Two New Closely Related Mo^V Hydroxymonophosphates Built Up of $Cd[Mo_6P_4O_{25}(OH)_6]_2$ and $Cd[Mo_6P_4O_{26}(OH)_5]_2$ Clusters

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Dedicated to Professor H. G. von Schnering on the occasion of his retirement

Abstract: Two new molybdenum(v) hydroxyphosphates have been synthesized hydrothermally, $Na_2Cd_3(Mo_2O_4OH)_6(PO_4)_2(PO_3OH)_6[N(CH_3)_4]_4 \cdot 10H_2O$ (**1**) and $Cd_9(Mo_2O_4OH)_{12}(PO_4)_6(PO_3OH)_{10}[N(CH_3)_4]_8 \cdot 15H_2O$ (**2**). Their structures have been determined from single-crystal X-ray diffraction. The water molecules and hydroxyl groups have been deduced from valence calculations. Both compounds crystallize in the triclinic space group $P\bar{1}$, with the cell parameters for **1** $a = 12.340(2)$, $b = 12.596(1)$, $c = 14.717(2)$ Å, $\alpha = 107.24(1)°$, $\beta = 89.83(1)°$, $\gamma = 114.31(1)°$, $V = 1972.3(4)$ Å^3, and for **2** $a = 11.942(1)$, $b = 13.339(2)$, $c = 26.765(3)$ Å, $\alpha = 85.33(1)°$, $\beta = 86.87(1)°$, $\gamma = 64.08(1)°$, $V = 3821.3(9)$ Å^3. The two frameworks can be described on the basis of similar $[Mo_6P_4X_{31}]^{n-}$ (X = O, OH) anionic clusters, but **1** is a tridimensional structure, whereas **2** exhibits a monodimensional structure.

Keywords
cadmium · crystal structure · hydrothermal synthesis · hydroxyphosphate · molybdenum

Introduction

Hydroxyphosphates of transition or post-transition elements involving amine derivatives as templating agents are of great interest for the construction of microporous compounds, demonstrated, for instance, for numerous oxyfluorinated compounds with open structures.[1] In this respect the chemistry of Mo^V phosphates offers great possibilities, owing to the particular configuration of the molybdenyl species, which allows great flexibility of the structure, as shown for many new tunnel and layered structures of anhydra molybdenum phosphates.[2, 3]

In the case of hydroxyphosphates, the association of Mo^V to sodium and/or to a second transition or post-transition element such as zinc or iron stabilised a new anionic cluster $[Mo_6P_4X_{31}]^{n-}$ (X = O, OH).[4–7] The connection of such clusters with MO_6 octahedra (M = Na, Zn, Fe etc.) suggests the possibility of generating a huge number of new frameworks, depending on the nature of the M cations and on the presence or not of a templating agent. During the study of the system Na–Mo–P–O–H, we discovered a new Mo^V hydroxyphosphate, $Na_8(Mo_2O_4OH)_3 \cdot (PO_4)_3(PO_3OH) \cdot nH_2O$,[8] whose $[NaMo_6P_4O_{27}(OH)_4]_2$ clusters had already been encountered in several other Mo^V hydroxyphosphates.[4, 5] But the great originality of this structure is its tridimensionality, resulting from the fact that such clusters are connected through NaO_6 octahedra, forming intersecting tunnels. In order to understand the influence of the other cations upon the stability of the $[Mo_6P_4X_{31}]^{n-}$ clusters we studied the introduction of cadmium in those phosphates, as its covalent character was likely to modify the crystal chemistry of Mo^V hydroxyphosphates significantly. Moreover, we introduced the tetramethylammonium cation as templating agent. The synthesis and crystal structures of two closely related new Mo^V hydroxymonophosphates, $Na_2Cd_3(Mo_2O_4OH)_6(PO_4)_2(PO_3OH)_6[N(CH_3)_4]_4 \cdot 10H_2O$ (**1**) and $Cd_9(Mo_2O_4OH)_{12}(PO_4)_6(PO_3OH)_{10}[N(CH_3)_4]_8 \cdot 15H_2O$ (**2**), are described here.

