

Poly[[$(\mu_2$ -biphenyl-2,4'-dicarboxylato)- $(\mu_2$ -1,4-bis(imidazol-1-ylmethyl)-benzene)cadmium(II)] 0.15-hydrate]

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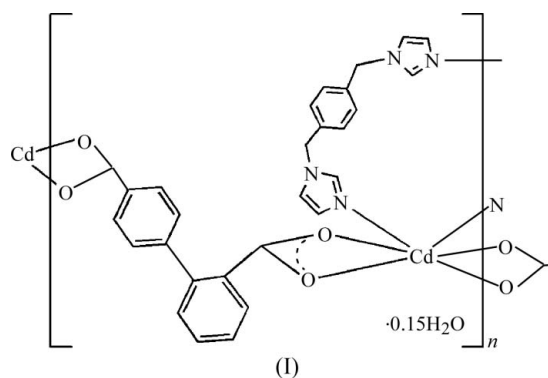
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The asymmetric unit of the title two-dimensional coordination polymer, $[\text{Cd}(\text{C}_{14}\text{H}_8\text{O}_4)(\text{C}_{14}\text{H}_{14}\text{N}_4)] \cdot 0.15\text{H}_2\text{O}$, is composed of one Cd^{II} cation, one biphenyl-2,4'-dicarboxylate (bpdc) anion, one 1,4-bis(imidazol-1-ylmethyl)benzene (bix) ligand and 0.15 solvent water molecules. The coordination environment of the Cd^{II} cation is defined by four carboxylate O atoms from two different bpdc anions in a chelating mode and two N atoms from two distinct bix ligands, constructing a distorted trigonal prism polyhedron. Two inversion-related Cd^{II} cations are bridged together by two positionally disordered bpdc anions, forming a 22-membered ring with a $\text{Cd} \cdots \text{Cd}$ distance of 9.1966 (9) Å. These rings are then further linked by two bix ligands, extending into a two-dimensional layer along (102) with 6^3 topology.

