

# Hydrothermal synthesis, characterization and crystal structures of two new zinc(II) phosphonates: $\text{Zn}_2[(\text{O}_3\text{PCH}_2)_2\text{NHCH}_2\text{CO}_2]$ and $\text{Zn}_2[\text{HO}_3\text{PCH}_2\text{NH}(\text{CH}_2\text{PO}_3)_2]$

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The hydrothermal reaction of zinc(II) acetate with *N,N*-bis(phosphonomethyl)aminoacetic acid  $[(\text{H}_2\text{O}_3\text{PCH}_2)_2\text{NCH}_2\text{CO}_2\text{H}, \text{H}_5\text{L}^1]$  and nitrilotris(methylenephosphonic acid)  $[\text{N}(\text{CH}_2\text{PO}_3\text{H}_2)_3, \text{H}_6\text{L}^2]$  at  $180^\circ\text{C}$  afforded two new zinc coordination polymers with a similar 3D network structure.  $\text{Zn}_2[(\text{O}_3\text{PCH}_2)_2\text{NHCH}_2\text{CO}_2]$  (complex **1**) is hexagonal,  $P6_1$ , with  $a = 8.0677(12)$ ,  $c = 27.283(6)$  Å,  $u = 1537.9(5)$  Å<sup>3</sup>,  $Z = 6$ . In complex **1**, the Zn(II) atoms are tetrahedrally coordinated by three phosphonate oxygen atoms and one carboxylate oxygen atom from four ligands. The  $\text{ZnO}_4$  tetrahedra are further interconnected through bridging phosphonate and carboxylate groups into a three dimensional network.  $\text{Zn}_2[\text{HO}_3\text{PCH}_2\text{NH}(\text{CH}_2\text{PO}_3)_2]$  (complex **2**) is also hexagonal,  $P6_1$  with  $a = 8.3553(8)$ ,  $c = 26.657(4)$  Å,  $u = 1611.6(3)$  Å<sup>3</sup>,  $Z = 6$ . The structure of complex **2** features a 3D network built from  $\text{ZnO}_4$  tetrahedra linked together by bridging phosphonate groups. One zinc and three phosphonate oxygen atoms are disordered. The two zinc atoms in the asymmetric unit are tetrahedrally coordinated by four phosphonate oxygen atoms of four ligands. Each ligand connects with eight zinc atoms. The effect of the extent of deprotonation of phosphonic acids and substitution groups on the type of complexes formed are discussed.

Metal phosphonate chemistry has been an area of interest to both inorganic and materials chemists in recent years due to potential applications in the areas of catalysis, ion exchange, proton conductivity, intercalation chemistry, photochemistry, and materials chemistry.<sup>1</sup> Most of the compounds studied are layered species in which the metal octahedra are bridged by phosphonate tetrahedra to form two-dimensional layers that are separated by the hydrophobic regions of the organic moieties.<sup>1</sup> Studies from our group and from others have shown that a variety of metal ions, including group 4 and 14 elements and divalent and trivalent ions, form this type of layered compound.<sup>1–3</sup>

Research on metal complexes with phosphonic acids attached with aza-crown ethers show those compounds have many unusual structural features.<sup>1,4</sup> Phosphonic acids with functional carboxylate groups, such as *N*-(phosphonomethyl)iminodiacetic acid ( $\text{H}_4\text{PMIDA}$ ) are also interesting, since they can adopt various kinds of coordination modes under different reaction conditions. A mixed phosphate-phosphonate layered zirconium compound was made by reaction of a zirconium salt with a mixture of phosphoric acid and  $\text{H}_4\text{PMIDA}$  solutions.<sup>5</sup> When the above reactions were carried out in the absence of phosphoric acid, a linear chain compound was isolated.<sup>6</sup> In both cases the iminodiacetic moieties are only involved in hydrogen bonding. Under less acidic conditions, we isolated two novel complexes,  $[\text{Co}_2(\text{PMIDA})(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$  whose structure contains double layers of Co(II) carboxylate interconnected by layers of Co(II) phosphonate, and a zinc carboxylate-phosphonate hybrid layered complex,  $[\text{Zn}_2(\text{PMIDA})(\text{CH}_3\text{CO}_2\text{H})] \cdot 2\text{H}_2\text{O}$ .<sup>7</sup> With the complete deprotonation by adding potassium hydroxide, Wood and his co-workers<sup>8</sup> obtained the canted antiferromagnet  $[\text{K}_2\text{Co}(\text{PMIDA})]_6 \cdot x\text{H}_2\text{O}$ , whose crystal structure features a hexameric ring in the chair conformation.

