A novel cadmium(II) coordination polymer with a four-connected (4,4)-net based on a trinuclear cadmium(II) node

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In the title cadmium(II) coordination polymer, poly[tri-μ_4-adipato-bis(2-phenyl-1H-1,3,7,8-tetraazacyclopenta[l]phenanthrene-$\kappa^2 N^7, N^8$)tricadmium(II)], [Cd$_3$(C$_6$H$_8$O$_4$)$_3$(C$_{19}$H$_{12}$N$_4$)$_2$]$_n$, one of the Cd atoms is in a distorted pentagonal bipyramidal coordination environment, surrounded by five O atoms from three adipate (adip) ligands and two N atoms from one 2-phenyl-1H-1,3,7,8-tetraazacyclopenta[l]phenanthrene (L) ligand. A second Cd atom occupies an inversion center and is coordinated by six O atoms from six adip ligands in a distorted octahedral geometry. The carboxylate ends of the adip ligands link Cd^{II} atoms to form unique trinuclear Cd^{II} clusters, which are further bridged by the adip linkers to produce a two-dimensional layer structure. Topologically, each trinuclear Cd^{II} cluster is connected to four others through six adip ligands, thus resulting in a unique two-dimensional four-connected framework of (4,4)-topology. This work may help the development of the coordination chemistry of 1,10-phenanthroline derivatives.

Comment

Metal–organic coordination polymers built up from polynuclear metal clusters and multicarboxylate building blocks have become an attractive area of research in recent years, owing to their interesting molecular topologies and potential applications as functional materials (Eddaoudi et al., 2001; Hagrman et al., 1999; Noveron et al., 2002). Polynuclear metal clusters can be very versatile in terms of coordination properties and rigidity, and can display intriguing physical properties that are not found in mononuclear species. So far, multicarboxylate building blocks with special configurations have been selected for use in the design of a wide range of polynuclear metal clusters. Following this direction, a variety of coordination polymers based on polynuclear metal clusters have been obtained using multicarboxylate building blocks. Typically, benzene-1,2-dicarboxylic acid and benzene-1,3-di-

carboxylic acid have been widely used for the design and synthesis of coordination polymers with polynuclear metal clusters (Yang, Li et al., 2007). However, far less effort has been expended on adipic acid (H$_2$adip; Yang, Ma et al., 2007). As a dicarboxylate ligand, H$_2$adip possesses flexibility owing to the presence of –CH$_2$– spacers between the two carboxylate groups, which is helpful for the formation of coordination polymers with polynuclear metal clusters.

On the other hand, the preparation of ordered functional crystalline solids, which display a variety of well defined supramolecular architectures mediated by supramolecular interactions, is currently of great interest and importance (Lehn, 1988, 2002). In this regard, 1,10-phenanthroline (phen) and 2,2′-bipyridyl have been widely used to build supramolecular architectures owing to their excellent coordinating ability and large conjugated systems that can easily form π–π interactions (Tong et al., 2000; Zheng et al., 2001). On this basis, a number of coordination polymers have been prepared from one-dimensional covalently bonded chains or layers, yielding extended two- or three-dimensional supramolecular structures through the π–π interactions (Zhang et al., 2005). However, far less attention has been given to their derivatives (Yang, Li et al., 2007; Yang, Ma et al., 2007). For example, the unusual phen derivative 2-phenyl-1H-1,3,7,8-tetraazacyclopenta[l]phenanthrene (L) possesses an extended aromatic

