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# The role of deprotonation of the ligand on the structures of metal phosphonates: synthesis, characterization and crystal structures of two new metal diphosphonates with a 1D double chain and a 2D layer structure

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Reactions of *N*-methyl-iminobis(methylenephosphonic acid), $CH_3N(CH_2PO_3H_2)_2$, ($H_4L$) with divalent metal nitrates in aqueous solution afforded two new metal diphosphonates with different structures. $Zn(H_2L)(H_2O)$ (**1**) features a 1D double chain built from $ZnO_4$ tetrahedra cross-linked by bridging phosphonate groups and ligands. Each zinc cation is tetrahedrally coordinated by three phosphonate oxygen atoms from three ligands and an aqua ligand. These double chains are interconnected into a <111> layer through N–H ··· O and O–H ··· O hydrogen bonds. In $Cd(H_3L)_2{\cdot}2H_2O$ (**2**) the Cd(II) ion is octahedrally coordinated by six phosphonate oxygen atoms from four ligands, two of them in a bidentate and two in a unidentate fashion. Each $CdO_6$ octahedron is further linked to four neighboring $CdO_6$ octahedra through four bridging phosphonate groups, resulting in a two-dimensional metal phosphonate (002) layer. These layers are held together by strong hydrogen bonds between uncoordinated phosphonate oxygen atoms. The effect of the extent of deprotonation of phosphonic acids on the type of complex formed is discussed.

## Introduction

Metal phosphonates have potential applications in the areas of catalysis, ion exchange, proton conductivity, intercalation chemistry, photochemistry, and materials chemistry.[1] Most of them are layered species in which the metal octahedra are bridged by phosphonic acid tetrahedra to form two-dimensional layers that are separated by the hydrophobic regions of the organic moieties.[1] Studies have shown that a variety of metal ions, including group 4 and 14 elements and divalent and trivalent ions, can form this type of layered compound.[1–3] One challenge for studying such materials is that they usually exhibit poor crystallinity which makes their structural analysis a difficult task. Divalent metal phosphonates usually have a larger solubility in various solvents than do zirconium(IV) or titanium(IV) phosphonates and they are more likely to be obtained in the form of single crystals, thus allowing more systematic structural studies to be carried out. Another method used to increase their solubility is to put additional functional groups on the phosphonic acids, such as an aza-crown ether, a carboxylate group or an amine group. Research on metal complexes with crown ether substituted phosphonic acids attached have many unusual structural features.[1,4,5d] Studies on metal complexes with phosphonic acids containing functional carboxylate groups, such as *N*-(phosphonomethyl)-iminodiacetic acid $H_2O_3PCH_2N(CH_2CO_2H)_2$ ($H_4$PMIDA), have shown that the extent of deprotonation of the ligand has a strong effect on the structures of the metal phosphonates that form. However, other factors also prove to be important. For example, a mixed phosphate–phosphonate layered zirconium compound was made by reaction of a zirconium salt with a mixture of phosphoric acid and $H_4$PMIDA solutions.[5] When the above reactions were carried out in the absence of phosphoric acid, a linear chain compound was isolated.[6] In both cases the iminodiacetic moieties are only involved in hydrogen bonding and are present as pendant groups between the layers or chains. The iminodiacetic acid groups are too large to fit on the layer requiring a spacer phosphate group to allow layers to form. In the absence of the spacer group, the linear compound spaces the pendant groups without crowding. In both cases, the iminonitrogen is protonated. Under less acidic conditions, we isolated two novel complexes, $[Co_2(PMIDA)(H_2O)_5]{\cdot}H_2O$ whose structure contains double layers of Co(II) carboxylate interconnected by layers of Co(II) phosphonate, and a zinc carboxylate-phosphonate hybrid layered complex, $Zn_2(PMIDA)(CH_3CO_2H)]{\cdot}2H_2O$.[7] In these compounds the imino-nitrogen was not protonated and was able to complex the metals. With the complete deprotonation by adding potassium hydroxide, Wood and his co-workers obtained the canted anti-ferromagnet $[K_2Co(PMIDA)]_6{\cdot}xH_2O$, whose crystal structure features a hexameric ring in the chair conformation.[8] Diphosphonic acids in which the two phosphonate groups are attached to diamine groups ($HO_3PCH_2HNRNHCH_2PO_3H$), can also form metal phosphonates with a variety of structures, such as mononuclear chelate complexes,[9] complexes with a 1D chain structure or 3D network structure based on dimeric units[10] and pillared layered compounds.[4,11] Only a few structural studies have been reported on metal complexes of iminodiphosphonic acids, $RN(CH_2PO_3H_2)_2$.[12–14] The crystal structure of a copper complex with *N*-ethyliminobis(methylphosphonate), was reported by Makaranets *et al.*[12] Recently the *N*-methyl-iminobis(methylenephosphonic acid) ($H_4L$) was structurally determined and its coordination behavior with metal ions has been studied in aqueous solution by potentiometric titration and NMR measurements. Its zinc complex was proposed to be a layered structure.[13] $Mn(H_3L)_2{\cdot}2H_2O$ with a layer structure, and $Zn_3(HL)_2$ whose structure features a 3D network, have been reported recently in our laboratory.[14] Subsequently systematic structural studies afforded a 1 : 1(M : L) zinc complex, $Zn(H_2L)(H_2O)$ (complex **1**), whose structure features a double chain, and $Cd(H_3L)_2{\cdot}2H_2O$ (complex **2**), which is isostructural with the Mn(II) complex we previously reported.[14]

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Herein we report their synthesis, characterization and crystal structures.