Few studies have been done on metal complexed with *N,N*-bis(phosphonomethyl)aminoacetic acid  $[(\text{H}_2\text{O}_3\text{PCH}_2)_2\text{NCH}_2\text{CO}_2\text{H}, \text{H}_5\text{L}^1]$ , which differs slightly from  $\text{H}_4\text{PMIDA}$  in that one acetate group in  $\text{H}_4\text{PMIDA}$  has been replaced by a phosphonate group. X-Ray structural analysis of its platinum(II) complexes indicated that the ligand forms a 5-member chelate ring with Pt(II) ion by using the amine group and the acetate group, the phosphonate groups remain uncoordinated.<sup>9</sup>

Many studies have been carried out in our laboratory on nitrilotris(methylenephosphonic acid)  $[\text{N}(\text{CH}_2\text{PO}_3\text{H}_2)_3, \text{H}_6\text{L}^2]$ , in which both acetate groups of  $\text{H}_4\text{PMIDA}$  have been substituted by phosphonate groups. The structures of nitrilotris(methylenephosphonic acid) with amines such as 1,7-phenanthroline, 1,10-phenanthroline, acridine and tripropylamine in a 1 : 1 ratio feature a hydrogen bonded 3D hexagonal network.<sup>10</sup> For its metal(II) phosphonate complexes, two different types of 1 : 1 (M:L) complexes have been isolated by using various metal–ligand ratios in the synthesis, namely,  $\text{M}[\text{NH}(\text{CH}_2\text{PO}_3\text{H})_3(\text{H}_2\text{O})_3]$  ( $\text{M} = \text{Mn}, \text{Co}, \text{Ni}, \text{Zn}, \text{Cu}, \text{Cd}$ ) whose structure features a hydrogen bonded 2D layer,<sup>11</sup> and the dehydrated  $\text{Mn}[\text{NH}(\text{CH}_2\text{PO}_3\text{H})_3]$  whose structure is a 3D network.<sup>12</sup> The metal ion in the hydrated complexes is octahedrally 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.<sup>12</sup> Hydrothermal reaction of zinc(II) acetate with *N,N*-bis(phosphonomethyl)aminoacetic acid  $[(\text{H}_2\text{O}_3\text{PCH}_2)_2\text{NCH}_2\text{CO}_2\text{H}, \text{H}_5\text{L}^1]$  and nitrilotris(methylenephosphonic acid) in a 2 : 1 (M:L) molar ratio at  $180^\circ\text{C}$  afforded two new zinc coordination polymers with a similar 3D network framework, namely,  $\text{Zn}_2[(\text{O}_3\text{PCH}_2)_2\text{NHCH}_2\text{CO}_2]$  (complex **1**) and  $\text{Zn}_2[\text{HO}_3\text{PCH}_2\text{NH}(\text{CH}_2\text{PO}_3)_2]$  (complex **2**). Herein we report their synthesis, characterization and crystal structures.

