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catena-Poly[bis{μ-dihydrogen [(5-carboxypentylimino)dimethylene]-diphosphonato-κ^2O:O'}cadmium(II)]

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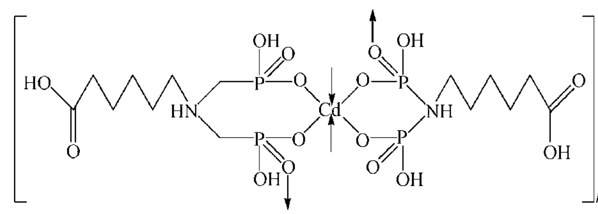
The title compound, $[Cd(C_8H_{18}NO_8P_2)_2]_n$, synthesized by hydrothermal methods, exhibits a layered structure in which the Cd^{II} ion, occupying a centre of symmetry, is coordinated by six O atoms from four phosphonate ligands. The cross-linkage of CdO_6 octahedra by bridging phosphonate ligands results in a cadmium(II) phosphonate layer. Within the layer, there exists a 16-membered ring incorporating four –Cd—O—P—O– linkages. The uncoordinated carboxyl group of the ligand is oriented so that it penetrates the adjacent layer, taking part in hydrogen bonding to two uncoordinated phosphonate O atoms to form a CO_2H/HO_2P motif.

Comment

In recent years, the chemistry of metal phosphonates has been an active research area owing to their potential applications in the area of catalysis, ion exchange, proton conductivity, surface modification, intercalation chemistry, photochemistry and materials chemistry (Clearfield, 1998). Metal phosphonates can exhibit structural types such as zero-dimensional (Ying, Chen *et al.*, 2008), one-dimensional chain (Yang *et al.*, 2005), two-dimensional layered (Zheng *et al.*, 2002) or three-dimensional microporous (Burkholder *et al.*, 2004). It has been proved that attaching an additional functional group, such as carboxyl, hydroxy, amine or crown ether groups, to the phosphonic acid group is a very useful method for building open-framework structures (Cheetham *et al.*, 1999; Stock, Frey *et al.*, 2000; Serpaggi & Férey, 1999; Ying *et al.*, 2006). Amongst these functional groups, the carboxyl group has been widely used because of its coordination ability. Phosphonic acids such as HOOC–*R*–PO_3H_2, HOOC–*R*–$N(CH_2PO_3H_2)_2$ and HOOC–*R*$NHCH_2PO_3H_2$, which contain only one carboxyl group, have been used extensively (Bauer *et al.*, 2005; Tang *et al.*, 2006; Stock, 2002; Stock, Stucky & Cheetham, 2000; Zhang *et al.*, 2005). Amongst these three types of phosphonic acid ligand, several metal phosphonates of the form HOOC–*R*–$N(CH_2PO_3H_2)_2$ have been reported (Bauer *et al.*, 2005; Tang *et al.*, 2006), but to the best of our knowledge (Cambridge Structural Database, Version 5.25, with updates to May 2009; Allen, 2002) metal phosphonates of the form HOOC–$(CH_2)_5$–$N(CH_2PO_3H_2)_2$ are rare. The only example, namely, $Pb_2[O_2C(CH_2)_5N(CH_2PO_3)(CH_2PO_3H)]$, has been reported by our group recently (Ying, Li *et al.*, 2008). This compound exhibits a three-dimensional structure and the metal ions are



(I)

five-coordinate. Transition metal phosphonates formed by this ligand have not been reported before. Hydrothermal reaction of Cd^{II} acetate and HOOC–$(CH_2)_5$–$N(CH_2PO_3H_2)_2$ resulted in the title compound, (I). We report here its synthesis, characterization and crystal structure.

