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RAPID COMMUNICATION

Isolation of a Zinc Phosphate Primary Building Unit, $[C_6N_2H_{18}]^{2+}[Zn(HPO_4)(H_2PO_4)_2]^{2-}$, and Its Transformation to an Open-Framework Phosphate, $[C_6N_2H_{18}]^{2+}[Zn_3(H_2O)_4(HPO_4)_4]^{2-}$

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A 4-membered ring zinc phosphate monomer, I, $[C_6N_2H_{18}]^{2+}[Zn(HPO_4)(H_2PO_4)_2]^{2-}$, has been isolated by the reaction of the Zn^{2+} with the amine, *N,N,N′,N′*-tetramethylethylenediamine (TMED) and H_3PO_4 at room temperature over an extended period of time. It could also be prepared by the reaction of the amine phosphate, $[C_6N_2H_{18}][HPO_4]$ $2H_2O$, with Zn^{2+} in the temperature range 30–80°C. The phosphate monomer consists of a network of ZnO_4, $PO_2(OH)_2$, and $PO_3(OH)$ tetrahedral units linked by their vertices, forming isolated 4-membered rings that are held by hydrogen bond interactions. Interestingly, I, on mild heating, transform into a layered structure, II, $[C_6N_2H_{18}]^{2+}[Zn_3(H_2O)_4(HPO_4)_4]^{2-}$. The structure of II consists of a network of ZnO_4, $ZnO_2(H_2O)_4$, and $PO_3(OH)$ moieties sharing the vertices, forming a layered architecture. The formation of a layered structure from the 4-membered ring monomer suggests that the 4-membered ring is likely to be the primary building unit of the open-framework phosphates. © 2000 Academic Press

INTRODUCTION

A myriad of open-framework metal phosphates possessing chain, ladder, and 3-dimensional structures have been prepared in recent years, with the broad objective of obtaining novel porous materials (1). These materials are generally produced hydrothermally in the presence of organic amines. A crucial aspect of open-framework metal phosphates that is yet to be understood relates to the pathway involved in the evolution of structures of different degrees of complexity. In the case of aluminophosphates (2), it has been proposed that a linear-chain precursor transforms to a ladder-type structure, followed by layer and 3-dimensional structures. The chain and ladder structures themselves contain 4-membered metal phosphate rings, which clearly constitute the fundamental building unit of these open-framework structures. It is believed that the 4-membered rings can readily transform to 6, 8, and other higher membered rings commonly found in layer and 3-dimensional structures (3). It is therefore of vital importance to isolate a monomeric 4-membered ring metal phosphate, and to examine whether it transforms to an open-framework structure under relatively mild conditions. With this objective in mind, we carried out the reaction of zinc ions with phosphoric acid in the presence of an organic amine, *N,N,N′,N′*-tetramethylethylenediamine (TMED), at room temperature over an extended period of time. Such a room temperature reaction yielded a monomeric zinc phosphate, **I**, of the composition $[C_6N_2H_{18}]^{2+}[Zn(HPO_4)(H_2PO_4)_2]^{2-}$. We have explored ways of preparing the zinc phosphate monomer, **I**, on a laboratory time scale and found that it could be obtained quantitatively by the reaction of the phosphate of TMED with zinc ions at room temperature. More interestingly, **I** transforms to a layered open-framework structure, **II**, $[C_6N_2H_{18}]^{2+}[Zn_3(H_2O)_4(HPO_4)_4]^{2-}$ on mild heating. To our knowledge, this is the first observation of a transformation of a plausible primary building unit to a complex open-framework phosphate.

EXPERIMENTAL

Compound **I** was synthesized by two different methods. In the first method, the direct reaction involving the amine, phosphoric acid, and the zinc salt was employed, and in the other, the reaction between the Zn^{2+} ions and the amine phosphate (TMED-P) was used; both reactions occurred at room temperature. TMED-phosphate, $[C_6N_2H_{18}]$ $[HPO_4]2H_2O$, was synthesized by the reaction between

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a methanolic solution of 85% H_3PO_4 (12 mM of H_3PO_4 in 50 mM of MeOH) and 10 mM of TMED. The mixture was warmed at 50°C for a few minutes and left to crystallize at room temperature. Colorless crystals of the 1:1 amine phosphate of composition $(TMEDH_2)^{2+}(HPO_4)^{2-}$ were obtained in quantitative yields. The crystals, thus obtained, were characterized using single crystal X-ray diffraction.

