

## Synthesis and Structural Characterization of a Homologous Series of Divalent-Metal Phosphonates, $M^{II}(O_3PR) \cdot H_2O$ and $M^{II}(HO_3PR)_2$

Guang Cao, Haiwon Lee, Vincent M. Lynch, and Thomas E. Mallouk\*

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Layered phosphonate salts of divalent metal ions (Mg, Mn, Zn, Ca, Cd) are precipitated by combining aqueous solutions of a phosphonic acid and a soluble metal salt. In this way compounds in the series  $M(O_3C_nH_{2n+1}) \cdot H_2O$  ( $M = Mg, Mn, Zn, n = 1-12$ ;  $M = Ca, Cd, n = 1-4$ ),  $M(O_3PC_6H_5) \cdot H_2O$  ( $M = Mg, Mn, Zn$ ),  $Ca(HO_3PC_6H_5)_2$ , and  $Ca(HO_3PC_nH_{2n+1})_2$  ( $n \geq 5$ ) were prepared. These compounds are insoluble in water at pH 7 but dissolve in dilute acid solutions. A preliminary X-ray structure for  $Mn(O_3PC_6H_5) \cdot H_2O$ , refined in the orthorhombic space group  $Pmn2_1$  with  $Z = 2$  and  $a = 5.734$  (5),  $b = 14.33$  (3), and  $c = 4.945$  (4) Å, is reported. The structure consists of layers of Mn atoms coordinated octahedrally by five phosphonate oxygen atoms and one water molecule. Each phosphonate group coordinates four Mn atoms, making a cross-linked Mn-O network. The phenyl groups lie above and below these approximately planar networks and make van der Waals contacts between layers. Compounds in the  $M(O_3PC_nH_{2n+1}) \cdot H_2O$  ( $M = Mg, Mn, Zn$ ) and  $M(O_3PC_6H_5) \cdot H_2O$  ( $M = Mg, Zn$ ) series crystallize in  $Pmn2_1$  with  $a = 5.61-5.74$  and  $c = 4.78-4.82$  Å and with  $b$  varying according to the size of the alkyl or phenyl group. A structural model for these compounds is discussed.

### Introduction

Layered phosphonate salts of transition-metal ions can be prepared via simple precipitation or redox reactions.<sup>1-5</sup> For example, the tetravalent metal salts  $M(O_3PR)_2$  are made by combining aqueous solutions containing  $M^{IV}$  and  $RPO_3H_2$ ,<sup>1-4</sup> and the vanadyl phosphonates  $VO(O_3PR) \cdot 2H_2O$  are made by reducing  $V^V$  with ethanol in the presence of  $RPO_3H_2$ .<sup>5</sup> These compounds are interesting because of their potential utility as sorbents and catalysts and because of the ease with which pillared<sup>4</sup> and intercalated<sup>3,5</sup> structures can be obtained. Recently, we have found that surface-bound multilayer structures, analogous to Langmuir-Blodgett films, can be grown on Si and Au substrates via sequential adsorption of the  $M^{IV}$  and bis(phosphonic acid) components of  $M^{IV}(O_3P-R-PO_3)$  salts.<sup>6</sup> This finding led us to investigate the crystal chemistry and surface adsorption of other metal phosphonate compounds. Since the tetravalent metal phosphonates derive structurally from the zirconium phosphate framework,<sup>7</sup> we were interested particularly in determining whether  $M^{II}(O_3PR) \cdot 3H_2O$  compounds, based on the layered newberyite ( $M^{II}(HOPO_3) \cdot 3H_2O$  ( $M = Mg, Mn$ )) structure,<sup>8</sup> could be prepared. Cunningham et al.<sup>9</sup> had reported the synthesis of divalent phosphonates  $M^{II}(O_3PR) \cdot H_2O$  ( $M = Mg, Mn, Co, Cu, Ni$ ) and deduced from electronic spectra that the metal coordination was approximately octahedral in all. Since it was not readily apparent how octahedral coordination was achieved with this stoichiometry, we prepared alkyl- and arylphosphonates of these and other divalent metal ions and obtained crystallographic data for representative compounds in the series. With  $M = Mg, Mn, Zn, Ca$ , and  $Cd$ , no phosphonate salts with the  $M^{II}-O-P$  framework found in newberyite were obtained; instead, two homologous series  $M^{II}(O_3PR) \cdot H_2O$  ( $M = Mg, Mn, Zn, Ca, Cd$ ) and  $M^{II}(HO_3PR)_2$  ( $M = Ca$ ) were found; a preliminary crystal structure of one member of the first series shows that it contains chelating phosphonate groups that occupy five of the six available metal coordination sites, the sixth being occupied by the water molecule.

### Experimental Section

**Materials and Methods.** Reagents and solvents used were of reagent grade quality and were obtained from commercial sources. Deionized water was purified to a resistivity of 18.3 MΩ cm with a Barnstead Nanopure system and was used in all experiments. Elemental analyses were performed by Atlantic Microlabs, Inc., Atlanta, GA. X-ray powder diffraction patterns were obtained with a Phillips diffractometer using monochromatized  $Cu K\alpha$  radiation.

