

A novel cadmium(II) coordination polymer with biphenyl-3,3',4,4'-tetracarboxylic acid and 4,4'-bipyridine

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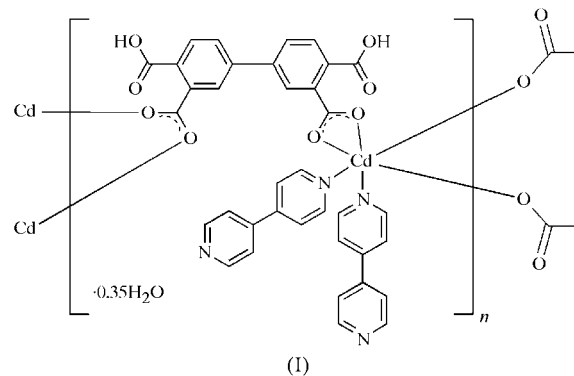
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A novel cadmium(II) coordination polymer, poly[[[bis(4,4'-bipyridine)cadmium(II)]- μ_3 -4,4'-dicarboxybiphenyl-3,3'-dicarboxylato] 0.35-hydrate], $[\{\text{Cd}(\text{C}_{16}\text{H}_8\text{O}_8)(\text{C}_{10}\text{H}_8\text{N}_2)_2\} \cdot 0.35\text{H}_2\text{O}]_n$, was obtained by reaction of $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 4,4'-bipyridine (4,4'-bpy) and biphenyl-3,3',4,4'-tetracarboxylic acid (H_4L) under hydrothermal conditions. Each Cd^{II} atom lies at the centre of a distorted octahedron, coordinated by four O atoms from three H_2L^{2-} ligands and N atoms from two monodentate 4,4'-bpy ligands. Each H_2L^{2-} ligand coordinates to three Cd^{II} atoms through two carboxylate groups, one acting as a bridging bidentate ligand and the other in a chelating bidentate fashion. Two Cd atoms, two H_2L^{2-} anions and four 4,4'-bpy ligands form a ring dimer node, which links into an extended broad zonal one-dimensional chain along the *c* axis.

Comment

Metal-carboxylate coordination polymers have emerged as an important family in the past few years (Rao *et al.*, 2004). It is also well known that the incorporation of carboxylic acid groups into coordination compounds gives interesting supra-molecular architectures (Puddephatt *et al.*, 2002). Multifunctional carboxylates and related species provide an effective means of designing novel hybrid structures with porous and other properties (Yaghi *et al.*, 2003; Kitagawa *et al.*, 2004). In some of these structures, the carboxylate group acts as a linker between two inorganic units. The biphenyl-3,3',4,4'-tetracarboxylic acid ligand (H_4L) has multifunctional possibilities: (a) it has four carboxyl groups that may be completely or partially deprotonated; (b) it can act not only as a hydrogen-bond acceptor but also as a hydrogen-bond donor, depending on the number of deprotonated carboxyl groups; (c) some of the carboxyl groups can be rotated out of the plane of the benzene ring upon complexation as a result of steric effects, and thus the ligand may connect metal ions in three



dimensions; (d) it is a flexible ligand. To the best of our knowledge, the crystal structure of a metal complex with the H_4L ligand has not been reported previously, although there are several crystal structures of complexes with analogous (but