In a typical synthesis of **I**, 10 mM of $ZnSO_4{\cdot}7H_2O$ was added to a mixture of 40 mM of water and 20 mM of 85% H_3PO_4 in a polypropylene bottle. TMED (10 mM) was added to the above under continuous stirring. The homogenized mixture was allowed to crystallize at room temperature. After several months, crystals of **I** were found in the bottle, which were filtered and dried. The product consisted entirely of **I**. In order to synthesize **I** on a laboratory time scale, the reaction of the amine phosphate and Zn^{2+} ions was carried out at room temperature. A mixture of 1 mM of $ZnSO_4{\cdot}7H_2O$, dissolved in 10 mM of H_2O and 2 mM of TMED-P, was stirred to obtain a homogeneous gel. The gel was, again, left to crystallize at room temperature. Colorless crystals of **I** were obtained within a week (yield ~60%).

The synthesis of zinc phosphate, **II**, was carried out by heating 25 mM of the dried crystals of **I** in 10 mM of water at 50°C for 2 days in a PTFE-lined stainless steel autoclave. The resultant plate-like single crystalline product was filtered, washed with water, and dried at room temperature. Initial characterization of both **I** and **II** was carried out using powder X-ray diffraction (XRD), thermogravimetric analysis (TGA), and EDAX. The powder XRD pattern is entirely consistent with the structure determined by single crystal X-ray diffraction. The powder XRD data for **I** are listed in Table 1.

A suitable colorless plate-like single crystal of each compound was carefully selected under a polarizing microscope and glued to a thin glass fiber with cyanoacrylate (superglue) adhesive. A crystal structure determination by X-ray diffraction (Mo*K*α) was performed on a Siemens Smart-CCD diffractometer. A hemisphere of intensity data were collected at room temperature in 1321 frames, with ω scans (width of 0.30° and exposure time of 10 s per frame). Crystal data for **I**: $[C_6N_2H_{18}]^{2+}[Zn(H_2PO_4)_2(HPO_4)]^{2-}$; $M = 473.37$; space group, $P(-1)$ (#2); $a = 8.627(2)$, $b = 8.894(9)$, $c = 12.674(2)$ Å, $\alpha = 88.94(3)$, $\beta = 75.17(0)$, $\gamma = 63.06(5)^\circ$; $V = 832.8(2)$ Å^3; $Z = 2$; $\rho_{\text{calc}} = 2.223$ g cm^{-3}; $\mu(\text{Mo}K\alpha) = 6.085$ mm^{-1}. Crystal data for **II**: $[C_6N_2H_{18}]^{2+}[Zn_3(H_2O)_4(HPO_4)_4]^{2-}$; $M = 770.11$; space group, $P2_1/c$ (#14); $a = 8.953(9)$, $b = 9.712(9)$, $c = 13.533(7)$ Å, $\beta = 95.98(6)^\circ$; $V = 1170.5(9)$ Å^3; $Z = 4$; $\rho_{\text{calc}} = 2.175$ g cm^{-3}; $\mu(\text{Mo}K\alpha) = 5.952$ mm^{-1}. For **I**, a total of 3555 total reflections were collected, and these were merged to give 2369 unique reflections ($R_{\text{merg}} = 0.05$) of which 2346 were considered to be observed with $I > 2\sigma(I)$. For **II**, a total of 4801 reflections were collected; these were merged to give 1679 unique reflections ($R_{\text{merg}} = 0.04$), of which 1343 were considered to be observed with $I > 2\sigma(I)$.

TABLE 1
Powder X-Ray Diffraction Pattern of I, $[C_6N_2H_{18}]^{2+}[Zn(H_2PO_4)_2(HPO_4)]^{2-}$

