

## Four New Mo(V) Phosphate Structures Built up of Isotypic $\text{Mo}_{12}\text{MP}_8\text{X}_{62}$ Clusters

A. Leclaire, A. Guesdon, F. Berrah, M. M. Borel, and B. Raveau

Laboratoire CRISMAT, UMR 6508 associée au CNRS, ISMRA et Université de Caen, 6, Boulevard de Maréchal Juin, 14050 CAEN Cedex, France

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Four new Mo(V) phosphates with different original structures built up of  $\text{Mo}_{12}\text{MP}_8\text{X}_{62}$  ( $X = \text{O}, \text{OH}$ ) clusters have been synthesized. Two of them are obtained with a tetramethylammonium cation as the organic template and for  $M = \text{Cd}$ :  $[\text{Mo}_{12}\text{CdP}_8\text{X}_{62}]\text{Cd}_3[\text{N}(\text{CH}_3)_4]_4 \cdot 10\text{H}_2\text{O}$  which exhibits a chain-like structure and  $[\text{Mo}_{12}\text{CdP}_8\text{X}_{62}]\text{Cd}[\text{N}(\text{CH}_3)_4]_2(\text{H}_3\text{O})_6 \cdot 5\text{H}_2\text{O}$  with a 3D intersecting tunnel structure. The two other phases contain octyldiammonium cations as templates and are both unidimensional with the formula  $[\text{Mo}_{12}\text{CdP}_8\text{X}_{62}]\text{Cd}_2[\text{NH}_3(\text{CH}_2)_8\text{NH}_3]_3 \cdot 7.3\text{H}_2\text{O}$  and  $[\text{Mo}_{12}\text{ZnP}_8\text{X}_{62}]\text{Zn}_2[\text{NH}_3(\text{CH}_2)_8\text{NH}_3](\text{H}_3\text{O})_4 \cdot 8\text{H}_2\text{O}$ . The distribution of hydrogen in the  $\text{Mo}_{12}\text{MP}_8\text{X}_{62}$  clusters is established from electrostatic bond valence calculations, for these new structures and for those previously studied, leading to a classification based on the nature and number of the  $\text{PO}_4$ ,  $\text{PO}_3\text{OH}$ , and  $\text{PO}_2(\text{OH})_2$  tetrahedra of the clusters. © 1999 Academic Press

### INTRODUCTION

Hydrothermal synthesis of Mo(V) phosphates at low temperature and at rather low pressure has allowed various structures, all characterized by the presence of identical clusters, with the composition  $\text{Mo}_{12}\text{MP}_8\text{X}_{62}$  ( $X = \text{O}, \text{OH}$ ) to be stabilized (1–7). Such clusters (Fig. 1) consist of two identical rings of six edge-sharing  $\text{MoX}_6$  octahedra, interconnected by one  $\text{MX}_6$  octahedron, whereas the  $\text{PX}_4$  tetrahedra which share their apices with the  $\text{MoX}_6$  octahedra are located only on one side of each  $\text{Mo}_6$  ring. Nine Mo(V) phosphates with such clusters have been isolated to date. The first compound was discovered by Haushalter and Lai (1) for  $M = \text{Na}$ , with the formula  $(\text{PPh}_4)_2[(\text{H}_3\text{O})_2\text{NaMo}_6\text{P}_4\text{O}_{24}(\text{OH})_7] \cdot 5\text{H}_2\text{O}$ . Recently, a second type of structure was observed for  $M = \text{Na}$ , with the compound  $\text{Na}_8(\text{Mo}_2\text{O}_4\text{OH})_3(\text{PO}_4)_3(\text{PO}_3\text{OH}) \cdot 12.25\text{H}_2\text{O}$  (2). Transition elements are susceptible to occupy the  $M$  site. This is the case for  $M = \text{Fe}(\text{II})$  for which two different structures with such clusters were isolated, with the formulas  $[(\text{CH}_3)_4\text{N}]_2(\text{NH}_4)_2[\text{Fe}_2\text{Mo}_{12}\text{O}_{30}(\text{H}_2\text{PO}_4)_6(\text{HPO}_4)_2] \cdot n\text{H}_2\text{O}$  and  $[(\text{CH}_3)_4\text{N}]_2\text{Na}_4[\text{Fe}_3\text{Mo}_{12}\text{O}_{30}(\text{H}_x\text{PO}_4)_8] \cdot n\text{H}_2\text{O}$ , re-

spectively (3), for  $M = \text{Mn}(\text{II})$  and  $\text{Co}(\text{II})$  with the compounds  $[(\text{CH}_3)_4\text{N}][\text{Mn}_2\text{Mo}_6\text{O}_{12}(\text{OH})_4(\text{PO}_4)(\text{HPO}_4)(\text{H}_2\text{PO}_4)_2] \cdot 4\text{H}_2\text{O}$  and  $[(\text{CH}_3)_4\text{N}]_2[\text{Co}_2\text{Mo}_6\text{O}_{12}(\text{OH})_4(\text{PO}_4)(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)] \cdot 5\text{H}_2\text{O}$ , respectively, both discovered by Lightfoot and Masson (4–5). IIB (IUPAC) elements are susceptible to stabilize such clusters, as shown for  $M = \text{Zn}$  with the compound  $(\text{TMA})_2(\text{H}_3\text{O})_2[\text{Zn}_3\text{Mo}_{12}\text{O}_{30}(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)_6] \cdot 11.5\text{H}_2\text{O}$  synthesized by Mundi and Haushalter (6) and for  $M = \text{Cd}$ , with the phases  $\text{Na}_2\text{Cd}_3(\text{Mo}_2\text{O}_4\text{OH})_6(\text{PO}_4)_2(\text{PO}_3\text{OH})_6[\text{N}(\text{CH}_3)_4]_4 \cdot 10\text{H}_2\text{O}$  and  $\text{Cd}_9(\text{Mo}_2\text{O}_4\text{OH})_{12}(\text{PO}_4)_6(\text{PO}_3\text{OH})_{10}[\text{N}(\text{CH}_3)_4]_8 \cdot 15\text{H}_2\text{O}$ , recently obtained by Guesdon *et al.* (7).

In spite of the existence of identical  $\text{Mo}_{12}\text{MP}_8\text{X}_{62}$  clusters, these compounds exhibit generally different structures, which may be three dimensional, bidimensional, or unidimensional. This great variety stems from the nature of the  $M$  site cation, but also from the nature and number of template cations that participate in the structure. The rather large number of Mo(V) phosphates involving the tetramethylammonium cation as the organic template (3–7) suggests the possibility of synthesizing other phases keeping this cation. Moreover, no other phase involving a different organic template such as an aliphatic diamine has been synthesized. For this reason we have investigated Mo(V) phosphates containing either cadmium or zinc with two sorts of organic templates, tetramethylammonium and octyldiammonium cations.

In the present work four new structures of Mo(V) phosphates, all built up of identical  $[\text{Mo}_{12}\text{MO}_{24}(\text{OH})_6(\text{PO}_4)_2(\text{PO}_3\text{OH})_6]^{10-}$  clusters, are described. Three of these compounds have cadmium as the  $M$  interconnecting cation, but differ by the nature and number of template cations. The first one contains  $\text{Cd}^{2+}$  and  $\text{N}(\text{CH}_3)_4^+$  cations as templates according to the formula  $[\text{Mo}_{12}\text{CdP}_8\text{X}_{62}]\text{Cd}_3[\text{N}(\text{CH}_3)_4]_4 \cdot 10\text{H}_2\text{O}$  and its structure can be described as 1D. The second one contains also  $\text{Cd}^{2+}$  and  $\text{N}(\text{CH}_3)_4^+$  cations but additional  $\text{H}_3\text{O}^+$  cations also play the role of templates leading to the formula  $[\text{Mo}_{12}\text{CdP}_8\text{X}_{62}]\text{Cd}[\text{N}(\text{CH}_3)_4]_2(\text{H}_3\text{O})_6 \cdot 5\text{H}_2\text{O}$  so that a 3D framework is obtained. The third one differs from the two other phases by the nature of the

organic template cation, which is a long chain diammonium cation  $[\text{NH}_3(\text{CH}_2)_8\text{NH}_3]^{2+}$ , so that a 1D structure is observed for this compound with the formula  $[\text{Mo}_{12}\text{CdP}_8\text{X}_{62}]\text{Cd}_2[\text{NH}_3(\text{CH}_2)_8\text{NH}_3]_3 \cdot 7.3\text{H}_2\text{O}$ . In the fourth compound, zinc plays the role of the *M* interconnecting cation, and three template cations are involved,  $\text{Zn}^{2+}$ ,  $\text{H}_3\text{O}^+$ , and  $[\text{NH}_3(\text{CH}_2)_8\text{NH}_3]^{2+}$ , according to the formula  $[\text{Mo}_{12}\text{ZnP}_8\text{X}_{62}]\text{Zn}_2[\text{NH}_3(\text{CH}_2)_8\text{NH}_3](\text{H}_3\text{O})_4 \cdot 8\text{H}_2\text{O}$ , leading to a 1D structure. Finally a comparison of the different Mo(V) phosphates involving such clusters allows a structural classification to be proposed.

### SYNTHESIS

The single crystals used for the structure determination of the above compounds were synthesized hydrothermally in teflon-lined autoclaves from mixtures of the following precursors and with the following temperature conditions:

For  $[\text{Mo}_{12}\text{CdP}_8\text{X}_{62}]\text{Cd}_3[\text{N}(\text{CH}_3)_4]_4 \cdot 10\text{H}_2\text{O}$ , a mixture of  $\text{CdMoO}_4$ ,  $\text{MoO}_3$ ,  $\text{Mo}$ ,  $\text{H}_3\text{PO}_4$  (75%),  $(\text{CH}_3)_4\text{NOH}$ ,  $5\text{H}_2\text{O}$ , and  $\text{H}_2\text{O}$  in the molar ratio of 9:20:4:16:8:888 was heated at  $220^\circ\text{C}$  for 37 h and then cooled at  $1.67^\circ \cdot \text{h}^{-1}$  down to  $20^\circ\text{C}$ .

For  $[\text{Mo}_{12}\text{CdP}_8\text{X}_{62}]\text{Cd}[\text{N}(\text{CH}_3)_4]_2(\text{H}_3\text{O})_6 \cdot 5\text{H}_2\text{O}$  a mixture of  $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ ,  $\text{Mo}$ ,  $\text{H}_3\text{PO}_4$  (75%)  $(\text{CH}_3)_4\text{NOH}$ ,  $5\text{H}_2\text{O}$ , and  $\text{H}_2\text{O}$  in the molar ratio of 9:3:4:16:8:444 was heated at  $200^\circ\text{C}$  for 12 h and then cooled at  $3.75^\circ \cdot \text{h}^{-1}$  to  $20^\circ\text{C}$ .

For  $[\text{Mo}_{12}\text{CdP}_8\text{X}_{62}]\text{Cd}_2[\text{NH}_3(\text{CH}_2)_8\text{NH}_3]_3 \cdot 7.3\text{H}_2\text{O}$  a mixture of  $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{MoO}_3$ ,  $\text{Mo}$ ,  $\text{H}_3\text{PO}_4$  (75%),  $\text{H}_2\text{N}(\text{CH}_2)_8\text{NH}_2$ , and  $\text{H}_2\text{O}$  in the molar ratio of 9:20:4:16:8:444 was heated at  $220^\circ\text{C}$  for 20 h and cooled at  $2.5^\circ \cdot \text{h}^{-1}$  to  $20^\circ\text{C}$ .

