

catena-Poly[[[*cis*-aquabis(4-carboxy-cyclohexane-1-carboxylato- κ^2 O,O')-cadmium(II)]- μ -4,4'-bipyridine- κ^2 N:N] monohydrate]

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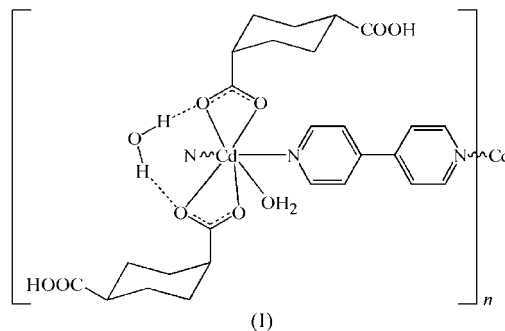
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The title complex, $\{[\text{Cd}(\text{C}_8\text{H}_{11}\text{O}_4)_2(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$, consists of linear chains formed through 4,4'-bipyridine ligands linking seven-coordinated Cd^{II} ions. Each Cd^{II} ion is in a distorted pentagonal-bipyramidal environment, coordinated by one water ligand, two 4-carboxycyclohexane-1-carboxylate ligands and one bridging 4,4'-bipyridine ligand to generate linear chains. The water molecules and the Cd atom on one side, and the 4,4'-bipyridine unit on the other, are bisected by two sets of twofold axes. The carboxylate group of the 4-carboxycyclohexane-1-carboxyl ligand chelates a Cd^{II} ion, while the (protonated) carboxyl group forms hydrogen bonds with adjacent chains, resulting in a layered structure. This is the first reported occurrence of a dicarboxycyclohexane ligand exhibiting a non-bridging coordination mode.

Comment

Considerable progress has recently been achieved on the crystal engineering of supramolecular architectures organized and sustained by means of coordinate covalent, supramolecular contacts (such as hydrogen bonds and π - π interactions), aurophilicity interactions (Colacio *et al.*, 2002; Roesky & Andruh, 2003; Guilera & Steed, 1999), *etc.* As an excellent building block in the design and construction of supramolecular polymers, 4,4'-bipyridine (4,4'-bipy) has been widely used. On the other hand, cyclohexane-1,4-dicarboxylic acid (H_2chdc) possesses a chair-type structure with *cis* and *trans* conformations, which can connect metal ions in different directions; it has two carboxylate groups and it has always been reported to link metal centers in a bridging mode (Qi *et al.*, 2003; Thirumurugan *et al.*, 2006). In spite of its being a good candidate for the construction of hydrogen-bonding networks, its supramolecular chemistry has rarely been explored, and so far mixed metal-organic complexes derived from 4,4'-bipy and chdc ligands have not been reported, even though the combination of 4,4'-bipy and chdc is expected to

construct an interesting variety of polymeric compounds. We report here the first occurrence of a one-dimensional Cd complex, $\{[\text{Cd}(\text{Hchdc})_2(4,4'\text{-bipy})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (I), with an unusual binding mode for the Hchdc ligand; it chelates one Cd^{II} ion, while its remaining (protonated) carboxylate group forms only hydrogen-bonding interactions.



Complex (I) consists of linear chains formed through 4,4'-bipy ligands linking seven-coordinated Cd^{II} ions. As shown in Fig. 1, the Cd^{II} ion adopts a distorted pentagonal-bipyramidal geometry. The water molecules and the Cd atom on one side, and the 4,4'-bipy unit on the other, are bisected by two sets of twofold axes. Two *trans*-related N atoms of two 4,4'-bipy ligands lie in the apical positions. One coordinated water molecule and four O atoms of two carboxylate groups of two chdc ligands form the equatorial plane (Table 1). The 4,4'-bipy ligand functions as a spacer between two Cd^{II} ions, the $\text{Cd}\cdots\text{Cd}$ separation being 11.645 (2) Å. The dihedral angle between two pyridine rings is 43.08 (3)°. As stated above, the Hchdc ligand chelates one Cd^{II} ion through one carboxylate group, while the remaining (protonated) carboxylate group does not participate in coordination, being only involved in hydrogen bonding. This is the first reported occurrence of a chdc ligand exhibiting a non-bridging coordination mode.

To our knowledge, this is the first example in the coordination chemistry of the chdc ligand in which it does not act in a bridging mode. As shown in Fig. 2, the Cd^{II} ions are interlinked by 4,4'-bipy ligands to generate linear chains along the *a* axis. The crystalline water molecule forms two $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds with two coordinated carboxylate O atoms.

