0.39 \text{ e \AA}^{-3}$ |
| 3693 reflections | Absolute structure: Flack (1983), 984 Friedel pairs |
| 307 parameters | Flack parameter: $-0.013 (19)$ |
| 6 restraints | |

Carbon-bound H atoms were positioned geometrically [C–H = 0.93 (aromatic) or 0.97 Å (methylene)] and included as riding atoms, with $U_{\text{iso}}(\text{H})$ values fixed at $1.2U_{\text{eq}}(\text{C})$. H atoms of water molecules were located in difference Fourier maps and refined isotropically with distance restraints of O–H = 0.85 (1) Å and H···H = 1.35 (1) Å, and

Table 1

Selected geometric parameters (Å, °).

| | | | |
|---------------------------------------|-------------|--|-------------|
| Cd1–N4 ⁱ | 2.244 (3) | Cd1–O1W | 2.465 (3) |
| Cd1–N1 | 2.282 (3) | Cd1–O1 | 2.499 (3) |
| Cd1–O3 ⁱⁱ | 2.384 (3) | Cd1–O4 ⁱⁱ | 2.554 (3) |
| Cd1–O2 | 2.423 (3) | | |
| N4 ⁱ –Cd1–N1 | 166.24 (13) | N1–Cd1–O1 | 87.43 (11) |
| N4 ⁱ –Cd1–O3 ⁱⁱ | 110.30 (11) | O3 ⁱⁱ –Cd1–O1 | 78.21 (9) |
| N1–Cd1–O3 ⁱⁱ | 82.34 (11) | O2–Cd1–O1 | 53.80 (10) |
| N4 ⁱ –Cd1–O2 | 92.80 (11) | O1W–Cd1–O1 | 140.62 (11) |
| N1–Cd1–O2 | 82.46 (11) | N4 ⁱ –Cd1–O4 ⁱⁱ | 86.42 (11) |
| O3 ⁱⁱ –Cd1–O2 | 130.03 (10) | N1–Cd1–O4 ⁱⁱ | 97.77 (11) |
| N4 ⁱ –Cd1–O1W | 83.67 (12) | O3 ⁱⁱ –Cd1–O4 ⁱⁱ | 52.44 (9) |
| N1–Cd1–O1W | 83.19 (12) | O2–Cd1–O4 ⁱⁱ | 177.49 (12) |
| O3 ⁱⁱ –Cd1–O1W | 137.45 (11) | O1W–Cd1–O4 ⁱⁱ | 90.53 (11) |
| O2–Cd1–O1W | 87.01 (12) | O1–Cd1–O4 ⁱⁱ | 128.69 (9) |
| N4 ⁱ –Cd1–O1 | 100.22 (10) | | |

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

Table 2

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--------------------------|----------|-------------|-------------|---------------|
| $O5-H5\cdots O4^{iii}$ | 0.81 (1) | 1.89 (2) | 2.675 (4) | 162 (5) |
| $O1W-HW12\cdots O3^{iv}$ | 0.85 (1) | 2.00 (2) | 2.813 (4) | 161 (5) |
| $O1W-HW11\cdots O1^v$ | 0.85 (1) | 2.29 (4) | 2.935 (4) | 133 (4) |

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

with $U_{iso}(H) = 1.5U_{eq}(O)$. The hydroxy H atom was located in a difference Fourier map and refined isotropically with a distance restraint of $O-H = 0.82(1)$ Å and with $U_{iso}(H) = 1.5U_{eq}(O)$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL-Plus* (Sheldrick, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3290). Services for accessing these data are described at the back of the journal.

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