Hydrothermal Synthesis of a Layered Zinc Molybdenum Phosphate with Octahedral and Tetrahedral Zinc: Structure of $(TMA)_2(H_3O)_2[Zn_3Mo_{12}O_{30}(HPO_4)_2(H_2PO_4)_6]\cdot11.5H_2O$

Linda A. Mundi[†] **and Robert C. Haushalter**[*,†]

Exxon Research and Engineering Company, Annandale, New Jersey 08801

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The reaction of Na_2MoO_4, Mo, ZnO, $(CH_3)_4NOH$ (=TMA(OH)), H_3PO_4, and H_2O in a mole ratio of 2:1:1:7:18:500 for 6 days at 200 °C gives a ca. 70% yield of the new layered zinc molybdenum phosphate $(TMA)_2(H_3O)_2[Zn_3Mo_{12}O_{30}(HPO_4)_2(H_2PO_4)_6]\cdot11.5H_2O$ (**1**). Orange crystals of **1** are monoclinic, space group $C2/m$, with a = 24.908 (9) Å, b = 13.036 (8) Å, c = 13.402 (4) Å, β = 98.83 (3)°, V = 4300 (3) Å^3, and R (R_w) = 0.069 (0.077) at 23 °C. The layers are built up from two $Mo_6O_{15}(HPO_4)(H_2PO_4)_3$ rings dimerized about an octahedral Zn atom and connected to other similar dimers by a tetrahedral Zn. The layers are held together via a complicated hydrogen-bonded network involving water molecules and terminal P–OH groups. The TMA cations are not located between the layers but rather are nestled into voids within the layers.

Recent synthetic and structural work has shown that inorganic oxides with very complicated structures are capable of existence. Examples include materials prepared at high temperatures, such as the superconducting cuprates with several different cations, and those formed at lower temperatures, like zeolites,[1] aluminophosphates,[2] and many minerals. Surprisingly complex structures exist in the mineral world. The 14.2-Å tunnel found in the iron aluminum phosphate cacoxenite[3] is the largest pore known in a crystalline solid-state material. The oxygen atoms in the framework of the molybdenum arsenate mineral betpaktalite[4] occupy only 46% of the available volume, but the remaining oxygens are still centered nearly exactly at the positions predicted from the dense closest packing of spheres. Most of these solids contain anionic frameworks which occlude cations which serve as the structure directing, or templating, agents. The complex structures result from the large amount of framework required to encapsulate organic cations, to accommodate the ordering of several different cations in a lattice, or from enclosing large amounts of water in a solid. Since these complex oxides have only recently been structurally characterized, even more complicated structures must certainly exist. Unfortunately, essentially nothing is known about the synthetic conditions required to prepare these materials since only tiny areas of the complicated parameter space have been surveyed.

We have recently studied the cation-directed hydrothermal synthesis of a new class of octahedral–tetrahedral framework solids based on MoO_6 octahedra and PO_4 tetrahedra.[5] The molybdenum phosphates are structurally very diverse and include examples of one dimensional (1-D) polymers,[6] two-dimensional layered materials,[7] and three-dimensional solids prepared both at high temperatures[8] and under hydrothermal conditions.[9] Several of the hydrothermally prepared 3-D compounds are microporous with internal void volumes in the range from 15 to nearly 40 volume %[10] and are the first large class of synthetic microporous solids composed of both octahedral and tetrahedral framework constituents.

We were interested in studying the possibility of ordering several different types of cation in a lattice using hydrothermal synthesis. To investigate incorporation of additional covalently bonded metal cations within octahedral–tetrahedral molybdenum phosphate frameworks, we initially attempted the syntheses by simply adding the cation oxide into typical molybdenum phosphate reactions. In this paper we report the synthesis and structural characterization of the new zinc molybdenum phosphate $(TMA)_2(H_3O)_2[Zn_3Mo_{12}O_{30}(HPO_4)_2(H_2PO_4)_6]\cdot11.5H_2O$ (**1**) (TMA = $(CH_3)_4N^+$), which contains both octahedral and tetrahedral zinc. Incorporation of the covalently bonded Zn into the anionic molybdenum phosphate lattice yields a solid with five different cationic sites.

