

***catena*-Poly[[aqua(11-chloropyrido[2',3':2,3]pyrimidino[5,6-*f*]-[1,10]phenanthroline- κ^2N^4,N^5)-cadmium(II)]- μ -benzene-1,4-dicarboxylato- $\kappa^3O^1,O^1':O^4$]: an inclined interpenetrating (6,3) network**

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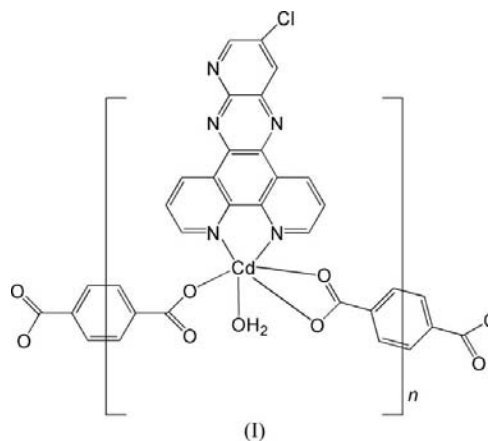
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The asymmetric unit of the title compound, $[\text{Cd}(\text{C}_8\text{H}_4\text{O}_4)(\text{C}_{17}\text{H}_8\text{ClN}_5)(\text{H}_2\text{O})]_n$, contains one Cd^{II} atom, two half benzene-1,4-dicarboxylate (1,4-bdc) anions, one 11-chloropyrido[2',3':2,3]pyrimidino[5,6-*f*][1,10]phenanthroline (*L*) ligand and one coordination water molecule. The 1,4-bdc ligands are on inversion centers at the centroids of the arene rings. The Cd^{II} atom is six-coordinated by two N atoms from one *L* ligand, three carboxylate O atoms from two different 1,4-bdc ligands and one water O atom in a distorted octahedral coordination sphere. Each Cd^{II} center is bridged by the 1,4-bdc dianions to give a one-dimensional chain. π - π stacking interactions between *L* ligands of neighboring chains extend adjacent chains into a two-dimensional supramolecular (6,3) network. Neighboring (6,3) networks are interpenetrated in an unusual inclined mode, resulting in a three-dimensional framework. Additionally, the water-carboxylate $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds observed in the network consolidate the interpenetrating nets.

Comment

The current interest in polymeric coordination networks is growing rapidly not only because of their potential applications in host-guest chemistry, ion exchange, gas storage and nonlinear optics, but also because of the intriguing variety of topologies (Batten & Robson, 1998; Yang *et al.*, 2008). Structural diversity in coordination polymers can occur as a result of various processes, including supramolecular isomerism, interpenetration or interweaving (Eddaoudi *et al.*, 2001; Carlucci *et al.*, 2003). Among these, entangled systems have attracted rapidly increasing interest because of their

potential applications as functional solid materials, and also because of their intriguing architectures and topologies (Batten, 2001). Interpenetrating networks, as an important subject in the area of entanglement, have provided a long-standing fascination for chemists (Ockwig *et al.*, 2005). These species can be regarded as infinite ordered polycatenanes or polyrotaxanes and are characterized by the presence of two or more independent networks that are inextricably entangled through the rings belonging to one framework. So far, a variety of appealing interpenetrated frameworks have been constructed and discussed in several excellent reviews (Batten & Robson, 1998; Batten, 2001; Carlucci *et al.*, 2003). Among the known interpenetrating coordination polymers with (6,3) networks, parallel interpenetration is the most common arrangement (Carlucci *et al.*, 2003). By contrast, inclined interpenetrating (6,3) networks are relatively scarce in coordination polymers, especially those constructed by π - π interactions (Carlucci *et al.*, 2003).