## Results

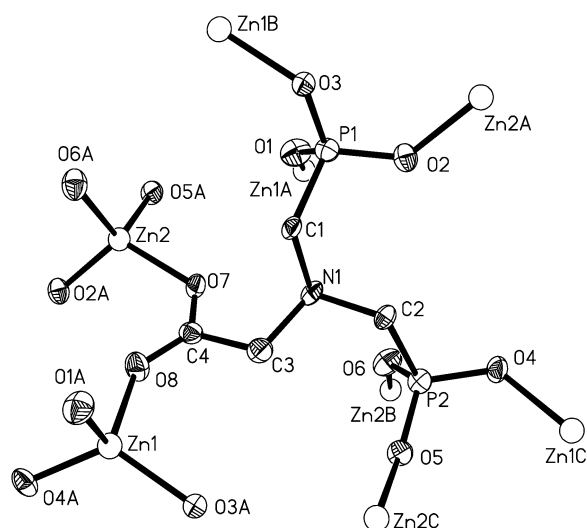
### Crystal structure of $\text{Zn}_2[\text{O}_2\text{CCH}_2\text{NH}(\text{CH}_2\text{PO}_3)_2]$ , **1**

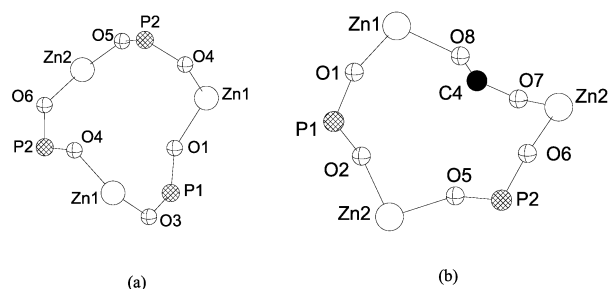
An ORTEP representation of the asymmetric unit of complex **1** is shown in Fig. 1. There are two zinc atoms in an asymmetric unit. Both Zn1 and Zn2 atoms are tetrahedrally coordinated by three phosphonate oxygen atoms and one carboxylate oxygen atom from four different ligands. The Zn–O(carboxylate) distances [1.992(7) and 1.988(6) Å, respectively, for Zn1 and Zn2] are slightly longer than the Zn–O<sub>p</sub> (phosphonate) bonds, which range from 1.909(6) to 1.937(6) Å (Table 1). Each ligand is connected with 8 zinc atoms. Both phosphonate and carboxylate groups of the ligand are deprotonated, but the amine group is still protonated, hence each ligand carries a charge of  $-4$ . Therefore, two Zn(II) ions are required to balance the negative charges. The ligand in the Pt(II) complex adopts a bidentate chelating coordination mode: only the amine group and one carboxylate oxygen are coordinated to the metal ion, the two phosphonate groups remain protonated and are not involved in the coordination bonding.<sup>9</sup>

The  $\text{ZnO}_4$  tetrahedra are further interconnected by bridging phosphonate and carboxylate groups, resulting in the formation of a 3D network (Fig. 2). It is interesting to note that two types of 12-membered rings are formed. One such ring contains 3 Zn, 3 P and 6 O atoms [Fig. 3(a)], whereas the other ring is composed of 3 Zn, 2 P, 1 C and 6 O atoms [Fig. 3(b)], that is one phosphonate group in Fig. 3(a) being substituted by a carboxylate group.

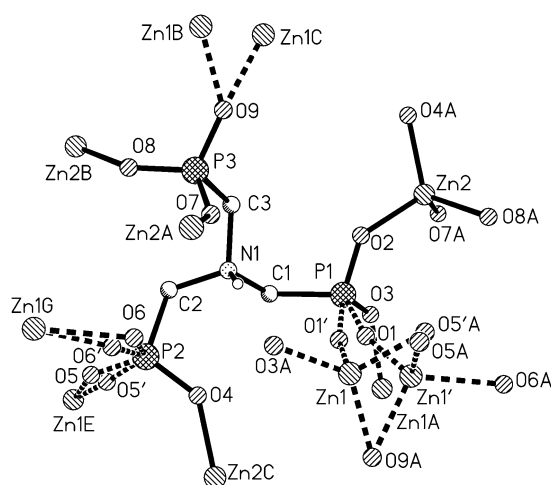
### Crystal structure of $\text{Zn}_2[\text{HPO}_3\text{CH}_2\text{NH}(\text{CH}_2\text{PO}_3)_2]$ , **2**

