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A six-connected *α*-polonium net based on tetranuclear Cd^{II} nodes

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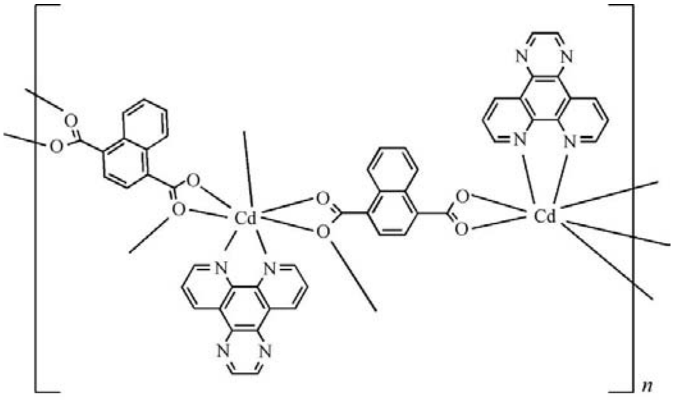
The cadmium(II) coordination polymer poly[[(pyrazino[2,3-*f*]-[1,10]phenanthroline-κ^2N^8,N^9)cadmium(II)]-μ_3-naphthalene-1,4-dicarboxylato-$\kappa^5O^1:O^1,O^{1'}:O^4,O^{4'}$], $[Cd(C_{12}H_6O_4)(C_{14}H_8N_4)]_n$, contains two Cd^{II} cations, two pyrazino[2,3-*f*][1,10]-phenanthroline (*L*) ligands and two naphthalene-1,4-dicarboxylate (1,4-ndc) anions in the asymmetric unit. Both Cd^{II} ions are in a distorted CdO_5N_2 monocapped octahedral coordination geometry. Both unique 1,4-ndc ligands are bonded to three Cd^{II} ions. In these modes, tetranuclear clusters are formed in which four Cd^{II} ions are bridged by the carboxylate groups of the 1,4-ndc ligands to form discrete rods. The tetranuclear cadmium carboxylate clusters act as rod-shaped secondary building units (SBUs) within the structure. The SBUs are connected together by the aromatic backbone of the dicarboxylate ligands, connecting the clusters into a three-dimensional *α*-polonium net. The title compound represents the first *α*-polonium net constructed from rod-like clusters in coordination polymers. The result indicates that an appropriate combination of dicarboxylate and aromatic chelating ligands is critical to the formation of high-dimensional structures based on metal clusters in these systems.

Comment

Recently, coordination polymers constructed of polynuclear metal clusters and polycarboxylates have attracted intense interest due to their interesting molecular topologies and potential applications as functional materials (Eddaoudi *et al.*, 2001). Polynuclear metal clusters can be very versatile in terms of coordination properties and rigidity, as well as displaying intriguing physical properties in comparison with mononuclear species (Hagrman *et al.*, 1999; Noveron *et al.*, 2002). Recent reviews of the framework topologies and other geometric characteristics of network solids reflect that it remains a challenge to achieve a true advance without understanding the structural aspects of such materials at a molecular or an atomic resolution (Eddaoudi *et al.*, 2001). In this regard, the skilful combination of bridging carboxylates, 2,2′-bipyridyl-like (bpy-like) chelating ligands and metal ions has generated many interesting coordination architectures. Unfortunately, owing to the termination effect of chelating bpy-like ligands, such coordination polymers containing both polycarboxylates and bpy-like ligands are usually only one- or two-dimensional coordination polymers (Hu *et al.*, 2006). As far as we know, high-dimensional complexes based on dicarboxylate and bpy-like ligands have rarely been reported. The utilization of polynuclear metal clusters as building blocks to construct high-dimensional frameworks has proved to be a feasible route (Wang *et al.*, 2005). One common approach to the synthesis of high-nuclearity clusters is to control the hydrolysis of metal salts with the aid of carboxylate ligands, where the carboxylate group may induce core aggregation, and it should be feasible to link discrete clusters into an extended network *via* the linear bridging ability of the carboxylate. In this work, we chose naphthalene-1,4-dicarboxylic acid (1,4-H_2ndc) as the carboxylate-containing ligand and pyrazino[2,3-*f*][1,10]phenanthroline (*L*) as the chelating ligand, yielding an unusual three-dimensional coordination polymer, [Cd(1,4-ndc)(*L*)]$_n$, (I), based on tetranuclear Cd^{II} clusters.