In the category of transition metal molybdenum phosphates, we have prepared one-dimensional and three-dimensional microporous ferric molybdenum phosphates, which will be reported elsewhere.[11]

Experimental Section

The reactions were carried out in polytetrafluoroethylene-lined stainless steel containers under autogeneous pressure. The Mo metal should have a particle size of less than 2 μm in order to achieve convenient reaction rates.

$(TMA)_2(H_3O)_2[Zn_3Mo_{12}O_{30}(HPO_4)_2(H_2PO_4)_6]\cdot11.5\ H_2O$ (1). The reaction of Na_2MoO_4, Mo, ZnO, $(CH_3)_4NOH$, H_3PO_4, and H_2O in a mole ratio of 2:1:1:7:18:500 for 6 days at 200 °C gives a ca. 70% yield of **1**. The solid is isolated by filtration and washing with water.

† Current address: NEC Research Institute, 4 Independence Way, Princeton, NJ 08540.

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Table I

empirical formula	$Mo_3Zn_{0.75}P_2O_{18.38}N_{0.5}C_2H_6$
fw	729.94
cryst color, habit	orange, plate
cryst dimens (mm)	0.150 × 0.100 × 0.040
lattice params	
a (Å)	24.908 (9)
b (Å)	13.036 (8)
c (Å)	13.402 (4)
β (deg)	98.83 (3)
V (Å^3)	4300 (3)
space group	$C2/m$ (No. 12)
Z value	8
D_{calc} (g/cm^3)	2.255
radiation (λ (Å))	Mo Kα (0.710 69)
μ(Mo Kα) (cm^{-1})	27.41
residuals:[a] R; R_w	0.069; 0.077

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

Comparison of the powder X-ray diffraction pattern of **1** with the pattern simulated from the atomic coordinates obtained from the single-crystal X-ray structure indicates the product is single phase. The water content was determined from thermogravimetric analysis of the sample.

The experimental crystallographic information is given in Table I, the atomic coordinates are given in Table II, and some selected bond distances and angles are collected in Table III. Additional crystallographic information is given in the supplementary material.

Results and Discussion

The simple addition of ZnO to the already rather complicated reaction mixtures of the typical molybdenum phosphate (MoPO) preparation[5] has a profound effect on the outcome of the reaction. In a reaction similar to the one used to prepare **1**, but without the ZnO (and using MoO_3 in place of Na_2MoO_4), a quantitative yield of the microporous, 3-D molybdenum phosphate $(Me_4N)_{1.3}(H_3O)_{0.7}[Mo_4O_8(PO_4)_{4/2}]\cdot 2H_2O$ (**2**) was obtained. While the molybdenum phosphate building block in **2** is the $[Mo_4O_8(PO_4)_{4/2}]^{2-}$ moiety, which has been found in several layered molybdenum phosphates,[7] the 3-D structure of **1** is built up from $[Mo_6O_{15}(HPO_4)(H_2PO_4)_3]^{5-}$ (**3**) units. The asymmetric unit and the atom-numbering scheme are shown in Figure 1. The hexameric molybdenum cluster consists of a six-membered ring of oxo-bridged Mo atoms with alternating Mo–Mo single bonds (ca. 2.6 Å) and nonbonded Mo–Mo interactions as shown in Figure 2. There are four phosphate groups, three around the periphery of the ring and one in the center. Hexamer **3** has been previously observed in the 1-D sodium-bridged polymer $(PPh_4)_2[(H_3O)_2NaMo_6P_4O_{24}(OH)_7]\cdot 5H_2O$[12] as well as in the phosphate $(Et_4N)_6Na_2[Na_{12}(H_3PO_4)\{Mo_{24}O_{60}(HPO_4)_4(H_2PO_4)_{12}\}]\cdot xH_2O$.[13] The molybdenum hexamers **3** are formulated as $[Mo_6O_{15}(HPO_4)(H_2PO_4)_3]^{5-}$ although it may be possible that not all of the P–O groups are protonated. This would require that some of the solvate water molecules are actually hydronium ions.

