Syntheses, Characterizations, and Crystal Structures of Three New Metal Phosphonocarboxylates with a Layered and a Microporous Structure

Bing-Ping Yang,[a] Jiang-Gao Mao,*[a] Yan-Qiong Sun,[a] Han-Hua Zhao,[b] and Abraham Clearfield[b]

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Hydrothermal reactions of *N*-(phosphonomethyl)proline (H_3L) with M^{II} (M = Cd, Pb, and Zn) chlorides resulted in three new metal amino-phosphono-carboxylates, namely, $[Cd_2LCl(H_2O)]$ (**1**) and $[Pb_2Cl_2(HL)]$ (**2**) with a layered structure, and $[Zn_7L_6][Zn(H_2O)_6]_2\cdot16H_2O$ (**3**) featuring a microporous structure built from centered octahedral $Zn_6(Zn)$ cluster anions. The cadmium(II) ions in complex **1** are octahedrally coordinated [$Cd(1)O_5Cl$, $Cd(2)O_4NCl$]. These cadmium octahedra form a 1D zigzag chain along the *b*-axis through edge sharing, and such chains are further interconnected via phosphonate tetrahedra to form a <002> layer. The organic rings of the ligands are orientated to the interlayer space. Complex **2** also has a layered structure, in which Pb(1) is six-coordinated by four phosphonate oxygen atoms and two carboxylate oxygen atoms from four ligands in a distorted octahedral geometry, three Pb–O distances are relatively longer than those of the remaining ones, whereas Pb(2) is six coordinated by three phosphonate oxygen atoms and one carboxylate oxygen from four ligands as well as two chloride anions in a distorted octahedral geometry, one Pb–O bond is much longer than the remaining ones. These two different types of Pb^{II} ions are further interconnected through bridging carboxylate and phosphonate groups to form a <200> layer. Complex **3** contains a novel heptanuclear zinc phosphonate cluster anion $[Zn_7L_6]^{4-}$ and two hexahydrated zinc(II) cations as well as 16 lattice water molecules. The seven Zn^{II} cations in an anion form an unusual centered $Zn_6(Zn)$ octahedron, packing of such cluster anions creates micropores that are occupied by the hexahydrated zinc(II) cations and lattice water molecules.

Introduction

The chemistry of metal phosphonates has been an active research area in recent years due to its potential applications in the areas of catalysis, ion exchange, proton conductivity, intercalation chemistry, photochemistry and materials chemistry.[1] Metal phosphonates also exhibit a variety of open frameworks such as layered and microporous structures.[1] Materials with open-framework and microporous structures are expected to find their use as hybrid composite materials in electro-optical and sensing applications in the future.[2] Attaching additional functional groups such as crown ethers and carboxylate groups to the phosphonic acid has been proved to be very useful methods in building open-framework and microporous structures. A number of porous metal phosphonates with crown ether moieties have been reported recently.[3,4] A series of metal carboxylate-phosphonates with a framework structure, using $H_2O_3PCH_2CO_2H$ and $H_2O_3PCH_2CH_2CO_2H$ as ligands, have also been isolated mainly by the Cheetham, Bujoli, and Sevov groups.[2,5,6] Results of our research and others indicate that amino-carboxylic-phosphonic acids are also capable of forming open frameworks. The structures of amino-carboxylate-phosphonates depend on the extent of deprotonation of the ligands as well as on the nature of the metal ions.[7–10] For example, *N*-(phosphonomethyl)iminodiacetic acid (H_4PMIDA) has been found to be able to adopt various kinds of coordination modes under different reaction conditions.[7–10] A layered zirconium compound of 4-[bis(phosphonomethyl)amino]butanoic acid was reported by the Vivani group,[11a] and two zinc(II) complexes with *N*,*N*-bis(phosphonomethyl)aminoacetic acid and *N*-(phosphonomethyl)-*N*-methylglycine have been also obtained in our laboratory.[11b,11c] The structure of the latter zinc(II) amino-carboxylate-phosphonate features a microporous structure built from heptanuclear $Zn_6(Zn)(ligand)_6$ cluster anions.[11c] A layered Co^{II} compound of *N*-(phosphonomethyl)proline (H_3L) with a 3:2 metal/ligand ratio, $Co_3L_2\cdot5H_2O$ and a layered Pb^{II} complex with $H_2O_3PCH_2NHCH_2CO_2H$ have been reported very recently.[11d,11e] Hydrothermal reactions of *N*-(phosphonomethyl)proline with other divalent metal salts resulted in two types of layered materials containing chloride anions, $[Cd_2LCl(H_2O)]$ (**1**) and $[Pb_2Cl_2(HL)]$ (**2**), and a microporous compound, $[Zn_7L_6][Zn(H_2O)_6]_2\cdot16H_2O$ (**3**). Herein we

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[a] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences,
Fuzhou 350002, P. R. China
Fax: (internat.) + 86-591-371-4946
E-mail: mjg@ms.fjirsm.ac.cn
[b] Department of Chemistry, Texas A&M University,
P. O. Box 30012, College Station, Texas 77843-3255, USA

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report their syntheses, characterizations and crystal structures.