For  $[\text{Mo}_{12}\text{ZnP}_8\text{X}_{62}]\text{Zn}_2[\text{NH}_3(\text{CH}_2)_8\text{NH}_3](\text{H}_3\text{O})_4 \cdot 8\text{H}_2\text{O}$  a mixture of  $\text{ZnO}$ ,  $\text{MoO}_3$ ,  $\text{Mo}$ ,  $\text{H}_3\text{PO}_4$  (75%),  $\text{H}_2\text{N}(\text{CH}_2)_8\text{NH}_2$ , and  $\text{H}_2\text{O}$  in the molar ratio of 3:10:2:8:3:278 was heated at  $220^\circ\text{C}$  for 20 h and cooled at  $2.5^\circ \cdot \text{h}^{-1}$  to  $20^\circ\text{C}$ .

All attempts to prepare each of the four compounds in the form of monophasic powder samples by hydrothermal synthesis were unsuccessful.

### X-RAY STRUCTURE DETERMINATION

The cell parameters were determined with a least square method using 25 reflections with  $18^\circ < \theta < 22^\circ$ . The reflections were measured with a CAD 4 Enraf Nonius diffractometer with the  $\text{MoK}\alpha$  radiation, isolated with a graphite monochromator. All the reflections were corrected for the Lorentz polarization and absorption effects. Extinction corrections were made for the cadmium compounds. The crystal parameters of the four compounds are listed in Table 1.

The structure were solved by the heavy atom method. The atomic coordinates and the thermal factors (Table 2) were refined, using a full matrix least square method.

### LOCATION OF HYDROGEN ATOMS

From the structure determination it appeared that the electroneutrality is not respected, suggesting the presence of additional hydrogen atoms, either as  $\text{H}_2\text{O}$  molecules or as OH groups or  $\text{H}_3\text{O}^+$  cations. In order to locate these hydrogen atoms, electrostatic bond valence sums received by each atom were calculated using the Brese and O'Keeffe formulation (8). The  $R_{ij}$  constants of 1.604 for P reported by Brese and O'Keeffe (8) and of 1.879 for Mo(V) calculated with 86 corner sharing Mo(V) octahedra were first used for these calculations. Calculated valences ranging from 4.63 to 5.05, with a mean value of 4.85, were obtained for Mo(V), whereas valences ranging from 4.60 to 5.27, with a mean value of 4.84, were obtained for phosphorus. Those ranges of values show that the  $R_{ij}$  values previously calculated for Mo(V) and P are not adequate. This can be explained in the case of Mo(V) by the fact that in the present compounds the Mo(V) octahedra share their edges instead of their apices.

In order to refine the  $R_{ij}$  values, new calculations were performed based on new data considering 328  $\text{PO}_4$  tetrahedra for phosphorus, and 42 Mo(V) octahedra sharing only edges in  $\text{Mo}_6$  rings (2–7). In this way,  $R_{ij}$  values of 1.890 and 1.615 were obtained for Mo(V) and P, respectively. With these new values, the sums of the electrostatic bond valences are centered on 4.99 for both polyhedra, Mo(V) and P, with valences ranging from 4.77 to 5.20 and from 4.73 to 5.40, respectively. These new  $R_{ij}$  values will be used for the calculations of the electrostatic bond valences of Mo(V) and P not only in the present compounds but also in all other previously studied Mo(V) phosphates which exhibit similar  $\text{Mo}_{12}\text{MP}_8\text{X}_{62}$  clusters.

### DESCRIPTION OF $\text{Mo}_{12}\text{MP}_8\text{X}_{62}$ CLUSTERS

All four compounds exhibit identical  $\text{Mo}_{12}\text{MP}_8\text{X}_{62}$  clusters ( $X = \text{O}, \text{OH}$ ) built up of two  $\text{Mo}_6$  rings of six edge-sharing  $\text{MoX}_6$  octahedra interconnected by a  $\text{CdO}_6$  or  $\text{ZnO}_6$  octahedron and sharing their apices with eight  $\text{PX}_4$  tetrahedra (Fig. 1). The examination of the electrostatic bond valences (Table 3) shows that there exists a lack of about 0.90 evu (electrostatic valence unit) for three oxygen atoms of the  $\text{Mo}_6\text{O}_{24}$  rings, so that the latter consist of six  $\text{MoO}_5\text{OH}$  octahedra leading to the formulation  $\text{Mo}_6\text{O}_{21}(\text{OH})_3$ . Three of the oxygen atoms of three  $\text{PO}_4$  tetrahedra out of four show also a lack of about 0.94 evu, so that six  $\text{PO}_3\text{OH}$  tetrahedra are formed per cluster. The distribution of the hydrogen atoms in the  $\text{Mo}_6$  rings is identical for the four compounds (Fig. 2), whereas the distribution of the  $\text{PO}_3\text{OH}$  tetrahedra for the phosphate

TABLE 1  
Summary of Crystal Data, Intensity Measurements, and Structure Refinement Parameters

	A	B	C	D
Crystal data				
Space group	$P2_1/c$	$Pn$	$P\bar{1}$	$P\bar{1}$
Cell dimensions	$a = 14.503(1) \text{ \AA}$ $b = 12.267(1) \text{ \AA}$ $c = 22.202(2) \text{ \AA}$ $\beta = 100.867(6)^\circ$	$a = 15.123(1) \text{ \AA}$ $b = 12.305(1) \text{ \AA}$ $c = 19.264(2) \text{ \AA}$ $\beta = 98.620(8)^\circ$	$a = 11.820(1) \text{ \AA}$ $b = 13.248(1) \text{ \AA}$ $c = 14.794(1) \text{ \AA}$ $\alpha = 68.593(6)^\circ$ $\beta = 82.067(7)^\circ$ $\gamma = 87.372(8)^\circ$	$a = 11.535(1) \text{ \AA}$ $b = 14.344(1) \text{ \AA}$ $c = 14.500(2) \text{ \AA}$ $\alpha = 67.772(8)^\circ$ $\beta = 71.517(9)^\circ$ $\gamma = 76.728(7)^\circ$
Volume ( $\text{\AA}^3$ )	3879.2(5)	3544.4(6)	2136.0(3)	2089.8(4)
Z	2	2	1	1
$\rho_{\text{calc}}$ ( $\text{g} \cdot \text{cm}^{-3}$ )	2.85	2.79	2.51	2.35
Intensity measurements				
$\lambda$ (MoK $\alpha$ )	0.71073	0.71073	0.71073	0.71073
Scan mode	$\omega$ -4/3 $\theta$	$\omega$ - $\theta$	$\omega$ - $\theta$	$\omega$ -4/3 $\theta$
Scan width ( $^\circ$ )	$1.0 + 0.35 \tan \theta$	$1.0 + 0.35 \tan \theta$	$1.05 + 0.35 \tan \theta$	$1.0 + 0.35 \tan \theta$
Slit aperture (mm)	$1.0 + \tan \theta$	$1.0 + \tan \theta$	$1.0 + \tan \theta$	$1.0 + \tan \theta$
Max $\theta$ ( $^\circ$ )	45	45	45	45
Standard reflections	3 measured every 3600 s	3 measured every 3600 s	3 measured every 3600 s	3 measured every 3600 s
Measured reflections	32767	30578	35601	24858
Reflections with $I > 3\sigma$	4063	4355	7006	3415
$\mu$ ( $\text{mm}^{-1}$ )	3.23	2.94	2.69	2.84
Structure solution and refinement				
Parameters refined	297	442	540	274
Agreement factors	$R = 0.058$ $R_w = 0.057$	$R = 0.036$ $R_w = 0.031$	$R = 0.036$ $R_w = 0.034$	$R = 0.055$ $R_w = 0.073$
Weighting scheme	$w = 1/\sigma^2$	$w = 1/\sigma^2$	$w = 1/\sigma^2$	$w = 1/\sigma^2$

Note. A =  $[\text{Mo}_{12}\text{CdP}_8\text{O}_{50}(\text{OH})_{12}]\text{Cd}_3[\text{N}(\text{CH}_3)_4]_4 \cdot 10\text{H}_2\text{O}$ ; B =  $[\text{Mo}_{12}\text{CdP}_8\text{O}_{50}(\text{OH})_{12}]\text{Cd}[\text{N}(\text{CH}_3)_4]_2(\text{H}_3\text{O})_6 \cdot 5\text{H}_2\text{O}$ ; C =  $[\text{Mo}_{12}\text{CdP}_8\text{O}_{50}(\text{OH})_{12}]\text{Cd}_2[\text{NH}_3(\text{CH}_2)_8\text{NH}_3]_3 \cdot 7.3\text{H}_2\text{O}$ ; D =  $[\text{Mo}_{12}\text{ZnP}_8\text{O}_{50}(\text{OH})_{12}]\text{Zn}_2[\text{NH}_3(\text{CH}_2)_8\text{NH}_3](\text{H}_3\text{O})_4 \cdot 8\text{H}_2\text{O}$ .

$[\text{Mo}_{12}\text{CdP}_8\text{X}_{62}]\text{Cd}[\text{N}(\text{CH}_3)_4]_2(\text{H}_3\text{O})_6 \cdot 4\text{H}_2\text{O}$  (Fig. 2a) is different from that observed in the three other Mo(V) phosphates (Fig. 2b). Such a different distribution is closely related to the noncentrosymmetric character of the  $\text{Mo}_{12}\text{CdP}_8\text{X}_{62}$  cluster in the first compound, contrary to the three other phases which exhibit a centrosymmetric cluster. Note that some other oxygen atoms of the  $\text{PO}_4$  tetrahedra show also a lack of valence but the latter is significantly smaller, i.e., of 0.66 or 0.37 evu. The examination of the environment of the latter oxygen atoms shows in fact that such a lack corresponds to the formation of one or several hydrogen bonds with  $\text{H}_2\text{O}$  molecules or  $\text{H}_3\text{O}^+$  cations.

Thus in the four compounds the clusters can be formulated  $[\text{Mo}_{12}\text{MO}_{24}(\text{OH})_6(\text{PO}_4)_2(\text{PO}_3\text{OH})_6]^{10-}$ .

#### ARRANGEMENTS OF THE CLUSTERS: FORMATION OF CHAIN-LIKE AND TRIDIMENSIONAL STRUCTURES

The arrangement of the  $\text{Mo}_{12}\text{MP}_8\text{X}_{62}$  clusters are fundamentally different in the four compounds (Figs. 3–6), lead-

ing to three chain-like type structures and one tridimensional framework.

The projection of the structure of the phosphate  $[\text{Mo}_{12}\text{CdP}_8\text{X}_{62}]\text{Cd}_3[\text{N}(\text{CH}_3)_4]_4 \cdot 10\text{H}_2\text{O}$  onto the (010) plane (Fig. 3) shows that its structure consists of  $[\text{Mo}_{12}\text{Cd}_4\text{P}_8\text{O}_{50}(\text{OH})_{12}(\text{H}_2\text{O})_6]^{4n-}$  chains running along **a**. In those chains each  $\text{Mo}_{12}\text{CdP}_8\text{O}_{50}(\text{OH})_{12}$  cluster is connected to the next one along **a** through a trioctahedral unit,  $\text{Cd}_3\text{O}_8(\text{H}_2\text{O})_6$ . The latter unit consists of three edge-sharing  $\text{CdO}_4(\text{H}_2\text{O})_2$  octahedra whose  $\text{H}_2\text{O}$  apices have been located from bond valence calculations (Table 3). The tetramethyl cations  $[\text{N}(\text{CH}_3)_4]^+$  are located between the chains, forming with the latter ionic bonds which are responsible for the cohesion of the structure. Moreover the stability of the whole framework is reinforced by the existence of hydrogen bonds between the chains, and between the chains and  $\text{H}_2\text{O}$  molecules that are located besides the tetramethylammonium cations.