The zinc molydenum phosphate **1** is prepared from the reaction of Na_2MoO_4, Mo, ZnO, $(CH_3)_4NOH$ (=TMA(OH)), H_3PO_4, and H_2O in a mole ratio of 2:1:1:7:18:500 for 6 days at 200 °C and is isolated in about 70% yield based on Mo. No attempt was made to optimize the yield of **1** by varying the reaction conditions. Although the Na^+ cations from Na_2MoO_4 did not appear in the product, the substitution of other Mo starting materials for Na_2MoO_4 was not investigated. As has been found with many of the hydrothermally synthesized MoPO materials,[5] a high yield of a structurally very complicated material is obtained from simple monomeric starting materials. It may be possible that the high yield is due to the fact that the product is merely the least soluble species present under these reaction conditions.

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Table II. Fractional Coordinates and B(eq) Values (Å^2) for **1**

atom	x	y	z	B(eq)[a]
Mo(1)	0.08909 (7)	0.2324 (1)	0.9617 (1)	1.85 (6)
Mo(2)	0.06432 (7)	0.1348 (1)	0.7933 (1)	1.63 (6)
Mo(3)	0.11799 (7)	0.0989 (1)	1.1895 (1)	1.63 (6)
Zn(1)	0.2389 (1)	0	0.8249 (2)	1.7 (1)
Zn(2)	0	0	1.0000	1.8 (2)
P(1)	0.1349 (3)	0	0.6504 (4)	2.0 (3)
P(2)	0.1518 (3)	0	0.9678 (4)	1.7 (3)
P(3)	0.3010 (2)	−0.2150 (4)	0.8686 (3)	2.8 (2)
O(1)	0.1059 (5)	0.0953 (8)	0.6773 (8)	2.1 (2)
O(2)	0.1921	0	0.696 (1)	3.0 (4)
O(3)	0.1313 (8)	0	0.535 (1)	2.6 (4)
O(4)	0.0182 (7)	0	0.751 (1)	1.6 (3)
O(5)	0.1290 (5)	0.2108 (9)	0.8492 (9)	2.5 (3)
O(6)	0.0341 (4)	0.1231 (7)	0.9196 (8)	1.4 (2)
O(7)	0.1391 (5)	0.0948 (8)	1.0272 (8)	1.7 (2)
O(8)	0.0697 (5)	0.2118 (8)	1.1078 (8)	1.7 (2)
O(9)	0.1135 (7)	0	0.864 (1)	1.8 (3)
O(10)	0.0617 (7)	0	1.130 (1)	2.1 (3)
O(11)	0.1776 (7)	0	1.213 (1)	2.1 (3)
O(12)	0.2108 (8)	0	0.955 (1)	2.9 (4)
O(13)	0.0535 (5)	0.343 (1)	0.935 (1)	3.2 (3)
O(14)	0.3406 (5)	−0.1968 (9)	0.9670 (9)	2.5 (3)
O(15)	0.0215 (5)	0.2180 (9)	0.7263 (9)	2.6 (3)
O(16)	0.3234 (5)	−0.2889 (8)	0.7977 (8)	2.0 (2)
O(17)	0.2886 (6)	−0.116 (1)	0.815 (1)	3.9 (3)
O(18)	0.0995 (5)	0.122 (1)	1.302 (1)	2.8 (3)
O(19)	0.2495 (6)	−0.271 (1)	0.899 (1)	4.5 (3)
O(20)	0.388 (1)	0	0.061 (2)	7.1 (7)
O(21)	0.762 (1)	0.500	0.141 (2)	6.1 (6)
O(22)	0.536 (1)	0.458 (2)	0.450 (2)	4.7 (7)
O(23)	0.066 (1)	0.230 (3)	0.504 (3)	7 (1)
O(24)	0.2500	0.2500	0.500	7 (1)
O(25)	0.833 (2)	0.386 (3)	0.268 (3)	7 (1)
O(26)	0.211 (3)	0	0.436 (6)	4 (2)
N(1)	0.0609 (6)	0.500	0.243 (1)	5.4 (4)
C(1)	0.062 (1)	0.500	0.133 (1)	5.4 (4)
C(2)	0.0043 (7)	0.500	0.261 (2)	5.4 (4)
C(3)	0.0887 (7)	0.592	0.288 (1)	5.4 (4)
C(4)	0.0888 (7)	0.408	0.288 (1)	5.4 (4)
H(11)	0.098 (1)	0.500	0.121 (2)	5.4 (4)
J(12)	0.044 (1)	0.440	0.104 (1)	5.4 (4)
H(13)	0.044 (1)	0.559	0.104 (1)	5.4 (4)
H(21)	−0.0137 (6)	0.559	0.232 (2)	5.4 (4)
H(22)	−0.0137 (6)	0.440	0.232 (2)	5.4 (4)
H(23)	0.004 (1)	0.500	0.332 (2)	5.4 (4)
H(31)	0.088 (1)	0.592	0.359 (1)	5.4 (4)
H(32)	0.1253 (7)	0.592	0.276 (2)	5.4 (4)
H(33)	0.0707 (7)	0.651	0.259 (1)	5.4 (4)
H(41)	0.088 (1)	0.408	0.359 (1)	5.4 (4)
H(42)	0.0708 (7)	0.348	0.259 (1)	5.4 (4)
H(43)	0.1254 (7)	0.408	0.276 (2)	5.4 (4)