**Compound Syntheses and Properties.** Alkyl- and arylphosphonate salts of Mg, Mn, Zn, Ca, and Cd were prepared by combining an aqueous solution of the phosphonic acid with a solution of the appropriate metal salt ( $MgSO_4$ ,  $MgCl_2 \cdot 6H_2O$ ,  $MnSO_4 \cdot H_2O$ ,  $ZnCl_2$ ,  $CaCl_2$ , or  $CdCl_2$

$\cdot 2.5H_2O$ ). Typically, one gram of the phosphonic acid was dissolved in 40 mL of water; methanol or ethanol was added in the case of long-chain alkylphosphonic acids in order to obtain clear solutions. One equivalent of the metal salt dissolved in 20 mL of water was added to the stirred phosphonic acid solution, followed by sufficient 0.1 M aqueous NaOH to make the pH 5-6. The phosphonate salts precipitate as poorly crystalline, flocculent solids. The degree of crystallinity is improved by stirring the filtered precipitate in water at 50 °C for several days. Samples prepared in this way were then filtered, washed with water and then ethanol or methanol, and dried in air. Elemental analyses for C and H agreed well with the formulations  $M(O_3PR) \cdot H_2O$  ( $M = Mg, Mn, Zn$ , R = alkyl, phenyl),  $M(O_3PC_nH_{2n+1}) \cdot H_2O$  ( $M = Ca, Cd, n \leq 5$ ), and  $M(HO_3PR)_2$  ( $M = Ca$ , R = phenyl, alkyl with six or more carbon atoms in the chain).

Unlike the tetravalent metal phosphonates  $M(O_3PR)_2$ , which are only sparingly soluble in strong acid solutions,<sup>3,4</sup> the divalent metal phosphonate salts are soluble at low pH. In the Mg series, compounds with short alkyl chains ( $C_1-C_4$ ) are soluble at pH 4-5, and those with longer chains (phenyl,  $C_5-C_{12}$ ) dissolve at pH 1-2. Short-chain ( $C_1-C_4$  and phenyl) compounds in the Ca, Cd, Mn, and Zn series are soluble at pH 2-3, while the  $Ca(HO_3PR)_2$  compounds dissolve only at pH  $\leq 1$ .

**Crystal Growth and X-ray Data Collection.** Single crystals of  $Mn(O_3PC_6H_5) \cdot H_2O$  were grown in an agar-filled glass U-tube. One end of the tube was immersed in 0.1 M  $MnSO_4$  solution, and the other end in a 0.1 M phenylphosphonic acid solution adjusted to pH 2.0 with NaOH. Clusters of colorless platelike single crystals grew near the Mn end of the tube over a period of 5 months. The gel was then cut from the tube and dissolved in warm water. Due to their extreme thinness, most crystals were unsuitable for data collection. After many trial crystals, a crystal of dimensions  $0.04 \times 0.11 \times 0.67$  mm was chosen for data collection. Data were collected on a Syntex P2<sub>1</sub> diffractometer, using  $Mo K\alpha$  radiation ( $\lambda = 0.71069$  Å), with a graphite monochromator and a Syntex LT-1 low-temperature delivery system (163 K). Laue symmetry and systematically absent reflections ( $h0l$  ( $h + l = 2n + 1$ ) and  $00l$  ( $l = 2n$

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\* To whom correspondence should be addressed.

**Table I.** Fractional Coordinates and Isotropic or Equivalent Isotropic<sup>a</sup> Thermal Parameters ( $\text{\AA}^2$ ) for Non-Hydrogen Atoms of  $\text{Mn}(\text{O}_3\text{PC}_6\text{H}_5)\cdot\text{H}_2\text{O}$  Refined in Space Group  $Pmn2_1$ 

atom	x	y	z	U
Mn	0.0	-0.01647 (12)	0.0	0.0149 (6)
P	0.5	-0.1191 (2)	0.0624 (8)	0.0138 (11)
O1	0.5	-0.0999 (6)	-0.238 (2)	0.020 (3)
O2	0.7136 (11)	-0.0778 (4)	0.2082 (12)	0.017 (2)
O3	0.0	-0.1276 (6)	-0.312 (2)	0.021 (3)
C1	0.5	-0.2424 (9)	0.108 (3)	0.021 (3)
C4	0.5	-0.433 (2)	0.173 (5)	0.071 (7)
C2	0.711 (4)	-0.2905 (14)	0.130 (4)	0.036 (5)
C3	0.706 (5)	-0.3899 (15)	0.162 (4)	0.045 (6)
C2A	0.5	-0.284 (3)	0.370 (8)	0.045 (9)
C3A	0.5	-0.378 (2)	0.403 (9)	0.061 (11)
C6A	0.5	-0.299 (3)	-0.132 (9)	0.064 (12)
C5A	0.5	-0.401 (4)	-0.108 (11)	0.09 (2)

<sup>a</sup>For anisotropic atoms, the  $U$  value is  $U_{\text{eq}}$ , calculated as  $U_{\text{eq}} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* A_{ij}$ , where  $A_{ij}$  is the dot product of the  $i$ th and  $j$ th direct space unit cell vectors.

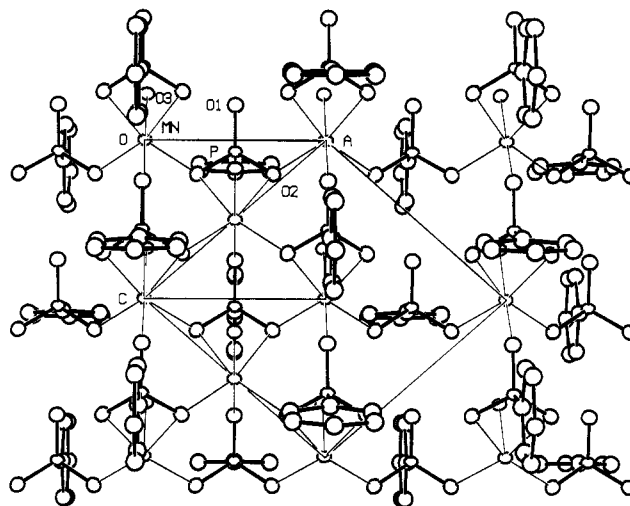
+ 1 absent)) were consistent with space groups  $Pmn2_1$  and  $Pmnm$  (standard setting  $Pmnm$ ). Lattice parameters were obtained from the least-squares refinement of 15 reflections with  $11.2 < 2\theta < 23.6^\circ$ ;  $a = 5.734$  (5),  $b = 14.334$  (26),  $c = 4.945$  (4)  $\text{\AA}$ ;  $V = 406.4$  (9)  $\text{\AA}^3$ ;  $\rho_x = 1.87$   $\text{g cm}^{-3}$  (163 K) for  $Z = 2$ . Data were collected by using the  $\omega$ -scan technique (334 reflections measured),  $2\theta$  range  $4\text{--}45^\circ$ ,  $1^\circ \omega$  scan at  $1\text{--}4^\circ/\text{min}$  ( $h = 0\text{--}6$ ,  $k = 0\text{--}15$ ,  $l = 0\text{--}5$ ). Four reflections ( $011$ ,  $131$ ,  $110$ ,  $010$ ) were remeasured every 196 reflections to monitor instrument and crystal stability. Data were corrected for Lp effects, absorption (based on crystal shape; transmission factor range  $0.8321\text{--}0.9277$ ;  $\mu = 17.23$   $\text{cm}^{-1}$ ), and decay (maximum correction for decay  $< 0.5\%$ ).<sup>10</sup> Data reduction procedures are described by Riley and Davis.<sup>11</sup> Reflections having  $F_o < 6(\sigma(F_o))$  were considered unobserved (21 reflections).

