

## Poly[[diaquacadmium(II)]- $\mu_4$ - [N-(phosphonomethyl)ammonio]- acetato]

Qian-Jun Deng,<sup>a,b</sup> Ming-Hua Zeng,<sup>c</sup> Hong Liang<sup>a,c\*</sup> and  
Ke-Long Huang<sup>a</sup>

<sup>a</sup>School of Chemistry and Chemical Engineering, Central South University, Changsha, Hunan 410000, People's Republic of China, <sup>b</sup>Science School, Foshan University, Foshan 528000, People's Republic of China, and <sup>c</sup>Department of Chemistry and Chemical Engineering, Guangxi Normal University, Guilin, Guangxi 541004, People's Republic of China  
Correspondence e-mail: dqj3927@163.com

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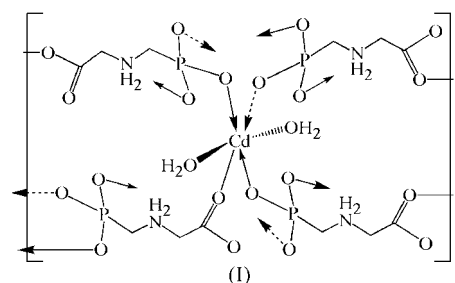
The title compound,  $[\text{Cd}(\text{C}_3\text{H}_6\text{NO}_5\text{P})(\text{H}_2\text{O})_2]_n$ , is a three-dimensional polymeric complex. The asymmetric unit contains one Cd atom, one *N*-(phosphonomethyl)glycine zwitterion  $[(\text{O}^-)_2\text{OPCH}_2\text{NH}_2^+\text{CH}_2\text{COO}^-]$  and two water molecules. The coordination geometry is a distorted  $\text{CdO}_6$  octahedron. Each *N*-(phosphonomethyl)glycine ligand bridges four adjacent water-coordinated Cd cations through three phosphonate O atoms and one carboxylate O atom, like a regular  $\text{PO}_4^{3-}$  group in zeolite-type frameworks. One-dimensional zigzag  $(-\text{O}-\text{P}-\text{C}-\text{N}-\text{C}-\text{C}-\text{O}-\text{Cd}-)$ <sub>n</sub> chains along the [101] direction are linked to one another *via* Cd—O—P bridges and form a three-dimensional network motif with three types of channel systems. The variety of O—H...O and N—H...O hydrogen bonds is likely to be responsible for stabilizing the three-dimensional network structure and preventing guest molecules from entering into the channels.

### Comment

Metal complexes containing phosphonic acids attached to a variety of functional groups, such as aza-crown ethers (Sharma & Clearfield, 2000), amines (Kong *et al.*, 2004; Jankovics *et al.*, 2002) and carboxylic acid groups (Zhu *et al.*, 2000; Mao *et al.*, 2002), have shown many unusual structural and functional features. The *N*-(phosphonomethyl)glycine ligand is a trifunctional aminocarboxylatephosphonate and features a diverse range of coordination modes in metal complexes (Stock, 2002; Ramstedt *et al.*, 2004). We report here a new polymeric  $\text{Cd}^{\text{II}}$  complex incorporating the trifunctional *N*-(phosphonomethyl)glycine (PMG) ligand, (I). The coordination mode of PMG has not previously been reported.