h	k	l	d_{obs}	d_{calc}	Δd	I_{rel}
0	0	1	12.181	12.187	−0.006	36.5
0	1	0	7.880	7.883	−0.003	94.6
1	0	0	7.391	7.392	−0.001	22.9
1	0	1	7.285	7.279	0.006	28.6
0	1	−1	6.991	6.990	0.001	7.7
1	1	1	6.838	6.839	−0.001	100.0
0	1	1	6.299	6.301	−0.002	10.1
0	0	2	6.088	6.093	−0.005	14.7
1	1	−1	5.872	5.873	−0.001	21.0
1	0	2	5.511	5.512	−0.001	10.1
1	−1	0	4.458	4.457	0.001	17.8
1	2	0	4.441	4.438	0.003	38.9
1	1	−2	4.341	4.344	−0.003	21.7
2	1	1	4.294	4.296	−0.002	9.3
1	2	1	4.221	4.223	−0.002	8.7
2	1	0	4.174	4.174	−0.000	9.4
1	0	−2	4.169	4.168	0.001	10.4
1	−1	−1	3.902	3.905	−0.003	8.1
0	2	−1	3.878	3.881	−0.003	43.6
1	1	3	3.845	3.845	0.000	70.6
0	1	−3	3.790	3.790	0.000	54.6
2	2	1	3.697	3.703	−0.006	40.9
2	0	0	3.697	3.696	0.001	46.3
2	2	0	3.678	3.681	−0.003	8.1
1	2	2	3.655	3.656	−0.001	17.1
2	0	2	3.637	3.639	−0.002	24.3
0	2	1	3.633	3.632	0.001	14.3
0	1	3	3.461	3.455	0.006	34.1
2	2	2	3.419	3.420	−0.001	9.2
1	1	−3	3.328	3.325	0.003	8.4
2	0	−1	3.305	3.292	0.013	15.4
0	2	−3	3.003	3.004	−0.001	24.6
2	−1	1	2.979	2.972	0.007	7.6
1	3	0	2.945	2.945	0.000	9.8
2	−1	0	2.873	2.872	0.001	8.8
3	1	1	2.845	2.845	0.000	14.3
2	3	1	2.842	2.842	0.000	9.5
1	−1	4	2.840	2.840	0.000	7.1
2	0	−2	2.830	2.831	−0.001	9.1
3	2	2	2.746	2.744	0.002	21.8
0	3	−1	2.632	2.631	0.001	7.5
2	1	−3	2.600	2.600	0.000	8.0
1	0	−4	2.580	2.576	0.004	7.4
0	2	−4	2.555	2.555	0.000	7.5
1	0	5	2.534	2.533	0.001	7.1
1	3	−3	2.404	2.403	0.001	8.5
2	4	−1	2.165	2.168	−0.003	8.0
0	4	0	1.971	1.971	0.000	9.8

Note. Refined lattice parameters (Cu*K*α): $a = 8.634(2)$, $b = 8.904(1)$, $c = 12.687(3)$ Å, $\alpha = 88.95(1)$, $\beta = 75.19(1)$, $\gamma = 63.01(2)^\circ$.

The crystal structure was determined by direct methods using SHELXS-86 (4) and difference Fourier syntheses. All the hydrogen positions were initially located in the difference map; for the final refinement the hydrogen atoms were placed geometrically and held in the riding mode. The last cycles of refinement included atomic positions for all the nonhydrogen atoms and isotropic thermal parameters for all the hydrogen atoms. Full-matrix least-squares refinement against $|F^2|$ was carried out using the SHELXTL-PLUS (5) suite of programs. The final Fourier maximum and minimum were 1.000 and -1.427 eÅ^{-3} for **I** and 0.561 and -0.799 eÅ^{-3} for **II**. The final R values, $R_1 = 0.05$, w$R_2 = 0.13$, and $S = 1.09$ for **I** and $R_1 = 0.03$, w$R_2 = 0.09$, and $S = 1.10$ for **II**, were obtained for 218 and 177 parameters, respectively.

RESULTS AND DISCUSSION

The final atomic coordinates of **I** are listed in Table 2. The asymmetric unit of **I** consists of 23 nonhydrogen atoms and is presented in Fig. 1a. There are three crystallographically independent phosphorus and a single zinc atom in the asymmetric unit. The Zn atoms are tetrahedrally coordinated with respect to oxygen with average Zn–O bond distances of 1.950 Å and O–Zn–O angles of 100.4°. The zinc atoms are connected to three distinct P atoms via Zn–O–P links, with average bond angles of 133.6°. Of the three independent P atoms, P(1) and P(3) are connected to Zn atoms via one P–O–Zn linkage and have three terminal P–O bonds, and P(2) is connected to Zn via two P–O–Zn linkages with two terminal P–O bonds. The average P–O distances of 1.536, 1.539, and 1.542 Å were obtained for P(1), P(2), and P(3), respectively. The P–O distances in the region of $\sim$1.561–1.588 Å are formally P–O(H) groups. The P–O distances with values in the range 1.506–1.531 Å are typically P=O bonds. This assignment is also consistent with the bond valence sum calculations (6). The structure of **I** consists of 4-membered rings formed by ZnO_4 and $PO_2(OH)_2$ tetrahedra. The $PO_3(OH)$ and $PO_2(OH)_2$ moieties hang from the Zn center, as shown in Fig. 1a, and are stabilized by extensive intra-molecular multi-point hydrogen bonding involving the phosphate units as well as the doubly protonated amine molecule, forming a sheet-like structure (Fig. 1b). To our knowledge, this is the first time such a structure has been isolated for a zinc phosphate material.