[a] $B(eq) = (8\pi^2/3)[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*(\cos\gamma) + 2U_{13}aa^*cc^*(\cos\beta) + 2U_{23}bb^*cc^*(\cos\alpha)]$.

The structure of **1** consists of the hexamers **3** bonded together with both octahedral and tetrahedral Zn into layers. The octahedral Zn(1), which resides at the $\bar{1}$ site at 000, forms a bridge between two of the hexamers **3** as shown in Figure 3. This Zn is bonded to three O atoms (those oxygens which bridge the metal–metal-bonded molybdenum atoms together), from each Mo_6 unit at distances of 2.18 (1) Å (×4) and 2.14 (2) Å (×2) to give centrosymmetric $Zn[Mo_6O_{15}(HPO_4)(H_2PO_4)_3]_2^{8-}$ dimers. The $Zn[Mo_6O_{15}(HPO_4)(H_2PO_4)_3]_2^{8-}$ units are bonded into the layer, and to the other $Zn[Mo_6O_{15}(HPO_4)(H_2PO_4)_3]_2^{8-}$ units in the structure, by contacting six different tetrahedral Zn.

These tetrahedral Zn, which are crystallographically identical, are coordinated to the terminal phosphate O atoms of the $[Mo_6O_{15}(HPO_4)(H_2PO_4)_3]^{5-}$ clusters as follows. The Zn–O contacts are 1.93 (2), 1.97 (2), 1.97 (1), and 1.98 (1) Å. Each $[Mo_6O_{15}(HPO_4)(H_2PO_4)_3]^{5-}$ unit has seven terminal phosphate O atoms (Figure 2), six on the periphery of the Mo_6 ring and one in the center oriented perpendicular to the plane of the six Mo. The two terminal phosphate O atoms on each of three peripheral phosphate groups can be considered as endo and exo with respect

Table III. Selected Interatomic Distances (Å)