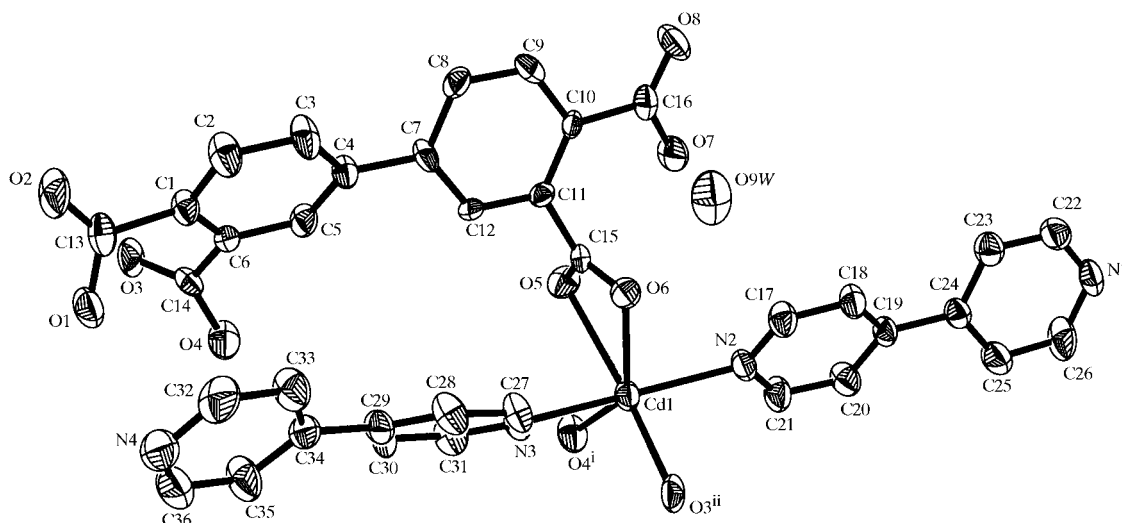
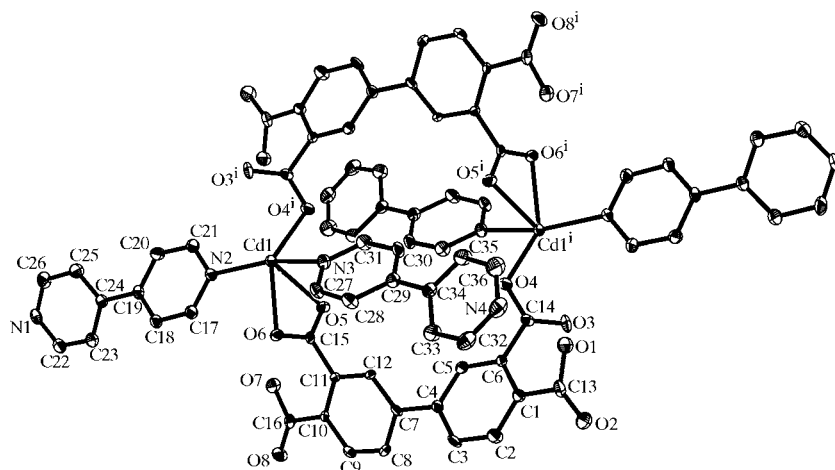
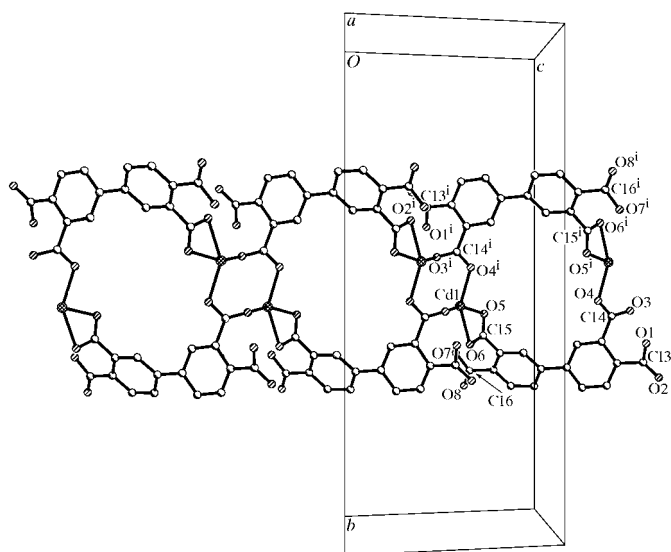


Figure 1

View of the local coordination of the Cd^{II} atom, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted. [Symmetry codes: (i) $2 - x, 1 - y, 2 - z$; (ii) $x, y, z - 1$.]