Compound **II** was obtained from **I** by heating the zinc phosphate monomer in water at 50°C for 2 days. The final atomic coordinates for **II** are presented in Table 3. The asymmetric unit consists of 35 nonhydrogen atoms, out of which 27 belong to the framework and 8 belong to the guest species. There are two crystallographically independent

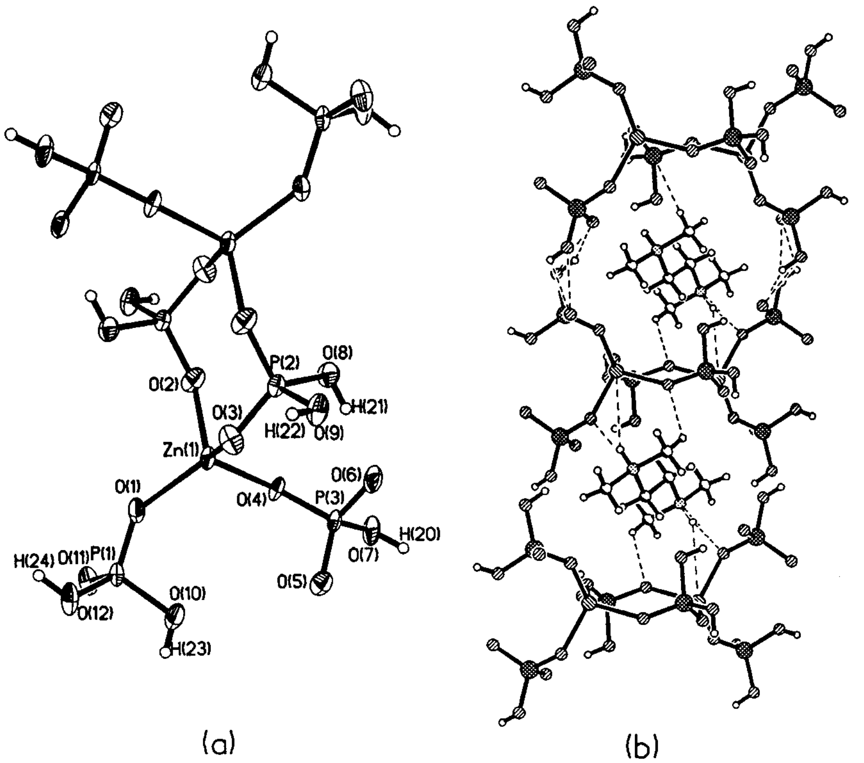

FIG. 1. (a) ORTEP plot of the structure of the 4-membered zinc phosphate monomer, **I**. Notice the HPO_4 and H_2PO_4 units hanging from the Zn center. Thermal ellipsoids are given at 50% probability. The asymmetric unit is labeled. (b) Hydrogen bonded assembly of the monomer and the amine. The sheet-like architecture has cavities where the amine molecules reside. Dotted lines represent hydrogen-bond interactions.