Up to now, 1,10-phenanthroline (phen) and its derivatives have been widely used to build supramolecular architectures because of their excellent coordinating ability; the resulting large conjugated system can easily form π - π interactions (Wang *et al.*, 2008; Qiao *et al.*, 2008; Yang *et al.*, 2007). However, to the best of our knowledge, coordination polymers based on its derivative 11-chloropyrido[2',3':2,3]pyrimidino[5,6-*f*][1,10]phenanthroline, (*L*), have not been reported. In this study, we selected the benzene-1,4-dicarboxylate dianion (1,4-bdc) as an organic linker and *L* as an *N*-donor chelating ligand, generating a new inclined interpenetrating three-dimensional coordination polymer, *viz.* $[\text{Cd}(1,4\text{-bdc})(L)(\text{H}_2\text{O})]_n$, (I).

The asymmetric unit of (I) contains one Cd^{II} atom, two half 1,4-bdc anions, one *L* ligand and one coordination water molecule (Fig. 1). The two independent 1,4-bdc ligands are on inversion centers located at the centroids of the arene rings. Each Cd^{II} atom is six-coordinated by two N atoms from one *L* ligand, three carboxylate O atoms from two different 1,4-bdc ligands and one water O atom in a distorted octahedral coordination arrangement. The average Cd-O and Cd-N distances in (I) (Table 1) are comparable to those observed for $[\text{Cd}(1,4\text{-ndc})(L')]_n$ (1,4-ndc = naphthalene-1,4-dicarboxylate and *L'* = pyrazino[2,3-*f*][1,10]phenanthroline) (Qiao *et al.*,

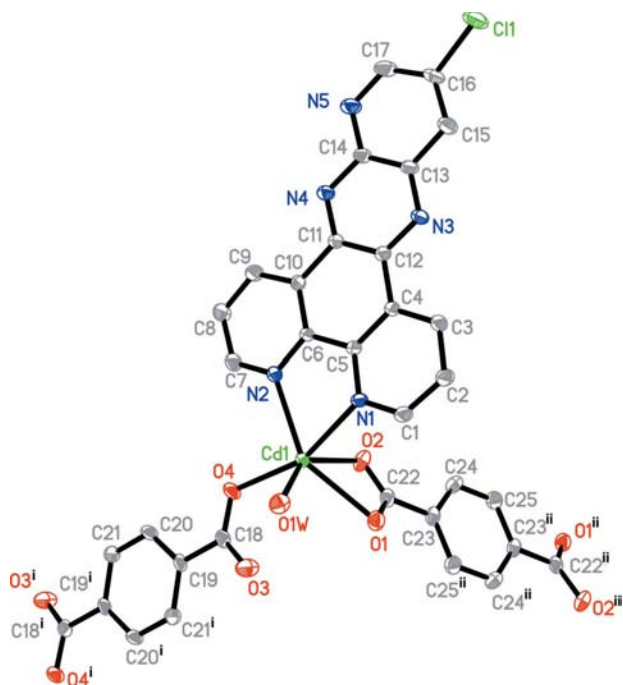


Figure 1

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

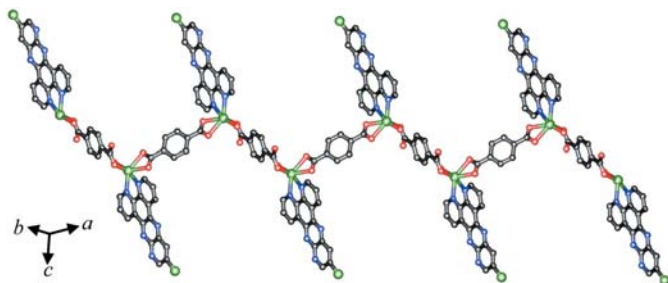


Figure 2

A view of the one-dimensional chain of (I).