Figure 2

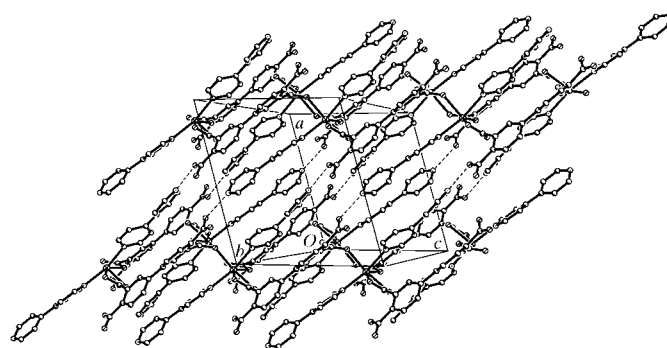
View of the dimer node, with displacement ellipsoids drawn at the 30% probability level. H atoms and water molecules have been omitted for clarity. [Symmetry code: (i) $2 - x, 1 - y, 2 - z$.]


Figure 3

The one-dimensional chain-like fragment (along c) in (I). H atoms, 4,4'-bpy groups and water molecules have been omitted for clarity. [Symmetry code: (i) $2 - x, 1 - y, 2 - z$.]

rigid) ligands, *viz.* terephthalic acid (Shi *et al.*, 2005), benzene-1,3,5-tricarboxylic acid (Rosi *et al.*, 2002; Li *et al.*, 1999; Millange *et al.*, 2002; Kepert & Rosseinsky, 1998), benzene-1,2,4,5-tetracarboxylic acid (Shi *et al.*, 2001, 2005; Cao *et al.*, 2002; Hou *et al.*, 2004), biphenyl-4,4'-dicarboxylic acid (Shi *et al.*, 2005; Pan *et al.*, 2003; Dai *et al.*, 2004; Mukherjee *et al.*, 2004; Shiu *et al.*, 2003) and its analogs. However, the H_4L coordination geometry is very different from those of the rigid ligands above because of the flexibility of its four carboxyl groups. We report here the preparation and crystal structure of a novel one-dimensional coordination polymer, *viz.* $\{[Cd(H_2L)(4,4'-bpy)_2] \cdot 0.35H_2O\}_n$ (4,4'-bpy is 4,4'-bipyridine), (I).

Single-crystal X-ray diffraction reveals that (I) is an extended broad zonal one-dimensional chain based on ring dimer building blocks constructed from two Cd atoms, two H_2L^{2-} ligands and four 4,4'-bpy ligands. Each Cd^{II} atom is six-


Figure 4

The two-dimensional supermolecular hydrogen-bonded framework in (I) (viewed approximately down the $[011]$ direction) formed *via* O—H...N interactions.

coordinate (Fig. 1), with two O atoms donated by one chelating bidentate H_2L^{2-} ligand, two from two separate bridging bidentate H_2L^{2-} ligands and two N atoms [Cd1—N2 = 2.312 (4) Å and Cd1—N3 = 2.404 (4) Å] from two 4,4'-bpy ligands, which, unusually, act as monodentate (not bridging bidentate) ligands. The four Cd1—O_{carboxyl} distances fall in the range 2.206 (3)–2.466 (4) Å and the O—Cd1—O angles vary from 54.6 (1) to 85.1 (1)°, similar to those in other cadmium–carboxylate coordination polymers (Shi *et al.*, 2005), with the Cd center displaying the typical distorted octahedral coordination geometry (Table 1). The H_2L^{2-} ligands exhibit an interesting connection mode with the metal ions, which is different from those in the other reported analogous ligands (Shi *et al.*, 2001, 2005). As shown in the scheme and Fig. 1, three types of coordination modes of H_2L^{2-} ligands are present in the structure, *viz.* (a) two carboxylate groups (C13 and C16) are not deprotonated and remain free [C13—O2 = 1.180 (6) Å, C13—O1 = 1.330 (6) Å, C16—O8 = 1.208 (6) Å and C16—O7 = 1.310 (6) Å]; (b) one carboxylate group (C15) adopts a bidentate chelating mode, chelating one Cd^{II} atom; (c) another carboxylate group (C14) adopts a bidentate bridging mode, connecting two Cd^{II} atoms. Each H_2L^{2-} ligand acts as a tetradentate ligand coordinating to three Cd^{II} atoms.