## Experimental

### Materials and methods

Deionized water used in all experiments was purified to a resistivity of 17.6 MΩ cm with a Barnstead Nanopure II System. All other chemicals were of reagent grade quality obtained from commercial sources and were used without further purification. Solution NMR was recorded on a Varian Unity Plus 300 spectrometer. The $^{31}$P solid state MAS NMR spectra were obtained on a modified Bruker MSL-300 unit operating at 121.5 MHz, spinning the 7.5 mm zirconium rotors at 2–5 kHz in the NMR probe and using a single pulse sequence (pulse delay = 20 s, 80 transients). $H_3PO_4$ (EM Science, 85%) was used as an external standard for both solution and solid state $^{31}$P NMR measurements. Elemental analysis data were obtained from Desert Analytics, Tucson, AZ. Thermogravimetric analysis was carried out with a TA 4000 unit, at a heating rate of 10 °C min$^{-1}$ under an oxygen atmosphere.

### Synthesis of *N*-methyl-iminobis(methylenephosphonic acid) ($H_4L$)

The ligand was prepared by a Mannich type reaction according to the procedures previously described.[14]

### Preparation of $Zn(H_2L)(H_2O)$ (1) and $Cd(H_3L)_2{\cdot}2H_2O$ (2)

The two metal phosphonates were synthesized by a similar method. Cadmium nitrate (Aldrich) (1.0 mmol) and the *N*-methyl-iminobis(methylenephosphonic acid) (2.0 mmol) were mixed and dissolved in 5.0 ml of water. Ethanol was allowed to diffuse into the resultant solution slowly. After ten days, colorless crystals of complex **2** were recovered in 45.7% yield. The zinc(II) complex was also synthesized by reaction of zinc nitrate (Aldrich) with the diphosphonic acid in a molar ratio of 1 : 2, colorless crystals of complex **1** were obtained in *ca.* 32.4% yield. Elemental analysis for complex **1**: C, 11.67; H, 3.41; N, 4.87; P, 20.79. Calc. C, 11.99; H, 3.69; N, 4.66; P, 20.62%. Elemental analysis for complex **2**: C, 12.20; H, 3.95; N, 4.84; P, 21.37. Calc. C, 12.33; H, 4.14; N, 4.79; P, 21.19%. The solid state $^{31}$P NMR spectrum of complex **1** shows two peaks at 11.7 and 14.9 ppm respectively, and that of complex **2** has four peaks at 9.4, 10.3, 11.7 and 15.0 ppm, respectively.

### Crystallography

Single crystals of complexes **1** and **2** were mounted on a Bruker Smart CCD using Mo-Kα radiation ($\lambda$ = 0.71069 Å), and a graphite monochromator at 110(2) K. The cell constants were indexed from reflections obtained from 60 frames collected with 10 seconds exposure per frame. A hemisphere of data (1271 frames at 5 cm detector distances) was collected by the narrow-frame method with scan widths of 0.30° in $\omega$ and exposure times of 20 and 30 seconds per frame for complexes **1** and **2**, respectively. The first 50 frames were recollected in the end of data collection to assess the stability of the crystal, and it was found that the decay in intensity was less than 1%. The data were corrected for Lorentz factor, polarization, air absorption and absorption due to variations in the path length through the detector faceplate and extinction. An absorption correction based on SADABS (for the data set of complex **1**) and the $\psi$ scan method (for the data set of complex **2**) were also applied.[15]

The space group was uniquely determined to be $P\bar{1}$ (no. 2) for both complexes. Both structures were solved using direct methods (SHELXTL) and refined by least-square methods with atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms.[20] All hydrogen atoms, except those for water molecules in complex **1**, were generated geometrically, assigned fixed isotropic thermal parameters and included in the structure factor calculations. The hydrogen atoms for the water molecules in complex **1** were located from difference Fourier maps, and were refined isotropically. However, in the case of complex **2**, the water hydrogens could not be similarly located even on truncating the data to $2\theta = 30°$, probably because of the presence of the heavier Cd atoms but the P–OH protons were located. Some of the data collection and refinement parameters are summarized in Table 1. Important bond lengths and angles for the two complexes are listed in Table 2 and hydrogen bond data in Table 3.

CCDC reference numbers 186596 and 186597.

See http://www.rsc.org/suppdata/dt/b2/b204270n/ for crystallographic data in CIF or other electronic format.