(I)
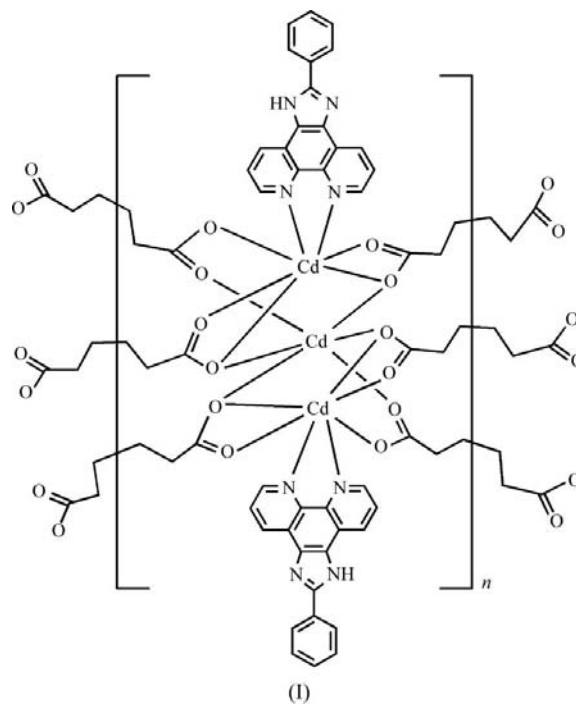
system and is a good candidate for the construction of metal–organic supramolecular architectures (Steck & Day, 1943). In this contribution, we selected H$_2$adip as a flexible linker and L as a secondary ligand, generating a new trinuclear Cd^{II} coordination polymer, (I), a rare example of a two-dimensional structure with four-connected (4,4)-topology based on trinuclear Cd^{II} nodes.

The asymmetric unit of (I) contains two crystallographically independent Cd^{II} atoms. As shown in Fig. 1, atom Cd1 is in a
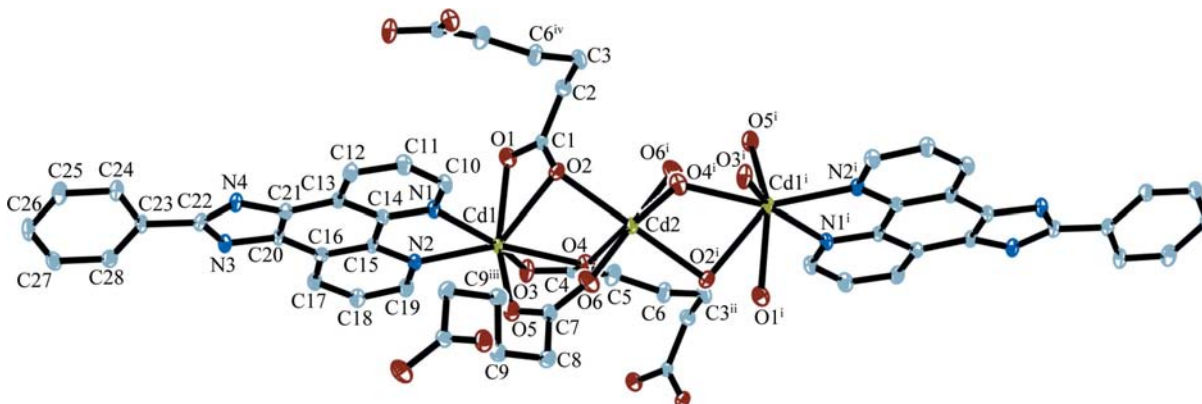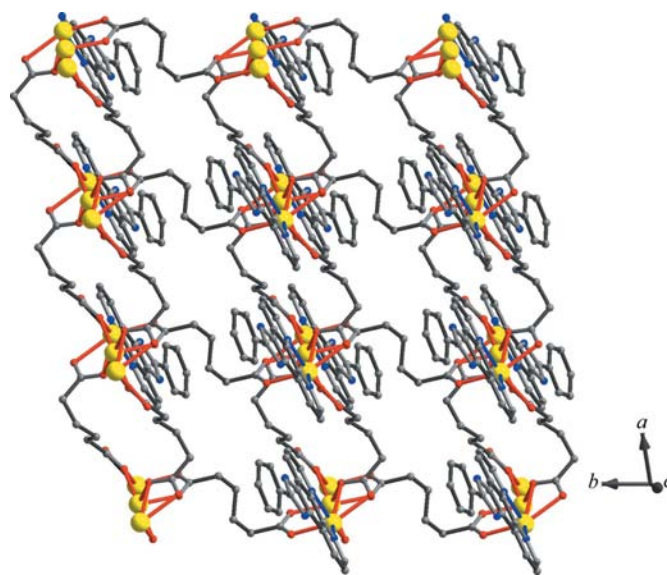
Figure 1
A view of the local coordination of the Cd^{II} cation in (I), showing the atom-numbering scheme. Displacement ellipsoids are shown at the 30% probability level. [Symmetry codes: (i) $-x, -y + 1, -z + 1$; (ii) $x + 1, y, z$; (iii) $-x, -y, -z + 1$; (iv) $-1 + x, y, z$.]