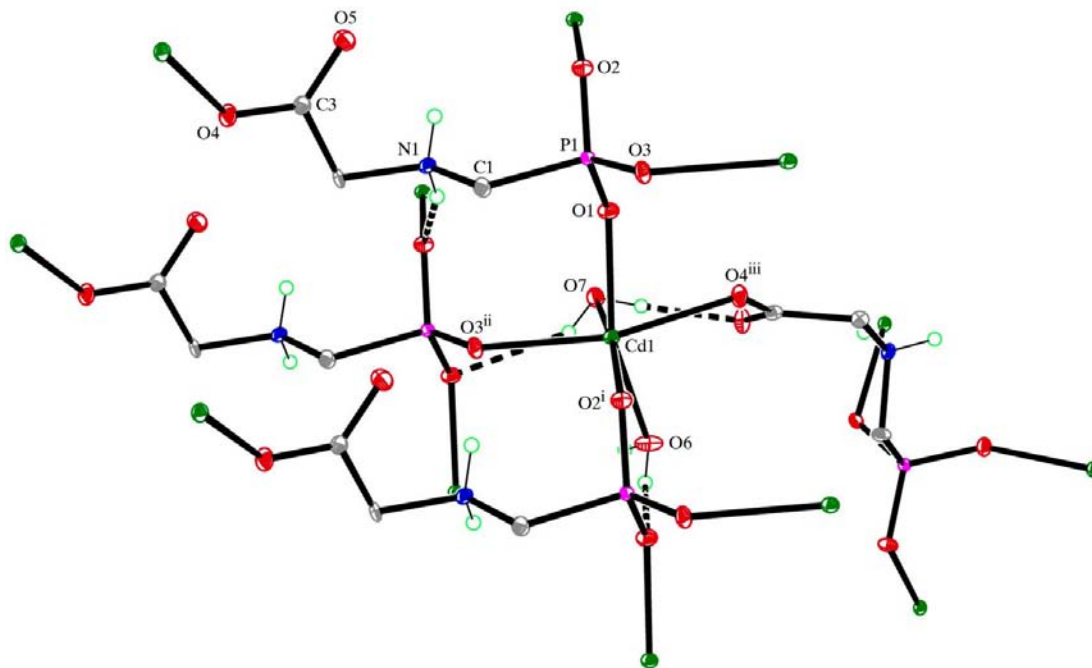
The structure of complex (I) is shown in Fig. 1. The asymmetric unit consists of one  $\text{Cd}^{\text{II}}$  ion, one PMG dianion and two water molecules. The  $\text{Cd}^{\text{II}}$  ion is six-coordinated and situated

in a distorted  $\text{CdO}_6$  octahedral environment, involving three O atoms from phosphonate groups of three neighbouring ligands, one carboxylate O atom from another ligand and two water O atoms. The Cd—O bond distances are in the range 2.208 (2)–2.387 (2) Å (Table 1), and are similar to those reported for another  $\text{Cd}^{\text{II}}$  aminocarboxylatephosphonate (Yang *et al.*, 2003). The equatorial plane of the coordination environment is defined by atoms O1, O3<sup>ii</sup>, O4<sup>iii</sup> and O6 [symmetry codes: (ii)  $x, y + 1, z$ ; (iii)  $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$ ], with a mean deviation of 0.0454°. The *trans*-axial positions are occupied by atoms O7 and O2<sup>i</sup> [symmetry code: (i)  $x + \frac{1}{2}, y + \frac{1}{2}, z$ ], with a O7—Cd1—O2<sup>i</sup> bond angle of 169.99 (9)°. The N atom is not coordinated. There are also O—H...O and N—H...O hydrogen-bond interactions in the structure (Fig. 1 and Table 2).

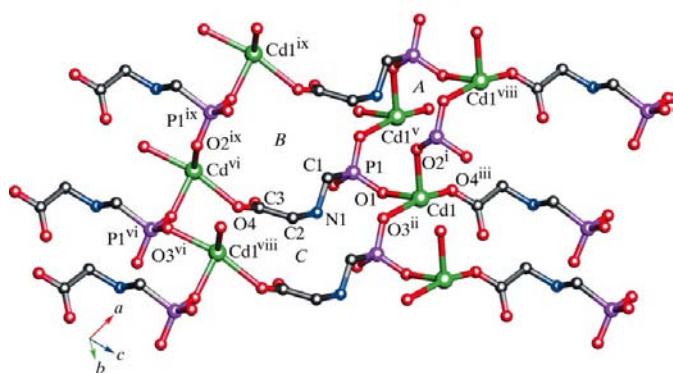


The X-ray crystal structure reveals that compound (I) has a metal-to-ligand ratio of 1. It is also clear that both phosphonate and carboxylate groups of the ligand are deprotonated, whereas the Cd atom has an oxidation state of +2. Thus, the only way in which the neutrality of compound (I) can be achieved is by considering the possibility that the secondary amine may be 2H-protonated, *viz.*  $-\text{NH}_2^+$ . Overall, the ligand coordinates to  $\text{Cd}^{\text{II}}$  carrying a double negative charge, as the zwitterion  $[(\text{O}^-)_2\text{OPCH}_2\text{NH}_2^+\text{CH}_2\text{COO}^-]$  (Stock, 2002). Three phosphonate O atoms and one terminal carboxylate O atom in one zwitterion are utilized to connect the  $\text{Cd}^{2+}$  site, and therefore each  $[(\text{O}^-)_2\text{OPCH}_2\text{NH}_2^+\text{CH}_2\text{COO}^-]$  zwitterion in effect behaves like a regular  $\text{PO}_4^{3-}$  group in zeolite-type frameworks (Zhu *et al.*, 2000) and is four-connected to four  $\text{Cd}^{2+}$  sites. Such a coordination mode is different from those previously reported for PMG. To maintain a metal-to-ligand ratio of 1, each  $\text{Cd}^{2+}$  site is also four-connected to  $[\text{O}_3\text{PCH}_2\text{NH}_2\text{COO}]^{2-}$  sites (see scheme and Fig. 1).