**Structure Solution and Refinement.** Intensity statistics and geometry of the phosphonate group indicated that the correct space group was  $Pmn2_1$  (alternate space group  $Pmnm$  requires P to lie on the position of  $mm$  symmetry). A preliminary structure (vide infra) was solved and refined in space group  $Pmn2_1$ , which requires that Mn, the water molecule, and the phosphonate group lie in the mirror plane. The  $z$  coordinate of Mn was fixed to define the origin during refinement. The Mn position was determined from a Patterson map, and the positions of other non-H atoms were determined from subsequent electron density maps. The structure was refined by full-matrix least-squares procedures<sup>12</sup> with anisotropic thermal parameters for Mn, P, and O atoms. C atoms were refined isotropically. CH type H atoms were calculated and fixed in idealized positions and were refined with isotropic thermal parameters riding at  $1.2U_{\text{iso}}$  of the relevant C atom. The HO3 position was determined from a  $\Delta F$  map and fixed during refinement, with  $U_{\text{iso}}$  fixed at  $1.2U_{\text{eq}}$  of O3. Sixty parameters were refined.  $\sum w(|F_o| - |F_c|)^2$  was minimized, where  $w = 1/(\sigma(F_o))^2$  and  $\sigma(F_o) = 0.5kI^{-1/2}[(\sigma(I))^2 + (0.02I)^2]^{1/2}$ . Intensity,  $I$ , was given by  $(I_{\text{peak}} - I_{\text{bgkd}})/(\text{scan rate})$ ; 0.02 is a factor to downweight intense reflections and to account for instrument instability, and  $k$  is the correction due to Lp effects, absorption, and decay.  $\sigma(I)$  was estimated from counting statistics:  $\sigma(I) = (I_{\text{peak}} + I_{\text{bgkd}})^{1/2}/(\text{scan rate})$ . Final  $R = 0.0364$  for 314 reflections;<sup>13</sup>  $R_w = 0.0429$  (for all reflections,  $R = 0.0394$  and  $R_w = 0.0432$ ); goodness of fit = 2.39. Maximum  $|\Delta/\sigma| < 0.1$  in the final refinement cycle, and the minimum and maximum peaks in the final  $\Delta F$  map were  $-0.60$  and  $0.56$   $\text{e}/\text{\AA}^3$ , respectively, in the region of the disordered phenyl groups. Scattering factors for the non-H atoms were taken from Cromer and Mann,<sup>14</sup> with anomalous-dispersion corrections from Cromer and Liberman,<sup>15</sup> while scattering factors for the H atoms were from Stewart et al.;<sup>16</sup> the linear absorption coefficient was taken from ref 17. The least-squares plane

**Table II.** Bond Lengths ( $\text{\AA}$ ) and Angles (deg) for Non-H Atoms of  $\text{Mn}(\text{O}_3\text{PC}_6\text{H}_5)\cdot\text{H}_2\text{O}$ <sup>a</sup>

1	2	3	1-2	1-2-3
O1 <sup>a</sup>	Mn	O2 <sup>b</sup>	2.113 (7)	91.7 (1)
O1 <sup>a</sup>	Mn	O2 <sup>d</sup>		85.5 (1)
O1 <sup>a</sup>	Mn	O3		173.7 (3)
O2 <sup>b</sup>	Mn	O2 <sup>c</sup>	2.129 (6)	101.0 (2)
O2 <sup>b</sup>	Mn	O2 <sup>d</sup>		97.7 (2)
O2 <sup>b</sup>	Mn	O2 <sup>e</sup>		161.2 (2)
O2 <sup>b</sup>	Mn	O3		92.3 (2)
O2 <sup>c</sup>	Mn	O2 <sup>d</sup>	2.129 (6)	161.2 (2)
O2 <sup>c</sup>	Mn	O2 <sup>e</sup>		97.7 (2)
O2 <sup>c</sup>	Mn	O3		92.3 (2)
O2 <sup>d</sup>	Mn	O2 <sup>e</sup>	2.326 (6)	63.6 (2)
O2 <sup>d</sup>	Mn	O3		89.2 (1)
O2 <sup>e</sup>	Mn	O3	2.326 (6)	89.2 (1)
O3	MN		2.218 (10)	
O1	P	O2	1.510 (11)	113.0 (3)
O2	P	O2 <sup>c</sup>	1.539 (6)	105.4 (4)
O2	P	C1		108.8 (3)
C1	P	O1	1.783 (13)	107.8 (6)
C2	C1	P	1.40 (2)	120.0 (9)
C2	C1	C2 <sup>c</sup>		120 (1)
C3	C2	C1	1.43 (3)	119 (2)
C4	C3	C2	1.33 (3)	119 (2)
C3	C4	C3 <sup>c</sup>	1.33 (3)	124 (2)
C2A	C1	C6A	1.43 (4)	121 (2)
C2A	C1	P		122 (2)
C6A	C1	P	1.44 (5)	117 (2)
C3A	C4	C5A	1.38 (5)	127 (3)
C5A	C4		1.47 (6)	
C3A	C2A	C1	1.36 (5)	122 (3)
C4	C3A	C2A		118 (4)
C5A	C6A	C1	1.47 (7)	120 (4)
C4	C5A	C6A		113 (4)

<sup>a</sup>Symmetry operators: (a)  $0.5 - x, -y, 0.5 + z$ ; (b)  $-1 + x, y, z$ ; (c)  $1 - x, y, z$ ; (d)  $0.5 - x, -y, -0.5 + z$ ; (e)  $-0.5 + x, -y, -0.5 + z$ .