distorted pentagonal bipyramidal coordination environment consisting of five O atoms from three adip ligands and two N atoms from one *L* ligand. Atoms O2, O3, O4, N1 and N2 form the equatorial plane, while atoms O1 and O5 occupy the axial positions. Atom Cd2 lies on an inversion center and is coordinated by six O atoms from six adip ligands in a distorted octahedral geometry, where atoms O2, O2^i, O6 and O6^i [symmetry code: (i) $-x, -y + 1, -z + 1$] are in one plane, and atoms O4 and O4^i lie perpendicular to this plane. The Cd—N [2.328 (3) and 2.387 (2) Å] and Cd—O distances [2.218 (2)–2.532 (2) Å] in (I) (Table 1) are comparable to those found in another crystallographically characterized multinuclear Cd^{II} complex, *viz.* [Cd$_4$(OH)$_2$(H$_2$O)$_2$(sip)$_2$(4,4′-bpy)$_4$]·H$_2$O (sip is 5-sulfoisophthalate and 4,4′-bpy is 4,4′-bipyridyl; Li *et al.*, 2005). Notably, in (I), two coordination modes for the adip ligands have been found. One type of adip linker coordinates to four Cd^{II} atoms in a bis-tridentate mode, while the other connects four Cd^{II} centers in a bis-bidentate mode. Interestingly, the carboxylate ends of the adip ligands link the Cd^{II} atoms to form a unique trinuclear Cd^{II} cluster. These clusters are further bridged by the adip linkers resulting in a two-dimensional layer structure (Fig. 2). It is noted that the *L* ligands are extended on both sides of the layers, and the planes of adjacent *L* ligands are nearly parallel. These parallel *L* ligands are paired to furnish strong aromatic π–π stacking interactions [with a centroid-to-centroid distance of 3.785 (2) Å, a vertical face-to-face distance of 3.442 (1) Å and a dihedral angle of 0.80 (3)°], which extend the layers into a three-dimensional supramolecular structure in the *bc* plane (Fig. 3).

A better insight into the structure of (I) can be achieved by the application of the topological approach, that is, reducing multidimensional structures to simple node-and-linker nets. As discussed above, each trinuclear Cd^{II} cluster is surrounded by eight organic ligands, namely six bridging adip and two chelating *L* ligands. Therefore, this defines a four-connected node. Each trinuclear Cd^{II} cluster core is further linked to four nearest neighbors through six adip ligands, thus resulting in a unique four-connected two-dimensional network (Fig. 4). Considering the trinuclear clusters as nodes and keeping the
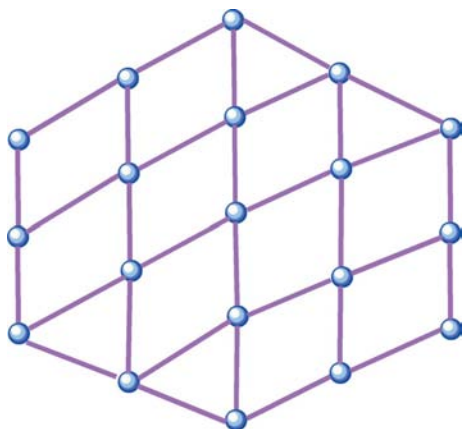
adip ligands as spacers, the overall topology of the two-dimensional framework is best described as a four-connected

Figure 2
The layer structure of (I) (*DIAMOND*; Brandenburg, 2006).
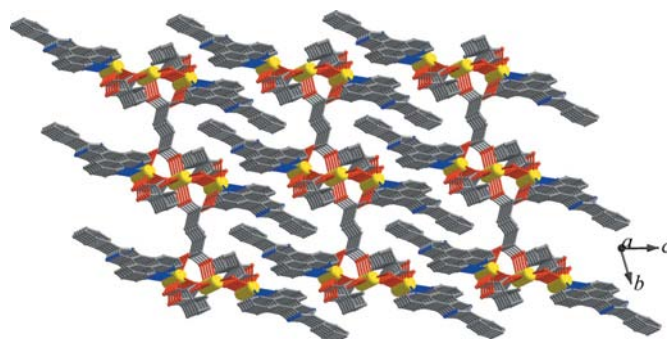
Figure 3
A view of the three-dimensional supramolecular structure formed through π–π stacking interactions (*DIAMOND*; Brandenburg, 2006).