A one-dimensional zigzag chain is formed, containing a repeating  $(-\text{O1}-\text{P1}-\text{C1}-\text{N1}-\text{C2}-\text{C3}-\text{O4}-\text{Cd1}-)$  unit, with a metal–metal distance of 9.586 Å along the [101] direction. These chains are further linked to one another *via* two types of Cd1—O2—P1 and Cd1—O3—P1 bridges in a different direction, as the  $\text{PO}_4^{3-}$  groups link to Cd atoms in different chains (Fig. 2), with O—Cd—O bond angles in the range 78.87 (8)–163.42 (7)° (Table 1). The result of cross-linking chains in this manner is the formation of a three-dimensional network motif containing three channel systems that are nearly perpendicular to one another. These channels are created by 12-, 20- and 20-membered rings, respectively. Each 12-membered ring (A) is formed of three Cd atoms and



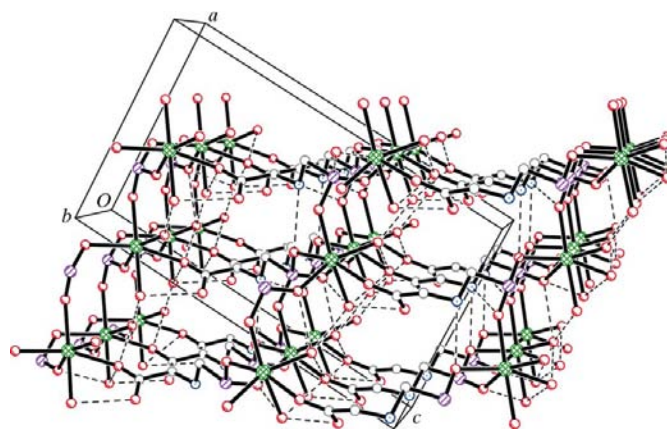
**Figure 1**  
A view of the molecular structure of compound (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines and carbon-bound H atoms have been omitted for clarity. [Symmetry codes: (i)  $\frac{1}{2} + x, \frac{1}{2} + y, z$ ; (ii)  $x, 1 + y, z$ ; (iii)  $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$ .]



**Figure 2**  
A view of the three types of 12-, 20- and 20-membered rings (A, B and C). The one-dimensional zigzag chains along the [101] direction are linked via two types of Cd1–O2–P1 and Cd1–O3–P1 bridges in different directions. Coordinated water molecules and H atoms have been omitted for clarity. [Symmetry codes: (i)  $\frac{1}{2} + x, \frac{1}{2} + y, z$ ; (ii)  $x, 1 + y, z$ ; (iii)  $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$ ; (v)  $x, y - 1, z$ ; (vi)  $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$ ; (vii)  $-\frac{1}{2} + x, \frac{3}{2} - y, -\frac{1}{2} + z$ ; (viii)  $x, -1 - y, \frac{1}{2} + z$ ; (ix)  $\frac{1}{2} + x, \frac{1}{2} + y, z - 1$ .]

three phosphonate groups,  $(-O-P-O-Cd-)_3$ . The two 20-membered rings (B and C) are similarly composed of two  $(-Cd-O-P-C-N-C-C-O-Cd-)$  units, sharing one Cd atom and one O–P–O bridge (Fig. 2).

Molecules of compound (I) show extensive hydrogen bonding between the coordinated water molecules and the phosphonate/carboxylate O atoms, between coordinated water molecules, and between the N atoms and the phosphonate O atoms. Such a complex hydrogen-bond network is likely to contribute to the overall stability of the



**Figure 3**  
The molecular packing in compound (I), showing the chains extending along different directions into a three-dimensional network motif via Cd–O–P bridges. Hydrogen bonds are shown as dashed lines and H atoms have been omitted for clarity.

crystal structure and prevents guest molecules entering into the above channels (Table 2 and Fig. 3).

### Experimental

A mixture of cadmium(II) acetate dihydrate (0.134 g, 0.5 mmol), *N*-(phosphonomethyl)glycine (0.078 g, 0.5 mmol) and deionized water (16 ml) was heated in a Teflon-lined stainless steel autoclave (25 ml) for 144 h at 433 K, after which the autoclave was cooled to room temperature over a period of 12 h at a rate of 10 K h<sup>-1</sup>. Colourless block-shaped single crystals of (I) were collected in about 18% yield.