**Figure 1.** Structure of  $\text{Mn}(\text{O}_3\text{PC}_6\text{H}_5)\cdot\text{H}_2\text{O}$  viewed down the  $b$  (stacking) axis. A possible ordered arrangement of the phenyl rings within a single layer is shown. Both the orthorhombic and primitive monoclinic cells are indicated. O, A, and C indicate the origin and unit translations along  $a$  and  $c$  in the orthorhombic cell.

program was supplied by Cordes;<sup>18</sup> other computer programs were from ref 11 of Gadol and Davis.<sup>19</sup>

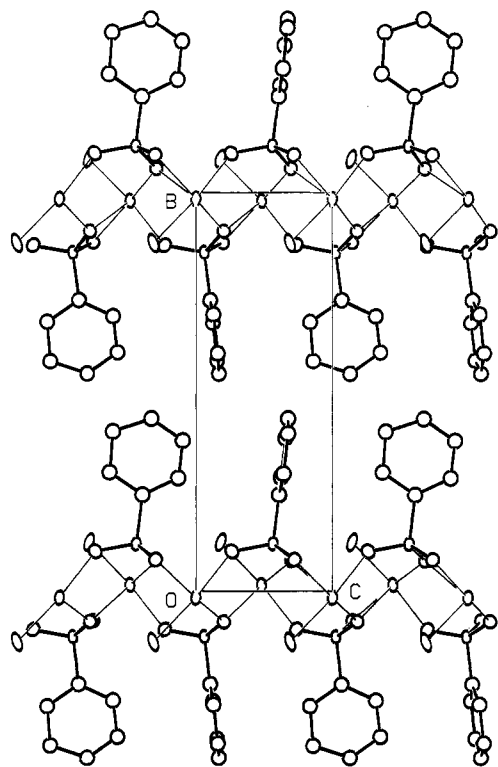
## Results and Discussion

**Preliminary Structure of  $\text{Mn}(\text{O}_3\text{PC}_6\text{H}_5)\cdot\text{H}_2\text{O}$ .** Positional parameters are given in Table I, and selected bond distances and angles are found in Table II. ORTEP views of the structure (Figures 1 and 2) show that it is layered. Polar groups (Mn, phosphonate oxygen, and lattice water) form a two-dimensional

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**Figure 2.** Structure of  $\text{Mn}(\text{O}_3\text{PC}_6\text{H}_5)\cdot\text{H}_2\text{O}$  viewed down the  $a$  axis. A single possible arrangement of the disordered phenyl rings is shown.

network in which the metal atoms are nearly coplanar; the P–C bond and the plane of the phenyl rings are approximately perpendicular to these metal planes, and the phenyl groups make van der Waals contacts between layers. Refinement of the structure in  $Pmn2_1$  showed that the phenyl ring was disordered over two principal orientations. In one orientation the ring was approximately perpendicular to the mirror plane, and in the other orientation the ring lay in the mirror plane (C atoms labeled with an A). The disorder was treated as resulting from a rotation about the P–C bond, and the positions of atoms C1 and C4 were assumed to be unaffected by the disorder. Refinement of the site occupancy factors of the atoms in the two orientations resulted in a site occupancy factor of 0.51 (2) for the atoms lying perpendicular to the mirror plane. Therefore, the two orientations were treated with equal weight in subsequent refinements. Atoms lying in the mirror plane are too close to atoms related by a  $c$  axis translation (contacts C3A...C5A (related by  $x, y, z + 1$ ) and C2A...C6 (related by  $x, y, z + 1$ ) are 2.44 (7) and 2.47 (6) Å, respectively, with H contacts less than 1 Å). Along  $a$ , atoms lying perpendicular to the mirror plane are also too close [contacts C2...C2 (related by  $x + 1, y, z$ ) and C3...C3 (related by  $x + 1, y, z$ ) are 3.32 (3) and 3.38 (4) Å, respectively, with H contacts of 1.59 (3) and 1.66 (4) Å, respectively]. There are no close contacts along  $b$ . Therefore, the disorder cannot occur in a totally random fashion. The orientation of the phenyl rings must alternate in a regular way along both the  $a$  and  $c$  directions within a single layer. However, there are no restrictions along  $b$ . The disorder must occur via stacking disorder or twinning in the  $b$  direction, resulting in the averaged orientation reported here.