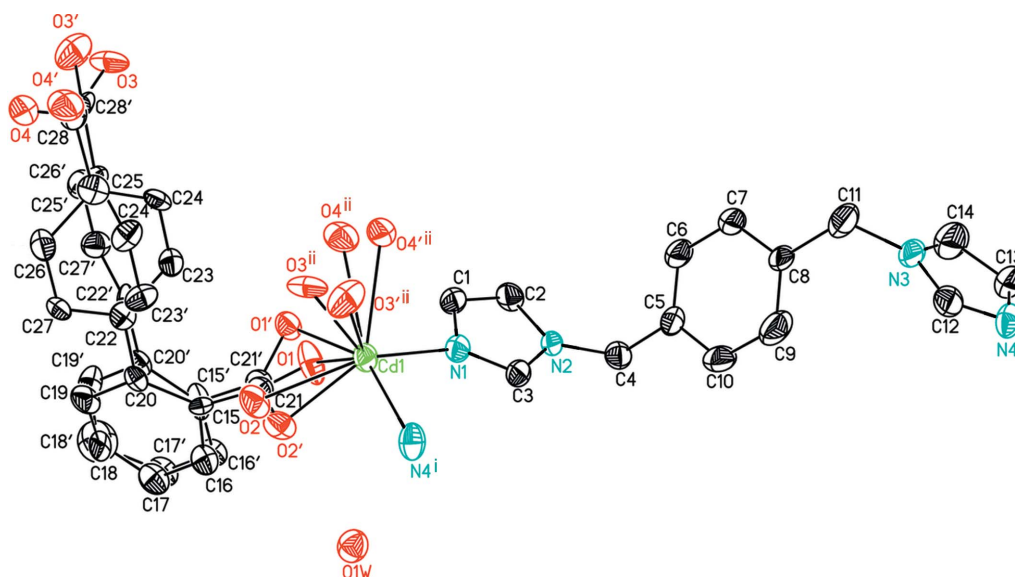
Comment

Currently, the rational design and synthesis of metal–organic frameworks (MOFs) have attracted considerable attention due to the diversity in their architectures and topologies (Lu, 2003). Selection of suitable organic bridging ligands plays a key role in the construction of MOFs. During the past decade many MOFs in which polycarboxylates are used as the bridging ligands to assemble coordination polymers have been successfully synthesized and reported (Duan *et al.*, 2007; Liu *et al.*, 2008; Ghosh *et al.*, 2009; Jiang *et al.*, 2009; Xu *et al.*, 2009; Li *et al.*, 2009).

Biphenyl-2,4'-dicarboxylic acid (H_2bpdc) is a flexible ligand coordinating to transition metals, with two carboxyl groups that can supply four potential O donor atoms. Moreover, the two rings in H_2bpdc can be rotated around the bridging C—C single bond and the two carboxyl groups are located asymmetrically, which makes it a good candidate for constructing various MOFs. However, to the best of our knowledge, coordination polymers involving H_2bpdc have rarely been reported (Liu *et al.*, 2010). We present here the title coordination polymer, (I).



As shown in Fig. 1, the asymmetric unit of (I) consists of one Cd^{II} cation, one biphenyl-2,4'-dicarboxylate (bpdc) anion


Figure 1

The asymmetric unit of (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) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + 1, -y + 1, -z$.]

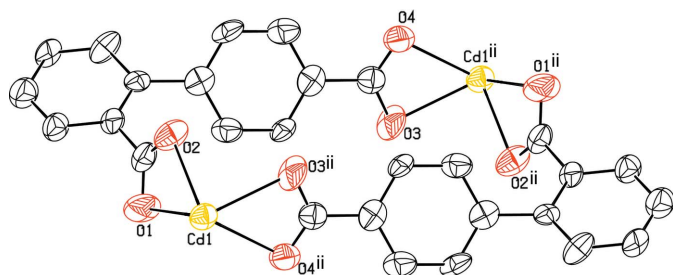


Figure 2

A view of the two inversion-related Cd^{II} cations bridged by two bpdC anions to form a 22-membered ring. H atoms have been omitted for clarity. [Symmetry code: (ii) $-x + 1, -y + 1, -z$.]

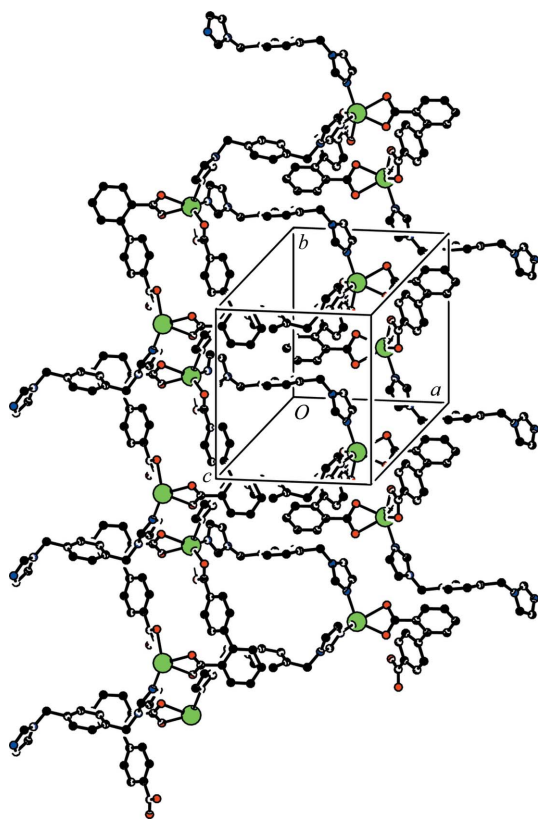


Figure 3

A view of the crystal packing in (I), illustrating the formation of the two-dimensional network in (102). H atoms have been omitted for clarity.