Mo(1)–Mo(2)	2.582 (2)	Zn(1)–O(12)	1.97 (2)
Mo(1)–O(5)	1.95 (1)	Zn(1)–O(17)	1.97 (1)
Mo(1)–O(6)	2.00 (1)	Zn(1)–O(17)	1.98 (1)
Mo(1)–O(7)	2.28 (1)	Zn(2)–O(6)	2.18 (1)
Mo(1)–O(8)	2.11 (1)	Zn(2)–O(6)	2.18 (1)
Mo(1)–O(13)	1.70 (1)	Zn(2)–O(6)	2.18 (1)
Mo(1)–O(14)	2.08 (1)	Zn(2)–O(6)	2.18 (1)
Mo(2)–O(1)	2.06 (1)	Zn(2)–O(10)	2.14 (2)
Mo(2)–O(4)	2.129 (9)	Zn(2)–O(10)	2.14 (2)
Mo(2)–O(5)	1.94 (1)	P(1)–O(1)	1.51 (1)
Mo(2)–O(6)	1.96 (1)	P(1)–O(1)	1.51 (1)
Mo(2)–O(9)	2.26 (1)	P(1)–O(2)	1.46 (2)
Mo(2)–O(15)	1.68 (1)	P(1)–O(3)	1.54 (2)
Mo(3)–Mo(3)	2.580 (4)	P(2)–O(7)	1.53 (1)
Mo(3)–O(7)	2.32 (1)	P(2)–O(7)	1.53 (1)
Mo(3)–O(8)	2.10 (1)	P(2)–O(9)	1.56 (2)
Mo(3)–O(10)	1.98 (1)	P(2)–O(12)	1.51 (2)
Mo(3)–O(11)	1.95 (1)	P(3)–O(14)	1.54 (1)
Mo(3)–O(16)	2.06 (1)	P(3)–O(16)	1.52 (1)
Mo(3)–O(18)	1.67 (1)	P(3)–O(17)	1.48 (1)
Zn(1)–O(2)	1.93 (2)	P(3)–O(19)	1.58 (2)

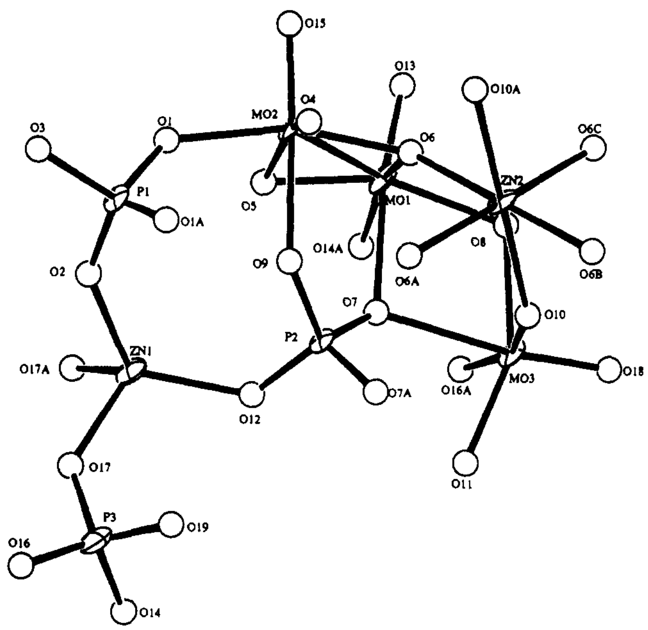

Figure 1. Atoms in the asymmetric unit of **1** and the numbering scheme for the atoms.

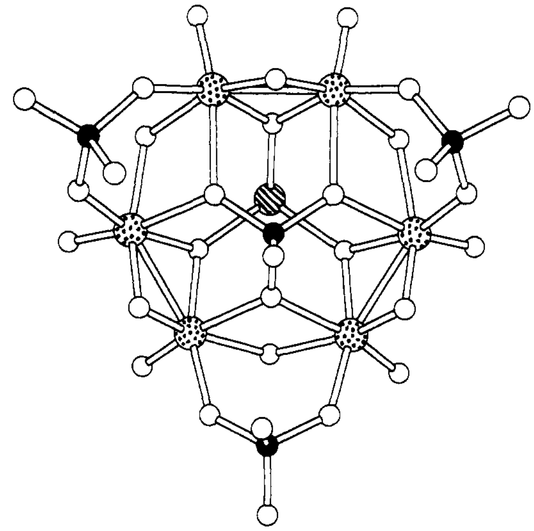

Figure 2. $[Mo_6O_{15}(HPO_4)(H_2PO_4)_3]^{5-}$ rings found in **1**. There are three Mo–Mo bonds near 2.6 Å and four PO_4 groups. Each of the three peripheral phosphate groups have two terminal P–O groups, while the central PO_4 has one terminal P–O. The stippled circles represent Mo, the striped circles Zn, and the black circles P.