The requirement that the phenyl rings be ordered within a given layer suggests that the true unit cell might be doubled along the  $a$  and  $c$  axes. Axial photographs taken along  $a^*$  and  $c^*$  showed a few, very faint diffraction spots (only three additional reflections along  $a^*$  and two along  $c^*$ ) indicating doubling of both axes. These additional reflections also appeared on photographs taken from a second crystal. No superlattice spots along  $b^*$  were observed. Because the positions of the Mn, P, O, C1, and C4 atoms from the  $Pmn2_1$  refinement are well-defined, the symmetry of the new, larger cell can be deduced. If the new cell is taken by simply doubling the  $a$  and  $c$  axes, there is loss of orthorhombic symmetry. The new cell can be  $B$ -centered monoclinic, which means that a

primitive monoclinic cell of half the volume can be obtained. Figure 1 shows the relation of this cell to the orthorhombic  $Pmn2_1$  cell. The monoclinic cell will be pseudo- $B$ -centered in space group  $Pa$  or  $Pc$  and will have two  $\text{Mn}(\text{O}_3\text{PC}_6\text{H}_5)\cdot\text{H}_2\text{O}$  groups per asymmetric unit. Of the two phenyl rings in this asymmetric unit, one must lie approximately in the mirror plane of the orthorhombic cell and the second must lie approximately perpendicular to the first. The choice of space group,  $Pa$  or  $Pc$ , is determined by the orientation of the phenyl rings only, and the direction of the glide is masked by the pseudo- $B$ -centering of the Mn, P, and O atoms.

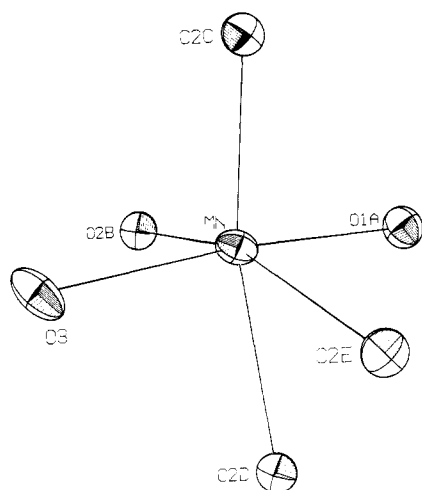
More data were needed to refine the monoclinic model, and a new data set was collected on a second crystal. The new monoclinic cell constants are as follows:  $a = 7.598$  (3),  $b = 14.930$  (5),  $c = 7.606$  (3) Å;  $\beta = 98.64$  (3)°;  $V = 822.1$  (5) Å<sup>3</sup>. A total of 3105 reflections were collected, of which 1554 were of the type  $h + l = 2n + 1$ . These reflections would not have been collected in the original data set. Of these, only 24 reflections were considered observed, with  $I > 3\sigma(I)$ . Refinement was begun by using the refined coordinates of the Mn, P, and O atoms from the orthorhombic refinement and their  $x, y, z + 1$  equivalents. The transformation matrix from orthorhombic to monoclinic coordinates was (0.5, 0, -0.5; 0, -1, 0; 0.5, 0, -0.5). Refinement was attempted in both  $Pa$  and  $Pc$ . Because of the pseudo- $B$ -centering, initial difference electron density maps showed disordered phenyl rings in both space groups. For each space group, two models, corresponding to the two possible orientations of the phenyl rings, were attempted. In neither case was the refinement satisfactory. There was very severe correlation between the two groups in the asymmetric unit with correlation coefficients as high as 0.9 between analogous atoms in the two groups.  $R_w$  for all monoclinic refinements was greater than 7%. Only the Mn atom could be refined anisotropically without resulting in nonpositive definite temperature factors. The bond lengths for the C atoms were widely scattered, ranging from 1.1 to 1.6 Å, and there were large deviations from planarity for the phenyl rings in all monoclinic models. However, if the data were transformed to correspond to the original  $Pmn2_1$  cell by eliminating the 24 observed monoclinic reflections and applying the appropriate transformation matrix, the refinement proceeded to convergence normally. The Mn, P, and O atoms could be refined anisotropically. The phenyl ring is planar, there is little scatter in the C–C bond lengths, and  $R_w = 5\%$ . By all measures, the refinement in space group  $Pmn2_1$  is superior to either ordered model in  $Pa$  or  $Pc$ . While the appearance of the extra diffraction spots indicates a supercell of some sort, the important features of the structure are well refined in the smaller orthorhombic cell. We are currently exploring precession and Weissenberg photographs of this material and considering twinning models, to see if additional insight can be gained into this problem.

Figure 1 shows the bonding of the polar network within a single layer, and a possible ordered arrangement of the phenyl rings. The coordination about the metal atom is a distorted octahedron of oxygen atoms, as shown in Figure 3; five coordination sites are occupied by phosphonate oxygens (O1, O2), and the sixth is occupied by the water oxygen (O3). The phosphonate oxygen atom (O1) lying in the mirror plane bonds to only one Mn atom, making a relatively close contact (2.113 Å) trans to the water oxygen. The other phosphonate oxygens (O2) each bond to two Mn atoms, making slightly longer contacts. One of the cis O–Mn–O angles in the  $\text{MO}_6$  octahedron is small (63.6°) because the two oxygen atoms are bonded to the same phosphorus. All the other cis O–Mn–O angles are in the range 85–101°. This polar Mn–O–P network resembles neither of the analogous networks in newburyite<sup>8</sup> ( $\text{MgO}_3\text{POH}\cdot 3\text{H}_2\text{O}$ ) or zirconium phosphate<sup>7</sup> ( $\text{Zr}(\text{O}_3\text{POH})_2\cdot\text{H}_2\text{O}$ ). In the latter structures each phosphonate oxygen in the network binds only one metal atom. The metal–phosphonate coordination is therefore 3:3 in newburyite and 6:3 in zirconium phosphate; in the  $\text{Mn}(\text{O}_3\text{PC}_6\text{H}_5)\cdot\text{H}_2\text{O}$  structure the coordination is 4:4.