Two Cd atoms, two H_2L^{2-} ligands and four 4,4'-bpy ligands act as a ring dimer node (see Fig. 2). Nodes are connected through Cd1—O4ⁱ and O4—Cd1ⁱ bonds [symmetry code: (i) $2 - x, 1 - y, 2 - z$] into an extended broad zonal one-dimensional chain along the *c* axis (see Fig. 3).

In the packing arrangement of (I) (see Fig. 4), adjacent one-dimensional chains are parallel to each other and associate into a two-dimensional supermolecular layer *via* hydrogen bonds between the N atoms of 4,4'-bpy groups and hydroxyl groups of the free carboxylates of the H_2L^{2-} ligands (Table 1).

Experimental

H_4L was purchased from TCI and was used without further purification. Compound (I) was synthesized hydrothermally under autogenous pressure. A mixture of Cd(CH₃COO)₂·3H₂O (0.303 g, 1 mmol), H_4L (0.330 g, 1 mmol), 4,4'-bpy (0.312 g, 2 mmol) and NaOH (0.080 g, 2 mmol) was stirred for 20 min and then sealed in a Teflon-lined stainless steel Parr vessel, which was heated at 443 K for 72 h. After slow cooling to ambient temperature, colorless block-shaped crystals of (I) were separated mechanically from the powder and washed with distilled water (yield *ca* 70% based on Cd). The compound is insoluble in common organic solvents and water. Analysis found: C 57.3, H 3.3, N 7.5%; C₃₆H_{24.70}CdN₄O_{8.35} requires: C 56.9, H 3.28, N 7.38%.

Crystal data

[Cd(C ₁₆ H ₈ O ₈)(C ₁₀ H ₈ N ₂) ₂]·0.35H ₂ O	$D_x = 1.661 \text{ Mg m}^{-3}$
$M_r = 759.34$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 18569 reflections
$a = 12.101 (5) \text{ \AA}$	$\theta = 1.7\text{--}28.2^\circ$
$b = 24.379 (5) \text{ \AA}$	$\mu = 0.79 \text{ mm}^{-1}$
$c = 10.679 (5) \text{ \AA}$	$T = 298 (2) \text{ K}$
$\beta = 105.413 (5)^\circ$	Block, colorless
$V = 3037 (2) \text{ \AA}^3$	$0.35 \times 0.26 \times 0.25 \text{ mm}$
$Z = 4$	

Data collection

Rigaku R-Axis RAPID diffractometer	7162 independent reflections
ω scans	3097 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	$R_{\text{int}} = 0.084$
$T_{\text{min}} = 0.784, T_{\text{max}} = 0.828$	$\theta_{\text{max}} = 28.3^\circ$
18797 measured reflections	$h = -7 \rightarrow 15$
	$k = -32 \rightarrow 32$
	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.048$	$w = 1/[\sigma^2(F_o^2) + (0.036P)^2]$
$wR(F^2) = 0.115$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.96$	$(\Delta/\sigma)_{\text{max}} = 0.074$
7162 reflections	$\Delta\rho_{\text{max}} = 0.62 \text{ e \AA}^{-3}$
454 parameters	$\Delta\rho_{\text{min}} = -0.64 \text{ e \AA}^{-3}$

Table 1

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 \cdots N1 ⁱ	0.82	2.04	2.677 (6)	134
O7—H7 \cdots N4 ⁱⁱ	0.82	1.80	2.590 (6)	163

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

All H atoms on C and O atoms were positioned geometrically and refined as riding atoms [C—H = 0.93 \AA and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$; O—H = 0.82 \AA and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$]. The water molecule O9W was partially occupied and free refinement of its occupancy gave a final value of 0.35 (2); the H atoms attached to O9W were not located.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *PROCESS-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990); 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: HJ1069). Services for accessing these data are described at the back of the journal.

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