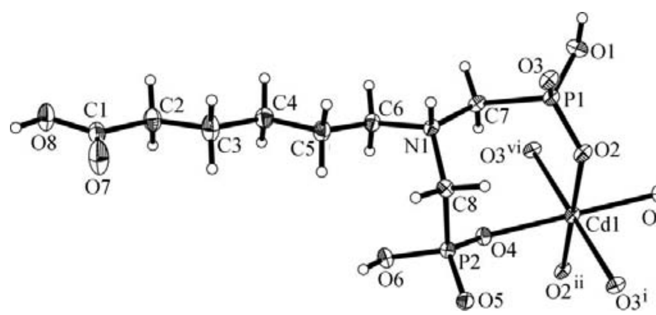


Figure 1
The molecular structure of the title compound, shown with 30% probability displacement ellipsoids. [Symmetry codes: (i) $-x + 1$, $y + \frac{1}{2}$, $-z + \frac{1}{2}$; (ii) $-x + 1$, $-y + 1$, $-z + 1$; (vi) x, $-y + \frac{1}{2}$, $z + \frac{1}{2}$.]

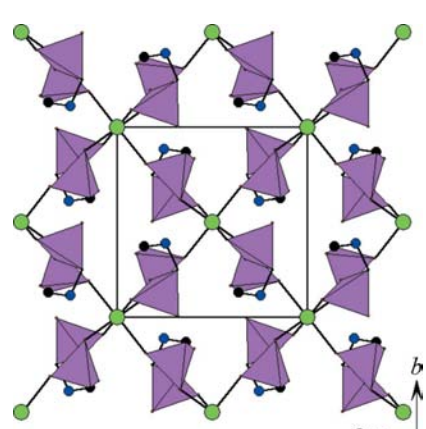


Figure 2
A view of the cadmium(II) phosphonate layer in the title compound, with the C–PO_3 tetrahedra shaded. The HOOC$(CH_2)_5$– group (which is approximately normal to this plane) and the H atoms have been omitted for clarity.

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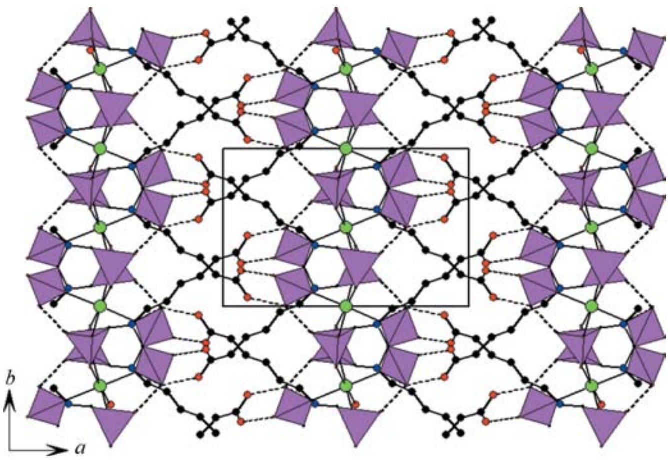

Figure 3
A view of the structure of the title compound, along the *c* axis. The C–PO_3 tetrahedra are shaded and H atoms have been omitted for clarity. Hydrogen bonding is shown by dashed lines.

As shown in Fig. 1, in the title compound, the cadmium(II) ions, which reside on centres of symmetry, are coordinated by six O atoms from four phosphonate ligands (O2, O4, $O2^{ii}$, $O4^{ii}$, $O3^{vi}$ and $O3^{i}$; see Fig. 1 for symmetry codes). The Cd—O distances range from 2.242 (2) to 2.287 (2) Å (Table 1). The cadmium(II) ions exhibit a distorted octahedral coordination geometry. The phosphonate anion chelates the Cd^{II} ion in a bidentate fashion, and also forms a bridge to a second Cd^{II} ion. The amine group and carboxyl group of the ligand remain uncoordinated. The crosslinkage of CdO_6 octahedra by bridging phosphonate ligands results in a cadmium(II) phosphonate layer (Fig. 2). Within the layer, there is a 16-membered ring made up of four –Cd—O2—P1—O3– sequences. If, for the purposes of classifying the net, we define the chelate ring as a single point of connection to Cd (making each ligand effectively a single linker), so that all Cd centres can be defined as four-connected nodes, then the layer can be described as a (4,4) grid. Within the layer there is a single hydrogen bond (Table 2). The uncoordinated carboxyl group at the end of the hydrocarbon arm of the molecule penetrates the adjacent layer to form a double hydrogen-bonded CO_2H/HO_2P motif (Fig. 3 and Table 2).