Figure 4
A schematic representation of the two-dimensional four-connected (4,4)-net.

Table 1
Selected geometric parameters (Å, °).

Cd1—N1	2.387 (2)	Cd1—O4	2.408 (2)
Cd1—N2	2.328 (3)	Cd1—O5	2.249 (2)
Cd1—O1	2.391 (3)	Cd2—O2	2.318 (2)
Cd1—O2	2.532 (2)	Cd2—O4	2.284 (2)
Cd1—O3	2.431 (2)	Cd2—O6	2.218 (2)
O5—Cd1—N2	103.07 (9)	N1—Cd1—O3	152.91 (8)
O5—Cd1—N1	86.65 (9)	O1—Cd1—O3	85.10 (9)
N2—Cd1—N1	70.66 (8)	O4—Cd1—O3	53.32 (8)
O5—Cd1—O1	153.45 (9)	O5—Cd1—O2	101.13 (9)
N2—Cd1—O1	98.78 (9)	N2—Cd1—O2	142.84 (8)
N1—Cd1—O1	86.53 (9)	N1—Cd1—O2	83.13 (8)
O5—Cd1—O4	84.01 (9)	O1—Cd1—O2	52.56 (7)
N2—Cd1—O4	136.70 (8)	O4—Cd1—O2	73.45 (8)
N1—Cd1—O4	152.51 (8)	O3—Cd1—O2	111.39 (8)
O1—Cd1—O4	90.38 (9)	O6—Cd2—O4	86.90 (9)
O5—Cd1—O3	111.41 (10)	O6—Cd2—O2	89.51 (10)
N2—Cd1—O3	85.23 (8)	O4—Cd2—O2	79.91 (9)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3···O1^v	0.86	2.04	2.770 (3)	142

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

(4,4)-net (Yang *et al.*, 2008). Occurrences of the (4,4)-net have been extensively reported; however, a (4,4)-net based on a trinuclear metal node is rarely observed (Batten & Robson, 1998). Therefore, to our knowledge, (I) is the first example of a two-dimensional (4,4)-net based on a trinuclear Cd^{II} node. The flexibility of the L ligand may play an important role in the formation of the unusual structure.

It is noteworthy that the structure of (I) is entirely different from that of the related compound $[Cd_2(Dpq)_2(BPDC)_2]$·1.5H$_2$O (Dpq is dipyrido[3,2-*d*:2′,3′-*f*]quinoxaline and BPDC is biphenyl-4,4′-dicarboxylate; Wang *et al.*, 2007), in which the BPDC ligands link the Cd^{II} centers to give an interesting six-connected twofold-interpenetrated three-dimensional α-Po-related architecture. The structure of (I) is also entirely different from that of the related polymer $[Cd_2(fum)Cl_2L_2]_n$ (fum is the fumarate dianion; Kong *et al.*, 2008). In that structure, the μ_2-Cl atoms and the bis-chelating fum dianions bridge neighboring Cd^{II} centers, yielding a coordination polymer chain structure along the c axis. N—H···O hydrogen bonds between the N atoms of L and the carboxylate O atoms of fum lead to a sheet structure in the bc plane.

Finally, an N—H···O hydrogen bond between the N atom of the L ligand and a carboxylate O atom further stabilizes the structure of (I) (Table 2).

Experimental

CdCl$_2$·2.5H$_2$O (0.114 g, 0.5 mmol), H$_2$adip (0.073 g, 0.5 mmol) and L (0.148 g, 0.5 mmol) were dissolved in distilled water (12 ml), and triethylamine was added until the pH value of the system was adjusted to about 5.5. 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 458 K for 10 d under autogenous pressure. Subsequently, 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 28%, based on Cd^{II}).

All H atoms were positioned geometrically (N—H = 0.86 Å and C—H = 0.93 or 0.97 Å) and refined as riding, with U_{iso}(H) values of 1.2U_{eq}(carrier).

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *PROCESS-AUTO*; 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: *SHELXL97*.

metal-organic compounds

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