Results and Discussion

Crystal Structure of [$Cd_2LCl(H_2O)$] (1)

Complex **1** features a 2D layer built from a zigzag chain of edge-sharing cadmium(II) octahedra. As shown in Figure 1, Cd2 is octahedrally coordinated by a tridentate chelating ligand (O11, N1, O2), one carboxylate (O1b), and one phosphonate oxygen (O12d) atom from two neighboring [Cd(L)] units and a chloride anion (Cl1), whereas Cd1 is octahedrally coordinated by two carboxylate (O1c, O2b) and two phosphonate oxygen (O11, O13a) atoms from four neighboring [Cd(L)] units, an aqua ligand and a chloride anion. These octahedra are severely distorted, probably due to the edge-sharing of the octahedra and the larger size of the chloride anion. The average Cd−N distance is 2.37(1) Å; Cd−O distances range from 2.18(1) to 2.48(1) Å, and the Cd−Cl bonds are in the range from 2.527(3) to 2.665(3) Å. These bond lengths are similar to those reported for other Cd^{II} phosphonates.[3c,12] The phosphonate-carboxylate ligand adopts a coordination mode different from those in the Co^{II} complex.[11d] Both carboxylate oxygen atoms are bidentately bridging, whereas one phosphonate oxygen (O11) is bidentate and the other two are unidentate.

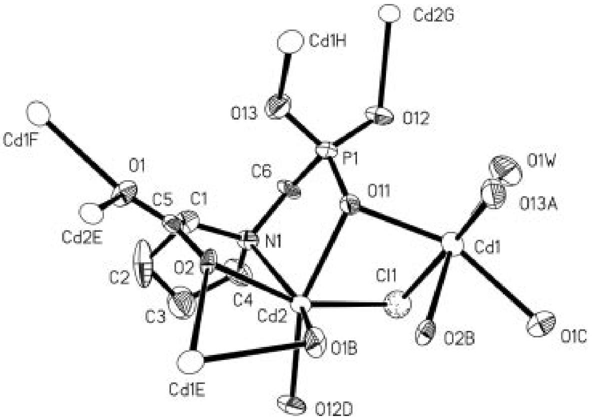


Figure 1. ORTEP representation of the asymmetric unit of complex **1**; thermal ellipsoids are drawn at 50% probability; symmetry codes for generated atoms: a. $x + 1, y + 1/2, -z + 1$; b. $x + 2, y + 1/2, -z + 1$; c. $x, y + 1, z$; d. $x + 1, y, z$; e. $x + 2, -1/2 + y, -z + 1$; f. $x, y - 1, z$; g. $x - 1, y, z$; h. $1 - x, -1/2 + y, 1 - z$

These two types of Cd^{II} octahedra are condensed by edge-sharing (O11−Cl1 and O2−O1b) to form a 1D zigzag chain along the *b* axis. Two types of four-membered rings are found: one is formed by Cd1−O11−Cd2−Cl1 and the other one is composed of Cd2, O2, Cd1e, and O1b atoms. Such 1D chains are further interconnected by bridging phosphonate tetrahedra to form a <002> 2D layer (Figure 2). There are small cavities formed within the 2D layer, each cavity is formed by three edge-sharing Cd^{II} octahedra from one chain and another Cd^{II} octahedron from a neighboring chain interconnected by two phosphonate tetrahedra. In the Co^{II} complex, the Co octahedra form a dimer by edge-sharing, and these dimers are interconnected into a 1D chain by corner-sharing. The 1D chains are interconnected through isolated dimers by bridging $C-PO_3$ tetrahedra, hence the cavities of the layered Co^{II} compound are much larger than those in the Cd^{II} complex.[11d] Similar to those in the Co^{II} complex, the double layers of complex **1** are held together by weak Van der Waals forces (Figure 3). The interlayer distance is about 10.3 Å, which is much smaller than that of the Co^{II} compound (11.9 Å) reported previously.[11d]

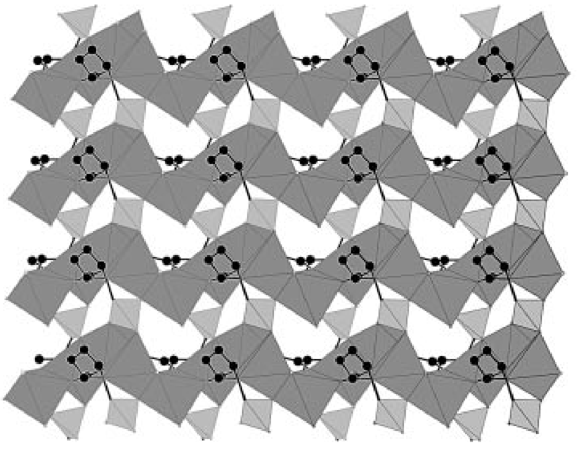


Figure 2. A <002> layer of complex **1**; the Cd^{II} octahedra and $C-PO_3$ tetrahedra are shaded in medium and light gray, respectively, and C atoms are drawn as black circles

