

A Mo(V) Monophosphate Built Up from Cd_2O_{10} and Mo_2O_{10} Bioctahedra: $\text{CdMoO}_2\text{PO}_4$

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A Mo(V) monophosphate involving cadmium has been synthesized for the first time. This new phase $\text{CdMoO}_2\text{PO}_4$ crystallizes in the $P2_1/c$ space group with $a = 4.9229(4) \text{ \AA}$, $b = 8.550(1) \text{ \AA}$, $c = 11.418(2) \text{ \AA}$, and $\beta = 109.193^\circ(9)$. This crystal structure can be described in two different ways. In a first description one considers a tridimensional host lattice $[\text{MoPO}_6]_z$ built up from Mo_2O_{10} bioctahedra and monophosphate groups sharing their corners and forming tunnels running along a and b , where the Cd^{2+} cations are located with a distorted octahedral coordination. The Mo_2O_{10} bioctahedra, that consist of two edge-sharing MoO_6 octahedra, exhibit a geometry characteristic of Mo(V), with two abnormally short Mo–O bonds in the *trans* position with respect to the basal plane of the unit, corresponding to the free oxygen apices. In the second description one considers a pure octahedral framework $[\text{CdMoO}_6]_z$ built up from Cd_2O_{10} and Mo_2O_{10} bioctahedra. The latter share their edges forming $[\text{Mo}_2\text{Cd}_2\text{O}_{18}]_z$ ribbons waving along b . The assemblage of these ribbons forms a rather close packed framework, whose tetrahedral cavities are occupied by phosphorus. © 1996

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Numerous molybdenum(V) monophosphates have been synthesized this past decade (see for a review Ref. 1). Most of them are stabilized by the presence of large cations such as alkaline or alkaline earth elements; the latter favor the formation of cages and tunnels which are generally bordered by the oxygen atoms of the molybdenyl group forming the MoO_6 octahedra. In contrast, very few Mo(V) phosphates of smaller cations are known, perhaps because of their coordination that is most of the time octahedral or trigonal prismatic so that they have a difficulty to accommodate the particular configuration of the $\text{Mo}^{\text{V}}\text{O}_6$ octahedra. In this respect, cadmium is an interesting candidate, since it is susceptible to exhibit distorted CdO_6 octahedra. For this reason, we have investigated the system $\text{Cd}-\text{Mo}^{\text{V}}-\text{P}-\text{O}$. We report herein on the first molybdenum(V) cadmium phosphate, $\text{CdMoO}_2\text{PO}_4$.

SYNTHESIS

Single crystals of the title compound were grown from a mixture of nominal composition $\text{CdMo}_3\text{P}_3\text{O}_{17}$. This com-

pound has been synthesized in two steps: first $\text{H}(\text{NH}_4)_2\text{PO}_4$, $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, and MoO_3 were mixed in an agate mortar in adequate ratios according to the composition $\text{CdMo}_{2.82}\text{P}_3\text{O}_{17}$ and heated at 600 K in a platinum crucible to decompose the ammonium phosphate and the cadmium acetate. In a second step the resulting mixture was then added to the required molybdenum (0.18 mol), sealed in an evacuated silica ampoule, heated for 1 day at 1103 K and cooled at 9.6 K per hour down to 873 K. The sample was finally quenched to room temperature.

Two sorts of crystals were extracted from the resulting product: yellow crystals identified as MoPO_5 and dark red crystals. The microprobe analysis of the latter confirmed the composition CdMoPO_6 deduced from the structure determination.

Attempts to prepare this phase in the form of a powder always yielded a purple violet compound as a major compound with the right composition CdMoPO_6 . Nevertheless, the microscopic observation using a binocular evidenced a secondary white phase identified as $\text{Cd}_2\text{P}_2\text{O}_7$. The powder X-ray diffraction pattern was however indexed in the monoclinic cell (Table 1) in agreement with the parameters obtained from the single crystal X-ray study.

STRUCTURE DETERMINATION

A dark red crystal with dimensions $0.12 \times 0.10 \times 0.05 \text{ mm}^3$ was selected for the structure determination. The cell parameters reported in Table 2 were determined and refined by diffractometric techniques at 294 K with a least squares refinement based upon 25 reflections with $18^\circ \leq \theta \leq 22^\circ$. The data were collected on a CAD 4 Enraf Nonius diffractometer with the data collection parameters of Table 2. The reflections were corrected for Lorentz, polarization, absorption (Gaussian method), and secondary extinction effects.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

There are two ways to describe this structure taking into consideration the relative sizes of cadmium and molybdenum (see Table 3).