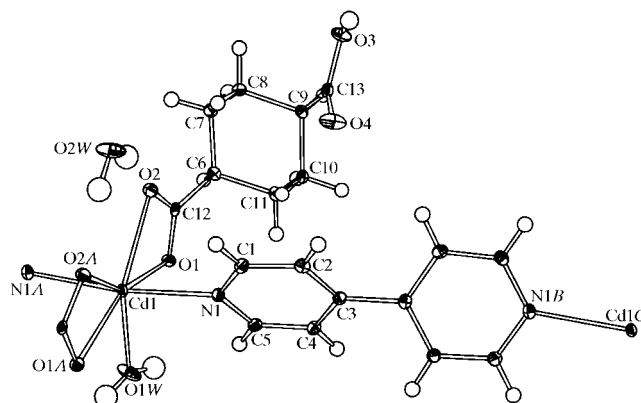
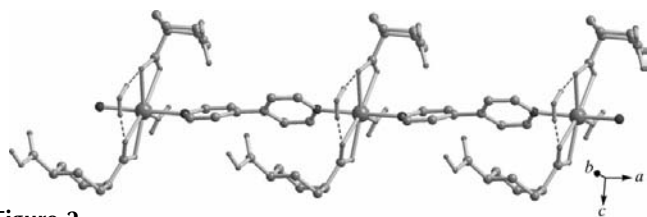
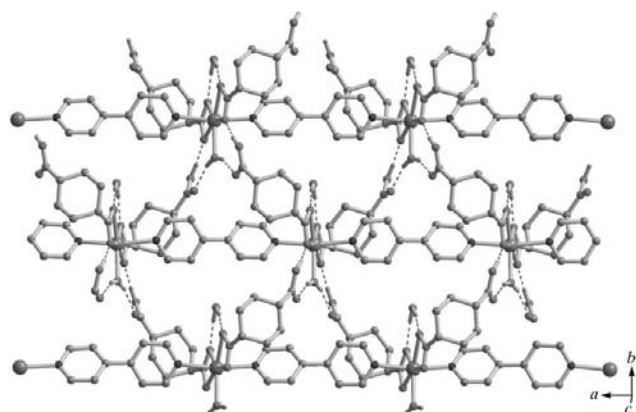


Figure 1
A view of (I) (30% probability displacement ellipsoids) [symmetry codes: (A) $-x + 1, y, -z + \frac{1}{2}$; (B) $-x, y, -z + \frac{1}{2}$; (C) $x - 1, y, z$].

**Figure 2**

The chain structure of (I). Hydrogen bonds are drawn as dashed lines. H atoms not involved in these interactions have been omitted.

**Figure 3**

The two-dimensional hydrogen-bonding network with (3,6)-topology. Hydrogen bonds are drawn as dashed lines. H atoms not involved in these interactions have been omitted.

A noteworthy feature of (I) is the two-dimensional hydrogen-bonding network (Fig. 3 and Table 2). Two uncoordinated carboxyl and two coordinated carboxylate groups, one aqua ligand and one solvent water molecule are linked through hydrogen-bonding interactions to form a butterfly-like unit. From a topological point of view, such six-membered butterfly-like units can be represented as a (3,6)-net (Li *et al.*, 2004).

Experimental

A mixture of CdCl₂ (0.184 g, 1 mmol), cyclohexane-1,4-dicarboxylic acid (0.087 g, 0.5 mmol), 4,4'-bipy (0.078 g, 0.5 mmol) and water (18 ml) was sealed in a 25 ml Teflon-lined stainless steel reactor and heated at 433 K for 3 d. On completion of the reaction, the reactor was cooled slowly to room temperature and the mixture was filtered, giving yellow single crystals suitable for X-ray analysis.

Crystal data

[Cd(C₈H₁₁O₄)₂(C₁₀H₈N₂)-
(H₂O)]·H₂O
M_r = 646.96
Orthorhombic, *Pbcn*
a = 11.6451 (5) Å
b = 15.1490 (8) Å
c = 15.1936 (8) Å
V = 2680.38 (7) Å³

Z = 4
D_x = 1.603 Mg m⁻³
Mo Kα radiation
μ = 0.88 mm⁻¹
T = 130 (2) K
Prism, yellow
0.50 × 0.34 × 0.23 mm

Data collection

Siemens SMART 1K CCD area-
detector diffractometer
φ and ω scans
Absorption correction: multi-scan
(SADABS; Sheldrick, 1996)
T_{min} = 0.59, T_{max} = 0.82

15765 measured reflections
2353 independent reflections
2319 reflections with I > 2σ(I)
R_{int} = 0.015
θ_{max} = 25.0°

Refinement

Refinement on F²
R[F² > 2σ(F²)] = 0.022
wR(F²) = 0.067
S = 1.06
2353 reflections
187 parameters

H atoms treated by a mixture of
independent and constrained
refinement

$w = 1/[\sigma^2(F_o^2) + (0.0389P)^2 + 2.4163P]$
where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ)_{max} = 0.001
Δρ_{max} = 0.31 e Å⁻³
Δρ_{min} = -0.51 e Å⁻³

Table 1

Selected bond lengths (Å).

Cd1—O1W	2.280 (2)	Cd1—O1	2.3961 (13)
Cd1—N1	2.3083 (19)	Cd1—O2	2.4880 (13)
Cd1—N1 ⁱ	2.3083 (19)	Cd1—O2 ⁱ	2.4880 (13)
Cd1—O1 ⁱ	2.3961 (13)		

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

Table 2

Hydrogen-bond geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
O1W—H1...O4 ⁱⁱ	0.87 (3)	1.82 (3)	2.672 (2)	168 (3)
O3—H3O...O1 ⁱⁱⁱ	0.83 (3)	1.76 (3)	2.5855 (19)	172 (2)
O2W—H2...O2	0.89 (3)	1.99 (3)	2.858 (2)	165 (3)

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

H atoms bonded to C atoms were positioned geometrically [aromatic C—H = 0.93 Å and aliphatic C—H = 0.97–0.98 Å; $U_{iso}(H) = 1.2U_{eq}(C)$]. H atoms bonded to O atoms were located in a difference Fourier map and refined freely; their displacement parameters were set at $1.2U_{eq}(O)$.

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: DIAMOND (Bergerhoff *et al.*, 1996); software used to prepare material for publication: SHELXTL (Siemens, 1996).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3020). Services for accessing these data are described at the back of the journal.

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