## Results

### Crystal structure of $Zn[(HO_3PCH_2)(O_3PCH_2)NHCH_3]$, $Zn[(H_2L)(H_2O)]$ 1

Another zinc complex with the same ligand, $Zn_3(HL)_2$, which was synthesized by hydrothermal reactions and whose structure features a 3D network, was reported previously in our laboratory.[14] Complex **1** has a very different structure from that of $Zn_3(HL)_2$. The asymmetric structural unit of complex **1** is shown in Fig. 1. The zinc atom is tetrahedrally coordinated by three phosphonate oxygen atoms from three ligands and an aqua ligand, whereas the zinc atom in $Zn_3(HL)_2$ is tetrahedrally coordinated by four phosphonate oxygen atoms from four ligands. The Zn–O distances range from 1.913(2) to 1.969(2) Å (Table 2), which are comparable with those of zinc phosphonates reported previously.[7,14] One phosphonate group of the ligand in complex **1** is in a bidentate bridging coordination mode (P1, O1, O2, O3), the other one adopts the unidentate coordinate mode (P2, O4, O5, O6), thus each ligand is tridentate, bridging with three Zn(II) ions. Each ligand in the hydrothermally synthesized $Zn_3(HL)_2$ complex is hexadentate, and connects with six Zn(II) ions.[14] From the 1 : 1 metal : ligand ratio, each ligand should carry two negative charges. The amino nitrogen and one phosphonate group must be 1H-protonated. By examination of the P–O distances, O6 is the most likely oxygen atom to be protonated because it has the longest P–O bond (Table 2). Furthermore, the amine group has a tetrahedral coordination geometry as deduced from the C–N–C bond angles which average 110.6°. The protonated phosphonate oxygen and the NH group are involved in hydrogen bonding, the O6–H6A ··· O1 and N(1)–H11A ··· O4 distances are 2.469 and 2.696 Å, respectively, and their bond angles are 159.6 [O(6)–H(6a) ··· O(1)] and 151.0° [N(1)–H(11a) ··· O(4)], respectively. The aqua ligand also forms strong hydrogen bonds with phosphonate oxygen atoms (see Table 2).

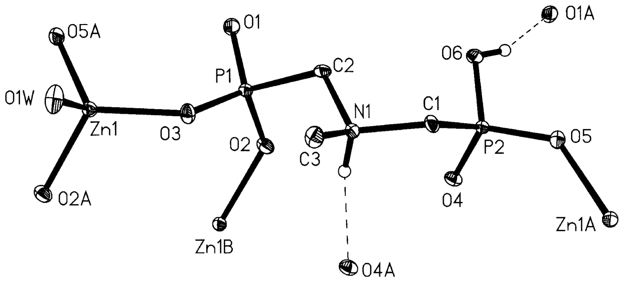


Fig. 1 ORTEP[21] representation of the asymmetry unit of complex **1**. Thermal ellipsoids are drawn at 50% probability. The dashed lines represent hydrogen bonds.

As shown in Fig. 2, each pair of $ZnO_4$ tetrahedra are bridged

**Table 1** Crystal data and structure refinement for complexes **1** and **2**[a]

| Complex | **1** | **2** |
|---|---|---|
| Empirical formula | $C_3H_{11}ZnNO_7P_2$ | $C_6H_{24}CdN_2O_{14}P_4$ |
| $M$ | 300.44 | 584.55 |
| Crystal system | Triclinic | Triclinic |
| Space group | $P\bar{1}$ (no. 2) | $P\bar{1}$ (no. 2) |
| $a$/Å | 7.6001(14) | 9.418(4) |
| $b$/Å | 7.9401(15) | 9.948(4) |
| $c$/Å | 8.5505(16) | 10.574(5) |
| $\alpha$/° | 89.175(3) | 82.408(7) |
| $\beta$/° | 64.549(3) | 73.694(7) |
| $\gamma$/° | 81.432(3) | 89.773(7) |
| $V$/Å$^3$ | 460.00(15) | 941.9(7) |
| $Z$ | 2 | 2 |
| $T$/K | 110(2) | 110(2) |
| $\mu$ (MoK$\alpha$)/mm$^{-1}$ | 3.030 | 1.571 |
| $F$(000) | 304 | 588 |
| Reflections collected | 2773 | 6003 |
| Independent reflections | 2041 ($R_{int}$ = 0.0246) | 4267 ($R_{int}$ = 0.0307) |
| Observed reflections [$I > 2\sigma(I)$] | 1804 | 3909 |
| $R1/wR2$ [$I > 2\sigma(I)$] | 0.0411/0.1119 | 0.0520/0.1351 |
| $R1/wR2$ (all data) | 0.0462/0.1158 | 0.0556/0.1375 |

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

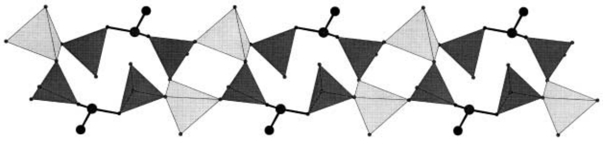


Fig. 2 A 1D double chain along the diagonal direction of the (001) plane. The $ZnO_4$ tetrahedra and C–$PO_3$ tetrahedra are shaded in light and dark gray, respectively.

by a pair of phosphonate groups to form a dimeric unit. Neighboring dimeric units are interconnected by bridging ligands, resulting in a 1D double chain along the diagonal axis of the (001) plane (Fig. 2). Two types of voids are created that alternate along the double chain. The small void is formed by an 8-membered ring (two $ZnO_4$ tetrahedra corner sharing with two phosphonate tetrahedra), and the larger one is created by a 16-membered ring composed of two $ZnO_4$ tetrahedra bridged by two ligands). These double chains are further interconnected into a <111> 2D layer by strong hydrogen bonds between uncoordinated phosphonate oxygen atoms (O6–H ··· O1, 2.469 Å) (Fig. 3). The methyl groups are orientated to the interchain spaces. These layers are held together *via* van der Waals forces.