(I)

The asymmetric unit of (I) consists of two crystallographically independent Cd^{II} atoms, two unique *L* chelating ligands and two unique bridging 1,4-ndc ligands (Fig. 1). Both Cd^{II} atoms are in a distorted seven-coordinate CdO_5N_2 monocapped octahedral coordination geometry. Atom Cd1 bonds to a μ_2-O atom [O4^{i}; symmetry code: (i) $x - 1$, y, z] from a carboxylate ligand chelated to the adjoining Cd2 atom, four O atoms [O1, O2, O7^{iii} and O8^{iii}; symmetry code: (iii) $x - 1$, $-y + \frac{1}{2}$, $z + \frac{1}{2}$] from three different 1,4-ndc ligands and two N atoms (N1 and N2) from one chelating *L* ligand. The coordination environment of atom Cd2 is completed by two N atoms (N5 and N6) from a chelating *L* ligand, four O atoms (O3, O4, O5 and O6) from two different 1,4-ndc ligands and a μ_2-O atom [O6^{ii}; symmetry code: (ii) $-x + 1$, $-y + 1$, $-z$] from a carboxylate ligand chelated to the adjoining Cd1 atom. Thus, both unique 1,4-ndc ligands are bonded to three Cd^{II} atoms.

Tetranuclear clusters are formed in which four Cd atoms are bridged by the carboxylate groups of the 1,4-ndc ligands to form discrete rods (Fig. 2). The distance between the Cd atoms at either end of these rods is about 10.92 (2) Å. Each cluster

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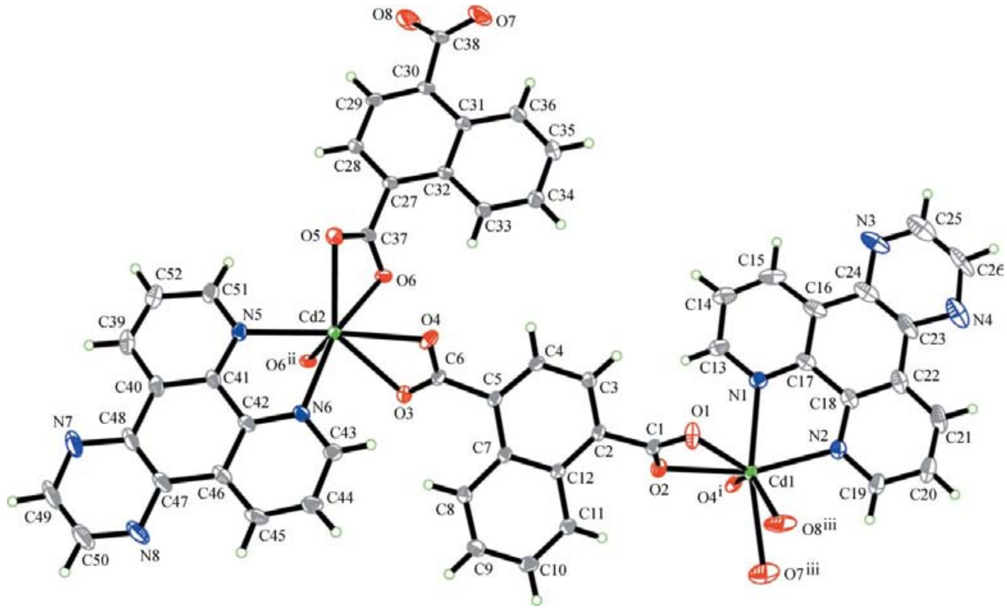

Figure 1

A view of the local coordination of the Cd^{II} cations in (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 20% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $x - 1, y, z$; (ii) $1 - x, 1 - y, -z$; (iii) $x - 1, \frac{1}{2} - y, \frac{1}{2} + z$.]

lies across an inversion centre, with the Cd2 atoms in the middle and the Cd1 atoms on the ends of the rod. To the best of our knowledge, this rod-like tetranuclear Cd cluster including the bpy-like chelating ligand *L* has not been reported so far, although other non-coplanar tetranuclear Cd clusters including bpy-like chelating ligands have been reported (Wei *et al.*, 2005).

The tetranuclear cadmium carboxylate clusters act as rod-shaped secondary building units (SBUs) within the structure of (I). The SBUs are connected together by the aromatic backbone of the dicarboxylate ligands, connecting the clusters into a three-dimensional network (Fig. 3). Each SBU has eight 1,4-ndc ligands radiating outwards. However, these only connect to six adjacent clusters (four by single bridges) to give (4,4) sheets parallel to the *yz* plane, and two by double bridges in the *z* direction, to give the three-dimensional net. Each SBU therefore acts as a six-connecting node, and the overall network topology is that of α-polonium (Batten & Robson, 1998; Yang *et al.*, 2008). Recently, several six-connected nets, such as $4^4.6^{11}$, LB-1 ($4^4 6^{10} 8$), pcu ($4^{12} 6^3$), roa ($4^4 6^{10} 8$), and rob ($4^8 6^6 8$), have been observed in coordination polymers (Zhang *et al.*, 2007). It is noteworthy that the α-polonium net presented here is clearly different from the six-connected three-dimensional nets mentioned above. To the best of our knowledge, the structure of (I) is the first α-polonium net constructed from rod-like clusters in coordination polymers. The result indicates that an appropriate combination of the dicarboxylate and aromatic chelating ligands is critical to the formation of high-dimensional structures based on metal clusters.