The structure of complex **2** also features a 3D network structure similar to that in complex **1**. As shown in Fig. 4, the asymmetric structural unit of complex **2** contains two zinc atoms and one ligand. The Zn1 atom is disordered and has two orientations (Zn1 and Zn1' with 89.6% and 10.4% occupancies, respectively). Three phosphonate oxygen atoms (O1, O5 and O6) are also disordered and each has two orientations (O1, O1', O5, O5', O6 and O6' with 50% occupancy each). Each zinc atom is tetrahedrally coordinated by four phosphonate oxygen atoms from four ligands. The Zn–O distances range from 1.79(2) to 2.18(2) Å (Table 1). These values represent too broad a range but are a reflection of the disorder. The





**Fig. 3** Two types of 12-membered rings in complex **1**/ Zn, P, C and O atoms are represented by open, hatched, black and crossed circles, respectively.



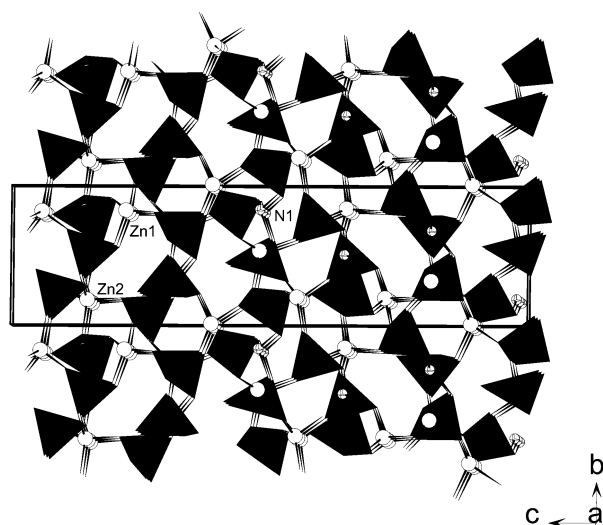
**Fig. 4** View of the asymmetric unit of complex **2**. Zn1 (Zn1'), O1 (O1'), O5 (O5') and O6 (O6') are disordered. The dashed lines represent the bonds related to disordered atoms.

The  $\text{ZnO}_4$  tetrahedra are interconnected by phosphonate groups, resulting in the formation of a complex 3D network as shown in Fig. 5, and rings of various sizes. Two types of 12-membered rings are created (Fig. 6). One such ring contains 3 Zn, 3 P and 6 O atoms, the other 12-membered ring is composed of 2 Zn, 3 P, 4 O, 2 C and one N atoms. We can view the latter ring is formed by replacing one  $\text{ZnO}_4$  tetrahedra in the former ring by an amine tetrahedron.

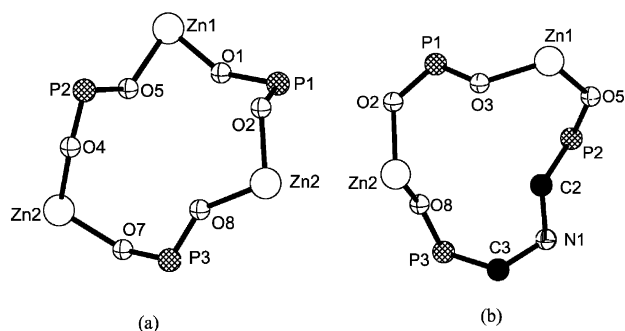
The ligand adopts an octadentate coordination mode, and bridges with 8 Zn(II) atom. This is different from that in its hydrated and non-hydrated divalent metal complexes. In the  $\text{M}[\text{NH}(\text{CH}_2\text{PO}_3\text{H})_3(\text{H}_2\text{O})_3]$  ( $\text{M} = \text{Co}, \text{Mn}, \text{Ni}, \text{Cu}, \text{Zn}, \text{Cd}$ ) complexes, all the phosphonate groups are 1-H protonated, each one is unidentately coordinated to a metal ion, forming a 1D chain. Such chains are further interconnected into a 2D layer *via* hydrogen bonding between the uncoordinated phosphonate oxygen atoms.<sup>11</sup> The ligand in the Mn  $[\text{NH}(\text{CH}_2\text{PO}_3\text{H})_3]$  complex is pentadentate, and bridges with five metal ions. Two phosphonate groups are bidentate, and the third one remains unidentate as in hydrated complexes. The 5-coordinated Mn(II) ions are interconnected by bridging phosphonate groups into a 3D network, instead of the layer structure in its hydrated complex.<sup>12</sup>