Results and Discussion

The two Mo^V hydroxymonophosphates **1** and **2** were synthesized hydrothermally from $Na_2MoO_4 \cdot 2H_2O$, Mo, CdO, H_3PO_4 and $(CH_3)_4NOH$, and their structures were determined from single-crystal X-ray diffraction data (Table 1) according to the experimental procedure described below. Solution of the single-crystal X-ray data for **1** and for **2** yields the chemical formulae $Na_2Cd_3Mo_{12}P_8N_4C_{16}O_{72}$ and $Cd_9Mo_{24}P_{16}N_8C_{32}O_{142}$, respectively. In spite of the good accuracy of the structure refinement it was not possible to localize the hydrogen atoms. Therefore an analysis of the electrostatic bond strengths was performed using the Brese and O'Keeffe relation[9] for Mo^V, P^V, Cd^{II} and Na^I and the Brown curve[10] for the valence H···O (acceptor) bond versus the O···O distance. These calculations[11] showed a lack of electrostatic valence of about 0.70 for one oxygen atom linked to molybdenum,

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Table 1. Summary of crystal data, intensity measurements and structure refinement parameters.

	1	**2**
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	12.340(2)	11.942(1)
b (Å)	12.596(1)	13.339(2)
c (Å)	14.717(2)	26.765(3)
α (°)	107.24(1)	85.33(1)
β (°)	89.83(1)	86.87(1)
γ (°)	114.31(1)	64.08(1)
volume (Å)^3	1972.3(4)	3821.3(9)
Z	2	2
ρ_{calcd} (g cm^{-3})	2.68	2.87
λ ($Mo_{K\alpha}$)	0.71073	0.71073
scan mode	$\omega-2\theta$	$\omega-\theta$
scan width (°)	$1.05 + 0.35\,\mathrm{tn}\theta$	$1.30 + 0.35\,\mathrm{tn}\theta$
slit aperture (mm)	$1.03 + \mathrm{tn}\theta$	$1.10 + \mathrm{tn}\theta$
max θ (°)	35	40
standard reflections	3 measured every 3600 s	3 measured every 3600 s
measured reflections	18083	47802
reflections with $I > 3\sigma$	2170	17399
μ (mm^{-1})	2.9	3.4
parameters refined	306, $R = 0.040$	961, $R = 0.040$
agreement factors	$R_w = 0.034$	$R_w = 0.044$
weighting scheme	$w = 1/\sigma^2$	$w = 1/\sigma^2$

and for one oxygen atom belonging to some of the phosphorus tetrahedra, so that the formulae of these hydroxyphosphates can be established as $Na_2Cd_3(Mo_2O_4OH)_6(PO_4)_2(PO_3OH)_6[N(CH_3)_4]_4 \cdot 10\,H_2O$ and $Cd_9(Mo_2O_4OH)_{12}(PO_4)_6(PO_3OH)_{10}[N(CH_3)_4]_8 \cdot 15\,H_2O$, respectively.

The projection of these two structures along $\vec{a}$ (Figures 1, 2) shows that they both contain $Cd[Mo_6P_4O_{25}(OH)_6]_2$ clusters but the hydroxyphosphate **2** exhibits a second sort of cluster, $Cd[Mo_6P_4O_{26}(OH)_5]_2$. The geometry of these clusters (Figure 3) is very similar to that observed for several sodium, iron or zinc hydroxyphosphates,[4–8] cadmium replacing these cations. It differs mainly from the latter in the distribution of the hydroxyl groups. Both clusters are built up of two rings of six $Mo(O_5OH)$ edge-sharing octahedra; the two "Mo_6" rings are connected through one CdO_6 octahedron (Figure 3) exactly as for $Na_8(Mo_2O_4OH)_3(PO_4)_3(PO_3OH) \cdot n\,H_2O$,[8] Cd replacing Na. The cluster $Cd[Mo_6P_4O_{25}(OH)_6]_2$ contains six PO_3OH tetrahedra and two PO_4 tetrahedra (Figure 3a) whereas the cluster $Cd[Mo_6P_4O_{26}(OH)_5]_2$ contains four PO_3OH tetrahedra and four PO_4 tetrahedra (Figure 3b). This distribution of the OH groups is slightly different from that observed for the cluster $Na[Mo_6P_4O_{27}(OH)_4]_2$,[8] where only two PO_3OH tetrahedra are observed per cluster (Figure 3c). This distribution of the hydrogen atoms is fundamentally different from that observed by Haushalter et al. in similar clusters;[4–7] these authors never found any evidence of $Mo(O_5OH)$ octahedra.