TABLE 2
Atomic Coordinates [×10^4] and Equivalent Isotropic Displacement Parameters [Å×10^3] for I, [$C_6N_2H_{18}$][$Zn(H_2PO_4)$ (HPO_4)]

Atom	*x*	*Y*	*z*	*U*(eq)[a]
Zn(1)	2567(1)	5192(1)	1537(1)	19(1)
P(1)	−1415(1)	7714(1)	3123(1)	19(1)
P(2)	6452(2)	4817(1)	1094(1)	17(1)
P(3)	3867(2)	2229(1)	3013(1)	18(1)
O(1)	198(4)	7054(4)	2141(3)	32(1)
O(2)	2999(5)	4569(4)	−14(3)	29(1)
O(3)	4455(4)	5760(4)	1685(3)	28(1)
O(4)	2871(4)	3046(4)	2141(3)	22(1)
O(5)	2969(4)	3315(4)	4105(3)	26(1)
O(6)	5871(4)	1784(4)	2590(3)	28(1)
O(7)	3750(4)	500(4)	3134(3)	28(1)
O(8)	7076(4)	2869(4)	880(3)	24(1)
O(9)	7568(4)	4910(4)	1869(3)	28(1)
O(10)	−800(5)	6667(4)	4073(3)	32(1)
O(11)	−3060(4)	7686(4)	2924(3)	27(1)
O(12)	−1919(5)	9582(4)	3525(3)	30(1)
N(1)	2549(5)	6377(5)	4968(3)	28(1)
C(1)	4122(8)	5456(8)	5461(5)	42(1)
C(2)	2623(9)	7677(8)	4236(5)	43(1)
C(3)	911(8)	7174(7)	5938(5)	40(1)
N(2)	12485(5)	896(5)	736(3)	24(1)
C(4)	14418(6)	−394(6)	315(4)	25(1)
C(5)	11428(7)	101(7)	1433(4)	34(1)
C(6)	11631(7)	1698(7)	−162(5)	35(1)

[a] *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

phosphorus and zinc atoms present in the asymmetric unit. Of the two crystallographically distinct Zn atoms, one is in tetrahedral environment [Zn(1)] and the other is octahedral [Zn(2)] with respect to oxygen atoms, with an average bond distance of 2.028 Å. Zn(2), which is octahedrally coordinated, occupies a special position with a site occupancy of 0.5. Zn(1) engages in four Zn–O–P linkages with nearest P neighbors and Zn(2) engages in only two Zn–O–P linkages, resulting in an average Zn–O–P bond angle of 128.1°. The remaining Zn–O linkages in the case of Zn(2) are terminal Zn–O linkages and are found to be water molecules. Such terminal water-coordinated-to-Zn centers are known to occur in zinc phosphates (7). It is to be noted, however, that an octahedral environment for Zn in framework phosphates is rather rare. Of the two phosphorus atoms, P(1) provides three P–O–Zn linkages with one terminal P–O bond, and P(2) provides two P–O–Zn linkages with two P–O terminal bonds. The average P–O bond distance is 1.535 Å for both P(1) and P(2). The terminal P–O

TABLE 3
Atomic Coordinates [×10^4] and Equivalent Isotropic Displacement Parameters [Å×10^3] for II, [$C_6N_2H_{18}$][$Zn_3(H_2O)_4$ $(HPO_4)_4$]

Atom	*x*	*Y*	*z*	*U*(eq)[a]
Zn(1)	400(1)	956(1)	6262(1)	22(1)
Zn(2)	0	5000	5000	22(1)
P(1)	525(1)	3724(1)	7276(1)	22(1)
P(2)	−2674(1)	204(1)	5053(1)	20(1)
O(1)	330(4)	−842(3)	6863(3)	31(1)
O(2)	858(4)	2187(3)	7388(2)	31(1)
O(3)	−1420(3)	1224(3)	5356(2)	24(1)
O(4)	2102(4)	1055(3)	5472(2)	28(1)
O(5)	−282(4)	4043(3)	6267(2)	32(1)
O(6)	1846(5)	6225(4)	5595(4)	34(1)
O(7)	−1552(4)	6519(4)	5556(3)	30(1)
O(8)	2053(4)	4554(4)	7330(2)	33(1)
O(9)	−3495(3)	−253(3)	5927(2)	27(1)
O(10)	−3776(4)	1049(3)	4306(2)	29(1)
N(1)	−3850(5)	4560(5)	6235(3)	35(1)
C(2)	−4229(7)	5724(6)	6883(4)	46(2)
C(3)	−3727(7)	3256(6)	6821(5)	52(2)
C(1)	−4981(6)	4386(6)	5346(4)	38(1)