#### Thermogravimetric study

A TGA diagram of complex **1** shows two weight losses. The first step is the loss of the carboxylate group of the ligand, which begins at about 403 °C and is completed at 541 °C. The



**Fig. 5** View of crystal structure of complex **2** along the *a* axis. C- $\text{PO}_3$  tetrahedra are in black. Zn and amine N atoms are shown as large open and octadent circles, respectively. For the sake of clarity, the structure is drawn with the ordered model.



**Fig. 6** Two types of 12-membered rings in complex **2**. Zn, P, N, C and O atoms are represented by open, hatched, octadent black and crossed circles, respectively. For the sake of clarity, the Zn1 atom is shown by only one orientation.

weight loss of 12.32% is in good agreement with the calculated value (11.29%). The second step corresponds to the burning of the remaining organic group, completed at about 800 °C. The final product is  $\text{Zn}_2\text{P}_2\text{O}_7$ , a metal pyrophosphate. The total weight loss of 21.8% is in good agreement with the calculated one (22.0%). Complex **2** is stable up to 394 °C. The TGA diagram for complex **2** shows two steps of major weight loss that are overlapped. The first step is the release of water molecules formed by the condensation of hydrogen phosphonate groups, which starts at 394 °C. The second step is the burning of organic groups, which is complete at about 950 °C. The total weight loss is 11.14%, which is in good agreement with the calculated weight loss of 11.73% if the final products are assumed to be zinc pyrophosphate ( $\text{Zn}_2\text{P}_2\text{O}_7$ ) and zinc metaphosphate [ $\text{Zn}(\text{PO}_3)_2$ ] in a 1 to 2 ratio. Our previous TGA studies indicate that metaphosphate phases can be formed when the number of phosphonate groups per metal ion in the initial metal phosphonates is larger than one, such as in divalent metal complexes with *N*-methyliminobis(methylene-phosphonic acid).<sup>13</sup>

#### NMR analysis

The  $^{31}\text{P}$  NMR spectra of the two ligands were acquired in  $\text{D}_2\text{O}$  solution while those of complexes **1** and **2** were solid  $^{31}\text{P}$  MAS

NMR spectra. The free ligands,  $H_5L^1$  and  $H_6L^2$ , show single phosphorus peaks of the phosphonate groups at 7.968 and 8.335 ppm, respectively, thus all phosphonate groups of each ligand have the same environment. Upon complexing with zinc(II) ions, their chemical shifts moved upfield to 6.871 and 6.496 ppm, respectively, for complexes **1** and **2**. There is no splitting of peaks, indicating that all phosphonate groups in each zinc complex have the same coordination environment.

## Discussion

Hydrothermal reaction of zinc(II) acetate with *N,N*-bis(phosphonomethyl)aminoacetic acid [ $H_2O_3PCH_2)_2NCH_2CO_2H$ ] and nitrilotris(methylenephosphonic acid) [ $N(CH_2PO_3H_2)_3$ ] resulted in two new zinc(II) phosphonates, namely,  $Zn_2[O_3PCH_2)_2NHCH_2CO_2]$  (complex **1**) and  $Zn_2[HO_3PCH_2NH(CH_2PO_3)_2]$  (complex **2**). Both complexes have a similar 3D network structure. In both complexes, the  $ZnO_4$  tetrahedra are interconnected through bridging phosphonate and/or carboxylate groups. The amine group in both complexes is protonated and hence has tetrahedral geometry.