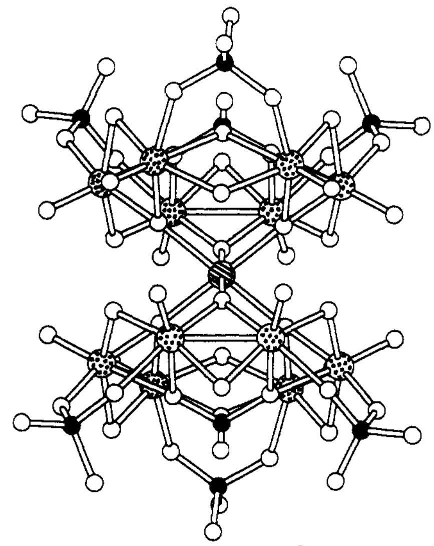

Figure 3. $Zn[Mo_6O_{15}(HPO_4)(H_2PO_4)_3]_2^{8-}$ dimers in **1**, showing the octahedral coordination of Zn(1). The stippled circles represent Mo, the striped circles Zn, and the black circles P.

to the central terminal O atom (Figure 2). Each Zn is coordinated to the O atoms of the four different phosphate groups. It is coordinated to the single terminal O atom of the central phosphate, P(2), and one of the endo oxygens from a phosphate, P(1), from the same $[Mo_6O_{15}(HPO_4)(H_2PO_4)_3]^{5-}$ unit. The two remaining O atoms in its coordination sphere are bonded to two different P(3) atoms from two different Mo_6 rings. Therefore, each tetrahedral Zn contacts phosphate groups from three different Mo_6 clusters, which in turn are each coordinated to three tetrahedral Zn. The way the Zn atoms bridge the ends of the $Zn[Mo_6O_{15}(HPO_4)(H_2PO_4)_3]_2^{8-}$ units to connect the Mo_6 units into the layer is shown in Figure 4.

A simplified schematic representation of how the tetrahedrally coordinated Zn^{2+} connects $Zn[[Mo_6O_{15}(HPO_4)(H_2PO_4)_3]_2^{8-}$ into the two-dimensional layers is shown in Figure 5.

Two of the three peripheral phosphates on one Mo_6 unit, containing P(3), are related by a mirror plane and are each coordinated to a Zn. These phosphate groups also contain a terminal P–O(19)H group. This O(19) is hydrogen bonded to another O(19) across a $\bar{1}$ site at 2.76 (3) Å. Another phosphate group with P(1) also has a terminal P–O(3)H group, but this P–OH group is oriented perpendicular to the plane of the layer and protrudes into the interlamellar space. It is hydrogen bonded to the water solvates between the layers as shown in Figure 6.

This connectivity generates layers with "voids" in them as shown in Figure 7, which is a view approximately perpendicular to the plane of the layer. This view shows that many of the atoms in the structure lie on mirror planes. The tetramethylammonium (=TMA) cations are nestled into these voids as shown in Figure 6. Note that when the TMA cations are in these voids, they are near the molybdenyl groups from the $Zn[Mo_6O_{15}(HPO_4)(H_2PO_4)_3]_2^{8-}$ dimers. We previously noted that in $(Et_4N)_6Na_2[Na_{12}(H_3PO_4)\{Mo_6O_{15}(HPO_4)(H_2PO_4)_3\}_4]\cdot xH_2O$,[13] and other molybdenum phosphates,[5] that the polar phosphate groups of the Mo_6 rings were associated in the solid state with the more polar cations in the structure (i.e. Na^+, H_3O^+, or NH_4^+ cations), while the molybdenyl groups were near the nonpolar Et_4N^+ cations. In the case of **1** the TMA cations are near the molybdenyl groups in the void, while the Zn^{2+} cations are associated with the polar phosphate groups. The exactly same situation has been obtained in the case of the certain 3-D ferric molybdenum phosphate frameworks.[11]