The structure of the Mo(V) phosphate  $[\text{Mo}_{12}\text{CdP}_8\text{X}_{62}]\text{Cd}_2[\text{NH}_3(\text{CH}_2)_8\text{NH}_3]_3 \cdot 7.3\text{H}_2\text{O}$  is closely related to the first one as shown from its projection along **a** (Fig. 4). It is

**TABLE 2**  
**Atomic Positional and Isotropic Displacement Parameters**  
**for [Mo<sub>12</sub>CdP<sub>8</sub>O<sub>50</sub>(OH)<sub>12</sub>]Cd<sub>3</sub>[N(CH<sub>3</sub>)<sub>4</sub>]<sub>4</sub> · 10H<sub>2</sub>O (A)**

Atom	x	y	z	$U_{eq}$ (Å <sup>2</sup> )
Mo(1)	0.3312(1)	0.3997(1)	0.35156(9)	0.0103(6) <sup>a</sup>
Mo(2)	0.3477(1)	0.2407(1)	0.48631(8)	0.0100(5) <sup>a</sup>
Mo(3)	0.3367(1)	0.3390(1)	0.58914(9)	0.0104(6) <sup>a</sup>
Mo(4)	0.3260(1)	0.6265(1)	0.59719(9)	0.0114(6) <sup>a</sup>
Mo(5)	0.3251(1)	0.7434(1)	0.49912(8)	0.0110(5) <sup>a</sup>
Mo(6)	0.3261(1)	0.6111(1)	0.35685(9)	0.0115(6) <sup>a</sup>
P(1)	0.1601(4)	0.7868(4)	0.3776(3)	0.014(2) <sup>a</sup>
P(2)	0.2250(3)	0.4864(4)	0.4659(2)	0.010(1) <sup>a</sup>
P(3)	0.1667(4)	0.4641(4)	0.6426(2)	0.014(2) <sup>a</sup>
P(4)	0.2012(4)	0.1768(5)	0.3560(3)	0.020(2) <sup>a</sup>
Cd(1)	1/2	1/2	1/2	0.0117(6) <sup>a</sup>
Cd(2)	0	1/2	1/2	0.0156(6) <sup>a</sup>
Cd(3)	0.0586(1)	0.5473(1)	0.34854(7)	0.0205(5) <sup>a</sup>
O(1)	0.383(1)	0.384(1)	0.2904(7)	0.020(3)
O(2)	0.4092(9)	0.283(1)	0.4094(6)	0.008(3)
O(3)	0.2710(9)	0.391(1)	0.4365(6)	0.010(3)
O(4)	0.236(1)	0.277(1)	0.3254(7)	0.020(3)
O(5)	0.4174(8)	0.507(1)	0.4007(5)	0.013(3)
O(6)	0.2289(8)	0.506(1)	0.3270(5)	0.012(3)
O(7)	0.411(1)	0.132(1)	0.5133(6)	0.019(3)
O(8)	0.2540(9)	0.160(1)	0.4203(6)	0.014(3)
O(9)	0.2465(9)	0.252(1)	0.5330(6)	0.013(3)
O(10)	0.425(1)	0.359(1)	0.5322(7)	0.016(3)
O(11)	0.393(1)	0.250(1)	0.6396(6)	0.018(3)
O(12)	0.228(1)	0.370(1)	0.6359(6)	0.017(3)
O(13)	0.3960(8)	0.482(1)	0.6303(5)	0.012(3)
O(14)	0.2588(8)	0.481(1)	0.5360(5)	0.008(3)
O(15)	0.376(1)	0.711(1)	0.6515(7)	0.022(4)
O(16)	0.220(1)	0.571(1)	0.6422(6)	0.016(3)
O(17)	0.2281(9)	0.711(1)	0.5481(6)	0.012(3)
O(18)	0.4128(9)	0.628(1)	0.5375(6)	0.011(3)
O(19)	0.379(1)	0.856(1)	0.5291(7)	0.022(4)
O(20)	0.2205(9)	0.821(1)	0.4384(6)	0.015(3)
O(21)	0.392(1)	0.726(1)	0.4223(6)	0.015(3)
O(22)	0.2607(9)	0.595(1)	0.4424(6)	0.012(3)
O(23)	0.373(1)	0.646(1)	0.2960(7)	0.018(3)
O(24)	0.222(1)	0.729(1)	0.3376(6)	0.015(3)
O(25)	0.118(1)	0.892(1)	0.3432(6)	0.022(3)
O(26)	0.0781(9)	0.716(1)	0.3859(6)	0.017(3)
O(27)	0.1200(9)	0.478(1)	0.4463(5)	0.014(3)
O(28)	0.1330(9)	0.457(1)	0.7066(6)	0.019(3)
O(29)	0.0725(9)	0.467(1)	0.5981(6)	0.015(3)
O(30)	0.201(1)	0.076(1)	0.3174(7)	0.035(4)
O(31)	0.096(1)	0.200(2)	0.3612(8)	0.047(5)
O(32)	-0.050(1)	0.324(1)	0.5004(7)	0.026(4)
O(33)	0.028(1)	0.393(2)	0.2963(8)	0.044(5)
O(34)	-0.035(1)	0.376(1)	-0.2513(8)	0.043(5)
O(35)	0.153(1)	0.774(2)	0.2143(8)	0.051(5)
O(36)	0.078(1)	0.194(2)	0.4692(8)	0.048(5)
N(1)	0.454(1)	0.010(2)	0.3196(8)	0.028(4)
N(2)	0.150(2)	0.023(2)	0.622(1)	0.053(7)
C(1)	0.428(2)	0.004(2)	0.384(1)	0.037(6)
C(2)	0.560(2)	0.010(2)	0.329(1)	0.043(7)
C(3)	0.409(2)	-0.088(2)	0.282(1)	0.043(7)
C(4)	0.423(2)	0.177(2)	0.288(1)	0.041(7)
C(5)	0.213(2)	0.009(3)	0.576(1)	0.051(7)
C(6)	0.208(3)	0.012(4)	0.684(2)	0.010(1)
C(7)	0.071(3)	-0.055(3)	0.607(2)	0.09(1)
C(8)	0.108(3)	0.142(3)	0.619(2)	0.09(1)

**TABLE 2—Continued**

Atomic Positional and Isotropic Displacement and Site Occupation Parameters for [Mo <sub>12</sub> CdP <sub>8</sub> O <sub>50</sub> (OH) <sub>12</sub> ]Cd[N(CH <sub>3</sub> ) <sub>4</sub> ] <sub>2</sub> (H <sub>3</sub> O) <sub>6</sub> · 5H <sub>2</sub> O (B)						
Atom	x	y	z	$U_{eq}$ (Å <sup>2</sup> )	Occupancy	
Mo(1)	0.4826(7)	0.3958(5)	0.6766(6)	0.0115(3) <sup>a</sup>	1	
Mo(2)	0.3764(6)	0.4927(5)	0.5760(6)	0.0112(4) <sup>a</sup>	1	
Mo(3)	0.2514(7)	0.3417(6)	0.4428(6)	0.0120(3) <sup>a</sup>	1	
Mo(4)	0.2620(6)	0.1305(6)	0.4439(6)	0.0116(3) <sup>a</sup>	1	
Mo(5)	0.4000(6)	-0.0036(5)	0.5790(6)	0.0107(3) <sup>a</sup>	1	
Mo(6)	0.4937(7)	0.1110(6)	0.6809(6)	0.0113(3) <sup>a</sup>	1	
Mo(7)	0.5023(7)	0.3927(5)	0.3220(6)	0.0113(3) <sup>a</sup>	1	
Mo(8)	0.5935(6)	0.5050(5)	0.4191(6)	0.0107(3) <sup>a</sup>	1	
Mo(9)	0.7351(6)	0.3692(6)	0.5591(6)	0.0116(3) <sup>a</sup>	1	
Mo(10)	0.7447(7)	0.1594(6)	0.5610(6)	0.0120(3) <sup>a</sup>	1	
Mo(11)	0.6149(6)	0.0004(5)	0.4252(6)	0.0112(4) <sup>a</sup>	1	
Mo(12)	0.5153(7)	0.1031(5)	0.3244(6)	0.0115(3) <sup>a</sup>	1	
P(1)	0.305(1)	0.241(2)	0.610(1)	0.010(1) <sup>a</sup>	1	
P(2)	0.465(1)	0.249(2)	0.823(1)	0.014(1) <sup>a</sup>	1	
P(3)	0.161(1)	0.514(2)	0.541(1)	0.019(1) <sup>a</sup>	1	
P(4)	0.183(1)	-0.048(2)	0.548(1)	0.015(1) <sup>a</sup>	1	
P(5)	0.700(1)	0.262(2)	0.394(1)	0.010(1) <sup>a</sup>	1	
P(6)	0.533(1)	0.242(2)	0.178(1)	0.014(1) <sup>a</sup>	1	
P(7)	0.810(1)	0.556(2)	0.458(1)	0.015(1) <sup>a</sup>	1	
P(8)	0.838(1)	-0.023(2)	0.462(1)	0.019(1) <sup>a</sup>	1	
Cd(1)	1/2	0.2457(7)	1/2	0.0100(4) <sup>a</sup>	1	
Cd(2)	0.0004(7)	0.7490(7)	0.5006(6)	0.0116(3) <sup>a</sup>	1	
O(1)	0.553(1)	0.493(2)	0.701(1)	0.016(2)	1	
O(2)	0.364(2)	0.470(2)	0.671(1)	0.011(2)	1	
O(3)	0.479(2)	0.391(2)	0.570(1)	0.008(2)	1	
O(4)	0.464(1)	0.356(1)	0.780(1)	0.010(2)	1	
O(5)	0.560(2)	0.254(3)	0.683(1)	0.011(2)	1	
O(6)	0.386(1)	0.249(2)	0.663(1)	0.008(2)	1	
O(7)	0.427(2)	0.617(2)	0.571(2)	0.019(2)	1	
O(8)	0.344(2)	0.461(2)	0.466(1)	0.008(2)	1	
O(9)	0.255(1)	0.569(2)	0.561(1)	0.011(2)	1	
O(10)	0.297(2)	0.341(2)	0.566(1)	0.008(2)	1	
O(11)	0.218(2)	0.369(3)	0.359(2)	0.020(2)	1	
O(12)	0.350(1)	0.248(2)	0.444(1)	0.010(2)	1	
O(13)	0.171(2)	0.225(2)	0.468(1)	0.012(2)	1	
O(14)	0.161(2)	0.444(4)	0.474(2)	0.017(2)	1	
O(15)	0.238(2)	0.096(2)	0.358(2)	0.015(2)	1	
O(16)	0.310(1)	0.145(2)	0.560(1)	0.006(2)	1	
O(17)	0.184(2)	0.007(3)	0.472(2)	0.015(2)	1	
O(18)	0.361(1)	0.018(2)	0.475(1)	0.008(2)	1	
O(19)	0.391(2)	0.013(2)	0.680(2)	0.012(2)	1	
O(20)	0.278(1)	-0.078(2)	0.581(1)	0.010(2)	1	
O(21)	0.469(2)	-0.116(2)	0.583(1)	0.018(3)	1	
O(22)	0.492(2)	0.116(3)	0.579(2)	0.010(2)	1	
O(23)	0.474(2)	0.158(2)	0.778(2)	0.019(2)	1	
O(24)	0.583(2)	0.028(3)	0.703(2)	0.018(2)	1	
O(25)	0.419(2)	0.473(2)	0.292(2)	0.018(2)	1	
O(26)	0.603(1)	0.259(2)	0.347(1)	0.008(2)	1	
O(27)	0.610(2)	0.476(2)	0.324(2)	0.012(2)	1	
O(28)	0.508(2)	0.392(3)	0.425(2)	0.010(2)	1	
O(29)	0.430(2)	0.239(3)	0.323(1)	0.011(2)	1	
O(30)	0.521(2)	0.354(2)	0.219(2)	0.019(2)	1	
O(31)	0.536(2)	0.615(2)	0.429(1)	0.018(3)	1	
O(32)	0.696(2)	0.366(2)	0.441(1)	0.006(2)	1	
O(33)	0.626(1)	0.482(2)	0.535(1)	0.008(2)	1	
O(34)	0.714(1)	0.590(2)	0.432(1)	0.010(2)	1	
O(35)	0.765(2)	0.390(2)	0.646(2)	0.015(2)	1	