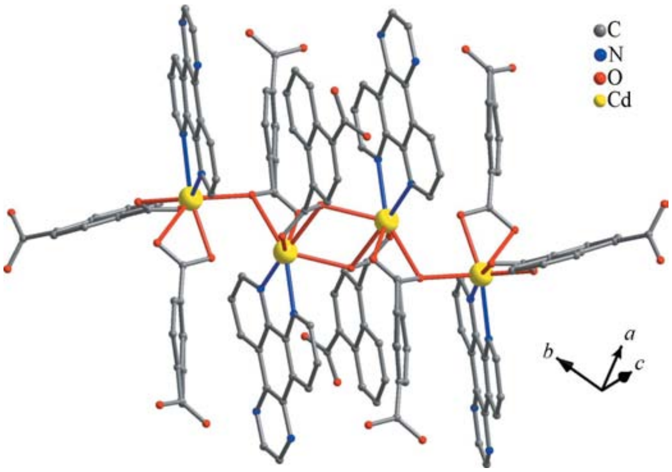

Figure 2

A view of the linkage of the tetranuclear core.

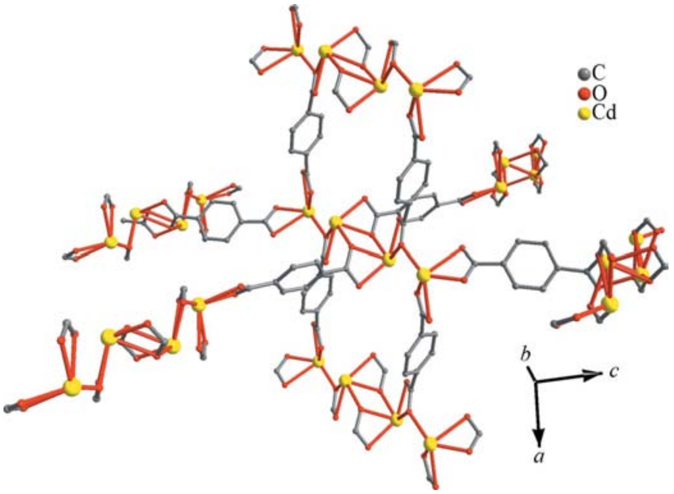

Figure 3

A view of the linkage of the tetranuclear core with six adjacent cores (H atoms and parts of the aromatic rings have been omitted for clarity).

Experimental

A mixture of $CdCl_2{\cdot}2.5H_2O$ (0.114 g, 0.5 mmol), 1,4-H_2ndc (0.110 g, 0.5 mmol) and *L* (0.123 g, 0.5 mmol) was dissolved in distilled water (12 ml), followed by addition of triethylamine until the pH of the system was about 5.7. 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 2 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 33%, based on Cd^{II}).

Crystal data

$[Cd(C_{12}H_6O_4)(C_{14}H_8N_4)]$
M_r = 558.81
Monoclinic, $P2_1/c$
a = 10.162 (2) Å
b = 18.040 (4) Å
c = 24.160 (5) Å
β = 92.78 (3)°
V = 4423.9 (15) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 1.03 mm^{-1}
T = 293 (2) K
0.31 × 0.29 × 0.24 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.721, T_{max} = 0.784
41917 measured reflections
10059 independent reflections
7470 reflections with $I > 2\sigma(I)$
R_{int} = 0.044

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.086
S = 1.05
10059 reflections
631 parameters
42 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.55 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}

All H atoms were positioned geometrically (C—H = 0.93 Å) and refined as riding, with $U_{iso}(H) = 1.2U_{eq}(C)$.

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*.

Table 1
Selected bond lengths (Å).

Cd1—N1	2.412 (3)	Cd2—O4	2.490 (2)
Cd1—N2	2.362 (3)	Cd2—O5	2.388 (2)
Cd2—N5	2.336 (3)	Cd2—O6	2.396 (2)
Cd2—N6	2.337 (3)	Cd1—$O8^{i}$	2.228 (3)
Cd1—O1	2.479 (3)	Cd1—$O4^{ii}$	2.280 (2)
Cd1—O2	2.358 (2)	Cd1—$O7^{i}$	2.599 (3)
Cd2—O3	2.431 (2)	Cd2—$O6^{iii}$	2.518 (2)

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

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3163). Services for accessing these data are described at the back of the journal.

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