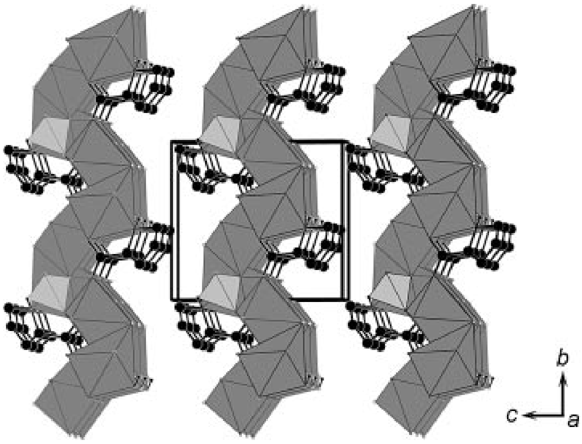


Figure 3. View of structure of complex **1** down the *a* axis; the Cd^{II} octahedra and $C-PO_3$ tetrahedra are shaded in medium and light gray, respectively; the C atoms are drawn as black circles

Crystal Structure of [$Pb_2Cl_2(HL)$] (2)

Complex **2** has a layered structure quite different from that of complex **1**. The asymmetric unit of complex **2** contains one [$Pb_2Cl_2(HL)$] unit (Figure 4). In addition to three regular Pb−O bonds (O1b, O11, O12a) with Pb−O distances ranging from 2.400(14) to 2.572(18) Å, the Pb(1) atom also forms three much weaker Pb−O bonds with the O2c, O13a, and O13c atoms. These weak bonds range from

2.824(14) to 2.851(19) Å (Table 1). Long Pb−O weak bonds have also been reported in other lead(II) phosphonates and lead(II) carboxylates — they are needed to satisfy the bond valences of the Pb^{II} ion.[9b,11e,13] Considering all these bonds, the coordination geometry around Pb(1) can be described as a severely distorted octahedron. Pb(2) is six-coordinated by three phosphonate and one carboxyl oxygen atoms, as well as two chloride anions, and also has a distorted octahedral geometry. The Pb2−O13b distance of 2.811(15) Å is much longer than those of the remaining Pb−O bonds, which range from 2.421(13) to 2.749(14) Å. The Pb−Cl distances are in the range of 2.684(7) to 2.767(5) Å (Table 1). The distortion of the lead polyhedron is due to the presence of the lone pair electrons of the lead(II) ion.

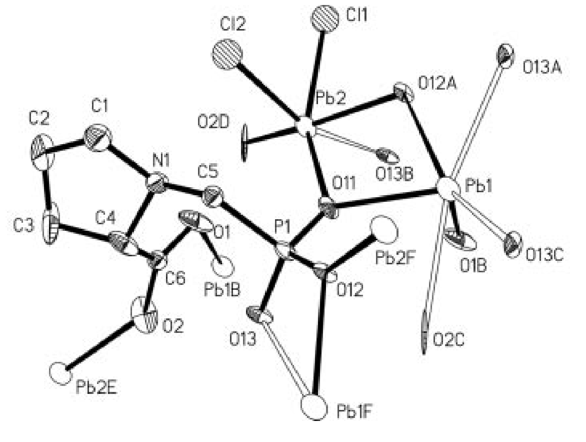


Figure 4. ORTEP representation of the asymmetric unit of complex **2**; thermal ellipsoids are drawn at 50% probability; the longer Pb−O contacts are represented by the open line; symmetry codes for generated atoms: a. *x*, −*y* + 1/2, *z* − 1/2; b. *x* + 1, −*y* + 1, −*z*; c. *x* + 1, *y* − 1/2, −*z* + 1/2; d. *x*, −*y* + 3/2, *z* − 1/2; e. *x*, 3/2 − *y*, 1/2 + *z*; f. *x*, 1/2 − *y*, 1/2 + *z*