[a] *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

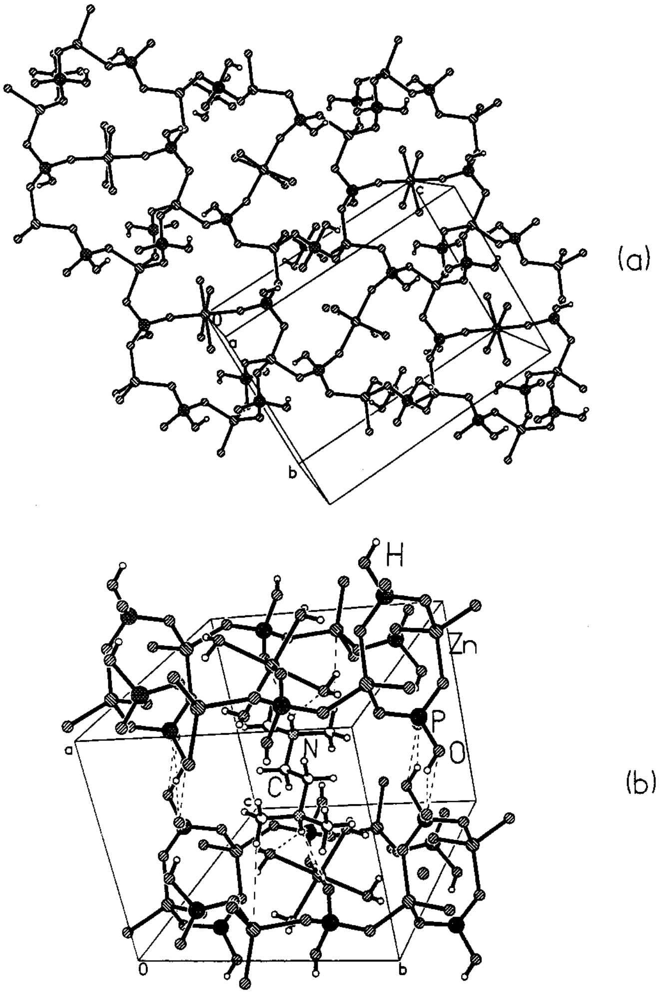

FIG. 2. (a) A single layer of **II**. Note that the octahedral Zn connects two phosphate units form the bifurcated 8-membered aperture. (b) Structure of the layered open-framework zinc phosphate, **II**, showing two layers with the amine in between. Hydrogens on the amine are omitted for clarity. The dotted lines represent inter-layer hydrogen bond interactions.

distances of 1.583 Å [P(1)–O(8)] and 1.569 Å [P(2)–O(10)] are formally –OH linkages. The O–P–O bond angles are in the expected range (ave. 109.4°). Bond valence sum calculations also agree with the above assignment (6). The structure of **II** comprises a network of $Zn(1)O_4$, $Zn(2)O_2(H_2O)_4$, and $PO_3(OH)$ moieties, in which the vertices are shared. The connectivity between these units gives rise to macroanionic layers, with bifurcated 8-membered apertures within each layer, as shown in Fig. 2a. Zn(2) links only with P(1) and the remaining Zn(2)–O linkages are terminal water molecules which point into the 8-membered aperture within the layers. As typical of layered structures, the charge compensating cationic amine molecules are situated in between the anionic inorganic layers, as shown in Fig. 2b. The doubly protonated amine molecule interacts with the framework via multi-point hydrogen bonding and is partly responsible for the observation of such an architecture.

The structures of **I** and **II** reveal that they are somewhat related. It is conceivable that a building unit of the type **I** can give rise to many framework architectures, although we have observed only one in the present study. In Fig. 3, we schematically show a plausible pathway of the transformations of **I** to open-framework structures. Thus, **I** (shown as 1 in Fig. 3) can assemble and transform into a corner-shared