For divalent metal complexes with nitrilotris(methylenephosphonic acid) it is interesting to note that the structures of the complexes obtained are affected by the ligand-to-metal ratio used in the synthesis. The hydrated complexes with a hydrogen bonded layer structure and a formula of  $M[NH(CH_2PO_3H)_3](H_2O)_3$  ( $M = Co, Mn, Ni, Cu, Zn, Cd$ ) were isolated when the ligand-to-metal ratio is in the range of 1 : 1 to 5 : 1. With the ratio increased to 10 : 1, the aqua ligands were replaced by phosphonate oxygen atoms and the Mn complex thus formed has a 3D network structure. The phosphonate groups in both hydrated and non-hydrated complexes are 1H-protonated.<sup>11,12</sup> Two more protons are removed and replaced by an additional divalent metal ion when the ratio of ligand-to-metal is equal to or less than 1 : 2, as in  $Zn_2[HPO_3NH(CH_2PO_3)_2]$  (complex **2**).

Another aspect of interest is the effect of the carboxylate group attached to the ligand on the structures of the metal phosphonates formed. The structures of nitrilotris(methylenephosphonic acid) and three of its carboxylate-substituted derivatives are shown in Scheme 1. The main difference between complexes **1** and **2** is that one of the phosphonate groups in complex **2** is replaced by a carboxylate group. This substitution results in only small changes in the structure of their metal phosphonates. When two phosphonate groups in nitrilotris(methylenephosphonic acid) are substituted by two carboxylate groups, the so-formed PMIDA ligand behaves very differently. It chelates Co(II) or Zn(II) ions with the nitrogen, two carboxylate and one phosphonate oxygen atoms. The interconnection of metal ions by bridging carboxylate and phosphonate groups resulted in metal carboxylate-phosphonate hybrid layered compounds,  $[Co_2(PMIDA)(H_2O)_3] \cdot H_2O$  and  $[Zn_2(PMIDA)(CH_3CO_2H)] \cdot 2H_2O$ . In both complexes the amine group of the  $H_4PMIDA$  is not protonated.<sup>7</sup> Many studies have been reported on the metal

complexes with nitrilotriacetic acid [ $N(CH_2COOH)_3$ ], which has three carboxylate groups instead of the three phosphonate groups in nitrilotris(methylenephosphonic acid).<sup>14,15</sup> Usually bases such as alkali hydroxide and amines are added to remove protons on the carboxylate groups during the preparation of the metal complexes. The ligand in these complexes chelates with a metal ion in two different ways. The first type of chelation involves three carboxylate oxygen atoms from three carboxylate groups and a nitrogen atom and three 5-membered chelate rings are formed,<sup>14</sup> whereas in the second type of chelation, only two carboxylate oxygen atoms and a nitrogen atom chelate with a metal ion, and thus only two 5-membered chelate rings are formed, the third carboxylate group remains uncoordinated.<sup>15</sup> Both types of chelation are adopted in the Fe(III) complex.<sup>16</sup> From these studies, it is concluded that with more carboxylate groups replacing the phosphonate groups in the ligand, the deprotonation of the amine group becomes much easier and chelation coordination modes are preferred.

## Experimental

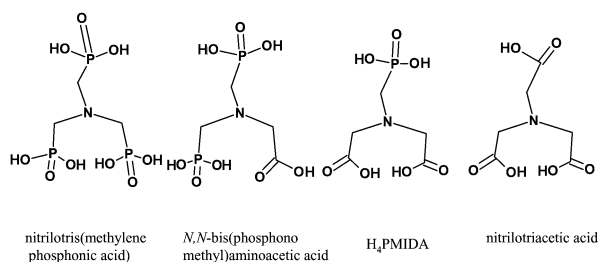
### Materials and methods

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 used without further purification. Solution NMR was recorded on a Varian Unity Plus 300 spectrometer.  $H_3PO_4$  (EM Science, 85%) was used as  $^{31}P$  standard reference. The  $^{31}P$  solid state MAS NMR spectra were obtained on a Bruker MSL-300 unit. 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<sup>-1</sup> under an oxygen atmosphere.