The nestling of the TMA cations is also evident in the view parallel to the layers as shown in Figure 6, which shows that the TMA cations are within, rather than in between, the layers. The layers are held together by a complicated hydrogen-bonded network involving the terminal phosphate P–OH groups, which

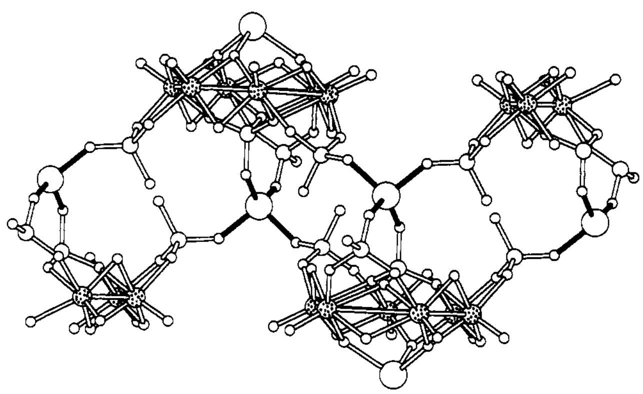

Figure 4. Portion of the structure of **1**, showing how the tetrahedral Zn(2) bridges the ends of the $Zn[Mo_6O_{15}(HPO_4)(H_2PO_4)_3]_2^{8-}$ dimers together. The nonbonded Mo–Mo contacts are connected with "bonds" to emphasize the planar disposition of the six molybdenum atoms. The stippled circles represent Mo, circles with black bonds represent tetrahedrally coordinated Zn, small tetrahedrally coordinated circles represent P, and smallest circles represent O.

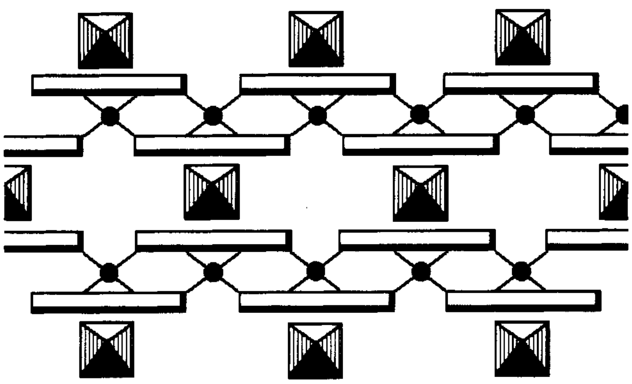

Figure 5. Simplified, schematic representation of the structure of **1**. The $[Mo_6O_{15}(HPO_4)(H_2PO_4)_3]^{5-}$ rings are represented as rectangles, the octahedral Zn as octahedra, and the tetrahedral Zn as black circles.

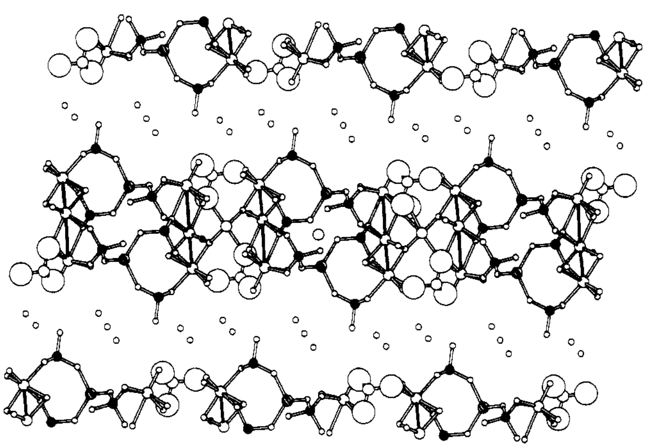

Figure 6. View parallel to the layers in **1**, which is also parallel to the plane of the Mo_6 rings. Note the terminal P–OH groups, which are hydrogen bonded to the water solvate (circles between the layers), protruding into the interlamellar space and the nestling of the TMA cations (largest circles) into the layers. Black circles represent P, and the striped circles tetrahedrally coordinated Zn. Both the bonded and nonbonded Mo–Mo interactions among the Mo atoms of the Mo_6 rings are darkened.