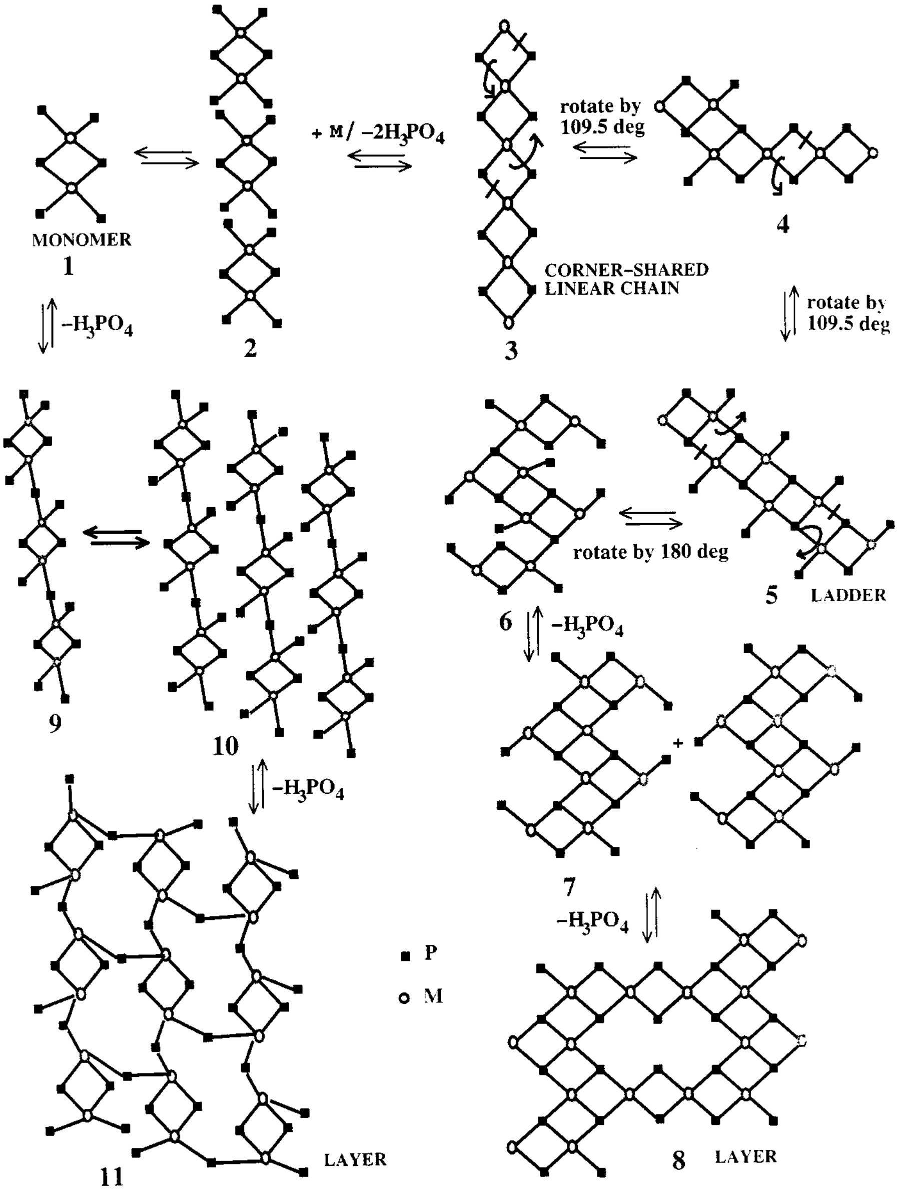

FIG. 3. A schematic reaction pathway showing the primary building unit **I** consisting of the 4-membered ring zinc phosphate monomer, 1 can transform into chain, 3, ladder, 5, and layer (8 and 11) structures. Note that **II** can be obtained by the reaction between 11 and Zn^{2+} ions.

linear chain, 3, via encapsulation of a metal ion between the hanging phosphate groups of two monomeric units, followed by condensation. The corner-shared chain can easily get converted into an edge-shared ladder, 5, by acid hydrolysis of the Zn–O–P bond, followed by a bond rotation, which can subsequently form the layer, 8. The formation of **II** can be visualized from **I** by the loss of a phosphate from 1 to form 9, which, after losing another phosphate, can condense to form a layered structure, 11 (via 10). The layers further react with Zn^{2+} ions and add on a $ZnO_2(H_2O_4)$ unit to yield **II**. This mechanism can be written as follows:

$$2[Zn(HPO_4)(H_2PO_4)_2] \xrightarrow{-H_2PO_4} [Zn_2(HPO_4)_2(H_2PO_4)_3] \xrightarrow[+Zn]{-H_2PO_4} [Zn_3(HPO_4)_4].$$

From the above, it is clear that the monomer containing the 4-membered ring is likely to be the primary building block of open-framework metal phosphates. The formation of **II** may require free Zn^{2+} ions in solution; it is possible that they are produced during the reaction by the dissociation of **I** (1). We propose to investigate the transformation of **I** to various types of open-framework structures by carrying out reactions under different conditions.

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