TABLE 2—Continued

Atomic Positional and Isotropic Displacement and Site Occupation Parameters for $[\text{Mo}_{12}\text{CdP}_8\text{O}_{50}(\text{OH})_{12}]\text{Cd}[\text{N}(\text{CH}_3)_4]_2(\text{H}_3\text{O})_6 \cdot 5\text{H}_2\text{O}$ (B)					
Atom	x	y	z	$U_{\text{eq.}} (\text{\AA}^2)$	Occupancy
O(36)	0.637(1)	0.263(2)	0.558(1)	0.010(2)	1
O(37)	0.817(2)	0.491(3)	0.523(2)	0.015(2)	1
O(38)	0.826(2)	0.266(2)	0.541(1)	0.012(2)	1
O(39)	0.771(2)	0.132(3)	0.647(2)	0.020(2)	1
O(40)	0.646(2)	0.028(2)	0.534(2)	0.008(2)	1
O(41)	0.832(2)	0.045(3)	0.529(2)	0.017(2)	1
O(42)	0.704(2)	0.160(2)	0.446(1)	0.008(2)	1
O(43)	0.559(2)	−0.114(3)	0.424(2)	0.019(2)	1
O(44)	0.748(1)	−0.057(2)	0.430(1)	0.011(2)	1
O(45)	0.524(2)	0.112(2)	0.423(1)	0.008(2)	1
O(46)	0.622(2)	0.028(2)	0.324(2)	0.011(2)	1
O(47)	0.428(2)	0.013(2)	0.304(2)	0.016(2)	1
O(48)	0.512(1)	0.147(2)	0.221(1)	0.010(2)	1
O(49)	0.214(2)	0.225(2)	0.642(1)	0.015(2)	1
O(50)	0.531(2)	0.248(2)	0.891(1)	0.014(2)	1
O(51)	0.363(2)	0.243(2)	0.837(2)	0.018(2)	1
O(52)	0.140(2)	0.445(2)	0.605(1)	0.021(3)	1
O(53)	0.094(1)	0.609(1)	0.528(1)	0.014(2)	1
O(54)	0.121(1)	−0.143(2)	0.547(1)	0.015(2)	1
O(55)	0.143(2)	0.032(2)	0.594(1)	0.018(3)	1
O(56)	0.774(2)	0.263(2)	0.355(1)	0.015(2)	1
O(57)	0.474(2)	0.236(2)	0.112(2)	0.014(2)	1
O(58)	0.634(2)	0.242(2)	0.162(2)	0.018(2)	1
O(59)	0.842(1)	0.475(2)	0.397(1)	0.018(3)	1
O(60)	0.867(1)	0.655(2)	0.467(1)	0.015(2)	1
O(61)	0.866(2)	0.070(2)	0.407(1)	0.021(3)	1
O(62)	0.916(1)	−0.090(1)	0.469(1)	0.014(2)	1
O(63)	0.473(1)	−0.044(2)	0.144(1)	0.018(4)	1
O(64)	0.019(3)	0.469(4)	0.370(3)	0.12(2)	1
O(65)	−0.039(2)	0.457(3)	0.641(2)	0.07(1)	1
O(66)	0.531(2)	−0.025(2)	0.874(2)	0.028(6)	1
O(67)	0.849(1)	0.247(3)	0.177(1)	0.035(5)	1
O(68)	0.125(2)	0.251(3)	0.812(1)	0.064(8)	1
O(69)	−0.024(2)	0.242(4)	0.316(2)	0.08(1)	1
O(70)	0.046(2)	0.257(2)	0.690(1)	0.041(6)	1
O(71)	0.255(2)	0.071(2)	0.761(2)	0.041(3)	1
O(72)	−0.024(3)	0.257(5)	0.455(2)	0.05(1)	0.5
O(73)	0.014(3)	0.201(3)	0.525(2)	0.05(1)	0.5
O(74)	0.735(2)	0.407(2)	0.236(2)	0.041(3)	1
N(1)	0.790(2)	0.256(3)	0.846(1)	0.024(6)	1
N(2)	0.219(2)	0.242(3)	0.147(2)	0.030(7)	1
C(1)	0.722(2)	0.166(2)	0.812(2)	0.028(7)	1
C(2)	0.723(2)	0.354(3)	0.838(2)	0.030(7)	1
C(3)	0.863(2)	0.264(4)	0.803(2)	0.05(1)	1
C(4)	0.788(2)	0.262(3)	0.931(2)	0.057(9)	1
C(5)	0.257(2)	0.350(3)	0.170(2)	0.039(9)	1
C(6)	0.253(2)	0.138(3)	0.180(2)	0.04(1)	1
C(7)	0.167(2)	0.250(3)	0.075(1)	0.038(6)	1
C(8)	0.127(2)	0.250(5)	0.178(2)	0.05(1)	1
Atomic Positional and Isotropic Displacement and Site Occupation Parameters for $[\text{Mo}_{12}\text{CdP}_8\text{O}_{50}(\text{OH})_{12}]\text{Cd}_2[\text{NH}_3(\text{CH}_2)_8\text{NH}_3]_3 \cdot 7.3\text{H}_2\text{O}$ (C)					
Atom	x	y	z	$U_{\text{eq.}} (\text{\AA}^2)$	Occupancy
Mo(1)	0.38380(5)	0.74178(5)	0.28824(5)	0.0183(2) <sup>a</sup>	1
Mo(2)	0.24937(5)	0.70154(5)	0.45133(5)	0.0166(2) <sup>a</sup>	1
Mo(3)	0.35517(5)	0.63266(5)	0.67988(5)	0.0151(2) <sup>a</sup>	1

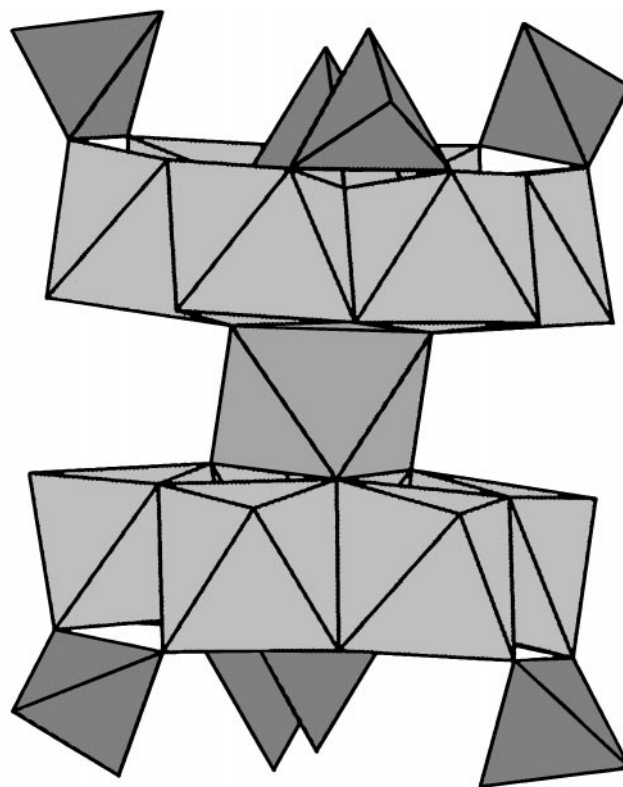
TABLE 2—Continued

Atomic Positional and Isotropic Displacement and Site Occupation Parameters for $[\text{Mo}_{12}\text{CdP}_8\text{O}_{50}(\text{OH})_{12}]\text{Cd}_2[\text{NH}_3(\text{CH}_2)_8\text{NH}_3]_3 \cdot 7.3\text{H}_2\text{O}$ (C)					
Atom	x	y	z	$U_{\text{eq.}} (\text{\AA}^2)$	Occupancy
Mo(4)	0.57669(5)	0.63158(5)	0.68023(5)	0.0156(2) <sup>a</sup>	1
Mo(5)	0.76291(5)	0.67865(5)	0.46060(5)	0.0153(3) <sup>a</sup>	1
Mo(6)	0.68525(5)	0.72605(5)	0.29352(5)	0.0169(2) <sup>a</sup>	1
Cd(1)	0.5	0.5	0.5	0.0151(3) <sup>a</sup>	1
Cd(2)	0.57516(5)	0.07754(4)	0.37736(4)	0.0210(2) <sup>a</sup>	1
P(1)	0.4958(2)	0.1988(1)	0.5355(1)	0.0147(6) <sup>a</sup>	1
P(2)	0.1931(2)	0.2095(2)	0.3782(2)	0.0193(7) <sup>a</sup>	1
P(3)	0.8180(2)	0.1610(2)	0.4027(2)	0.0193(7) <sup>a</sup>	1
P(4)	0.5644(2)	0.9113(2)	0.1196(2)	0.0229(7) <sup>a</sup>	1
O(1)	0.3026(5)	0.7018(4)	0.2236(4)	0.032(2) <sup>a</sup>	1
O(2)	0.3730(4)	0.6162(4)	0.4126(4)	0.018(2) <sup>a</sup>	1
O(3)	0.2865(4)	0.8342(4)	0.3418(4)	0.025(2) <sup>a</sup>	1
O(4)	0.5418(4)	0.6735(4)	0.2525(4)	0.019(2) <sup>a</sup>	1
O(5)	0.4484(4)	0.8822(4)	0.1823(4)	0.029(2) <sup>a</sup>	1
O(6)	0.5223(4)	0.7962(4)	0.3624(3)	0.015(2) <sup>a</sup>	1
O(7)	0.1336(4)	0.6499(4)	0.4297(4)	0.029(2) <sup>a</sup>	1
O(8)	0.1558(4)	0.7987(4)	0.5179(4)	0.022(2) <sup>a</sup>	1
O(9)	0.2484(4)	0.5846(4)	0.6001(4)	0.017(2) <sup>a</sup>	1
O(10)	0.3891(4)	0.7446(4)	0.5187(4)	0.016(2) <sup>a</sup>	1
O(11)	0.3124(4)	0.5447(4)	0.7930(4)	0.025(2) <sup>a</sup>	1
O(12)	0.2320(4)	0.7470(4)	0.6773(4)	0.023(2) <sup>a</sup>	1
O(13)	0.4767(4)	0.5494(4)	0.6347(4)	0.015(2) <sup>a</sup>	1
O(14)	0.4588(4)	0.7367(4)	0.6910(4)	0.017(2) <sup>a</sup>	1
O(15)	0.5871(5)	0.5482(4)	0.7946(4)	0.028(2) <sup>a</sup>	1
O(16)	0.6902(4)	0.7472(4)	0.6765(4)	0.023(2) <sup>a</sup>	1
O(17)	0.7151(4)	0.5715(4)	0.6086(4)	0.018(2) <sup>a</sup>	1
O(18)	0.6000(4)	0.7341(4)	0.5215(4)	0.016(2) <sup>a</sup>	1
O(19)	0.8841(4)	0.6131(4)	0.4438(4)	0.025(2) <sup>a</sup>	1
O(20)	0.8295(4)	0.7734(4)	0.5237(4)	0.024(2) <sup>a</sup>	1
O(21)	0.6537(4)	0.6018(4)	0.4184(4)	0.016(2) <sup>a</sup>	1
O(22)	0.7634(4)	0.8123(4)	0.3478(4)	0.022(2) <sup>a</sup>	1
O(23)	0.7876(4)	0.6748(4)	0.2334(4)	0.026(2) <sup>a</sup>	1
O(24)	0.6605(4)	0.8683(4)	0.1823(4)	0.026(2) <sup>a</sup>	1
O(25)	0.7427(4)	0.0607(4)	0.4422(4)	0.023(2) <sup>a</sup>	1
O(26)	0.4965(4)	0.0869(4)	0.5313(4)	0.018(2) <sup>a</sup>	1
O(27)	0.4333(5)	0.0773(5)	0.2830(5)	0.045(3) <sup>a</sup>	1
O(28)	0.6918(5)	0.0386(4)	0.2570(4)	0.036(2) <sup>a</sup>	1
O(29)	0.0997(4)	0.2579(4)	0.3155(4)	0.026(2) <sup>a</sup>	1
O(30)	0.1920(5)	0.0839(4)	0.4021(4)	0.030(2) <sup>a</sup>	1
O(31)	0.9352(4)	0.1276(4)	0.3576(4)	0.025(2) <sup>a</sup>	1
O(32)	0.5744(5)	0.8778(4)	0.0323(4)	0.032(2) <sup>a</sup>	1
O(33)	0.5779(5)	1.0388(4)	0.0873(4)	0.032(2) <sup>a</sup>	1
O(34)	0.1617(9)	0.2647(8)	0.1126(7)	0.117(6) <sup>a</sup>	1
O(35)	0.269(1)	0.049(1)	0.152(1)	0.097(8) <sup>a</sup>	0.64(2)
N(1)	0.0043(6)	0.9172(6)	0.3704(6)	0.041(3) <sup>a</sup>	1
N(2)	0.0020(6)	0.4428(6)	0.3574(5)	0.035(3) <sup>a</sup>	1
N(3)	0.356(1)	0.3220(7)	−0.0292(7)	0.079(5) <sup>a</sup>	1
C(1)	0.021(2)	0.955(2)	0.262(1)	0.185(9) <sup>a</sup>	1
C(2)	0.030(2)	0.864(2)	0.226(1)	0.185(9) <sup>a</sup>	1
C(3)	0.070(2)	0.916(2)	0.114(1)	0.185(9) <sup>a</sup>	1
C(4)	−0.019(2)	−0.012(2)	0.057(1)	0.185(9) <sup>a</sup>	1
C(5)	0.0465(8)	0.5370(8)	0.2649(8)	0.049(5) <sup>a</sup>	1
C(6)	0.0066(9)	0.5202(8)	0.1777(7)	0.050(4) <sup>a</sup>	1
C(7)	0.053(1)	0.612(1)	0.0797(9)	0.080(6) <sup>a</sup>	1
C(8)	0.185(1)	0.599(1)	0.052(1)	0.106(8) <sup>a</sup>	1
C(9)	0.762(1)	0.303(1)	0.040(1)	0.096(8) <sup>a</sup>	1
C(10)	0.637(1)	0.324(1)	0.068(1)	0.104(9) <sup>a</sup>	1
C(11)	0.560(1)	0.3226(9)	−0.0043(9)	0.072(6) <sup>a</sup>	1
C(12)	0.438(1)	0.328(1)	0.0385(9)	0.081(7) <sup>a</sup>	1