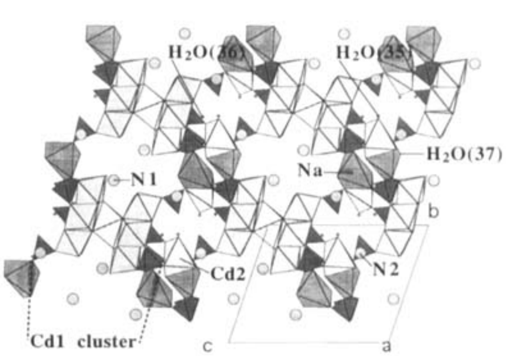

Figure 1. Projection of **1** along $\vec{a}$.

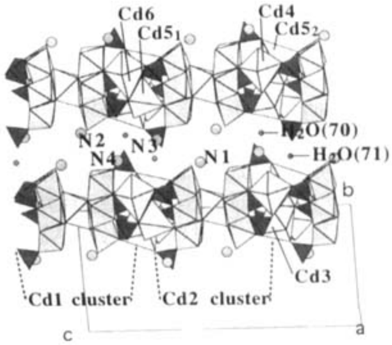

Figure 2. Projection of **2** along $\vec{a}$.

Abstract in French: *Deux nouveaux hydroxyphosphates de molybdène(V) ont été obtenus par synthèse hydrothermale:* $Na_2Cd_3(Mo_2O_4OH)_6(PO_4)_2(PO_3OH)_6[N(CH_3)_4]_4 \cdot 10\,H_2O$ *(**1**) et* $Cd_9(Mo_2O_4OH)_{12}(PO_4)_6(PO_3OH)_{10}[N(CH_3)_4]_8 \cdot 15\,H_2O$ *(**2**). Leurs structures ont été déterminées par diffraction des rayons X sur monocristaux. Les molécules d'eau et les groupements hydroxyles ont été déduits des calculs de valence électrostatique. Les deux composés cristallisent dans le groupe d'espace triclinique* $P\bar{1}$, *avec les paramètres de maille suivants:* $a = 12.340(2)$, $b = 12.596(1)$, $c = 14.717(2)$ Å, $\alpha = 107.24(1)°$, $\beta = 89.83(1)°$, $\gamma = 114.31(1)°$, $V = 1972.3(4)$ Å^3 *pour **1** et* $a = 11.942(1)$, $b = 13.339(2)$, $c = 26.765(3)$ Å, $\alpha = 85.33(1)°$, $\beta = 86.87(1)°$, $\gamma = 64.08(1)°$, $V = 3821.3(9)$ Å^3 *pour **2**. Les deux charpentes comportent des clusters anioniques de type* $[Mo_6P_4X_{31}]^{n-}$ $(X = O, OH)$, *mais **1** présente une structure tridimensionnelle tandis que **2** a une structure monodimensionnelle.*

The analysis of selected bond lengths for **1** and **2** shows that the MoO_6 octahedra in both structures present the characteristic geometry of Mo^V, with a short Mo–O bond (ranging from 1.65 to 1.69 Å) opposed to an abnormally long Mo–O bond (ranging from 2.22 to 2.36 Å) and four intermediate equatorial Mo–O bonds with distances ranging from 1.91 to 2.13 Å.[11] Nevertheless, one can see that the equatorial distances can be assigned to three categories: a) the shortest ones (ranging from 1.91 to 1.99 Å) correspond to the oxygen atoms that bridge two edge-sharing octahedra (i.e., to Mo–O–Mo bonds); b) intermediate distances (from 2.05 to 2.10 Å) characterize the Mo–O–P bonds; c) the longest Mo–O distances (from 2.08 to 2.13 Å) correspond to the hydroxyl groups bridging two MoO_6 octahedra, Mo–OH–Mo. The valence calculation confirmed the pentavalent character of molybdenum atoms, since values ranging from 4.76 to 4.94 were obtained. The Mo–Mo distances observed in Mo_6O_{22} rings show that these rings can be considered more as an association of three Mo_2O_{10} dimers than as a ring of six edge-sharing octahedra. There are indeed two types of Mo–Mo distances: three short distances (from 2.60 to 2.61 Å) on one hand and three longer ones (from 3.52 to 3.57 Å) on the other hand.