Table 1. Selected bond lengths (Å) for complexes **1**, **2**, and **3**

Complex **1**[a]			
Cd(1)−O(13)#1	2.181(10)	Cd(1)−O(1 W)	2.294(10)
Cd(1)−O(11)	2.299(10)	Cd(1)−O(2)#2	2.440(7)
Cd(1)−O(1)#3	2.447(10)	Cd(1)−Cl(1)	2.527(3)
Cd(1)−Cd(2)	3.4148(12)	Cd(2)−O(12)#4	2.205(8)
Cd(2)−O(1)#2	2.336(8)	Cd(2)−O(11)	2.371(7)
Cd(2)−O(2)	2.372(9)	Cd(2)−N(1)	2.374(11)
Cd(2)−Cl(1)	2.665(3)		
Complex **2**[b]			
Pb(1)−O(11)	2.400(14)	Pb(1)−O(12)#1	2.482(13)
Pb(1)−O(1)#2	2.572(18)	Pb(1)−O(13)#1	2.824(14)
Pb(1)−O(13)#3	2.842(13)	Pb(1)−O(2)#3	2.851(19)
Pb(2)−O(12)#1	2.421(13)	Pb(2)−Cl(2)	2.684(7)
Pb(2)−O(2)#4	2.747(16)	Pb(2)−O(11)	2.749(14)
Pb(2)−Cl(1)	2.767(5)	Pb(2)−O(13)#2	2.811(15)
Complex **3**[c]			
Zn(1)−O(11)#1	1.966(8)	Zn(1)−O(22)#1	1.982(7)
Zn(1)−O(3)	2.061(8)	Zn(1)−O(23)	2.125(7)
Zn(1)−N(2)	2.138(9)	Zn(2)−O(23)#2	2.115(7)
Zn(2)−O(23)	2.115(7)	Zn(2)−O(23)#1	2.115(7)
Zn(2)−O(13)	2.122(7)	Zn(2)−O(13)#2	2.122(7)
Zn(2)−O(13)#1	2.122(7)	Zn(3)−O(12)#1	1.955(7)
Zn(3)−O(21)	1.985(8)	Zn(3)−O(2)	2.033(8)
Zn(3)−O(13)	2.135(7)	Zn(3)−N(1)	2.165(9)
Zn(4)−O(1 W)#3	2.089(13)	Zn(4)−O(1 W)#4	2.089(13)
Zn(4)−O(1 W)	2.089(13)	Zn(4)−O(2 W)#3	2.110(12)
Zn(4)−O(2 W)	2.110(12)	Zn(4)−O(2 W)#4	2.110(12)
Zn(5)−O(3 W)#1	2.093(10)	Zn(5)−O(3 W)	2.093(10)
Zn(5)−O(3 W)#2	2.093(10)	Zn(5)−O(4 W)#2	2.099(11)
Zn(5)−O(4 W)	2.099(11)	Zn(5)−O(4 W)#1	2.099(11)
Hydrogen bonds:			
O(1)···O(3w)#5	2.650(13)	O(4)···O(2w)	2.817(15)
O(4)···O(8w)#6	2.792(15)	O(2w)···O(5w)#7	2.691(17)
O(3w)···O(4w)#1	2.819(15)	O(4w)···O(6w)#8	2.839(16)
O(5w)···O(7w)#9	2.785(15)	O(6w)···O(7w)#9	2.716(14)
O(6w)···O(7w)#2	2.824(15)	O(7w)···O(8w)	2.780(18)
O(9w)···O(10w)	2.830(30)		

[a] Symmetry transformations used to generate equivalent atoms: For **1**: #1: − *x* + 1, *y* + 1/2, −*z* + 1; #2: − *x* + 2, *y* + 1/2, −*z* + 1; #3: *x*, *y* + 1, *z*; #4: *x* + 1, *y*, *z*. [b] For **2**: #1: *x*, −*y* + 1/2, *z* − 1/2; #2: − *x* + 1, −*y* + 1, −*z*; #3: − *x* + 1, *y* − 1/2, −*z* + 1/2; #4: *x*, −*y* + 3/2, *z* − 1/2. [c] For **3**: #1: *y* − 1, *z*, *x* + 1; #2: *z* − 1, *x* + 1, *y*; #3: *y* − 1/2, −*z* + 3/2, −*x*+1; #4: − *z* + 1, *x* + 1/2, −*y* + 3/2; #5: − *z* + 1, *x* + 3/2, −*y* + 3/2; #6: −*x* + 1/2, −*y* + 2, *z* − 1/2; #7: −*x*, *y* − 1/2, −*z* + 3/2; #8: −*x* − 1/2, −*y* + 2, *z* − 1/2; #9 *x* − 1/2, −*y* + 5/2, −*z* + 2.

The phosphonate-carboxylate ligand adopts a coordination mode that is different from those in its Co^{II} and Cd^{II} complexes. The amine group is protonated, hence it remains non-coordinated. Two phosphonate oxygen atoms (O11 and O12) are bidentate, whereas the third one (O13) forms a weak Pb−O bond. Each carboxylate oxygen atom is bridged to one Pb^{II} ion, however O(2) also forms a weak Pb−O bond with the Pb(1) center.

The interconnection of the above two types of Pb^{II} ions via bridging carboxylate and phosphonate groups results in a <200> layer (Figure 5), and such layers are packed together by weak Van der Waals forces (Figure 6). The d-spacing is about 12.0 Å, very close to that of complex **1**.

Crystal Structure of $[Zn_7L_6][Zn(H_2O)_6]_2\cdot 16H_2O$ (3)

The structure of complex **3** is similar to that of the Zn^{II} complex with $CH_3N(CH_2CO_2H)CH_2PO_3H_2$ that we reported recently,[11] although the symmetry of the structure is lower due to the presence of the pyrrolidine ring in the ligand. The compound contains a novel heptanuclear zinc(II) phosphonate anion, two hexahydrated zinc(II) cations and 16 lattice water molecules. As shown in Figure 7, Zn1 is five-coordinated by a chelate ligand (N2, O3, O23), and two phosphonate oxygen atoms (O11a and O22a) from neighboring [ZnL] units in a distorted trigonal bipyramidal geometry. The Zn1−N2 and Zn1−O3 distances are 2.138(9) and 2.061(8) Å, respectively. The Zn1−O (phosphonate) distances are in the range of 1.966(8) to 2.125(7) Å. Zn3 is also five-coordinated by a chelate ligand (N1, O2, O13), and two phosphonate oxygen atoms (O21 and O12a) from two neighboring [ZnL] units in a distorted trigonal bipyramidal geometry. The Zn3−N1 and Zn3−O2 bond