TABLE 2—Continued

Atomic Positional and Isotropic Displacement Parameters for [Mo <sub>12</sub> ZnP <sub>8</sub> O <sub>50</sub> (OH) <sub>12</sub> ]Zn <sub>2</sub> [NH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> NH <sub>3</sub> ](H <sub>3</sub> O) <sub>4</sub> · 8H <sub>2</sub> O (D)				
Atom	x	y	z	U <sub>eq.</sub> (Å <sup>2</sup> )
Mo(1)	0.7807(2)	0.3118(2)	0.5579(2)	0.013(1) <sup>a</sup>
Mo(2)	0.5961(2)	0.2719(2)	0.7197(2)	0.012(1) <sup>a</sup>
Mo(3)	0.3031(2)	0.2907(2)	0.6872(2)	0.013(1) <sup>a</sup>
Mo(4)	0.2720(2)	0.3477(2)	0.5044(2)	0.012(1) <sup>a</sup>
Mo(5)	0.5225(2)	0.3960(2)	0.2851(2)	0.013(1) <sup>a</sup>
Mo(6)	0.7399(2)	0.3829(2)	0.3079(2)	0.013(1) <sup>a</sup>
Zn(1)	1/2	1/2	1/2	0.014(2) <sup>a</sup>
Zn(2)	0.4352(3)	0.0053(2)	0.3479(3)	0.018(2) <sup>a</sup>
P(1)	0.5611(6)	0.2210(5)	0.5170(6)	0.012(3) <sup>a</sup>
P(2)	0.4266(7)	0.0825(5)	0.8365(6)	0.016(3) <sup>a</sup>
P(3)	0.9364(6)	0.1849(5)	0.3970(6)	0.017(3) <sup>a</sup>
P(4)	0.3296(7)	0.2331(5)	0.3342(6)	0.016(3) <sup>a</sup>
O(1)	0.873(2)	0.357(1)	0.598(1)	0.016(5)
O(2)	0.619(1)	0.390(1)	0.593(1)	0.012(4)
O(3)	0.808(1)	0.421(1)	0.408(1)	0.008(4)
O(4)	0.737(1)	0.185(1)	0.664(1)	0.014(4)
O(5)	0.923(2)	0.220(1)	0.487(1)	0.020(5)
O(6)	0.681(1)	0.272(1)	0.469(1)	0.008(4)
O(7)	0.641(2)	0.305(1)	0.802(1)	0.021(5)
O(8)	0.528(2)	0.142(1)	0.825(1)	0.019(5)
O(9)	0.411(2)	0.335(1)	0.752(1)	0.019(5)
O(10)	0.501(1)	0.228(1)	0.628(1)	0.008(4)
O(11)	0.167(2)	0.339(1)	0.743(2)	0.023(5)
O(12)	0.265(1)	0.218(1)	0.615(1)	0.011(4)
O(13)	0.317(2)	0.154(1)	0.799(1)	0.016(4)
O(14)	0.356(1)	0.408(1)	0.563(1)	0.012(4)
O(15)	0.127(2)	0.410(1)	0.525(2)	0.022(5)
O(16)	0.239(1)	0.274(1)	0.417(1)	0.010(4)
O(17)	0.346(1)	0.451(1)	0.362(1)	0.012(4)
O(18)	0.471(2)	0.280(1)	0.451(1)	0.014(4)
O(19)	0.533(2)	0.487(1)	0.169(2)	0.028(6)
O(20)	0.584(1)	0.457(1)	0.358(1)	0.010(4)
O(21)	0.665(2)	0.299(1)	0.270(1)	0.016(5)
O(22)	0.432(2)	0.300(1)	0.263(1)	0.018(5)
O(23)	0.803(2)	0.470(1)	0.201(2)	0.024(5)
O(24)	0.891(2)	0.273(1)	0.315(1)	0.015(4)
O(25)	0.599(2)	0.108(1)	0.521(1)	0.017(5)
O(26)	0.476(2)	0.001(1)	0.787(2)	0.023(5)
O(27)	0.377(2)	0.026(1)	0.957(1)	0.021(5)
O(28)	0.066(2)	0.140(1)	0.364(1)	0.021(5)
O(29)	0.852(2)	0.096(1)	0.436(1)	0.017(5)
O(30)	0.378(2)	0.125(1)	0.387(2)	0.022(5)
O(31)	0.250(2)	0.236(1)	0.263(1)	0.020(5)
O(32)	0.384(2)	0.001(2)	0.613(2)	0.036(6)
O(33)	0.267(2)	0.007(1)	0.311(1)	0.023(5)
O(34)	0.634(2)	0.165(2)	0.015(2)	0.053(7)
O(35)	0.708(2)	0.148(2)	0.183(2)	0.057(8)
O(36)	0.354(3)	0.166(2)	0.066(2)	0.10(1)
O(37)	0.061(3)	0.488(2)	0.324(3)	0.11(1)
C(1)	0.036(4)	0.019(3)	0.940(3)	0.07(1)
C(2)	0.928(3)	0.084(3)	0.886(3)	0.06(1)
C(3)	0.991(3)	0.137(2)	0.760(3)	0.036(9)
C(4)	0.044(3)	0.052(3)	0.711(3)	0.04(1)
N(1)	0.103(2)	0.103(2)	0.597(2)	0.021(6)

<sup>a</sup>Atom has been refined anisotropically and is given in the form of an isotropic equivalent displacement parameter defined as:  $U_{eq} = 1/3(U_{11} + U_{22} + U_{33})$ .

FIG. 1. Mo<sub>12</sub>MP<sub>8</sub>X<sub>62</sub> Cluster (X = O, OH).

built up of [Mo<sub>12</sub>Cd<sub>3</sub>P<sub>8</sub>O<sub>50</sub>(OH)<sub>12</sub>(H<sub>2</sub>O)<sub>4</sub>]<sup>6n-</sup> chains running along **b**. In each chain, one Mo<sub>12</sub>CdP<sub>8</sub>O<sub>50</sub>(OH)<sub>12</sub> cluster is connected to the next one along **b**, through a biotetrahedral unit, Cd<sub>2</sub>O<sub>6</sub>(H<sub>2</sub>O)<sub>4</sub>. The biotetrahedra are built up of two edge sharing CdO<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub> octahedra, similar to those observed in the first compound. Thus the chains of this second phase are deduced from those of the first one by replacing the trioctahedral units Cd<sub>3</sub>O<sub>8</sub>(H<sub>2</sub>O)<sub>6</sub> by biotetrahedral units Cd<sub>2</sub>O<sub>6</sub>(H<sub>2</sub>O)<sub>4</sub>. The octyldiammonium cations are oriented transversally to the chains (Fig. 4) forming ionic bonds with the latter, in such a way that each diammonium cation ensures the bonding between two different chains. Moreover the cohesion of the structure is reinforced by the existence of hydrogen bonds which are developed between the MoPCd chains, the [NH<sub>3</sub>(CH<sub>2</sub>)<sub>8</sub>NH<sub>3</sub>]<sup>2+</sup> cations, and additional H<sub>2</sub>O molecules that are inserted in the framework (Fig. 4).