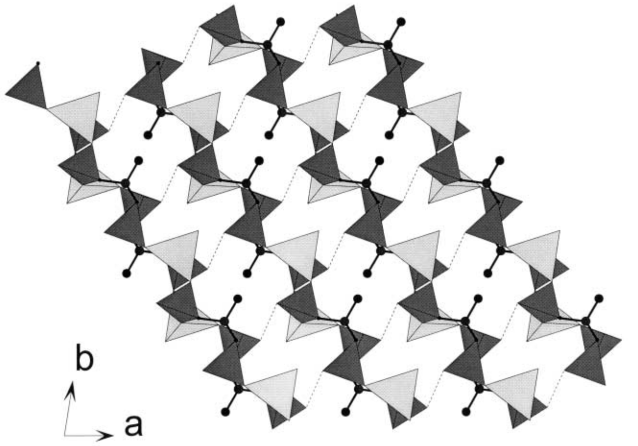


Fig. 3 A <111> hydrogen bonded 2D metal phosphonate layer of complex **1**. The $ZnO_4$ tetrahedra and C–$PO_3$ tetrahedra are shaded in light and dark gray, respectively.

### Crystal structure of $Cd[(HO_3PCH_2)_2NHCH_3]_2\cdot 2H_2O$, $Cd(H_3L)_2\cdot 2H_2O$ 2

The structure of complex **2** is isostructural with that of the Mn(II) complex we reported previously.[14] An ORTEP representation of the asymmetric unit of complex **2** is shown in Fig. 4. Both Cd1 and Cd2 atoms lie on centers of symmetry and are octahedrally coordinated by four oxygen atoms from two chelating ligands and two phosphonate oxygen atoms from two neighboring $Cd(H_3L)_2$ units. Each ligand acts as a tridentate ligand, chelating with one Cd(II) ion and bridging with another Cd(II), thus forming two different kinds of 8-membered chelate rings. One such ring is composed of Cd1, O1, P1, C1, N1, C2, P2, O5 atoms, and the other one contains Cd2, O8, P3, C5, N2, C4, P4, O10 atoms (Fig. 4). The Cd–O distances range from 2.235(3) Å to 2.292(4) Å, which are slightly longer than those in the Mn(II) complex.[14] The nitrogen atom and both phosphonate groups of the ligand are 1H-protonated, thus each ligand carries a negative charge of one, and two ligands are needed to balance the two positive charges of a Cd(II) ion. The lattice water molecules (O1W, O2W) are not coordinated to the Cd(II) ions, but form strong hydrogen bonds with phosphonate oxygen atoms (O9 ··· O1W, 2.727, O1W–O12, 2.969, O2W ··· O2, 2.688 and O2W ··· O6, 2.876 Å) or with neighboring water molecules (O1W ··· O1W, 2.633 and O2W ··· O2W, 2.743 Å) (Table 3). The POH oxygens of each phosphonate group are O3, O6, O9, O12. In each group, except the P4 group, the P–O bond is significantly longer than the

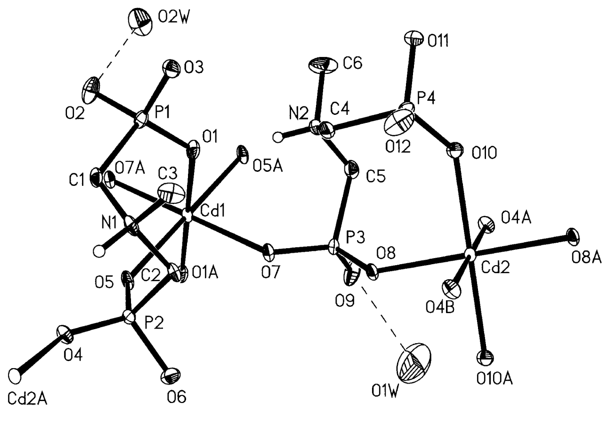


Fig. 4 ORTEP representation of the asymmetric unit of complex **2**. Thermal ellipsoids are drawn at 50% probability. The dashed lines indicate hydrogen bonds.

**Table 2** Selected bond lengths (Å) and angles (°) for complexes **1** and **2**

| Complex **1** | | | |
|---|---|---|---|
| Zn(1)–O(5)#1 | 1.913(2) | Zn(1)–O(3) | 1.915(2) |
| Zn(1)–O(2)#2 | 1.967(2) | Zn(1)–O(1W) | 1.969(2) |
| O(2)–Zn(1)#2 | 1.967(2) | O(5)–Zn(1)#3 | 1.913(2) |
| P(1)–O(1) | 1.511(2) | P(1)–O(3) | 1.524(2) |
| P(1)–O(2) | 1.538(2) | P(2)–O(4) | 1.512(2) |
| P(2)–O(5) | 1.521(2) | P(2)–O(6) | 1.542(2) |
| | | | |
| O(5)#1–Zn(1)–O(3) | 117.52(10) | O(5)#1–Zn(1)–O(2)#2 | 109.51(10) |
| O(3)–Zn(1)–O(2)#2 | 117.78(10) | O(5)#1–Zn(1)–O(1W) | 110.52(10) |
| O(3)–Zn(1)–O(1W) | 98.48(10) | O(2)#2–Zn(1)–O(1W) | 100.84(10) |