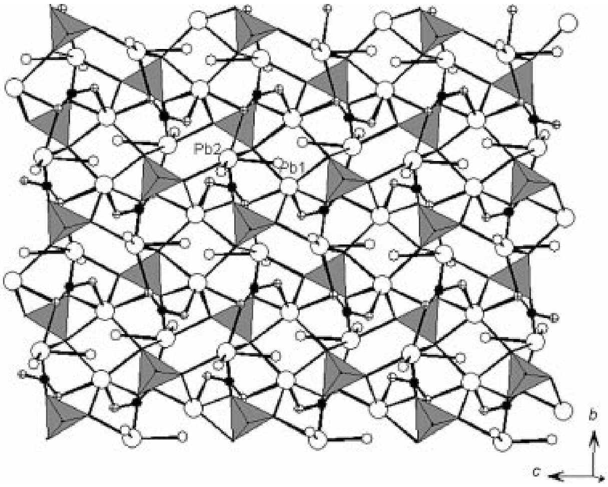


Figure 5. A <200> layer of lead(II) phosphonocarboxylate in complex **2**; the $C-PO_3$ tetrahedra are shaded in gray, Pb, Cl, C, and O atoms are drawn as open (large), open (small), black, and crossed circles, respectively; the pyrrolidine ring of the ligand has been omitted for clarity

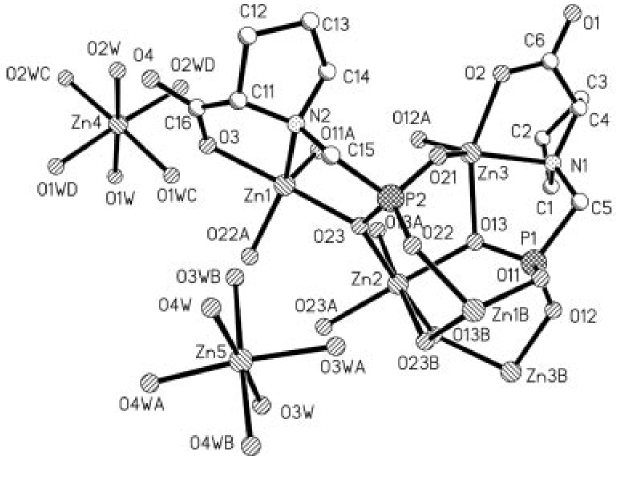


Figure 7. The asymmetric unit of complex **3** with atomic labeling; the lattice water molecules have been omitted for clarity; symmetry codes for generated atoms: a. $y - 1, z, x + 1$; b. $z - 1, x + 1, y$; c. $y - 1/2, -z + 3/2, -x+1$; d. $z + 1, x + 1/2, -y + 3/2$

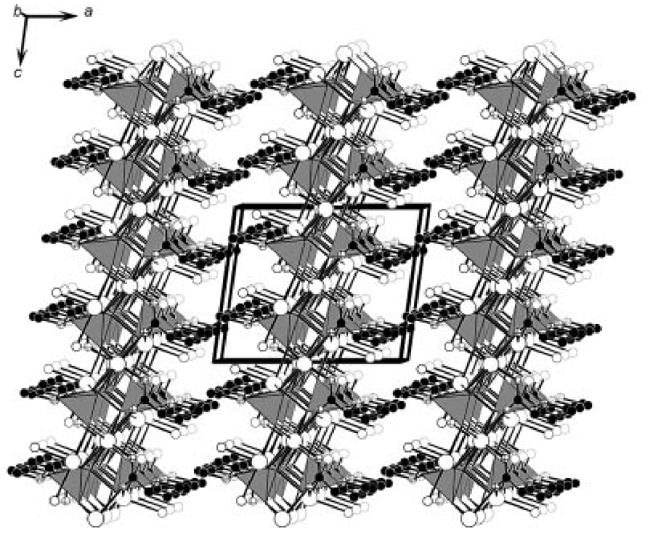


Figure 6. View of the structure of complex **2** down the *b* axis; the $C-PO_3$ tetrahedra are shaded in gray, Pb, Cl, N, C, and O atoms are drawn as open (large), open (small), octand, black, and crossed circles, respectively

lengths are 2.165(9) and 2.033(8) Å, respectively. The Zn3−O (phosphonate) distances range from 1.955(7) to 2.135(7) Å (Table 1); these distances are similar to those reported for other zinc(II) amino-carboxylate-phosphonates.[9,11]

The Zn2 atom lies on a position with threefold symmetry; it is octahedrally coordinated by six phosphonate oxygen atoms from three [Zn(1)(L)] and three [Zn(3)(L)] units. The Zn−O distances of 2.115(7) Å and 2.122(7) Å are close to those for the Zn1 and Zn3 atoms. The *N*-(phosphonomethyl)proline acts as a hexadentate ligand. It chelates to a Zn1 or a Zn3 atom and bridges three neighboring Zn^{II} ions. The O23 of $P(2)O_3C$ group bridges one Zn1 and one Zn2 atom, and O13 of the $P(1)O_3C$ group connects one Zn3 and one Zn2 atom. Such a coordination mode has been found in Co^{II} and Zn^{II} complexes with *N*-(phosphonomethyl)iminodiacetic acid.[9] Two carboxylate oxygen atoms (O1 and O4) remain non-coordinated. Since all C−O and P−O bonds have very short distances, we would expect both phosphonate and carboxylate groups of the ligand to be completely deprotonated. Each ligand carries three negative charges, thus the heptanuclear anion has a 4− charge.