The third Mo(V) phosphate, [Mo<sub>12</sub>ZnP<sub>8</sub>X<sub>62</sub>]Zn<sub>2</sub>[NH<sub>3</sub>(CH<sub>2</sub>)<sub>8</sub>NH<sub>3</sub>](H<sub>3</sub>O)<sub>4</sub> · 8H<sub>2</sub>O, exhibits also a 1D structure. The projection of its structure along **a** (Fig. 5) shows that it consists of [Mo<sub>12</sub>ZnP<sub>8</sub>O<sub>50</sub>(OH)<sub>12</sub>(H<sub>2</sub>O)<sub>4</sub>]<sup>6n-</sup> chains running along **b**. In those chains, the Mo<sub>12</sub>ZnP<sub>8</sub>O<sub>50</sub>(OH)<sub>12</sub> clusters are interconnected through ZnO<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> bipyramids. Like in the second phosphate, the octyldiammonium cations are oriented transversally with respect to

TABLE 3  
Electrostatic Bond Valence Sums Received by Oxygen Atoms in the A, B, C and D Compounds

A			B			C			D					
O(1)	1.76	F	O(1)	2.05	F	O(32)	1.86 <sup>a</sup>	O(1)	1.82	F	O(1)	1.69	F	
O(2)	1.07	H*	O(2)	1.75		O(33)	0.88	H*	O(2)	1.97	O(2)	1.95		
O(3)	1.89 <sup>a</sup>		O(3)	1.73		O(34)	1.88 <sup>a</sup>		O(3)	1.78	O(3)	1.05	H*	
O(4)	1.87 <sup>a</sup>		O(4)	1.73 <sup>a</sup>		O(35)	1.76	F	O(4)	1.09	H*	O(4)	1.70	
O(5)	1.92		O(5)	1.27	H*	O(36)	1.89		O(5)	1.94 <sup>a</sup>	O(5)	1.85 <sup>a</sup>		
O(6)	1.84		O(6)	2.16 <sup>a</sup>		O(37)	2.02 <sup>a</sup>		O(6)	1.84 <sup>a</sup>	O(6)	1.93 <sup>a</sup>		
O(7)	1.86	F	O(7)	1.60	F	O(38)	1.90		O(7)	1.78	F	O(7)	1.69	F
O(8)	2.01 <sup>a</sup>		O(8)	1.21	H*	O(39)	1.73	F	O(8)	1.86 <sup>a</sup>	O(8)	1.91 <sup>a</sup>		
O(9)	1.68	RHB	O(9)	1.80 <sup>a</sup>		O(40)	0.97	H*	O(9)	1.02	H*	O(9)	1.14	H*
O(10)	1.97		O(10)	2.12 <sup>a</sup>		O(41)	1.75 <sup>a</sup>		O(10)	1.92 <sup>a</sup>	O(10)	1.83 <sup>a</sup>		
O(11)	1.86	F	O(11)	1.87	F	O(42)	1.73 <sup>a</sup>	RHB	O(11)	1.78	F	O(11)	1.92	F
O(12)	2.00 <sup>a</sup>		O(12)	2.10		O(43)	1.96	F	O(12)	1.95 <sup>a</sup>	O(12)	1.78		
O(13)	1.13	H*	O(13)	1.70	RHB	O(44)	1.99		O(13)	1.92	O(13)	1.91 <sup>a</sup>		
O(14)	1.86 <sup>a</sup>		O(14)	1.93 <sup>a</sup>		O(45)	2.24		O(14)	2.00	O(14)	1.99		
O(15)	1.91	F	O(15)	1.74	F	O(46)	1.81		O(15)	1.82	F	O(15)	1.69	F
O(16)	1.84 <sup>a</sup>		O(16)	1.97 <sup>a</sup>		O(47)	1.55	F	O(16)	1.92 <sup>a</sup>	O(16)	1.85 <sup>a</sup>		
O(17)	1.73	RHB	O(17)	1.67 <sup>a</sup>	RHB	O(48)	2.00 <sup>a</sup>		O(17)	1.06	H*	O(17)	1.13	H*
O(18)	1.91		O(18)	1.35	H*	O(49)	1.03 <sup>a</sup>	H	O(18)	2.00 <sup>a</sup>	O(18)	1.93 <sup>a</sup>		
O(19)	1.86	F	O(19)	1.62	RHB	O(50)	1.69 <sup>a</sup>		O(19)	1.78	F	O(19)	1.75	F
O(20)	1.92 <sup>a</sup>		O(20)	1.90 <sup>a</sup>		O(51)	1.03 <sup>a</sup>	H	O(20)	1.88 <sup>a</sup>	O(20)	1.98		
O(21)	1.06	H*	O(21)	1.56	F	O(52)	1.11 <sup>a</sup>	H	O(21)	1.95	O(21)	1.79		
O(22)	1.85 <sup>a</sup>		O(22)	1.96		O(53)	1.62 <sup>a</sup>	RHB	O(22)	1.74	O(22)	1.83 <sup>a</sup>		
O(23)	1.76	F	O(23)	2.29 <sup>a</sup>		O(54)	1.68 <sup>a</sup>	RHB	O(23)	1.82	F	O(23)	1.90	F
O(24)	1.79 <sup>a</sup>		O(24)	1.67	F	O(55)	1.33 <sup>a</sup>	RHB	O(24)	1.94 <sup>a</sup>	O(24)	2.00 <sup>a</sup>		
O(25)	1.16 <sup>a</sup>	H	O(25)	2.00	F	O(56)	1.59 <sup>a</sup>	RHB	O(25)	1.66 <sup>a</sup>	RHB	O(25)	1.62 <sup>a</sup>	RHB
O(26)	1.74	RHB	O(26)	1.71 <sup>a</sup>	RHB	O(57)	1.99 <sup>a</sup>		O(26)	2.01 <sup>a</sup>	O(26)	1.90 <sup>a</sup>		
O(27)	1.98 <sup>a</sup>		O(27)	1.86		O(58)	1.03 <sup>a</sup>	H	O(27)	0.32	H <sub>2</sub>	O(27)	1.07 <sup>a</sup>	H
O(28)	1.07 <sup>a</sup>	H	O(28)	2.07		O(59)	0.84 <sup>a</sup>	H	O(28)	0.35	H <sub>2</sub>	O(28)	1.39 <sup>a</sup>	RHB
O(29)	1.87 <sup>a</sup>		O(29)	1.00	H*	O(60)	1.71 <sup>a</sup>	RHB	O(29)	1.34 <sup>a</sup>	RHB	O(29)	1.03 <sup>a</sup>	H
O(30)	1.33 <sup>a</sup>	RHB	O(30)	1.59 <sup>a</sup>	RHB	O(61)	0.93 <sup>a</sup>	H	O(30)	1.13 <sup>a</sup>	H	O(30)	1.90 <sup>a</sup>	
O(31)	1.13 <sup>a</sup>	H	O(31)	1.98	F	O(62)	1.93 <sup>a</sup>		O(31)	1.13 <sup>a</sup>	H	O(31)	1.13 <sup>a</sup>	H
O(32)	0.36	H <sub>2</sub>	O(63)	0	H <sub>2</sub>	O(69)	0	H <sub>2</sub>	O(32)	1.36 <sup>a</sup>	RHB	O(32)	0.20	H <sub>2</sub>
O(33)	0.43	H <sub>2</sub>	O(64)	0	H <sub>2</sub>	O(70)	0	H <sub>2</sub>	O(33)	1.08 <sup>a</sup>	H	O(33)	0.29	H <sub>2</sub>
O(34)	0.32	H <sub>2</sub>	O(65)	0	H <sub>2</sub>	O(71)	0	H <sub>2</sub>	O(34)	0	H <sub>2</sub>	O(34)	0	H <sub>2</sub>
O(35)	0	H <sub>2</sub>	O(66)	0	H <sub>2</sub>	O(72)	0	H <sub>2</sub>	O(35)	0	H <sub>2</sub>	O(35)	0	H <sub>2</sub>
O(36)	0	H <sub>2</sub>	O(67)	0	H <sub>2</sub>	O(73)	0	H <sub>2</sub>			O(36)	0	H <sub>2</sub>	
			O(68)	0	H <sub>2</sub>	O(74)	0	H <sub>2</sub>			O(37)	0	H <sub>2</sub>	

Note. A,  $[\text{Mo}_{12}\text{CdP}_8\text{O}_{50}(\text{OH})_{12}]\text{Cd}_3[\text{N}(\text{CH}_3)_4]_4 \cdot 10\text{H}_2\text{O}$ ; B,  $[\text{Mo}_{12}\text{CdP}_8\text{O}_{50}(\text{OH})_{12}]\text{Cd}[\text{N}(\text{CH}_3)_4]_2(\text{H}_3\text{O})_6 \cdot 5\text{H}_2\text{O}$ ; C,  $[\text{Mo}_{12}\text{CdP}_8\text{O}_{50}(\text{OH})_{12}]\text{Cd}_2[\text{NH}_3(\text{CH}_2)_8\text{NH}_3]_3 \cdot 7.3\text{H}_2\text{O}$ ; D,  $[\text{Mo}_{12}\text{ZnP}_8\text{O}_{50}(\text{OH})_{12}]\text{Zn}_2[\text{NH}_3(\text{CH}_2)_8\text{NH}_3](\text{H}_3\text{O})_4 \cdot 8\text{H}_2\text{O}$ . H\*, OH bridging two Mo atoms; H, OH linked to a P atom; H<sub>2</sub>, water molecule; RHB, receives hydrogen bond, completing the valence lack; F, molybdenyl apex.

<sup>a</sup>Oxygen atom of a phosphate group.

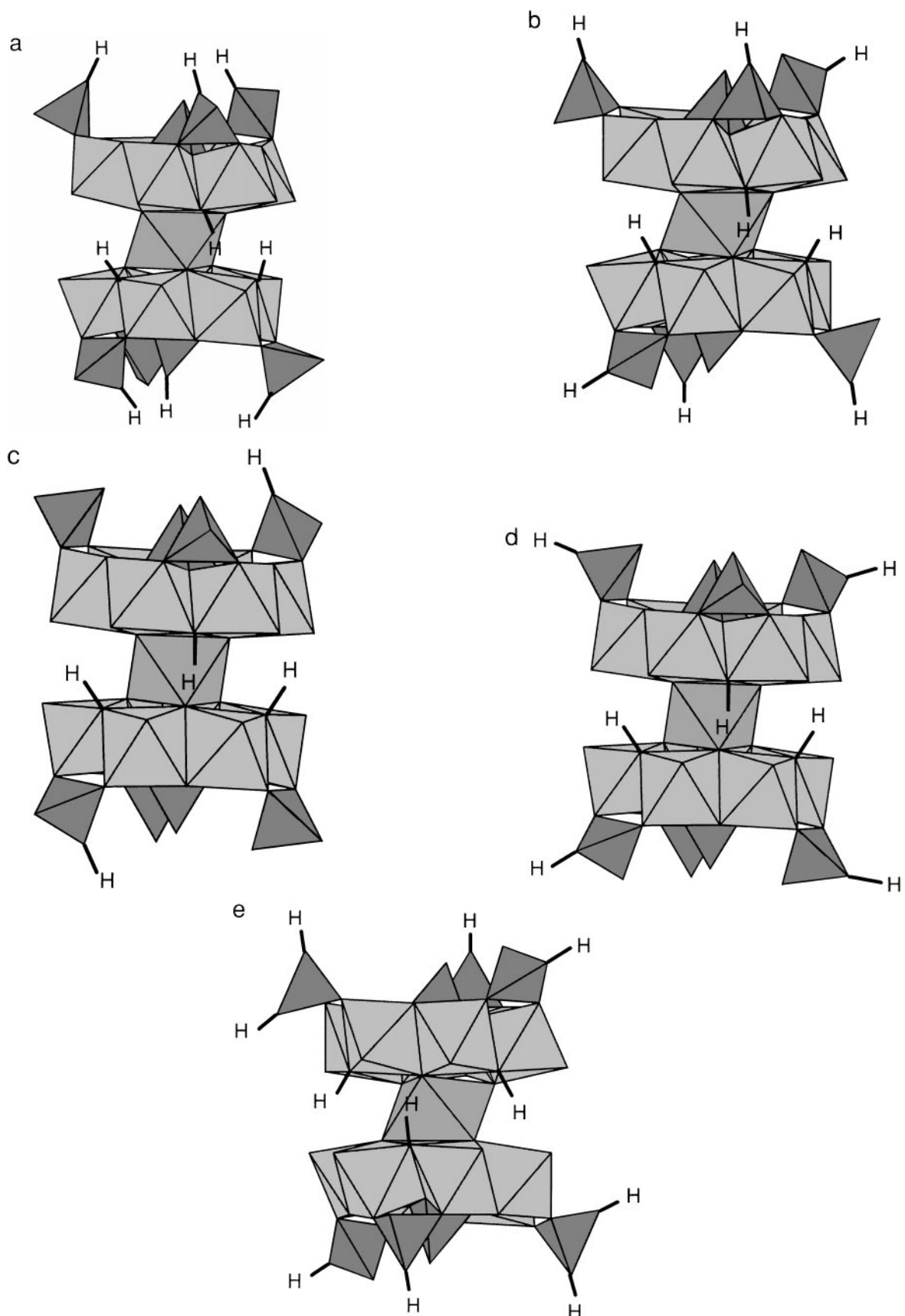
the chains, ensuring the cohesion of the structure by interconnecting two chains through ionic bonds. Moreover H<sub>3</sub>O<sup>+</sup> cations and H<sub>2</sub>O molecules are inserted between these chains.