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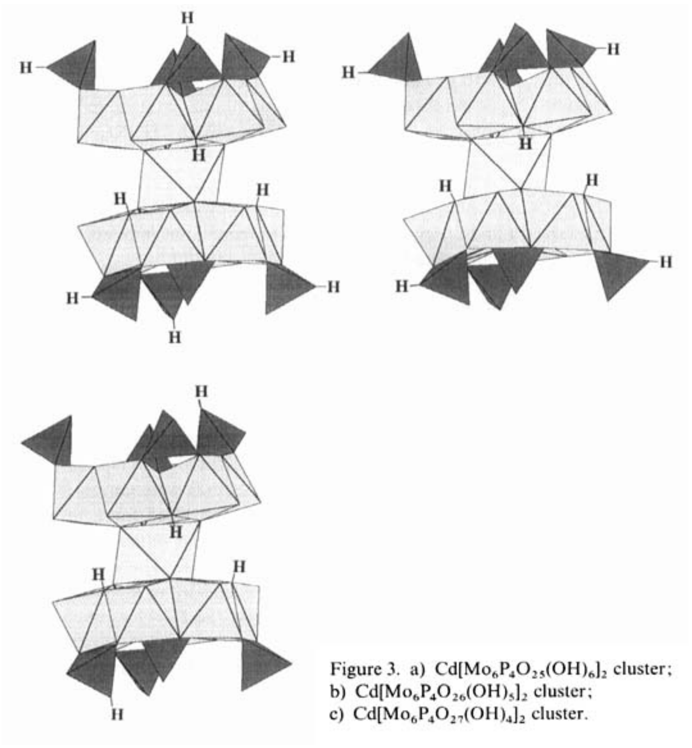


Figure 3. a) $Cd[Mo_6P_4O_{25}(OH)_6]_2$ cluster; b) $Cd[Mo_6P_4O_{26}(OH)_5]_2$ cluster; c) $Cd[Mo_6P_4O_{27}(OH)_4]_2$ cluster.

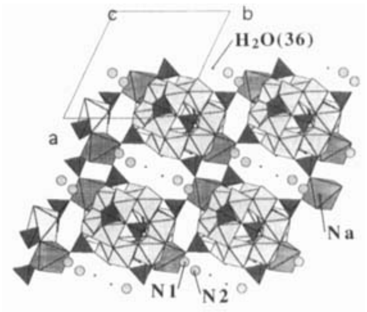


Figure 4. Projection of **1** along $\vec{c}$.

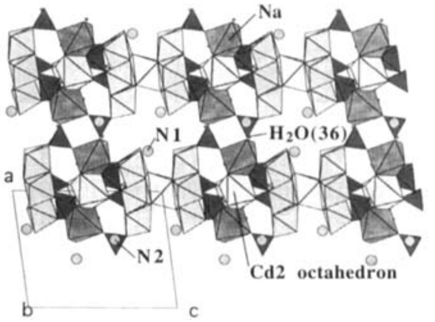


Figure 5. Projection of **1** along $\vec{b}$.

The central CdO_6 octahedra are fairly regular, with Cd–O distances ranging from 2.24 to 2.32 Å. The monophosphate groups, with P–O distances ranging from 1.48 to 1.60 Å, are less regular than those observed in many monophosphates. Note that the longer P–O distances correspond either to P–O–H or to P–O–Mo bonds.