## Crystal data

[Cd(C<sub>3</sub>H<sub>6</sub>NO<sub>5</sub>P)(H<sub>2</sub>O)<sub>2</sub>]  
*M<sub>r</sub>* = 315.49  
 Monoclinic, *Cc*  
*a* = 9.827 (2) Å  
*b* = 4.9326 (10) Å  
*c* = 16.795 (4) Å  
 $\beta$  = 93.910 (4)°  
*V* = 812.2 (3) Å<sup>3</sup>

*Z* = 4  
*D<sub>x</sub>* = 2.580 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 $\mu$  = 2.90 mm<sup>-1</sup>  
*T* = 153 (2) K  
 Block, colourless  
 0.30 × 0.25 × 0.07 mm

## Data collection

Rigaku Mercury diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan  
 (Jacobson, 1998)  
*T<sub>min</sub>* = 0.430, *T<sub>max</sub>* = 0.817

3642 measured reflections  
 1359 independent reflections  
 1348 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.021  
 $\theta_{\max}$  = 25.4°

## Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.015  
*wR* (*F*<sup>2</sup>) = 0.035  
*S* = 1.09  
 1359 reflections  
 127 parameters  
 H atoms treated by a mixture of  
 independent and constrained  
 refinement

$w = 1/[\sigma^2(F_o^2) + (0.0137P)^2 + 0.0465P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.60 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.47 \text{ e \AA}^{-3}$   
 Absolute structure: Flack (1983),  
 with 616 Friedel pairs  
 Flack parameter: -0.03 (2)

Table 1

Selected geometric parameters (Å, °).

Cd1—O1	2.208 (2)	Cd1—O3 <sup>iii</sup>	2.321 (2)
Cd1—O6	2.253 (2)	Cd1—O4 <sup>iii</sup>	2.369 (2)
Cd1—O2 <sup>i</sup>	2.271 (2)	Cd1—O7	2.387 (2)
O1—Cd1—O6	159.25 (9)	O2 <sup>i</sup> —Cd1—O4 <sup>iii</sup>	106.12 (8)
O1—Cd1—O2 <sup>i</sup>	100.24 (8)	O3 <sup>iii</sup> —Cd1—O4 <sup>iii</sup>	163.45 (8)
O6—Cd1—O2 <sup>i</sup>	92.94 (9)	O1—Cd1—O7	89.29 (9)
O1—Cd1—O3 <sup>iii</sup>	92.01 (8)	O6—Cd1—O7	78.81 (9)
O6—Cd1—O3 <sup>iii</sup>	104.27 (8)	O2 <sup>i</sup> —Cd1—O7	169.98 (8)
O2 <sup>i</sup> —Cd1—O3 <sup>iii</sup>	88.99 (8)	O3 <sup>iii</sup> —Cd1—O7	87.58 (9)
O1—Cd1—O4 <sup>iii</sup>	78.89 (9)	O4 <sup>iii</sup> —Cd1—O7	78.59 (9)
O6—Cd1—O4 <sup>iii</sup>	82.10 (9)		

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

H atoms on C and N atoms were positioned geometrically and were included in the refinement in the riding-model approximation, with C—H distances of 0.97 Å and N—H distances of 0.90 Å, and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ . The water H atoms were located in a difference Fourier map and were refined subject to an O—H distance restraint of 0.82 (1) Å.

Data collection: *CrystalClear* (Rigaku, 1999); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MS, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997);

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1A...O3 <sup>iv</sup>	0.90	2.07	2.881 (4)	149
N1—H1D...O2 <sup>ii</sup>	0.90	2.05	2.888 (4)	155
O6—H6A...O1 <sup>i</sup>	0.82	1.88	2.646 (3)	156
O6—H6A...O7 <sup>i</sup>	0.82	2.60	2.991 (3)	111
O6—H6B...O4 <sup>v</sup>	0.82 (3)	1.88 (3)	2.697 (3)	174 (5)
O7—H7A...O5 <sup>iii</sup>	0.82	1.95	2.710 (3)	153
O7—H7B...O1 <sup>ii</sup>	0.82 (1)	2.28 (3)	2.924 (3)	136 (4)
O7—H7B...O4 <sup>v</sup>	0.82 (1)	2.38 (3)	3.077 (3)	143 (4)

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

molecular graphics: *SHELXTL* (Sheldrick, 2000); 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: DN3020). Services for accessing these data are described at the back of the journal.

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