2008). Each Cd^{II} center is bridged by the 1,4-bdc dianions to give a one-dimensional chain running approximately along the *a* axis (Fig. 2). Notably, the *L* ligands are arranged in a parallel fashion on both sides of the chain, leading to a structure suitable for forming aromatic intercalation. The π - π stacking interactions between *L* ligands of neighboring chains [centroid-centroid distance = 3.52 (3) Å and face-to-face distance = 3.45 (4) Å] extend adjacent chains into a two-dimensional supramolecular network (Fig. 3). If the *L* ligand and the π - π stacking interaction are considered as linkers, and the Cd^{II} atom is taken as a three-connected node, the two-dimensional supramolecular network can be classified as a three-connected (6,3) topology. Interestingly, neighboring (6,3) networks are interpenetrated in an unusual inclined mode, resulting in a three-dimensional framework (Fig. 4). The manner of interpenetration is such that the smallest hexagonal circuit of each sheet has parts of two other sheets

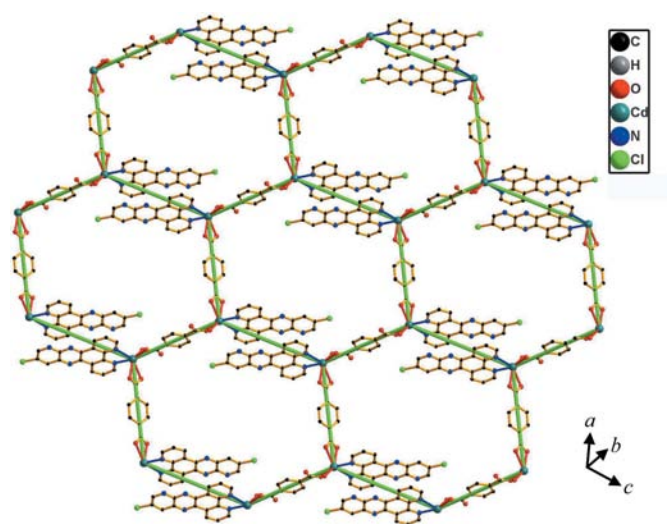


Figure 3

A view of the two-dimensional (6,3) network structure of (I).

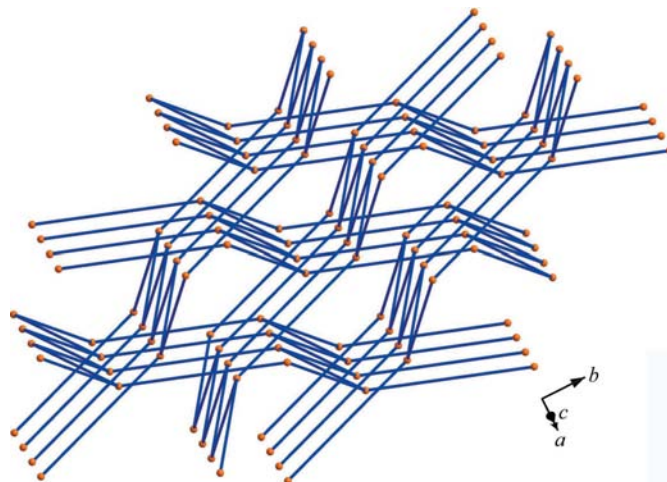


Figure 4

A view of the inclined interpenetrating (6,3) network structure of (I).

passing through it (Fig. 4). To the best of our knowledge, complex (I) is among only a few compounds having such inclined interpenetrating topology. Similar modes have so far only been reported in the structures of [Zn(SO₄)(bib)_{1.5}(H₂O)]·6H₂O [bib = 1,1'-(butane-1,4-diyl)bis(imidazole)] (Ma *et al.*, 2000) and [Ag₂(H₂bpd)₃·(cucurbituril)₃](NO₃)₈·40H₂O [bpd = *N,N'*-bis(4-pyridylmethyl)-1,4-diaminobutane] (Whang & Kim, 1997). Additionally, the O1W molecule, as the donor, forms hydrogen bonds with carboxylate O atoms (Table 2). The water-carboxylate O—H···O hydrogen bonds observed in the network consolidate the interpenetrating nets of (I).

Notably, when the similar phen derivative *L'* was used to react with Cd^{II} atoms in the presence of 1,4-ndc, a structurally different three-dimensional α -polonium structure [Cd(1,4-ndc)(*L'*)_n] was obtained (Qiao *et al.*, 2008). The topological difference between (I) and the reported material is mainly attributed to the structural difference of the dicarboxylates.