### Syntheses

***N,N*-Bis(phosphonomethyl)aminoacetic acid [ $(H_2O_3PCH_2)_2NCH_2CO_2H$ ,  $H_5L^1$ ].** The diphosphonic acid with a functional carboxylate group was prepared by a Mannich type reaction. Glycine (Aldrich, 7.6 g, 100 mmol) was mixed with hydrochloric acid (EM Science, 17.0 cm<sup>3</sup>), deionized water (17 cm<sup>3</sup>) and phosphorous acid (Aldrich, 32.8 g, 400 mmol). The mixture was allowed to reflux at 120 °C for 1 h, then paraformaldehyde (Aldrich, 9.0 g, 300 mmol) was added in small portions over a period of 1 h, and the mixture was then refluxed for an additional hour. Removal of solvents afforded a white powder, which was dissolved in 10 cm<sup>3</sup> of water and recrystallized by adding 100 cm<sup>3</sup> of acetone, yielding 19.5 g of *N,N*-bis(phosphonomethyl)aminoacetic acid (yield 74.1%). Its purity was confirmed by NMR measurements and elemental analysis.  $^{31}P$  NMR shows only a single peak at 7.968 ppm.  $^1H$  NMR: 4.203 ppm ( $-CH_2CO_2$ , 2H, s), 3.499 ppm ( $-CH_2-PO_3$ , d, 4H,  $J_{H-P} = 12.9$  Hz). Elemental analysis for  $C_4H_{11}NO_8P_2$ : C, 18.33%; H, 4.27%; N, 5.15%; P, 23.38%. Calcd: C, 18.25%; H, 4.18%; N, 5.32% P, 23.57%.

**Preparation of  $Zn_2[O_3PCH_2)_2NHCH_2CO_2]$  (complex **1**) and  $Zn_2[HO_3PCH_2NH(CH_2PO_3)_2]$  (complex **2**).** Both complexes were synthesized by hydrothermal reactions. A mixture of 2.0 mmol of zinc acetate (Fisher Chem.), 1.0 mmol of *N,N*-bis(phosphonomethyl)aminoacetic acid or nitrilotris(methylenephosphonic acid) (Fluka) and 10.0 ml of deionized water was sealed into a bomb equipped with a Teflon liner, and then heated at 180 °C for 5 days. Colorless crystals for complexes **1** and **2** were recovered in ca. 45.6% and 37.3% yields, respectively. Results of the  $^{31}P$  solid state MAS NMR



**Scheme 1** Nitrilotris(methylene phosphonic acid) and its derivatives substituted by one, two and three carboxylate groups.

measurements showed a single peak at 6.871 ppm for complex **1** and a single peak at 6.496 ppm for complex **2**. Elemental analysis for complex **1**,  $C_4H_7Zn_2NO_8P_2$ : C, 12.20%; H, 1.65%; N, 3.48%; P, 15.74%. Calcd: C, 12.31%; H, 1.80%; N, 3.59%; P, 15.91%. Elemental analysis for complex **2**,  $C_3H_8Zn_2NO_9P_3$ : C, 8.33%; H, 1.74%; N, 3.15%; P, 21.96%. Calcd: C, 8.46%; H, 1.88%; N, 3.29%; P, 21.84%.

## Crystallography

Single crystals of complexes **1** and **2** were mounted on a Bruker Smart CCD and reflections collected using MoK $\alpha$  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 s exposure per frame. A hemisphere of data (1271 frames at 5 cm detector distance) was collected by the narrow-frame method with scan widths of  $0.30^\circ$  in  $\omega$  and exposure time of 30 s per frame. The first 50 frames were recollected at 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. An empirical absorption correction based on the  $\Psi$  scan method was also applied.