Symmetry transformations used to generate equivalent atoms: For complex **1**: #1 $x + 1, y - 1, z$; #2 $-x, -y + 2, -z + 2$; #3 $x - 1, y + 1, z$; #4 $1 - x, 1 - y, -z$; #5 $x, -1 + y, z$; #6 $-x, 1 - y, 1 - z$. For complex **2**: #1 $-x + 1, -y + 1, -z + 1$; #2 $-x + 2, -y, -z + 1$; #3 $x, y - 1, z$; #4 $-x + 2, -y + 1, -z + 1$; #5 $x, y + 1, z$; #6 $1 - x, -y, 2 - z$; #7 $1 - x, 1 - y, -z$; #8 $2 - x, 1 - y, -z$; #9 $2 - x, -y, -z$.

| Hydrogen bonds<br>D–H ··· A | *d*(D–H)/Å | *d*(H ··· A)/Å | (D–H–A)/° | *d*(D ··· A)/Å | Symmetry operation |
|---|---|---|---|---|---|
| N1–H11A–O4 | 0.910 | 1.864 | 151.04 | 2.696 | $[-x, -y + 1, -z + 1]$ |
| O1W–H1W–O2 | 0.811 | 1.857 | 171.91 | 171.91 | $[x, y - 1, z]$ |
| O1W–H2W–O4 | 0.992 | 1.652 | 168.51 | 2.631 | $[x, y - 1, z]$ |
| O6–H6A–O1 | 0.820 | 1.684 | 159.58 | 2.469 | $[-x + 1, -y + 1, -z]$ |

| Complex **2** | | | |
|---|---|---|---|
| Cd(1)–O(5)#1 | 2.256(3) | Cd(1)–O(5) | 2.256(3) |
| Cd(1)–O(7)#1 | 2.260(3) | Cd(1)–O(7) | 2.260(3) |
| Cd(1)–O(1)#1 | 2.292(4) | Cd(1)–O(1) | 2.292(4) |
| Cd(2)–O(8) | 2.235(3) | Cd(2)–O(8)#2 | 2.235(3) |
| Cd(2)–O(10) | 2.285(4) | Cd(2)–O(10)#2 | 2.285(4) |
| Cd(2)–O(4)#3 | 2.290(3) | Cd(2)–O(4)#4 | 2.290(3) |
| P(1)–O(1) | 1.502(4) | P(1)–O(2) | 1.521(4) |
| P(1)–O(3) | 1.574(4) | P(2)–O(4) | 1.502(4) |
| P(2)–O(5) | 1.502(3) | P(2)–O(6) | 1.584(4) |
| P(3)–O(8) | 1.503(3) | P(3)–O(7) | 1.506(4) |
| P(3)–O(9) | 1.580(4) | P(4)–O(10) | 1.511(4) |
| P(4)–O(12) | 1.532(4) | P(4)–O(11) | 1.535(4) |
| O(4)–Cd(2)#5 | 2.290(3) | | |
| | | | |
| O(5)#1–Cd(1)–O(5) | 180.00(17) | O(5)#1–Cd(1)–O(7)#1 | 91.57(13) |
| O(5)–Cd(1)–O(7)#1 | 88.43(12) | O(5)#1–Cd(1)–O(7) | 88.43(12) |
| O(5)–Cd(1)–O(7) | 91.57(13) | O(7)#1–Cd(1)–O(7) | 180.0 |
| O(5)#1–Cd(1)–O(1)#1 | 93.93(13) | O(5)–Cd(1)–O(1)#1 | 86.07(13) |
| O(7)#1–Cd(1)–O(1)#1 | 81.30(13) | O(7)–Cd(1)–O(1)#1 | 98.70(13) |
| O(5)#1–Cd(1)–O(1) | 86.07(13) | O(5)–Cd(1)–O(1) | 93.93(13) |
| O(7)#1–Cd(1)–O(1) | 98.70(13) | O(7)–Cd(1)–O(1) | 81.30(13) |
| O(1)#1–Cd(1)–O(1) | 180.0 | O(8)–Cd(2)–O(8)#2 | 180.000(1) |
| O(8)–Cd(2)–O(10) | 93.83(12) | O(8)#2–Cd(2)–O(10) | 86.17(12) |
| O(8)–Cd(2)–O(10)#2 | 86.17(12) | O(8)#2–Cd(2)–O(10)#2 | 93.83(12) |
| O(10)–Cd(2)–O(10)#2 | 180.00(2) | O(8)–Cd(2)–O(4)#3 | 90.85(13) |
| O(8)#2–Cd(2)–O(4)#3 | 89.15(13) | O(10)–Cd(2)–O(4)#3 | 83.03(12) |
| O(10)#2–Cd(2)–O(4)#3 | 96.97(12) | O(8)–Cd(2)–O(4)#4 | 89.15(13) |
| O(8)#2–Cd(2)–O(4)#4 | 90.85(13) | O(10)–Cd(2)–O(4)#4 | 96.97(12) |
| O(10)#2–Cd(2)–O(4)#4 | 83.03(12) | O(4)#3–Cd(2)–O(4)#4 | 180.00(14) |