**Structure of the  $\text{M}(\text{O}_3\text{PC}_n\text{H}_{2n+1})\cdot\text{H}_2\text{O}$  Series.** X-ray powder diffraction patterns for compounds in this series show that for  $\text{M} = \text{Mg}, \text{Mn},$  and  $\text{Zn}$  the space group is  $Pmn2_1$  and that the unit

**Table III.** X-ray Powder Diffraction Data for  $\text{Zn}(\text{O}_3\text{PCH}_3)\cdot\text{H}_2\text{O}$  (Orthorhombic;  $a = 5.681$  (3),  $b = 8.733$  (2),  $c = 4.784$  (1) Å)

<i>hkl</i>	$1/d_{\text{calcd}}^2$	$1/d_{\text{obsd}}^2$	$I_{\text{rel}}$	<i>hkl</i>	$1/d_{\text{calcd}}^2$	$1/d_{\text{obsd}}^2$	$I_{\text{rel}}$
010	0.013 11	0.013 24	100	300	0.278 83		
100	0.030 98			141	0.284 45	0.284 72	4.8
001	0.043 69			231	0.285 62		
110	0.044 09	0.044 30	4.7	310	0.291 94		
020	0.052 44	0.052 62	2.0	032	0.292 77	0.292 85	3.5
011	0.056 80	0.056 96	7.2	202	0.298 69	0.298 93	3.0
101	0.074 67	0.074 94	2.4	212	0.311 80	0.311 93	4.5
120	0.083 42			301	0.322 52		
111	0.987 78	0.088 08	13.3	132	0.323 75	0.323 49	3.5
021	0.096 13	0.096 36	4.8	050	0.327 78	0.327 80	3.3
030	0.118 00	0.118 26	1.1	320	0.331 28		
200	0.123 92	0.124 34	10.0	240	0.333 70		
121	0.127 11	0.127 38	25.1	311	0.335 64	0.335 17	4.3
210	0.137 03	0.137 33	4.4	222	0.351 14	0.351 17	3.0
130	0.148 98	0.149 06	0.1	150	0.358 76	0.358 56	4.2
031	0.161 69	0.161 91	55.1	051	0.371 47		
201	0.167 62			321	0.374 97	0.375 13	4.9
002	0.174 77	0.174 80	2.7	241	0.377 40		
220	0.176 37			042	0.384 55	0.384 21	2.6
211	0.180 73	0.181 06	3.6	003	0.393 23		
012	0.187 88	0.188 20	2.5	330	0.396 83	0.396 75	1.1
131	0.192 67	0.192 87	17.7	151	0.402 45		
102	0.205 75			013	0.406 34	0.405 90	1.0
040	0.209 78			142	0.415 53	0.415 43	3.4
112	0.218 86			232	0.416 69		
221	0.220 06	0.220 35	4.6	103	0.424 21	0.423 91	1.8
022	0.227 21	0.227 34	3.1	113	0.437 32	0.437 76	2.4
140	0.240 76	0.241 12	7.4	331	0.440 53	0.440 15	3.5
230	0.241 92			023	0.445 67		
041	0.253 47	0.253 61	1.1	250	0.451 70	0.451 40	4.8
122	0.258 19	0.258 22	8.6	302	0.453 60		

**Figure 3.** Coordination environment of the Mn atom in  $\text{Mn}(\text{O}_3\text{PC}_6\text{H}_5)\cdot\text{H}_2\text{O}$ . 50% probability thermal ellipsoids are shown. Labels A–E refer to symmetry operations designated in Table II.

cell is similar to that of  $\text{Mn}(\text{O}_3\text{PC}_6\text{H}_5)\cdot\text{H}_2\text{O}$ . No extra reflections that would suggest a lower symmetry supercell could be detected by powder diffraction. For  $M = \text{Ca}$  and  $\text{Cd}$  the powder patterns could not be indexed in the orthorhombic system, although the  $\text{Ca}(\text{O}_3\text{PR})\cdot\text{H}_2\text{O}$  and  $\text{Cd}(\text{O}_3\text{PR})\cdot\text{H}_2\text{O}$  patterns resembled each other. Powder patterns from the  $\text{Ca}(\text{HO}_3\text{PR})_2$  series were also complex and were not successfully indexed; it was however possible to determine layer spacings in this series from the progression of layer axis lines.<sup>20</sup> Data from a typical powder pattern, for  $\text{Zn}(\text{O}_3\text{PCH}_3)\cdot\text{H}_2\text{O}$ , are given in Table III. Observed systematic absences are consistent with space group  $Pmn2_1$ , and the  $a$  and  $c$  unit cell dimensions are close to those found for  $\text{Mn}(\text{O}_3\text{PC}_6\text{H}_5)\cdot\text{H}_2\text{O}$ . Unit cell dimensions for related Mg, Mn, and Zn compounds are given in Table IV. Again, these compounds may be indexed in  $Pmn2_1$  with nearly identical  $a$  and  $c$  dimensions.

(20) Cao, G.; Lee, H.; Lynch, V. M.; Mallouk, T. E. *Solid State Ionics*, in press.**Table IV.** Unit Cell Dimensions for  $\text{M}(\text{O}_3\text{PR})\cdot\text{H}_2\text{O}$  Compounds Indexed in Space Group  $Pmn2_1$ 