The great novelty of these new hydroxymonophosphates lies in the relative positions of their clusters and their mode of connection through NaO_6 or CdO_6 octahedra, which are fundamentally different from all other hydroxyphosphates that contain similar units. The hydroxyphosphate **1** exhibits a tridimensional structure (Figure 1). Each $Cd[Mo_6P_4O_{25}(OH)_6]_2$ cluster (called Cd 1) is linked to the next one along $\vec{c}$ through two distorted $CdO_3(H_2O)_3$ octahedra (Cd 2) in the following way: each Cd 2 octahedron shares two apices with two P tetrahedra of one Cd 1 cluster (the central PO_4 tetrahedron and one PO_3OH peripheral tetrahedron), and one apex with one PO_3OH tetrahedron of another Cd 1 cluster located below or above it along $\vec{c}$. This assemblage of Cd 1 clusters and Cd 2 octahedra forms $[Cd_3(Mo_2O_4OH)_6(PO_4)_2(PO_3OH)_6 \cdot 8\,H_2O]_\infty$ columns running along $\vec{c}$ (Figure 1). Laterally, that is, in the (001) plane (Figure 1), columns are held together through $NaO_3OH(H_2O)_2$ octahedra (Na): each Na octahedron shares one edge with one Cd 2 octahedron of one column and two apices with two PO_3OH tetrahedra of two other columns. This tridimensional framework built up of "CdMoP" clusters, Cd and Na octahedra forms large tunnels running along $\vec{a}$ (Figure 1) and along $\vec{c}$ (Figure 4) and smaller tunnels running along $\vec{b}$ (Figure 5). The $[N(CH_3)_4]^+$ cations and the additional H_2O molecules (a fully occupied O(35) site and 74% occupied O(36) site) are located at the intersection of the [100] and [001] tunnels. Thus the Mo^V hydroxyphosphate **1** can be described as an intersecting tunnel structure, whose microporous character is further enhanced by the fact that one of the H_2O sites (O(37)) that forms the $NaO_3OH(H_2O)_2$ octahedron is partially occupied (29%). It must be emphasized that the Cd(2)–O distances of the $CdO_3(H_2O)_3$ octahedra (2.29 to 2.36 Å), as well as the Na–O bonds corresponding to the $NaO_3OH(H_2O)_2$ octahedra (2.24 to 2.40 Å, excepting O(37), which does not contribute to the stability of the structure) are short. This feature strongly supports the description of this structure as a tridimensional framework, the specific role of the clusters $Cd[Mo_6P_4O_{25}(OH)_6]_2$ being considerably attenuated comparatively to other Mo^V hydroxyphosphates that exhibit similar units. In this respect the compound **1** is rather similar to $Na_8(Mo_2O_4OH)_3(PO_4)_3 \cdot (PO_3OH) \cdot nH_2O$.[8]

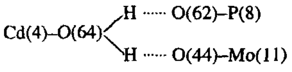
In contrast to the compound **1**, the hydroxyphosphate **2** that contains no sodium exhibits a unidimensional structure. In this structure (Figure 2), the clusters $Cd[Mo_6P_4O_{25}(OH)_6]_2$ and $Cd[Mo_6P_4O_{26}(OH)_5]_2$, Cd 1 and Cd 2 respectively, alternate along $\vec{c}$. Two successive "Cd 1/Cd 2" clusters are linked through four cadmium octahedra, Cd 3, Cd 4, Cd 5 and Cd 6. The Cd 3 and Cd 4 sites correspond to CdO_5H_2O and $CdO_3OH(H_2O)_2$ octahedra, respectively; they are both fully occupied with Cd–O distances ranging from 2.220 to 2.509 Å for Cd 3 and from 2.253 to 2.542 Å for Cd 4.[11] Cd 3 shares two adjacent apices with the two "central" tetrahedra of two different clusters, one apex with a "peripheral" PO_4 tetrahedron of one cluster, and a fourth corner with a bridging oxygen atom of two edge-sharing molybdenum octahedra of the other cluster. The Cd 4 octahedron shares one apex with a "peripheral" tetrahedron of one cluster, one apex with two edge-sharing MoO_6 octahedra of the same cluster, and one edge with a peripheral tetrahedron of the next cluster. The Cd 5 site is split over two sites, Cd 5_1 and Cd 5_2, that are 70% and 30% occupied, respectively. Cd 5_1 forms a CdO_5H_2O octahedron that shares one face with one Cd 3 octahedron, whereas Cd5_2, corresponding to a $CdO_3OH(H_2O)_2$ octahedron, shares one edge with Cd 3, but also one apex with