The Mo(V) phosphate  $[\text{Mo}_{12}\text{CdP}_8\text{X}_{62}]\text{Cd}[\text{N}(\text{CH}_3)_4]_2(\text{H}_3\text{O})_6 \cdot 5\text{H}_2\text{O}$  has very different structure from the three others as shown from the projections along **b** (Fig. 6a) and along [111] (Fig. 6b). In this structure, the Mo<sub>12</sub>CdP<sub>8</sub>X<sub>62</sub> clusters share the apices of their PO<sub>4</sub> tetrahedra with CdO<sub>6</sub> octahedra, forming large tunnels running along **b** (Fig. 6a) and along [111] (Fig. 6b). In this intersecting tunnel framework the cross-shaped tunnels running along **b** and [111]

are occupied by  $[\text{N}(\text{CH}_3)_4]^+$  cations, whereas the elliptic ones running along **b** and [111] are occupied by H<sub>3</sub>O<sup>+</sup> cations and H<sub>2</sub>O molecules. Note that the localization of the protons on the H<sub>2</sub>O molecules cannot be determined from the present study. A delocalization of H<sup>+</sup> can be considered, suggesting a possible protonic conduction.

#### GEOMETRY OF THE MX<sub>6</sub> AND PX<sub>4</sub> POLYHEDRA

The minimum and maximum Mo–X and P–X interatomic distances observed for the four compounds are listed in Table 4.



**FIG. 2.** Hydrogen distribution in the  $\text{Mo}_{12}\text{MP}_8\text{X}_{62}$  clusters leading to (a) the noncentrosymmetric “260” type; (b) the centrosymmetric “260” type; (c) the “620” type; (d) the “440” type; (e) the “242” configuration.



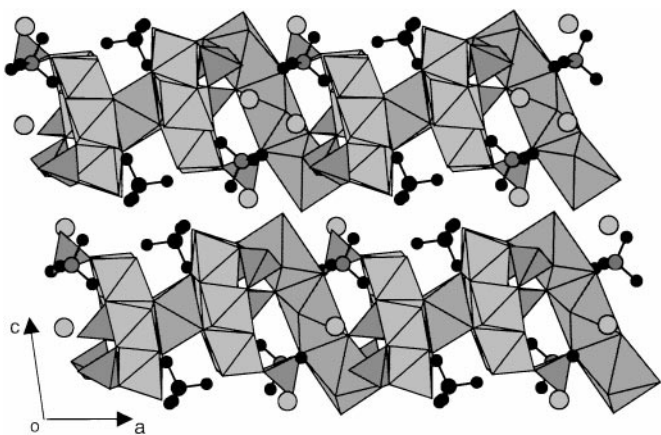


FIG. 3. Projection along **b** of the structure of  $[\text{Mo}_{12}\text{CdP}_8\text{O}_{50}(\text{OH})_{12}]\text{Cd}_3[\text{N}(\text{CH}_3)_4]_4 \cdot 10\text{H}_2\text{O}$  showing the 1D structure of clusters linked through  $\text{Cd}_3\text{O}_8(\text{H}_2\text{O})$  trioctahedral units.

The geometry of the  $\text{MoO}_5\text{OH}$  octahedra is characteristic of Mo(V), with one abnormally short Mo–O bond (1.62 to 1.73 Å), corresponding to the free oxygen apex, and one abnormally long opposite Mo–O bond (2.21 to 2.38 Å), corresponding to the oxygen atom shared by two Mo and one P atoms. The four other bond lengths are intermediate. Two series of shorter Mo–O bonds are observed: the first one which corresponds to the oxygen atoms bridging two Mo atoms and the central atom (Cd or Zn) range from 1.89 to 2.07 Å, whereas the second one bridging only two Mo atoms ranges from 1.86 to 2.00 Å. The third series of interatomic distances which correspond to Mo–O–P bonds

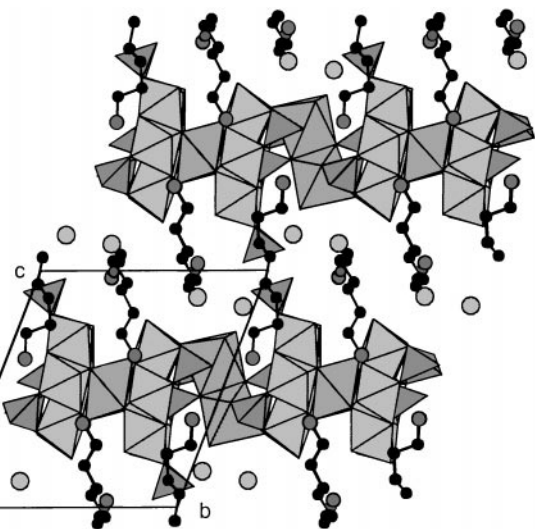


FIG. 4. Projection along **a** of the structure of  $[\text{Mo}_{12}\text{CdP}_8\text{O}_{50}(\text{OH})_{12}]\text{Cd}_2[\text{NH}_3(\text{CH}_2)_8\text{NH}_3]_3 \cdot 8\text{H}_2\text{O}$  structure showing the clusters connected through  $\text{Cd}_2\text{O}_6(\text{H}_2\text{O})$  bioctahedral units leading to rows linked by octyl-diammonium cation.

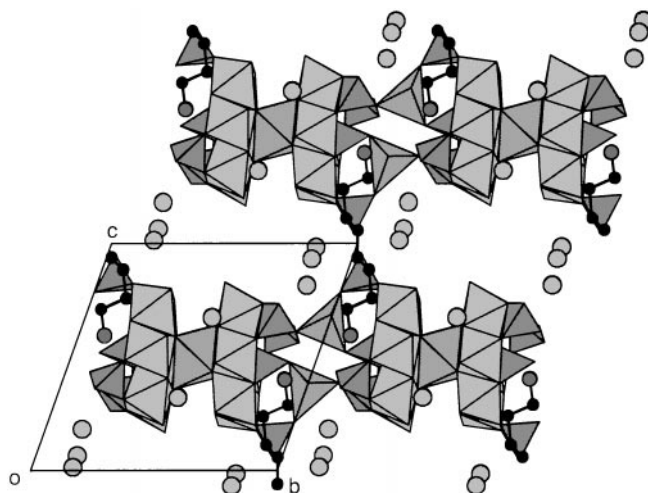


FIG. 5. Projection of the structure of  $[\text{Mo}_{12}\text{ZnP}_8\text{O}_{50}(\text{OH})_{12}]\text{Zn}_2[\text{NH}_3(\text{CH}_2)_8\text{NH}_3](\text{H}_3\text{O})_4 \cdot 8\text{H}_2\text{O}$  along **a**, showing the  $\text{ZnO}_3(\text{H}_2\text{O})_2$  bipyramids that connect the clusters.

are slightly longer (2.02 to 2.12 Å), whereas the fourth series of intermediate distance are the longest (2.01 to 2.24 Å), corresponding to Mo–OH bonds.

The P–O distances of the  $\text{PX}_4$  tetrahedra do not vary in a large range. They are correlated to the type of interaction received by the oxygen atom. The P–O–H bonds are the longest, ranging from 1.56 to 1.68 Å, whereas the P–O bonds corresponding to a free apex, receiving hydrogen bonds, are the shortest, ranging from 1.43 to 1.54 Å. The P–O–Mo bonds are intermediate, ranging from 1.44 to

1.61 Å as well as the P–O  $\begin{matrix} \text{Mo} \\ | \\ \text{P}-\text{O} \\ | \\ \text{Mo} \end{matrix}$  bonds (1.49 to 1.60 Å).

#### CLASSIFICATION OF THE Mo(V) PHOSPHATES WITH A CLUSTER LIKE STRUCTURE

Twelve Mo(V) phosphates involving similar  $\text{Mo}_{12}\text{MP}_8\text{X}_{62}$  clusters have been synthesized to date, including the four present compounds. In a great number of them, the localization of the hydrogen atoms was not determined previously. In order to establish a comparison between all these phases, electrostatic bond valence sums were calculated in the conditions described above, for all these compounds. We first observed a lack of about 0.90 evu for each of the three oxygen atoms of the  $\text{Mo}_6$  rings, leading for all the compounds to the formation of  $\text{MoO}_5\text{OH}$  octahedra instead of  $\text{MoO}_6$  octahedra. For the phosphate groups some oxygen atoms have a lack of valence either of 0.90 evu leading to the formation of P–OH bond or of 0.65 evu implying the formation of hydrogen bonds.

From these calculations, a “developed” formula can be obtained (Table 5) and the different polyhedra – $\text{MoO}_5\text{OH}$ ,

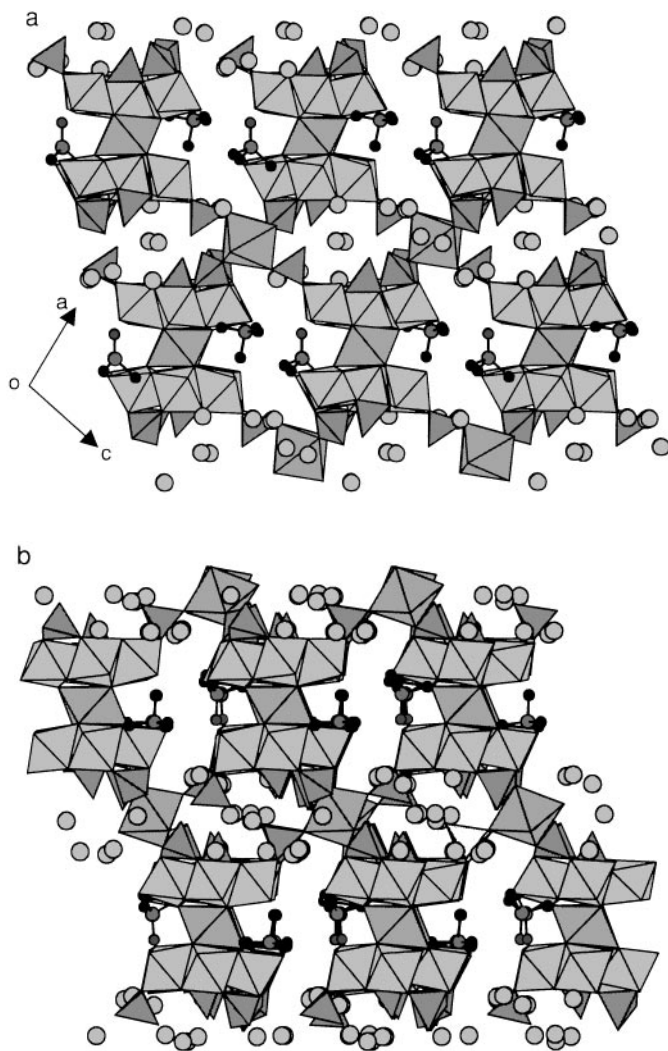


FIG. 6. Projection of the structure of  $[\text{Mo}_{12}\text{CdP}_8\text{O}_{50}(\text{OH})_{12}]\text{Cd}[\text{N}(\text{CH}_3)_4]_2(\text{H}_3\text{O})_6 \cdot 4\text{H}_2\text{O}$  showing the tridimensional character of the framework: (a) along **b** and (b) along  $[111]$ .