Experimental

The phosphonic acid ligand was synthesized by a Mannich-type reaction according to a previously reported procedure (Ying, Li *et al.*, 2008). A mixture of cadmium acetate (0.5 mmol, 0.130 g) and 6-[bis(phosphonomethyl)amino]hexanoic acid (0.5 mmol, 0.078 g) in distilled water (15 ml) was sealed in an autoclave equipped with a Teflon liner (20 ml) and then heated at 423 K for 4 d. Crystals of the title compound (colourless blocks) were obtained. Analysis found: C 25.62, H 4.87, N 3.70%; calculated for $C_{16}H_{36}CdN_2O_{16}P_4$: C 25.64, H 4.81, N 3.74%. IR data (KBr, cm^{-1}): 3436 (*m*), 3106 (*s*), 2960 (*s*), 1712 (*m*), 1677 (*m*), 1472 (*m*), 1437 (*m*), 1419 (*m*), 1375 (*w*), 1325 (*s*), 1290 (*m*), 1259 (*s*), 1235 (*s*), 1158 (*s*), 1083 (*s*), 1049 (*s*), 970 (*m*), 931 (*s*), 792 (*m*), 771 (*m*), 734 (*m*), 582 (*s*), 570 (*s*), 533 (*m*), 469 (*s*).

Crystal data

$[Cd(C_8H_{18}NO_8P_2)_2]$
M_r = 748.75
Monoclinic, $P2_1/c$
a = 15.4321 (17) Å
b = 9.4632 (11) Å
c = 9.9958 (11) Å
β = 108.414 (2)°
V = 1385.0 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.10 mm^{-1}
T = 273 K
0.23 × 0.11 × 0.07 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (North *et al.*, 1968)
T_{min} = 0.787, T_{max} = 0.927
10035 measured reflections
3219 independent reflections
2092 reflections with $I > 2\sigma(I)$
R_{int} = 0.095

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.089
S = 0.87
3219 reflections
179 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.27 e Å^{-3}
$\Delta\rho_{min}$ = −1.20 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cd1—O2	2.280 (2)	Cd1—O4	2.242 (3)
Cd1—$O3^{i}$	2.2875 (19)		
O2—Cd1—O4	91.82 (9)	O2—Cd1—$O4^{ii}$	88.18 (9)
O2—Cd1—$O3^{i}$	87.83 (7)		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···$O5^{iii}$	0.82	1.87	2.652 (4)	159
O6—H6C···$O7^{iv}$	0.82	1.79	2.605 (4)	178
O8—H8C···$O5^{iv}$	0.82	1.90	2.718 (4)	176
N1—H10A···$O2^{iii}$	0.91	2.13	2.823 (4)	132
N1—H10A···$O4^{v}$	0.91	2.42	3.172 (4)	140

Symmetry codes: (iii) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$; (iv) $-x, -y, -z$; (v) $x, -y-\frac{1}{2}, z-\frac{3}{2}$.

C- and N-bound H atoms were positioned geometrically (C—H = 0.97 Å and N—H = 0.91 Å). The hydroxy H atoms were placed (O—H = 0.82 Å) by considering the best staggered orientations of each O—H group with respect to the parent C—O or P—O bonds that also resulted in an appropriate orientation to interact with the nearest hydrogen-bond acceptor. All H atoms were refined in the riding-model approximation [U_{iso}(H) = 1.2U_{eq}(C), 1.5U_{eq}(O) or 1.2U_{eq}(N)].

Data collection: *SMART* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3111). Services for accessing these data are described at the back of the journal.

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