**Table 3** Hydrogen bonds for complex **2**

| D–H ··· A | *d*(D–H)/Å | *d*(H ··· A)/Å | (D–H–A)/° | *d*(D ··· A)/Å | Symmetry operation |
|---|---|---|---|---|---|
| O3–H3D–O12 | 0.820 | 1.771 | 176.98 | 2.590 | $[-x + 2, -y + 1, -z]$ |
| O6–H6D–O12 | 0.820 | 1.871 | 168.57 | 2.679 | $[-x + 2, -y + 1, -z + 1]$ |
| O9–H9A–O1W | 0.820 | 1.999 | 147.52 | 2.727 | |
| O12–H12A–O6 | 0.820 | 1.887 | 162.31 | 2.679 | $[-x + 2, -y + 1, -z + 1]$ |
| N1–H11A–O10 | 0.910 | 2.070 | 146.49 | 2.872 | $[x, y + 1, z]$ |
| N1–H11A–O8 | 0.910 | 2.379 | 125.81 | 3.004 | $[-x + 2, -y + 1, -z + 1]$ |
| N2–H22A–O1 | 0.910 | 2.026 | 149.47 | 2.847 | |
| O9–H9A–O2 | 0.923 | 1.771 | 166.8 | 2.678 | $[-x + 1, -y + 1, -z + 1]$ |
| N2–H22A–O5 | 0.910 | 2.436 | 122.72 | 3.027 | $[-x + 1, -y + 1, -z + 1]$ |
| O1W–[a]H–O12 | | | | 2.969 | $[-x + 2, -y, -z + 1]$ |
| O1W–[a]H–O1W | | | | 2.633 | |
| O2W–[a]H–O2W | | | | 2.743 | $[-x + 1, -y + 1, -z]$ |
| O2W–[a]H–O6 | | | | 2.876 | $[-x + 1, -y + 1, -z + 1]$ |
| O2W–[a]H–O2 | | | | 2.692 | |

[a] H = H not found in Fourier maps.

other two. The lack of elongation of the P–O12 bond may stem from the fact that O12 forms three hydrogen bonds, one as donor and two as acceptor. The same situation holds for the manganese compound.[14]

The $Cd(H_3L)_2$ units are interconnected by bridging phosphonate groups, forming a 2D metal phosphonate layer along the (002) plane (Fig. 5) and 16-membered rings. Each ring is composed of four phosphonate tetrahedra and four $CdO_6$ octahedra interconnected *via* corner-sharing. The unidentate-coordinating phosphonate groups (P1 and P4) are attached above and below the plane. The methyl groups are oriented towards the cavity created by the 16-membered rings as shown in Fig. 5. Hydrogen bonds are formed between phosphonate oxygen atoms within a layer, O9–H9A ··· O2, 2.678 Å, 166.8° and O6–H6D ··· O12, 2.679 Å, 168.6°, O12–H12A ··· O6, 2.679 Å, 162.3°), as well as between the nitrogen atom and phosphonate oxygen atoms within the layer (N1–H11A ··· O8, 3.004 Å (125.8°), N1–H11A ··· O(10), 2.872 Å (146.5°); N2–H22A ··· O1, 2.847 Å (149.5°), N2–H22A ··· O5, 3.027 Å (122.7°) (Table 3).

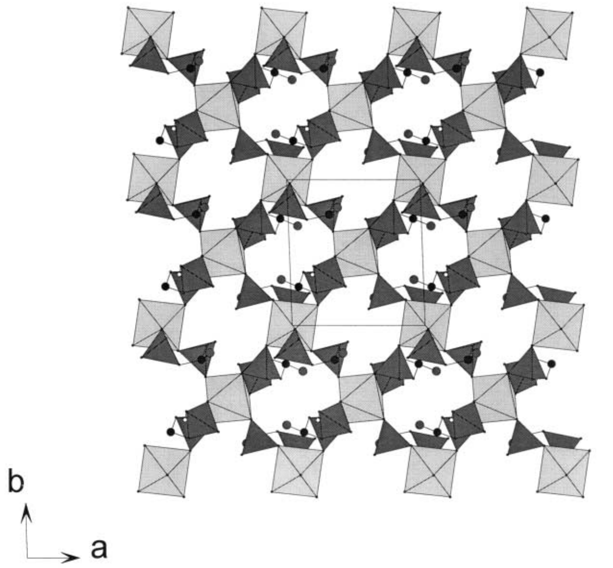


**Fig. 5** Polyhedral representation of a cadmium(II) phosphonate layer along the (002) plane. $CdO_6$ octahedra and C–$PO_3$ tetrahedra are shaded in light and dark gray, respectively. N and methyl C atoms are shown as gray and black circles, respectively.

These metal phosphonate layers are further inter-linked by inter-layer hydrogen bonds (Fig. 6). In addition to the hydrogen bonds between phosphonate oxygen atoms and lattice water molecules discussed above, there are also strong hydrogen bonds formed between phosphonate oxygen atoms from two neighboring metal phosphonate layers (O3–H3D ··· O12, 2.590 Å, 177.0°).