The seven Zn^{II} cations in the anion form an unusual centered octahedron similar to the Zn^{II} complex with $CH_3N(CH_2CO_2H)CH_2PO_3H_2$. The octahedron is created by six five-coordinate zinc(II) cations (Zn1 and Zn3) with the six-coordinate Zn2 atom as the central atom. The edge Zn···Zn contacts are in the range of 4.515(2) to 5.758(2) Å, and the distances from the central Zn to the octahedral apexes range from 3.610(2) to 3.665(2) Å. It is interesting to compare our heptanuclear zinc(II) phosphonate anions with the hexanuclear zinc(II) cages containing phosphonate and pyrazole reported by the Chandrasekhar group, in which the six zinc atoms are arranged in a chair-like conformation.[14]

The four negative charges of the cluster are balanced by two hexa-hydrated zinc(II) cations. These zinc(II) ions (Zn4 and Zn5) are located at positions with a threefold symmetry. The Zn4−O distances are 2.089(13) and 2.110(12) Å, respectively, and the Zn5−O distances are 2.093(10) and 2.099(11) Å, respectively. Its coordination geometry is a slightly distorted octahedron.

In a similar fashion to the Zn^{II} complex with $CH_3N(CH_2CO_2H)CH_2PO_3H_2$,[11] packing of the cluster anions create large cavities occupied by the hexahydrated zinc(II) cations as well as lattice water molecules (Figure 8). The diameter of the pore is estimated to be around 8.0 Å. The polynuclear cluster anions are located at the centers of the cell edges and the cell body center. A number of hydrogen bonds are formed among the non-coordinated carboxylate oxygen atoms, and coordinated and lattice water molecules (Table 1).

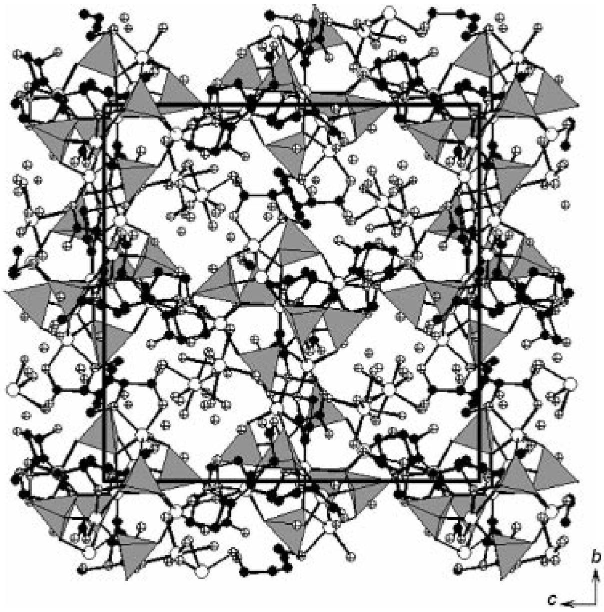


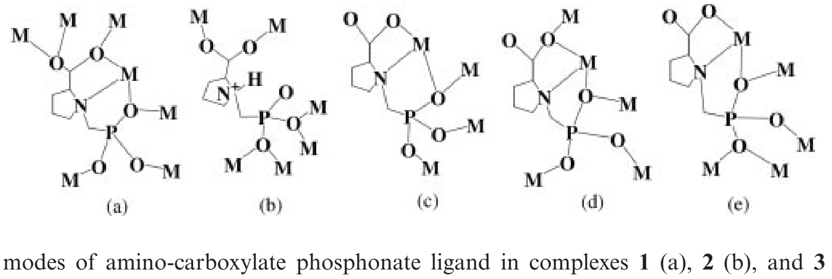
Figure 8. View of structure of complex **3** down the *a* axis; the C−PO_3 tetrahedra are shaded in gray, the Zn, N, C, and O atoms are drawn as open, octand, black, and crossed circles, respectively

Thermogravimetric Analysis

1The TGA diagram for complex **1** shows two main steps of weight loss. The first step, which corresponds to the loss of one aqua ligand and the chloride anion, starts at about 150 °C and ends at about 350 °C. The weight loss of 9.9% is slightly less than the calculated weight loss of 11.2%. The second step corresponds to the decomposition of the organic groups that starts at about 441 °C and is complete at 926 °C. The final products are $Cd_3(PO_4)_2$ and CdO in a 1:1 molar ratio. The total weight loss of 31.4% is close to the calculated weight loss of 32.3%. The TGA curves of the Pb^{II} complex show only one main weight loss. The compound is stable up to 240 °C. It then starts to decompose from 240 °C and continues up to 800 °C; this process corresponds to the loss of the chloride anions and the burning of the organic groups of the carboxylate-phosphonate ligand. The total weight loss is 32.4%, which is slightly less than the calculated one (35.5%) if the final products are assumed to be PbO. However, the total weight loss is much larger than the calculated value (25.3%) if the final products are $Pb_2P_2O_7$ and PbO in a 1:2 molar ratio. Thus we think our final products are mainly PbO mixed with a small amount of $Pb_2P_2O_7$. The TGA diagram for complex **3** shows two main steps of weight loss. The first step, which corresponds to the loss of 16 lattice water molecules and 12 coordinated water molecules, starts at about 60 °C and is complete at about 250 °C. The weight loss of 28.9% is slightly less than the calculated value (29.6%). The second step corresponds to the decomposition of organic groups starting at about 360 °C and continues up to 800 °C. The total weight loss of 33.7% is less than the calculated weight loss of 50.3% if the final products are assumed to be $Zn_2P_2O_7$ and ZnO; hence, the decomposition process is not complete at 800 °C. The use of N_2 gas to provide an inert atmosphere may be another reason for the incomplete decomposition.