which is positionally disordered, one 1,4-bis(imidazol-1-ylmethyl)benzene (bix) ligand and 0.15 solvent water molecules. The Cd^{II} cation is coordinated by four carboxylate O atoms [O1, O2, O3ⁱⁱ and O4ⁱⁱ; symmetry code: (ii) $-x + 1, -y + 1, -z$] from two different bpdC anions and two N atoms [N1 and N4ⁱ; symmetry code: (i) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$] from two distinct bix ligands, constructing a distorted CdO₄N₂ trigonal prism polyhedron. The four Cd–O bond lengths range from 2.288 (12) to 2.421 (12) Å, and the Cd–N distances are 2.256 (5) and 2.275 (5) Å (Table 1). In the CdO₄N₂ trigonal prism, two sets of atoms, O1(or O1ⁱ)/O4ⁱⁱ/N1 and O2(or O2ⁱ)/O3ⁱⁱ/N4ⁱ, occupy the corners of the upper and lower triangular faces.

For the bix ligand, the two terminal imidazole groups (N1/N2/C1–C3 and N3/N4/C12–C14) assume an *anti* conformation

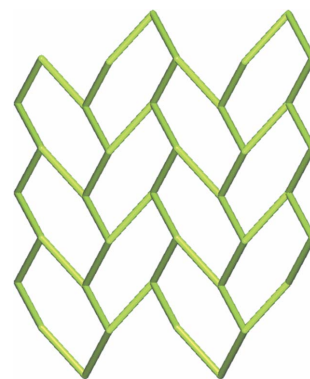


Figure 4

A view of the 6³ net (node: Cd) in the crystal structure of (I).

about the benzene ring and their planes are steeply tilted, by 71.8 (4) and 75.7 (4)°, respectively, with respect to the mean plane of the benzene ring (C5–C10).

Two inversion-related Cd^{II} cations are bridged by two disordered bpdC anions, forming a 22-membered ring with a Cd^{II}–Cd^{II} distance of 9.1966 (9) Å (Fig. 2). Each Cd^{II} cation is then linked by two bix ligands so that these rings are further extended into a two-dimensional layer along (102) (Fig. 3). Overall, each Cd^{II} cation is linked to three neighbouring Cd^{II} cations through one pair of bpdC anions and two bix ligands. For bpdC, each carboxylate group coordinates to a different Cd^{II} cation in a chelating mode, with dihedral angles of 46.8 (7)° between the two rings of the major component (C15–C20 and C22–C27) and 41.5 (9)° between those of the minor disordered component (C15ⁱ–C20ⁱ and C22ⁱ–C27ⁱ).

A pair of bpdC anions and bix ligands can be considered as a 2-connector, while the Cd^{II} cation can be considered as a 3-connected node, so that the structure of (I) is further simplified into a 6³ topological network (Blatov *et al.*, 2000) (Fig. 4) in which each node links neighbouring 3-connected nodes, corresponding to Cd^{II}–Cd^{II} distances of 9.1966 (9), 13.4004 (13) and 13.4004 (13) Å, respectively.

To the best of our knowledge, compounds related to 2,4'-bpdC have rarely been reported (Liu *et al.*, 2010). In [Co(2,4'-bpdC)(bix)] (Liu *et al.*, 2010), which is different to the arrangement in (I), the bpdC anion has two coordination modes connecting two Co centres: the 2-carboxylate group coordinates to one Co^{II} cation as a monodentate ligand, while the 4'-carboxylate group coordinates to one Co^{II} cation in a chelating mode. Alternating Co^{II} cations and bpdC anions construct an infinite chain propagating along [010]. Adjacent chains are further pillared by bix ligands to form a two-dimensional wave-like network with (4,4) topology. The coordination environment of the Co^{II} cation in this structure is defined by three O atoms from two bpdC anions and two N atoms from two bix ligands, affording a distorted trigonal bipyramid. Compound (I) is also entirely different from another related compound, [Co(2,4'-bpdC)(bix)_{0.25}]-0.25H₂O (Liu *et al.*, 2010). In that structure, although the bpdC ligand also assumes two coordination modes, it coordinates to three Co^{II} cations: the 2-carboxylate group coordinates to two Co^{II} cations in a bidentate bridging mode, while the 4'-carboxylate