The space group was determined to be either  $P6_1$  (No. 169) or  $P6_5$  (No. 170) for both complexes **1** and **2**. Both structures were solved using direct methods (SHELXTL) in space group  $P6_1$  (No. 169) and refined by least-square methods with atomic coordinates and anisotropic thermal parameters for non-hydrogen atoms.<sup>17</sup> Absolute structure parameters thus refined are  $-0.04(3)$  and  $0.04(3)$  for complexes **1** and **2**, respectively. Refinements of both structures using space group  $P6_5$  (No. 170) resulted in higher final  $R_1$  values (for observed data, 0.0573 and 0.0784, for complexes **1** and **2**, respectively) and very large absolute structure parameters [0.738(4) and 0.939(4), respectively, for complexes **1** and **2**]. Hence  $P6_1$  (No. 169) was used for all refinements of both structures. All atoms in complex **1** are well behaved. However, disorder problems exist for some atoms in complex **2**. An ordered model gave large thermal parameters for Zn1, O1, O5 and O6, and also a residual of  $3.5 e \text{ \AA}^3$ , which is  $1.50 \text{ \AA}$  from Zn1. The  $R_1$  was about 8.0%. After splitting O1, O5 and O6 atoms into two orientations (O1, O1', O5, O5', O6 and O6') with 50% occupancy for each site, the  $R_1$  value was lowered to 7.5%, but the residual around Zn1 remained as high as before. Careful examination of the environment around the residual peak indicate it also had a tetrahedral geometry. At this point, we realized that the Zn1

atom is disordered and thus has two orientations. A disordered model of the zinc atom (Zn1 and Zn1' at 89.6% and 10.4% occupancies, respectively) resulted in a lower  $R_1$  value (6.56%) and a featureless residual ( $1.246 e \text{ \AA}^3$ ,  $0.56 \text{ \AA}$  from C1). The disordered oxygen atoms, as well as C1 and C2 atoms were refined with isotropic thermal parameters. All hydrogen atoms were generated geometrically, assigned fixed isotropic thermal parameters and included in the structure factor calculations. Some of the data collection and refinement parameters are summarized in Table 2. Important bond lengths and angles for complexes **1** and **2** are listed in Table 1.

CCDC reference numbers 187598 and 187599. See <http://www.rsc.org/suppdata/nj/b2/b2020296n/> for crystallographic data in CIF format or other electronic format.

## Acknowledgements

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**Table 2** Crystal data and structure refinement for complexes **1** and **2**

Complex	<b>1</b>	<b>2</b>
Empirical formula	$C_4H_7Zn_2NO_8P_2$	$C_3H_8Zn_2NO_9P_3$
$M$	389.79	425.75
Crystal system	Hexagonal	Hexagonal
Space group	$P6_1$ (No. 169)	$P6_1$ (No. 169)
$a/\text{\AA}$	8.0677(12)	8.3553(8)
$c/\text{\AA}$	27.283(6)	26.657(4)
$U/\text{\AA}^3$	1537.9(5)	1611.6(3)
$Z$	6	6
$T/\text{K}$	110(2)	110(2)
$\mu(\text{Mo-K}\alpha)/\text{mm}^{-1}$	5.021	4.952
Reflections collected	3597	9968
Independent reflections	1851	2599
$R_{\text{int}}$	0.0764	0.0716
Observed reflections [ $I > 2\sigma(I)$ ]	1380	2599
$R_1^a$	0.0443	0.0656
$wR_2$ [ $I > 2\sigma(I)$ ] <sup>a</sup>	0.0941	0.1132
$R_1$ (all data) <sup>a</sup>	0.0686	0.0918
$wR_2$ (all data) <sup>a</sup>	0.1030	0.1269

<sup>a</sup>  $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ ,  $wR_2 = \{\Sigma w[(F_o)^2 - (F_c)^2]^2 / \Sigma w[(F_o)^2]\}^{1/2}$ .