## Thermogravimetric analysis

The TGA diagram for complex **1** indicates three main steps of weight loss. The first step is the loss of the coordination water molecule, which starts at 160 °C and completed at 212 °C. The observed weight loss of 5.94% is very close to the calculated value (5.99%). The following two steps are overlapped; first, the release of water molecule formed by the condensation of hydrogen phosphonate groups which started at about 356 °C; second, the burning of the organic group which continued up to 1000 °C. The total weight loss is 27.25%, which is in good agreement with the calculated weight loss of 25.64% if the final products are assumed to be zinc metaphosphate [$Zn(PO_3)_2$]. The TGA diagram of complex **2** is similar to that of the layered Mn(II) phosphonate.[14] It shows four major weight losses. The first step is the loss of two lattice water molecules, which is completed at 198 °C. The weight loss of 5.95% is in good agreement with the calculated value (6.16%). There are two processes taking place between 300 °C and 600 °C; first, the release of two water molecules formed by the condensation of hydrogen phosphonate groups; second, the pyrolysis of the organic group. However, these two processes overlap. The weight loss continues after 600 °C, even to 1000 °C. The final product is mainly $Cd(PO_3)_2$, a metal metaphosphate, the calculated weight loss of 53.74% is larger than the observed one (43.77%), thus the reaction is not complete at 1000 °C, as evidenced by the fact that the weight is still decreasing.

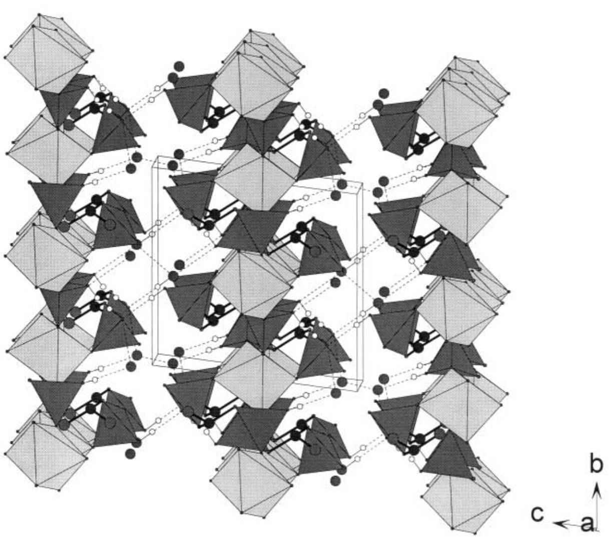


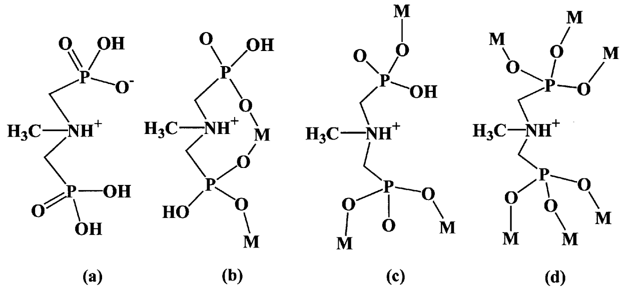
**Fig. 6** View of the crystal structure of complex **2** as viewed down the *a* axis showing the separation of the layers and the hydrogen bonding scheme. The $CdO_6$ octahedra are light gray, $CPO_3$ tetrahedra are dark gray, water oxygens between the layers are medium gray. Nitrogen atoms connecting the tetrahedra are black and the methyl carbon atoms bonded to N are medium gray.

## NMR analysis

The free ligand, $H_4L$, shows only a single phosphorus peak of the phosphonate groups at 8.1 ppm (solution NMR in $D_2O$ with 85% $H_3PO_4$ as standard reference), thus the two phosphonate groups have the same chemical environment.[14] Upon complexing with zinc(II) ions, the two phosphonate groups of the ligand are no longer identical. The spectrum of complex **1** shows two peaks at 11.7 and 14.9 ppm respectively, both are shifted downfield compared to that for the free ligand. From the crystal structure of complex **1** (see Fig. 1), we know that one phosphonate group (P2) is 1H-protonated and is unidentately coordinated, whereas the other one (P1) is non-protonated and is in a bidentate bridging mode with two Zn(II) atoms (Fig. 1), hence we can assign the peak at 11.7 ppm to P2 and that at 14.9 ppm to P1. The spectrum of the layered Cd(II) complex is more complicated, it has four peaks at 9.4, 10.3, 11.7 and 15.0 ppm, respectively, which are also shifted downfield from the peak position for the free ligand. The asymmetric unit of complex **2** has two ligands, therefore four phosphorus atoms (see Fig. 4). All four phosphonate groups are 1H-protonated, two of them (P1 and P4) exhibit a unidentate coordination to the Cd(II) ion, whereas the other two (P2 and P3) each bridges with two Cd(II) atoms (Fig. 4). The chemical environment around the P1 atom is slightly different from that of P4 due to the different Cd–O distances and O ··· O contacts, the same is true for the P2 and P3 atoms (See Table 2). We assigned the peak at 9.4 ppm to P1 and that at 10.3 ppm to P4, since the Cd–O bond and O ··· O hydrogen bonds are slightly stronger for phosphonate group P4. For the same reason, the peak at 11.7 ppm was assigned to P2 and that at 15.0 ppm to P3.