Conclusion

Hydrothermal reactions of *N*-(phosphonomethyl)proline (H_3L) with divalent metal ions afforded four different complexes, $[Cd_2LCl(H_2O)]$ (**1**), $[Pb_2Cl_2(HL)]$ (**2**), a microporous compound, $[Zn_7L_6][Zn(H_2O)_6]_2\cdot 16H_2O$ (**3**), and the previously reported layered $Co_3L_2\cdot 5H_2O$.[11d] *N*-(phosphonomethyl)proline (H_3L) exists as a zwitterion where one proton of a phosphonate group has been transferred to the amine group. The molecular units of *N*-(phosphonomethyl)proline (H_3L) are further interconnected by O−H···O and N−H···O hydrogen bonds into a 2D layer.[15] Upon partial or complete replacement of protons by divalent metal ions, three types of layered structures and a microporous structure are formed. As shown in Scheme 1, the carboxylate-phosphonate ligand adopts five different coordination modes in these four complexes. In the Cd^{II} complex, the phosphonate-carboxylate ligand chelates a Cd^{II} ion and bridges six other metal ions, both carboxylate oxygen atoms are bidentate, and one of the phosphonate oxygen atoms is also bidentate. The other two phosphonate oxygen atoms are unidentate (Scheme 1, a). In the lead(II) complex, the amine group of the ligand is protonated, hence it is not coordinated to the Pb^{II} ion. Without consideration of those weak Pb−O contacts, its coordination mode can be described as a hexadentate bridging mode, where two phosphonate O atoms behave as μ^2 metal linkers and the third phosphonate O remains non-coordinated (Scheme 1, b). In the zinc(II) cluster compound, the ligand chelates in a tridentate manner with a Zn^{II} ion and bridges three other Zn^{II} ions; only one phosphonate O is a μ^2 metal linker (Scheme 1, c). In the layered cobalt(II) complex,



Scheme 1. Coordination modes of amino-carboxylate phosphonate ligand in complexes **1** (a), **2** (b), and **3** (c) as well as in its Co^{II} complex (d and e)

Co_3L_2·$5H_2O$, two types of chelating and bridging modes are found, the ligand in one CoL unit chelates with a Co^{II} ion in a tridentate fashion (one N, one carboxyl O and one phosphonate O) and bridges other four metal ions; one carboxyl O and one phosphonate O act as bidentate metal linkers (Scheme 1, d). In another CoL unit, the ligand also chelates a Co^{II} ion and bridges four other metal ions. However, two phosphonate O atoms behave as μ^2 metal linkers (Scheme 1, e).[11d] Transition metal ions such as Co^{II}, Zn^{II}, and Cd^{II} ions have a greater affinity for the nitrogen atom than the Pb^{II} ion, thus the ligand can form a chelate ring with a Co^{II} (or Cd^{II} or Zn^{II}) ion through the amine nitrogen, a phosphonate, and a carboxylate oxygen atom, whereas in the lead(II) complex the amine group remains protonated. The lead(II) complexes also have a coordination geometry different from the transition metal complexes due to the presence of the lone pair of electrons.

We are especially interested in the cluster unit and microporous structure in the zinc(II) complex. This complex has a structure similar to that of zinc(II) complexes with *N*-(phosphonomethyl)-*N*-methylglycine previously reported by us.[11c] Thus, we would expect that each $Zn_6(Zn)$ cluster unit and the microporous structure built from the packing of the cluster units should be relatively stable. Currently, we are investigating the possibility of isolating a similar cluster unit with other magnetic transition metal ions, such as Mn^{II}, Cu^{II}, Ni^{II}, etc.; such materials may be used as single molecular magnets. Due to the number of lattice water molecules and hexahydrated zinc(II) cations located in the micropore of the structure, it would be interesting to replace the hydrated zinc(II) cations with alkaline earth cations or diamines such as ethylenediamine, methylenediamine etc. Such research efforts are in progress and the results will be published later.

Experimental Section

Materials and Methods: All of the starting materials were of reagent grade and were used without further purification. *N*-(Phosphonomethyl)proline (H_3L) was synthesized by a Mannich-type reaction according to the procedures previously described.[11d,15] Elemental analyses were performed on a German Elementary Vario EL III instrument. The FT-IR spectra were recorded on a Nicolet Magna 750 FT-IR spectrometer on KBr pellets in the range of 4000−400 cm^{-1}. Thermogravimetric analyses were carried out with a TGA/SBTA851 unit, at a heating rate of 15 °C/ min under a nitrogen atmosphere.