compd	$a$ , Å	$b$ , Å	$c$ , Å
$\text{Mg}(\text{O}_3\text{PCH}_3)\cdot\text{H}_2\text{O}$	5.68 (1)	8.72 (1)	4.79 (1)
$\text{Mn}(\text{O}_3\text{PC}_2\text{H}_5)\cdot\text{H}_2\text{O}$	5.67 (1)	10.21 (1)	4.78 (1)
$\text{Mg}(\text{O}_3\text{PC}_3\text{H}_7)\cdot\text{H}_2\text{O}$	5.65 (1)	12.28 (3)	4.76 (1)
$\text{Mg}(\text{O}_3\text{PC}_4\text{H}_9)\cdot\text{H}_2\text{O}$	5.67 (2)	15.10 (3)	4.80 (2)
$\text{Mg}(\text{O}_3\text{PC}_5\text{H}_{11})\cdot\text{H}_2\text{O}$	5.67 (2)	17.05 (3)	4.78 (2)
$\text{Mg}(\text{O}_3\text{PC}_6\text{H}_{13})\cdot\text{H}_2\text{O}$	5.66 (2)	19.50 (3)	4.79 (2)
$\text{Mg}(\text{O}_3\text{PC}_7\text{H}_{15})\cdot\text{H}_2\text{O}$	5.74 (10)	21.57 (6)	4.78 (5)
$\text{Mg}(\text{O}_3\text{PC}_8\text{H}_{17})\cdot\text{H}_2\text{O}$		22.94 (6) <sup>a</sup>	
$\text{Mg}(\text{O}_3\text{PC}_9\text{H}_{19})\cdot\text{H}_2\text{O}$		25.35 (6) <sup>a</sup>	
$\text{Mg}(\text{O}_3\text{PC}_{10}\text{H}_{21})\cdot\text{H}_2\text{O}$		27.39 (10) <sup>a</sup>	
$\text{Mg}(\text{O}_3\text{PC}_{11}\text{H}_{23})\cdot\text{H}_2\text{O}$		29.19 (10) <sup>a</sup>	
$\text{Mg}(\text{O}_3\text{PC}_{12}\text{H}_{25})\cdot\text{H}_2\text{O}$		31.04 (10) <sup>a</sup>	
$\text{Mg}(\text{O}_3\text{PC}_6\text{H}_5)\cdot\text{H}_2\text{O}$	5.61 (1)	14.28 (2)	4.82
$\text{Zn}(\text{O}_3\text{PCH}_3)\cdot\text{H}_2\text{O}$	5.68 (1)	8.73 (1)	4.78 (1)
$\text{Zn}(\text{O}_3\text{PC}_2\text{H}_5)\cdot\text{H}_2\text{O}$	5.67 (1)	10.14 (2)	4.79 (1)
$\text{Zn}(\text{O}_3\text{PC}_6\text{H}_5)\cdot\text{H}_2\text{O}$	5.66 (1)	14.45 (2)	4.80 (1)
$\text{Mn}(\text{O}_3\text{PCH}_3)\cdot\text{H}_2\text{O}$	5.82 (1)	8.79 (1)	4.91 (1)
$\text{Mn}(\text{O}_3\text{PC}_6\text{H}_5)\cdot\text{H}_2\text{O}$	5.73 (1)	14.33 (2)	4.95 (1)

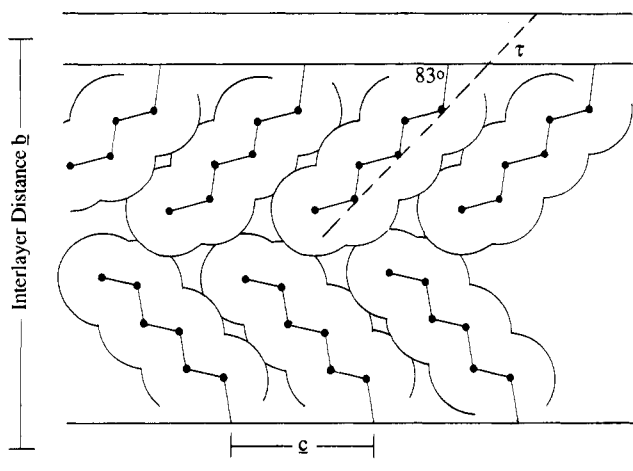
<sup>a</sup> Indexed on the basis of  $0k0$  lines only.

The  $b$  (stacking) axis dimension changes according to the length of the alkyl chain.

It is apparent from the similarity of unit cells that the metal–oxygen–phosphorus–water network in these compounds must be similar to that shown in Figure 1. This observation is consistent with the nearly identical ionic radii of  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Zn}^{2+}$  (0.86, 0.81, and 0.74 Å, respectively<sup>21</sup>). The larger  $\text{Ca}^{2+}$  (1.14 Å) and  $\text{Cd}^{2+}$  (1.09 Å) ions are not accommodated by this structure. Infrared spectra show that the alkyl chains adopt an all-trans configuration in the  $\text{M}(\text{O}_3\text{PR})\cdot\text{H}_2\text{O}$  series.<sup>20</sup> For those compounds crystallizing in  $Pmn2_1$  ( $M = \text{Mg}, \text{Mn}, \text{Zn}$ ), symmetry requires that the carbon atoms in the chains lie in planes perpendicular to the  $a$  axis.

The packing of alkyl chains in the  $\text{Mg}(\text{O}_3\text{PR})\cdot\text{H}_2\text{O}$  series may be inferred from the change in  $b$  axis spacing as more carbon atoms

(21) (a) Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1969**, *B25*, 952. (b) *Ibid.* **1970**, *B26*, 1046.



**Figure 4.** Packing model for alkyl chains in  $M(\text{O}_3\text{PC}_n\text{H}_{2n+1})\cdot\text{H}_2\text{O}$ . The angle between the P-C bond and the  $c$  axis ( $83^\circ$ ) is taken from the  $\text{Mn}(\text{O}_3\text{PC}_6\text{H}_5)\cdot\text{H}_2\text{O}$  structure. The tilt angle  $\tau$  is the angle between the  $c$  axis and the alkyl chain axis.

are added to the chain. From the angle between the P-C bond and the  $ac$  plane in  $\text{Mn}(\text{O}_3\text{PC}_6\text{H}_5)\cdot\text{H}_2\text{O}$  ( $82.7^\circ$ ) and an average C-C-C bond angle<sup>22</sup> of  $111-112^\circ$ , we anticipate an "ideal" tilt angle  $\tau$ , the angle between the chain axis and the  $ac$  plane, of approximately  $49^\circ$ . From the C-C single bond distance ( $1.53 \text{ \AA}$ ) we calculate an average increase in  $b$  of  $1.91 \text{ \AA}$  per carbon atom added to the chain. Experimentally, we observe in the Mg series  $\Delta b/\Delta n = 1.78 \text{ \AA}$  for  $\text{C}_1-\text{C}_3$  and  $1.99 \text{ \AA}$  for  $\text{C}_4-\text{C}_{12}$ , implying tilt angles of  $45$  and  $52^\circ$ , respectively. That the tilt angle is smaller for  $\text{C}_1-\text{C}_3$  than for  $\text{C}_4-\text{C}_{12}$  follows from a packing model shown