point into the space between the layers, as well as the H_3O^+ cations and several waters of solvation. It could be that the O atoms of the water within the layers (i.e. nearer the negatively charged layer framework) are the H_3O^+ cations and the O atoms from the waters are between the layers farther from the negative

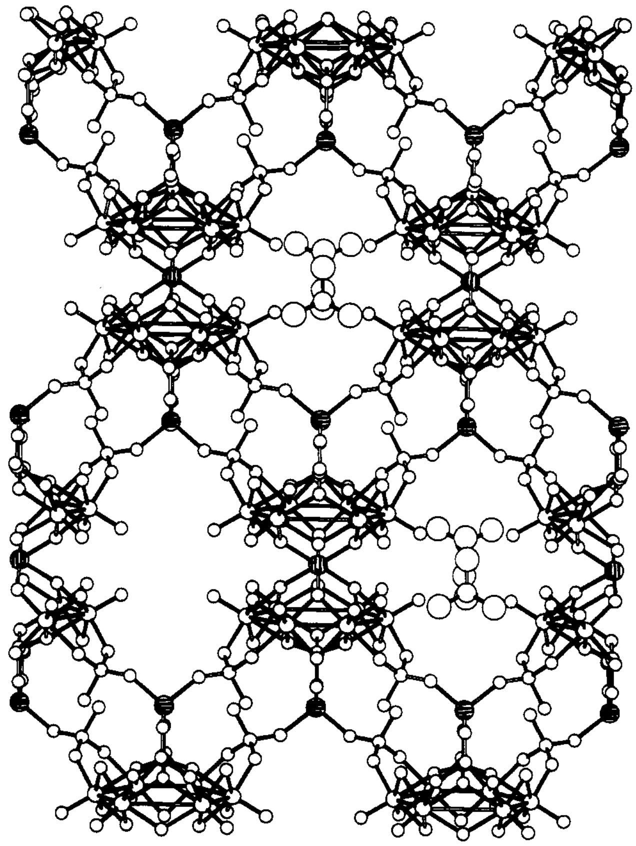

Figure 7. View approximately perpendicular to the layer illustrating how the TMA cations nestle into the voids created when Zn connects the $[Mo_6O_{15}(HPO_4)(H_2PO_4)_3]^{5-}$ units together. Vertically striped circles represent octahedrally coordinated Zn, horizontally striped circles represent tetrahedral Zn, nonstriped, tetrahedrally coordinated circles represent P, smallest circles represent O, and the largest circles represent the C and N atoms of the TMA cations. Note that one of the intralayer voids is depicted with no TMA cation.

charges. In the case of $(PPh_4)_2[(H_3O)_2NaMo_6P_4O_{24}(OH)_7]\cdot 5H_2O$,[12] hydronium cations were found between the Mo_6 rings.

The thermogravimetric analysis of **1**, with a heating rate of 10 °C·min^{-1} under He shows that most of the water in the structure is lost below 100 °C. There is a rather broad weight loss beginning above 300 °C and peaking at ca. 425 °C that corresponds to the thermal decomposition of the TMA cations. Water absorption isotherms obtained after the cation decomposition were somewhat reversible and showed a final uptake of 6–8 weight ‰ water, but the isotherms were not of type 1.

Conclusions

The ready incorporation of a second d-block element in an ordered, stoichiometric manner into a molybdenum phosphate, as illustrated by these zinc molybdenumn phosphates and the ferric molybdenumn phosphates,[11] shows that the potentially serious problem of segregation of the metals into binary phosphates does not necessarily occur. The relatively high-yield synthesis of an oxide with five different cations in the lattice certainly suggests that there are large number of other structurally complicated inorganic solids yet to be discovered.

Acknowledgment. We are grateful to Dr. Bev Vincent of Molecular Structure Corp. for the crystal structure analysis.

Supplementary Material Available: Tables listing experimental crystallographic details and complete distances and angles (13 pages); a listing of observed and calculated structure factors (34 pages). Ordering information is given on any current masthead page.