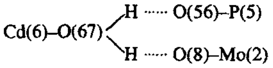
Cd 4. The Cd 5_1 and Cd 5_2 octahedra are severely distorted, with Cd–O distances ranging from 2.178 to 2.567 Å and from 2.213 to 2.84 Å, respectively. The $CdO_4(H_2O)_2$ octahedra corresponding to Cd 6 are half occupied with Cd–O distances ranging from 2.222 to 2.61 Å. This octahedron shares one edge with one unit and two apices with the other unit. Note that when Cd 6 and Cd 5_2 are simultaneously present in the structure, their octahedra share one edge (O(52) and O(62)).

This assemblage of $Cd[Mo_6P_4O_{25}(OH)_6]_2$ and $Cd[Mo_6P_4O_{26}(OH)_5]_2$ clusters through cadmium octahedra results in $[Cd_9(Mo_2O_4OH)_{12}(PO_4)_6(PO_3OH)_{10}\cdot 11\,H_2O]_\infty$ columns running along $\vec{c}$ (Figure 2). The cohesion of the structure is ensured by hydrogen bonds in the following way:

a) Along $\vec{b}$ the "free" (i.e., not bonded to Cd) water molecules (O(70) and O(71)) link two columns according to the scheme:
Cd(4)–O(65)H ··· O(70) ··· HO(59)–P(7)
P(6)–O(58) ··· HO(70) ··· HO(59)–P(7)
Mo(1)–O(2) ··· HO(70) ··· HO(59)–P(7)
P(6)–O(57)H ··· O(71) ··· HO(68)–Cd(6)
P(6)–O(57)H ··· O(71)H ··· O(60)–P(7)
P(6)–O(57)H ··· O(71)H ··· O(40)–Mo(10)

b) Along $\vec{a}$ it is principally the water molecules O(67) and O(64) that ensure the bonding according to the scheme:


$$\text{Cd(4)–O(64)}\begin{cases}\text{H} \cdots\cdots \text{O(62)–P(8)}\\ \text{H} \cdots\cdots \text{O(44)–Mo(11)}\end{cases}$$


$$\text{Cd(6)–O(67)}\begin{cases}\text{H} \cdots\cdots \text{O(56)–P(5)}\\ \text{H} \cdots\cdots \text{O(8)–Mo(2)}\end{cases}$$

As in **1**, the $[N(CH_3)_4]^+$ cations are located between the infinite columns (Figure 2).

Experimental Section

Synthesis: Single crystals of **1** and **2** were synthesized hydrothermally (heated for 36 hours at 220 °C and then cooled at 1.67° per hour to 20 °C) in Teflon-lined autoclaves from $Na_2MoO_4\cdot 2H_2O$, Mo, CdO, H_3PO_4 (75%), $(CH_3)_4NOH$ and water in the molar ratio of 2:1:1:18:7:500. The resulting mixture was filtered off, washed with water and air-dried at ambient temperature. The result was a mixture of reddish-brown powder with well-formed orange crystals of **1** and **2**. Several attempts to prepare large amounts of each phase in the form of powdered samples were unsuccessful.

Structure determination: Two orange crystals with dimensions 0.058 × 0.045 × 0.039 mm for **1** and 0.167 × 0.103 × 0.128 mm for **2** were selected for the structure determinations. The cell parameters reported in Table 1 were determined and refined by diffractometric techniques at 294 K with a least-squares refinement based upon 25 reflections with $18 \leq \theta \leq 22°$. The data were collected with an Enraf Nonius CAD4 diffractometer with the parameters reported in Table 1. Of the 18083 and 47802 reflections that were measured for **1** and **2**, respectively, 2170 and 17399 with $I \geq 3\sigma(I)$ were corrected for Lorentz and polarization effects for **1** and **2**, for absorption for **1** and for secondary extinction for **2**. Structure determinations and refinements were performed with the aid of the XTALL program package. The atoms were located with the heavy atom method and the refinements led to $R = 0.040$ and $R_w = 0.034$ for 1 and to $R = 0.040$ and $R_w = 0.044$ for **2**.

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[11] Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-406698 (**1**) and CSD-406699 (**2**).