Synthesis of [$Cd_2LCl(H_2O)$] (1): $CdCl_2$·2·$5H_2O$ (0.4 mmol, 0.091 g), H_3L (0.2 mmol, 0.042 g) and 25% ethanol aqueous solution (13 cm^3) were mixed and the pH was adjusted to between 4 and 5 by addition of Bu_4NOH. The resultant solution was heated at 170 °C in a Teflon-lined stainless steel autoclave for four days. Colorless plate-shaped crystals of **1** were collected in about 86% yield (83 mg). $C_6H_{11}Cd_2ClNO_6P$ (484.38): calcd. C 14.86, H 2.29, N 2.89; found C 15.58, H 1.89, N 2.94%. IR data (KBr, cm^{-1}): 3502−2899 (br), 1535 (s), 1417 (m), 1115 (s), 1051 (s), 964 (s), 559 (s).

Synthesis of [$Pb_2Cl_2(HL)$] (2): A mixture of $PbCl_2$ (0.4 mmol, 0.111 g), H_3L (0.2 mmol, 0.042 g), and H_2O (10 cm^3) with the pH value adjusted to between 4 and 5 by addition of Bu_4NOH, was heated at 160 °C in a Teflon-lined stainless steel autoclave for two days. Colorless plate crystals were recovered in about 26% yield (36 mg). $C_6H_{10}Cl_2NO_5PPb_2$ (692.40): calcd. C 10.41, H 1.46, N 2.02; found C 10.29, H 1.10, N 1.85%. IR data (KBr, cm^{-1}): 3600−2825 (br), 1566 (s), 1400 (m), 1340 (m), 1292 (w), 1030 (s), 964 (s), 764 (m), 569(m), 478 (m) cm^{-1}.

Synthesis of [Zn_7L_6][$Zn(H_2O)_6$]$_2$·$16H_2O$ (3): Complex **3** was synthesized by a method similar to that of complex **2**. Yield: 80% (155 mg) based on L. $C_{36}H_{110}N_6O_{58}P_6Zn_9$ (2329.45): calcd. C 18.56, H 4.76, N 3.61; found C 18.65, H 4.64, N 3.57%. IR (KBr, cm^{-1}): 3600−2864 (br), 1605 (s), 1400 (m), 1333 (w), 1234 (w), 1111 (s), 1078 (s), 989 (s), 931 (m), 580 (m).

X-ray Crystallographic Study: Data collections were performed on a Siemens Smart CCD diffractometer, using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Intensity data were collected by using narrow frame method with 0.3° per frame in at 293 K. A total of 1389, 2179 and 4713 independent reflections, respectively, for **1**, **2**, and **3**, were collected among which 1361 (for **1**), 1520 (for **2**), and 3341 (for **3**) with $I > 2.0\sigma(I)$ were considered observed. For data of complexes **1** and **3**, absorption corrections

Table 2. Summary of crystal data and details of intensity collection and refinement

	1	2	3
Empirical formula	$C_6H_{11}Cd_2ClNO_6P$	$C_6H_{10}Cl_2NO_5PPb_2$	$C_{36}H_{110}N_6O_{58}P_6Zn_9$
Formula mass	484.38	692.40	2329.45
Space group	$P2_1$	$P2_1/c$	$P2_13$
a, Å	6.5038(9)	11.9851(8)	20.203(2)
b, Å	8.9677(12)	10.4696(4)	20.203(2)
c, Å	10.3081(14)	10.0066(6)	20.203(2)
β, °	90	98.039(3)	90
V, Å^3	577.01(14)	1243.28(12)	8245.6(16)
Z	2	4	4
D_{calcd}, g·cm^{-3}	2.788	3.699	1.876
T, K	293(2)	293(2)	293(2)
μ, mm^{-1}	4.069	27.612	2.798
GOF	1.121	1.076	1.126
$R1, wR2$ [$I > 2\sigma(I)$][a]	0.0427, 0.1225	0.0597, 0.0999	0.0651, 0.1096
$R1, wR2$ (all data)	0.0435, 0.1239	0.1050, 0.1198	0.1159, 0.1336

[a] $R1 = \Sigma(\Sigma F_o - F_c)/\Sigma F_o$; $wR2 = [\Sigma w(F_o - F_c)^2/\Sigma w F_o{}^2]^{1/2}$.

were performed by using the SADABS program.[12] Absorption corrections based on the Ψ scan technique were applied to the data set of complex **2**. From E-value statistics and systematic absence, the space group is either $P2_1$ or $P2_1/m$ for **1**, $P2_1/c$ for **2**, and $P213$ for **3**. When $P2_1/m$ was used for the refinements of complex **1**, the structure was severely distorted, even for the cadmium atom, thus we refined the structure in the non-centrosymmetric $P2_1$ and the results were satisfactory. All three structures were solved by direct methods and refined by full-matrix least-square fitting on F^2 by SHEXLS.[16] All of the non-hydrogen atoms, except C(1), C(5), and C(6) atoms in **2**, were refined anisotropically. All hydrogen atoms were located at geometrically calculated positions and refined with isotropic thermal parameters. The hydrogen atoms for the aqua ligands and lattice water molecules in all three complexes were not refined. A summary of the crystallographic data for these three complexes is listed in Table 2. Selected bond lengths for complexes **1**, **2**, and **3** are given in Table 1.

CCDC-212383 (**1**), -212384 (**2**), and -212385 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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