## Discussion

Strong hydrogen bond formation has been found to exist in the parent ligand *N*-methyl-iminobis(methylenephosphonic acid) and its derivatives.[13,16] Reaction of *N*-methyl-iminobis-(methylenephosphonic acid) ($H_4L$) with divalent metal salts, yielded four metal phosphonates with three types of structures, namely, layered metal phosphonates, $M(H_3L)_2\cdot 2H_2O$ (M = Mn, Cd); $Zn(H_2L)(H_2O)$ which has a double chain structure; and $Zn_3(HL)_2$ with a 3D network structure. It provides another good example demonstrating that the deprotonation of the phosphonic acid plays an important role in the structural types of the resulting metal phosphonates and the M : L ratios. Scheme 1 shows the ligand $H_4L$ (a), and different coordination modes it adopts in its layered complexes (M = Mn, Cd) (b) and zinc(II) complex with a 1D double chain structure (c), as well as zinc(II) complex which has a 3D network structure (d).



**Scheme 1** Ligand $H_4L$ and its coordination modes in its divalent metal complexes.

*N*-Methyl-iminobis(methylenephosphonic acid) occurs in a zwitterionic form (Scheme 1a), which is a common form for phosphonic acids containing amine groups.[4,13] These zwitterions are interconnected into a 3D network based on tetramers through strong intermolecular hydrogen bonding (2.446(2), 2.525(2) and 2.572(2) Å).[13] Upon reaction with manganese(II) acetate or cadmium(II) nitrate at room temperature, one more proton on another phosphonate group is removed, thus complexes with 1 : 2 (M : L) are formed. The ligand adopts a tridentate chelate and bridging coordinate mode (Scheme 1b) to form the layer structure. The uncoordinated phosphonate oxygens are available for intra- and inter-layer hydrogen bonding. The reaction of zinc(II) nitrate with the ligand at the molar ratio of 1 : 2 under room temperature conditions afforded a Zn(II) complex with a double chain structure with a M : L ratio of 1 : 1, each ligand is also tridentate as in the layered complexes, however, no chelate rings are formed and it bridges with three metal ions instead of two metal ions in the layered species. Furthermore, one phosphonate group is deprotonated completely while the other one remains 1H-protonated. Under hydrothermal conditions at a higher temperature (165 °C), all of the protons on both phosphonate groups have been removed, but the amine group is still protonated. The ligand with a negative three charge forms a 3 : 2 (M : L) complex with zinc(II) acetate, $Zn_3(HL)_2$, in which the ligand acts as a hexadentate ligand and connects with six zinc ions (Scheme 1d). The structures of both zinc complexes are very different from the layer structure proposed by the solution studies.[13] The amine group of the ligand in four metal complexes is protonated. However, under weak basic condition (pH ~ 8), the proton on the amine group can be deprotonated, as reported in the copper complex with ethylaminebis(methylphosphonate).[12] The remaining phosphonate oxygen atoms in this compound are connected to Cs(I) ions as $Cs_2CO_3$ was used to increase the pH. Deprotonation of the amine groups also depends on the affinity of the metal ions for the nitrogen atom and the property of the chelate rings. In metal polyaminephosphonates, such as those in which the phosphonate groups are attached to ethylene diamine or polyaza-crown ether, the nitrogen atoms of the ligand are coordinated to the metal ion even under weakly acidic conditions.[9,17]

In the recent past we have prepared a number of complexes of nitrilotris(methylphosphonic acid) ($H_6L$) representing the triphosphonic acid. It is clear that the degree of deprotonation and the resultant hydrogen bonding determines the type of complex formed. $H_6L$ forms unique 3D hexagonal structures when a single proton is transferred to an amine. This reaction triggers formation of a hexagonal 3D-hydrogen bonded array that encapsulates the amines as templates.[18] If two protons are removed, by an addition of 2 moles of amine, linear chain structures are obtained. These negatively charged chains then combine with the positively charged amines to form a variety of layered compounds, whose final structure depends upon the shape of the amine.[18] In contrast, in the presence of divalent ions, Mn, Co, Ni, Cu, Zn and Cd a single linear chain structure is obtained, which is dictated by the hydrogen bonding scheme, involving the ligand and coordinated water molecules.[19] This behavior stands in contrast to the results reported here where under almost identical preparation conditions, Mn and Cd removed one proton while Zn removed two from the ligand. This difference apparently stems from the distinct preference of Mn(II) and Cd(II) for octahedral coordination which requires more ligand than the four coordinate zinc. However, in the case of nitrilotris(methylene phosphonic acid), removal of two protons by divalent metal still leaves four protons on the ligand as directing agents. Upon using a large excess of $H_6L$, an anhydrous $Mn(H_4L)$ derivative with a 3D structure was obtained.[19] The metal ion in hydrated complexes is octahedraly coordinated by three aqua ligands and three phosphonate oxygen atoms, whereas Mn(II) ion in the non-hydrated complex is five coordinated by five phosphonate oxygen atoms with a distorted square pyramid geometry.[19] Under hydrothermal conditions, four protons were removed, the resultant zinc complex, $Zn_2(H_2L^2)$ has a 3D network structure which is built from $ZnO_4$ tetrahedra cross-linked by the bridging phosphonate groups.[20]

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