$\text{PO}_4$ ,  $\text{PO}_3\text{OH}$ ,  $\text{PO}_2(\text{OH})_2$ —in the  $\text{Mo}_6\text{MP}_8\text{X}_{62}$  clusters can be identified. This table shows that a classification of the compounds according to the nature of the polyhedra can be made, using three digits corresponding in the following order to the number of  $\text{PO}_4$ , of  $\text{PO}_3\text{OH}$ , and  $\text{PO}_2(\text{OH})_2$  tetrahedra, respectively, in each cluster, with a total number of eight  $\text{PX}_4$  tetrahedra per cluster.

One observes that all the compounds exhibit an identical distribution of the protons on the Mo octahedra, leading to the formation of identical  $\text{Mo}_6\text{O}_{21}(\text{OH})_3$  rings built up of six  $\text{MoO}_5\text{OH}$  edge-sharing octahedra. Nine compounds exhibit identical “260” type clusters, i.e., involving two  $\text{PO}_4$  tetrahedra and six  $\text{PO}_3\text{OH}$  tetrahedra (Figs. 2a, 2b). Thus in these nine Mo(V) phosphates, all the clusters can be formulated  $\text{Mo}_{12}\text{M}(\text{OH})_6\text{O}_{24}(\text{PO}_4)_2(\text{PO}_3\text{OH})_6$ . A larger

number of  $\text{PO}_4$  tetrahedra is only observed for two compounds. The maximum number is obtained for a  $M = \text{Na}$  phase, whose clusters exhibit the “620” configuration, i.e.,  $\text{Mo}_{12}\text{Na}(\text{OH})_6(\text{PO}_4)_6(\text{PO}_3\text{OH})_2$  clusters (Fig. 2c). Only one compound exhibits two kinds of cluster “260” and “440” (Fig. 2d). Finally it must be emphasized that 11 compounds

TABLE 4  
Ranges and Mean Values of the Bond Lengths (Å)  
in the Polyhedra of the  $\text{Mo}_{12}\text{MP}_8\text{X}_{62}$  Clusters

		A	B	C	D	Mean value
Mo=O	Min	1.65(1)	1.62(3)	1.668(5)	1.65(2)	
	Max	1.68(1)	1.73(3)	1.677(5)	1.70(2)	
	< >	1.664	1.677	1.673	1.679	← 1.673
Mo—O—Mo   P	Min	2.23(1)	2.21(3)	2.221(5)	2.26(2)	
	Max	2.34(1)	2.38(3)	2.366(5)	2.33(2)	
opposed to the Mo=O bond	< >	2.295	2.292	2.285	2.284	← 2.289
Mo—OH	Min	2.09(1)	2.01(3)	2.103(5)	2.08(2)	
	Max	2.13(1)	2.24(3)	2.179(5)	2.14(2)	
Mo	< >	2.113	2.113	2.127	2.109	← 2.116
Mo—O—Mo   M	Min	1.96(1)	1.89(3)	1.958(5)	1.95(2)	
	Max	1.99(1)	2.07(3)	1.977(5)	1.98(2)	
	< >	1.982	1.970	1.970	1.963	← 1.971
Mo—O—O   Mo	Min	1.92(1)	1.86(3)	1.924(5)	1.91(2)	
	Max	1.97(1)	2.00(3)	1.956(5)	1.96(2)	
	< >	1.950	1.937	1.943	1.939	← 1.942
Mo—O   P	Min	2.05(1)	2.02(3)	2.040(5)	2.03(2)	
	Max	2.09(1)	2.12(3)	2.085(5)	2.11(2)	
	< >	2.069	2.072	2.055	2.069	← 2.066
Mo—Mo	Min	2.598(3)	2.56(1)	2.591(1)	2.578(4)	
	Max	2.613(3)	2.65(1)	2.605(1)	2.596(4)	
	< >	2.605	2.602	2.605	2.587	← 2.600
P—O   Mo	Min	1.49(1)	1.44(3)	1.520(5)	1.50(2)	
	Max	1.55(1)	1.61(3)	1.535(5)	1.54(2)	
	< >	1.521	1.533	1.525	1.526	← 1.526
external $\text{PO}_4$ group						
P—OH	Min	1.51(1)	1.43(3)	1.501(5)	1.50(2)	
	Max	1.53(1)	1.54(3)	1.516(5)	1.51(2)	
external $\text{PO}_4$ group < >		1.515	1.492	1.508	1.502	← 1.504
P—O—Mo   Mo	Min	1.56(1)	1.58(3)	1.570(5)	1.57(2)	
	Max	1.59(1)	1.68(3)	1.588(5)	1.60(2)	
external $\text{PO}_4$ group < >		1.576	1.62	1.576	1.589	← 1.590
P—O	Min	1.54(1)	1.49(3)	1.522(5)	1.52(2)	
	Max	1.55(1)	1.60(3)	1.552(5)	1.57(2)	
central $\text{PO}_4$ group < >		1.547	1.545	1.542	1.547	← 1.545
P—O “free apex” of central $\text{PO}_4$ group		1.51(1)	1.44(3)	1.506(5)	1.57(2)	
			1.60(3)			

Note. A,  $[\text{Mo}_{12}\text{CdP}_8\text{O}_{50}(\text{OH})_{12}]\text{Cd}_3[\text{N}(\text{CH}_3)_4]_4 \cdot 10\text{H}_2\text{O}$ ;  
B,  $[\text{Mo}_{12}\text{CdP}_8\text{O}_{50}(\text{OH})_{12}]\text{Cd}[\text{N}(\text{CH}_3)_4]_2(\text{H}_3\text{O})_6 \cdot 5\text{H}_2\text{O}$ ;  
C,  $[\text{Mo}_{12}\text{CdP}_8\text{O}_{50}(\text{OH})_{12}]\text{Cd}_2[\text{NH}_3(\text{CH}_2)_8\text{NH}_3]_3 \cdot 7.3\text{H}_2\text{O}$ ;  
D,  $[\text{Mo}_{12}\text{ZnP}_8\text{O}_{50}(\text{OH})_{12}]\text{Zn}_2[\text{NH}_3(\text{CH}_2)_8\text{NH}_3](\text{H}_3\text{O})_4 \cdot 8\text{H}_2\text{O}$ .

TABLE 5  
Developed Formula and Classification

	<i>M</i>	MoO <sub>5</sub> OH	PO <sub>4</sub>	PO <sub>3</sub> OH	PO <sub>2</sub> (OH) <sub>2</sub>	Structure	Ref.
[Mo <sub>12</sub> FeP <sub>8</sub> O <sub>50</sub> (OH) <sub>12</sub> ]Fe[N(CH <sub>3</sub> ) <sub>4</sub> ] <sub>2</sub> (NH <sub>4</sub> ) <sub>2</sub> (H <sub>3</sub> O) <sub>3</sub> · nH <sub>2</sub> O	Fe	12	2	6	0	3D	(3)
[Mo <sub>12</sub> FeP <sub>8</sub> O <sub>50</sub> (OH) <sub>12</sub> ]FeNa <sub>2</sub> [N(CH <sub>3</sub> ) <sub>4</sub> ] <sub>2</sub> · xH <sub>2</sub> O	Fe	12	2	6	0	3D	(3)
[Mo <sub>12</sub> ZnP <sub>8</sub> O <sub>50</sub> (OH) <sub>12</sub> ]Zn <sub>2</sub> [N(CH <sub>3</sub> ) <sub>4</sub> ] <sub>2</sub> (H <sub>3</sub> O) <sub>4</sub> · 9.5H <sub>2</sub> O	Zn	12	2	6	0	2D	(6)
[Mo <sub>12</sub> ZnP <sub>8</sub> O <sub>50</sub> (OH) <sub>12</sub> ]Zn <sub>2</sub> [NH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> NH <sub>3</sub> ](H <sub>3</sub> O) <sub>4</sub> · 8H <sub>2</sub> O	Zn	12	2	6	0	1D	This work (D)
[Mo <sub>12</sub> CoP <sub>8</sub> O <sub>50</sub> (OH) <sub>12</sub> ]Co <sub>3</sub> [N(CH <sub>3</sub> ) <sub>4</sub> ] <sub>4</sub> · 10H <sub>2</sub> O	Co	12	2	6	0	1D	(5)
[Mo <sub>12</sub> MnP <sub>8</sub> O <sub>48</sub> (OH) <sub>14</sub> ]Mn <sub>3</sub> [N(CH <sub>3</sub> ) <sub>4</sub> ] <sub>2</sub> · 8H <sub>2</sub> O	Mn	12	2	4	2	1D	(4)
[Mo <sub>12</sub> NaP <sub>8</sub> O <sub>54</sub> (OH) <sub>8</sub> ]Na <sub>15</sub> · 24.5H <sub>2</sub> O	Na	12	6	2	0	3D	(2)
[Mo <sub>12</sub> CdP <sub>8</sub> O <sub>50</sub> (OH) <sub>12</sub> ]Na <sub>2</sub> Cd <sub>2</sub> [N(CH <sub>3</sub> ) <sub>4</sub> ] <sub>4</sub> · 10H <sub>2</sub> O	Cd	12	2	6	0	3D	(7)
[Mo <sub>12</sub> CdP <sub>8</sub> O <sub>50</sub> (OH) <sub>12</sub> ]Cd <sub>2</sub> [NH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> NH <sub>3</sub> ] <sub>3</sub> · 7.3H <sub>2</sub> O	Cd	12	2	6	0	1D	This work (C)
[Mo <sub>12</sub> CdP <sub>8</sub> O <sub>50</sub> (OH) <sub>12</sub> ]Cd <sub>2</sub> [N(CH <sub>3</sub> ) <sub>4</sub> ] <sub>2</sub> (H <sub>3</sub> O) <sub>6</sub> · 5H <sub>2</sub> O	Cd	12	2	6	0	3D	This work (B)
[Mo <sub>12</sub> CdP <sub>8</sub> O <sub>50</sub> (OH) <sub>12</sub> ]Cd <sub>3</sub> [N(CH <sub>3</sub> ) <sub>4</sub> ] <sub>4</sub> · 10H <sub>2</sub> O	Cd	12	2	6	0	1D	This work (A)
[Mo <sub>12</sub> CdP <sub>8</sub> O <sub>52</sub> (OH) <sub>10</sub> ][Mo <sub>12</sub> CdP <sub>8</sub> O <sub>50</sub> (OH) <sub>12</sub> ]Cd <sub>7</sub> } [N(CH <sub>3</sub> ) <sub>4</sub> ] <sub>8</sub> · 15H <sub>2</sub> O }	Cd	{12 12}	{4 2}	{4 6}	{0 0}	1D	{(7) (7)}

out of 12 contain only PO<sub>4</sub> and PO<sub>3</sub>OH tetrahedra. The only compound that shows PO<sub>2</sub>(OH)<sub>2</sub> tetrahedra belongs to the “242” class (Fig. 2e), forming Mo<sub>12</sub>Mn(OH)<sub>6</sub>O<sub>24</sub>(PO<sub>4</sub>)<sub>2</sub>(PO<sub>3</sub>OH)<sub>4</sub>(PO<sub>2</sub>(OH)<sub>2</sub>) clusters.

This classification shows also that there exists a great diversity of structures, most of the frameworks being either 3D or 1D. Only one 2D structure has been observed to date. It is remarkable that most of the compounds have been obtained with an organic template cation, since nine of them contain the methyltetrammonium cation and two the octyl diammonium cation, and only one is obtained without any organic template. This suggests that many new frameworks built up of such clusters should be generated in the future by varying the nature of the organic and inorganic templates

and their ratios, as well as the nature of the central *M* atom of the cluster.

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