Experimental

A mixture of CdCl₂·2.5H₂O (0.5 mmol), 1,4-H₂bdc (0.5 mmol) and L (0.5 mmol) was dissolved in distilled water (12 ml), followed by addition of triethylamine until the pH of the system was adjusted to about 5.6. 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 428 K for 5 d under autogenous pressure. Afterwards, the reaction system was 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 46%, based on Cd^{II}).

Crystal data

| | |
|---|---|
| [Cd(C ₈ H ₄ O ₄)(C ₁₇ H ₈ ClN ₅)(H ₂ O)] | $V = 2292.9 (10) \text{ \AA}^3$ |
| $M_r = 612.26$ | $Z = 4$ |
| Monoclinic, $P2_1/n$ | Mo $K\alpha$ radiation |
| $a = 10.412 (3) \text{ \AA}$ | $\mu = 1.12 \text{ mm}^{-1}$ |
| $b = 14.466 (3) \text{ \AA}$ | $T = 293 \text{ K}$ |
| $c = 15.411 (4) \text{ \AA}$ | $0.32 \times 0.27 \times 0.22 \text{ mm}$ |
| $\beta = 98.956 (2)^\circ$ | |

Data collection

| | |
|---|--|
| Bruker SMART APEX diffractometer | 18357 measured reflections |
| Absorption correction: multi-scan (SADABS; Sheldrick, 1996) | 5256 independent reflections |
| $T_{\min} = 0.752$, $T_{\max} = 0.891$ | 3492 reflections with $I > 2\sigma(I)$ |
| | $R_{\text{int}} = 0.042$ |

Refinement

| | |
|---------------------------------|--|
| $R[F^2 > 2\sigma(F^2)] = 0.032$ | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.066$ | |
| $S = 0.89$ | $\Delta\rho_{\text{max}} = 1.42 \text{ e \AA}^{-3}$ |
| 5256 reflections | $\Delta\rho_{\text{min}} = -0.65 \text{ e \AA}^{-3}$ |
| 342 parameters | |

Table 1

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

| | | | |
|------------|------------|------------|------------|
| Cd1—O1 | 2.424 (2) | Cd1—O1W | 2.301 (2) |
| Cd1—O2 | 2.337 (2) | Cd1—N1 | 2.336 (2) |
| Cd1—O4 | 2.197 (2) | Cd1—N2 | 2.351 (2) |
| O4—Cd1—O1W | 89.70 (9) | N1—Cd1—N2 | 70.99 (8) |
| O4—Cd1—N1 | 159.27 (8) | O2—Cd1—N2 | 94.68 (8) |
| O1W—Cd1—N1 | 91.42 (9) | O4—Cd1—O1 | 111.97 (8) |
| O4—Cd1—O2 | 103.35 (8) | O1W—Cd1—O1 | 87.56 (8) |
| O1W—Cd1—O2 | 142.64 (8) | N1—Cd1—O1 | 88.76 (8) |
| N1—Cd1—O2 | 88.12 (8) | O2—Cd1—O1 | 55.08 (7) |
| O4—Cd1—N2 | 90.67 (8) | N2—Cd1—O1 | 144.81 (7) |
| O1W—Cd1—N2 | 120.38 (9) | | |

Table 2

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-----------------------------------|----------|-------------|-------------|---------------|
| O1W—HW11 \cdots O3 | 0.84 (4) | 1.84 (4) | 2.643 (4) | 160 (3) |
| O1W—HW12 \cdots O1 ⁱ | 0.81 (3) | 1.94 (3) | 2.752 (3) | 178 (3) |

Symmetry code: (i) $-x + 1, -y, -z$.

Carbon-bound H atoms were positioned geometrically ($C-H = 0.93 \text{ \AA}$) and refined as riding, with $U_{\text{iso}}(H)$ values fixed at $1.2U_{\text{eq}}(C)$. The water H atoms were located in a difference Fourier map and were thereafter refined freely.

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, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3222). Services for accessing these data are described at the back of the journal.

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