group coordinates to one Co^{II} cation in a monodentate mode. The 2,4'-bpdc ligands and the Co^{II} cations construct two-dimensional sheets, which are linked by bix ligands into a three-dimensional network with (6³). $(6^3 \cdot 10^3)$ topology.

Experimental

A mixture of CdSO₄·8H₂O (0.17 mmol, 0.13 g), H₂bpdc (0.5 mmol, 0.17 g), bix (0.5 mmol, 0.10 g), NaOH (1 mmol, 0.04 g) and H₂O (15 ml) was placed in a Parr Teflon-lined stainless steel vessel (23 ml), which was then sealed and heated at 403 K for 3 d. After the mixture had cooled slowly to room temperature, a large quantity of colourless block-like crystals of (I) were obtained.

Crystal data

[Cd(C ₁₄ H ₈ O ₄)(C ₁₄ H ₁₄ N ₄)]·0.15H ₂ O	$V = 2622.1 (4) \text{ \AA}^3$
$M_r = 593.61$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 11.0099 (9) \text{ \AA}$	$\mu = 0.87 \text{ mm}^{-1}$
$b = 12.558 (1) \text{ \AA}$	$T = 298 \text{ K}$
$c = 19.2362 (15) \text{ \AA}$	$0.15 \times 0.12 \times 0.10 \text{ mm}$
$\beta = 99.635 (2)^\circ$	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	17539 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	5157 independent reflections
$T_{\min} = 0.870$, $T_{\max} = 0.918$	3405 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.083$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.068$	45 restraints
$wR(F^2) = 0.138$	H-atom parameters constrained
$S = 1.07$	$\Delta\rho_{\text{max}} = 0.56 \text{ e \AA}^{-3}$
5157 reflections	$\Delta\rho_{\text{min}} = -0.71 \text{ e \AA}^{-3}$
458 parameters	

In the initial refinement, the whole bpdc molecule was found to be disordered over two orientations. Two positions were defined for all atoms of the ligand and similarity restraints were applied to all bond lengths and angles involving the disordered atoms (SIMU restraint with default estimated standard deviation; Sheldrick, 2008). In addition, the C atoms of the benzene rings of the disordered ligand were constrained to fit perfect hexagons. The most satisfactory occupancies for the disordered major (C15–C20 and C22–C27) and minor (C15'–C20' and C22'–C27') components were found to be 0.55 and 0.45, respectively. Atom O1W was assigned from a crystallographic point of view, with an occupancy of only 0.15. All H atoms were positioned geometrically and refined using a riding model, with C–H = 0.93 (aromatic) or 0.97 Å (methylene), and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The coordinates of the O1W H atoms were calculated

Table 1

Selected geometric parameters (Å, °).

Cd1–N4 ⁱ	2.256 (6)	Cd1–O4 ⁱⁱ	2.400 (12)
Cd1–N1	2.275 (5)	Cd1–O3 ⁱⁱ	2.420 (13)
Cd1–O2	2.288 (12)	Cd1–O1	2.421 (12)
<hr/>			
N2–C4–C5	113.1 (5)	N3–C11–C8	113.6 (6)

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

using the CAL-OH command in the program PLATON (Spek, 2009) and they were refined with the O1W–H distances fixed at 0.82 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$.

Data collection: SMART (Bruker, 2007); cell refinement: SAINT-Plus (Bruker, 2007); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: TOPOS (Blatov *et al.*, 2000) and PLATON (Spek, 2009); software used to prepare material for publication: PLATON.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SU3055). Services for accessing these data are described at the back of the journal.

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