(22) (a) Wyckoff, R. W. G. *Crystal Structures*; Wiley-Interscience: New York, 1966; Vol. 5, pp 589-612. (b) Kitaigorodskii, A. I. *Molecular Crystals and Molecules*; Academic: New York, 1973; pp 48-62.

in Figure 4. The  $n$ th carbon atom in a given chain makes closest contact with the  $n+3$  carbon in a neighboring chain (related by a  $c$  axis translation). For  $\text{C}_1-\text{C}_3$  there is no  $n+3$  carbon, and the smaller tilt angle allows more efficient packing of the alkyl groups.

For  $\text{C}_{\geq 4}$ , the avoided  $n, n+3$  contacts cause the tilt angle to increase. Even with the higher tilt angle, unreasonably close ( $<3.0 \text{ \AA}$ )  $\text{C}_n, \text{C}_{n+3}$  contacts are calculated if all carbon atoms are forced to lie in the mirror ( $bc$ ) planes. There is, however, sufficient room in the structure for the chains to twist out of these planes via rotation about P-C and C-C bonds: the chain width<sup>22</sup> perpendicular to the  $bc$  plane is ca.  $4.0 \text{ \AA}$ , but the  $a$  axis spacing (the separation distance between chains) is  $5.7 \text{ \AA}$ . It is reasonable that the chains might twist alternately above and below the mirror planes, while maintaining an approximately all-trans configuration, as shown in Figure 4. Calculations of alkyl chain density<sup>23</sup> for  $\text{Mg}(\text{O}_3\text{PR})\cdot\text{H}_2\text{O}$  give an average value of  $0.85 \text{ g/cm}^3$ . This is comparable to the densities of crystalline  $n$ -alkanes, e.g.  $\text{CH}_3(\text{C}-\text{H}_2)_{16}\text{CH}_3$  ( $0.78 \text{ g/cm}^3$ ),  $\text{CH}_3(\text{CH}_2)_{20}\text{CH}_3$  ( $0.79 \text{ g/cm}^3$ ), and  $\text{CH}_3(\text{CH}_2)_{34}\text{CH}_3$  ( $0.96 \text{ g/cm}^3$ ), and suggests that the chains are packed reasonably efficiently despite the long ( $5.7 \text{ \AA}$ ) separation distance between them along the  $a$  axis.

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**Supplementary Material Available:** For  $\text{Mn}(\text{O}_3\text{PC}_6\text{H}_5)\cdot\text{H}_2\text{O}$  refined in space group  $Pmn2_1$ , listings of anisotropic thermal parameters, hydrogen coordinates, and hydrogen bond angles and distances (Supplementary Tables I-IV) (2 pages); a listing of observed and calculated structure factor amplitudes (Supplementary Table V) (2 pages). Ordering information is given on any current masthead page.

(23) The average chain density of the  $\text{C}_1-\text{C}_{12}$  compounds in the  $\text{Mg}(\text{O}_3\text{PR})\cdot\text{H}_2\text{O}$  series is calculated as

$$\rho = [2M_r(\text{C}_{11}\text{H}_{22})]/[6.022 \times 10^{23}ac(b_{\text{C}_{12}} - b_{\text{C}_1})]$$

Contribution from the Instituto de Ciencia de Materiales CSIC, Serrano 115 dpdo, 28006 Madrid, Spain

## Proton-Sodium Exchange in Magadiite. Spectroscopic Study (NMR, IR) of the Evolution of Interlayer OH Groups

J. M. Rojo,\* E. Ruiz-Hitzky, and J. Sanz

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The formation process of the layered silicic acid H-magadiite, obtained after hydrochloric acid treatment of magadiite, has been studied by IR and ( $^1\text{H}$  and  $^{23}\text{Na}$ ) NMR spectroscopies combined with X-ray diffraction, chemical, and thermogravimetric analyses. This study shows that magadiite is a hydrogen silicate of layer structure, in which the negative charge of the layers is compensated by sodium ions or by protons ( $\text{Si}-\text{O}^-\text{Na}^+/\text{Si}-\text{OH}$  ratio  $\sim 2/3$ ). The progressive exchange of sodium ions by protons decreases the average H-H distance between OH groups from  $\sim 4 \text{ \AA}$  in magadiite to  $\sim 2.5 \text{ \AA}$  in H-magadiite. When all the sodium ions have been exchanged, the silicic structure collapses as a consequence of the establishment of hydrogen bonds between adjacent layers. These interactions prevent the interlayer water adsorption in H-magadiite.

### Introduction

The mineral magadiite, first described by Eugster<sup>1</sup> as a sodium layered silicate, is available as a powder with an average particle size of  $1-2 \text{ \mu m}$  and can be easily synthesized under hydrothermal conditions.<sup>2,3</sup> By acid treatment, sodium ions are exchanged by protons, yielding the layered silicic acid called H-magadiite in a topotactic process. Although the crystalline structures of both magadiite and H-magadiite are unknown at the present,  $^{29}\text{Si}$  NMR spectroscopy has allowed us to identify two types of  $\text{SiO}_4$  tet-

rahedra:<sup>4,5</sup> those within the layers sharing four oxygens with neighboring  $\text{SiO}_4$  tetrahedra and those located at the interlamellar surface that share three oxygens with other tetrahedra and bear one OH group. Silanol groups in H-magadiite have been characterized by IR and  $^1\text{H}$  NMR spectroscopies, showing two types of OH groups: those that are involved in relatively strong hydrogen bonds between adjacent layers and those more free, probably pointing to holes of the next layers.<sup>6</sup> The two types of OH groups

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