TABLE 1
Interreticular Distances

<i>h k l</i>	<i>d</i> _{calc.} (Å)	<i>d</i> _{obs.} (Å)	<i>I</i> (%)	<i>h k l</i>	<i>d</i> _{calc.} (Å)	<i>d</i> _{obs.} (Å)	<i>I</i> (%)
0 1 1	6.700	6.662	3.0	1 3 0	2.430	2.429	4.2
0 0 2	5.392	5.370	9.1	1 3 -2	2.373	2.372	8.3
1 0 0	4.649	4.645	1.8	2 1 -2	2.353	2.348	9.7
0 1 2	4.561	4.558	3.3	2 1 -1	2.350		
1 1 -1	4.248	4.238	34.7	0 2 4	2.280	2.280	0.6
1 1 0	4.084	4.076	36.2	2 1 -3	2.251	2.249	3.7
0 2 1	3.974	3.964	23.9			2.203	9.3
1 1 -2	3.832	3.820	10.7	1 3 -3	2.196	2.194	6.7
1 1 1	3.500	3.495	31.9	1 1 -5	2.186	2.184	16.0
		3.419	7.0			2.178	6.2
0 2 2	3.350	3.345	6.7	0 4 0	2.138	2.138	3.2
1 2 -1	3.220	3.216	30.2	2 2 -1	2.122	2.119	4.7
1 1 -3	3.194	3.190	6.4	1 3 2	2.085	2.084	11.4
1 2 0	3.147	3.142	8.4	2 1 -4	2.079	2.078	7.7
		3.095	2.1	2 1 1	2.069	2.069	8.0
1 0 2	3.059	3.060	6.6	1 0 4	2.057	2.057	4.4
1 2 -2	3.027	3.021	19.5	2 2 0	2.042	2.041	5.1
		2.951	3.6	1 1 4	2.000	1.997	6.1
1 1 2	2.880	2.877	16.9	1 2 -5	1.998		
1 2 1	2.855	2.853	4.1	0 4 2	1.987	1.987	7.6
		2.832	2.7	1 3 -4	1.982	1.981	7.3
0 3 1	2.755	2.750	100.0	1 4 -1	1.959	1.957	1.7
0 2 3	2.751			0 3 4	1.959		
0 0 4	2.696	2.692	7.1	2 2 1	1.908	1.908	10.5
1 1 -4	2.625	2.622	11.5	1 0 -6	1.900	1.902	4.7
0 1 4	2.571	2.570	8.0	2 1 -5	1.881	1.880	6.6
0 3 2	2.520	2.517	7.2	1 3 3	1.870	1.867	21.9
1 2 2	2.488	2.486	4.3	1 4 1	1.867		
1 3 -1	2.463	2.460	12.8	2 3 -2	1.857	1.861	8.9
				2 3 -1	1.855	1.853	7.0
				1 1 -6	1.854		
				1 2 4	1.854		

In the first description, cadmium, due to its size being significantly larger than molybdenum, can be considered as an interpolated cation distributed in the tunnels formed by the $[\text{MoPO}_6]_\infty$ host lattice. This is illustrated by the projections of the structure along **a** (Fig. 1) and **b** (Fig. 2). One observes Mo_2O_{10} bioctahedra built up of two edge-sharing MoO_6 octahedra sharing their apices with PO_4 tetrahedra. It results in rather large S-shape tunnels running along **a** (Fig. 1) and smaller tunnels running along **b** (Fig. 2). The cadmium cations are located at the intersection of these two kinds of tunnels. Along **c** and **b** (Fig. 1) the Mo_2O_{10} bioctahedra are linked through single PO_4 tetrahedra, so that two successive columns of bioctahedra running along **b** are located at two different levels along **a** (compare the two types of bioctahedra on Fig. 1). In fact, a very simple description of this framework can be made by considering the $[\text{MoPO}_8]_\infty$ chains running along **a** (Fig. 2).

In such chains, observed in many molybdenum(V) phosphates, one octahedron alternates with one tetrahedron, these two polyhedra sharing an apex (Fig. 3a). It must nevertheless be noticed that several kinds of $[\text{MoPO}_8]_\infty$ chains exist, depending on the types of apices linked; here, an octahedron shares one of its apical and one of its equatorial apices with two tetrahedra (Fig. 3a). Two $[\text{MoPO}_8]_\infty$ chains are linked together in order to form $[\text{Mo}_2\text{P}_2\text{O}_{14}]_\infty$ columns running along **a**: each octahedron of one chain shares an edge with an octahedron of the other chain, leading to the Mo_2O_{10} bioctahedra and to six-sided windows (delimited by two Mo_2O_{10} units and two PO_4 groups) (Fig. 3b). The assemblage of the $[\text{Mo}_2\text{P}_2\text{O}_{14}]_\infty$ columns, which gives the $[\text{MoPO}_6]_\infty$ framework, is made in the following way: each tetrahedron of one column shares one apex with one octahedron of another column. As a result, each column is connected to four similar ones and four columns delimit one tunnel running along **a** (Fig. 1).

TABLE 2
Summary of Crystal Data, Intensity Measurements, and
Structure Refinement Parameters for CdMoO₂PO₄

Crystal data	
Space group	$P2_1/c$
Cell dimensions	$a = 4.9229(4) \text{ \AA}$ $b = 8.550(1) \text{ \AA}$ $c = 11.418(2) \text{ \AA}$
	$\beta = 109.193(9)^\circ$
Volume	$453.9(2) \text{ \AA}^3$
Z	4
d_{calc}	4.91
Intensity measurements	
λ (MoK α)	0.71073 \AA
Scan mode	$\omega - 4/3\theta$
Scan width ($^\circ$)	$1. + 0.35 \tan \theta$
Slit aperture (mm)	$1. + \tan \theta$
Max θ ($^\circ$)	45°
Measured reflections	4023
Standard reflections	3 (every 3000 s)
Reflections with $I > 3\sigma$	2998
μ (mm^{-1})	7.67
Structure solution and refinement	
Parameters refined	83
Agreement factors	$R = 0.018, R_w = 0.022$
Weighting scheme	$w = f(\sin \theta/\lambda)$
Δ/σ max	< 0.01
$\Delta\rho$ ($\text{e}\text{\AA}^{-3}$)	< 1.6

TABLE 3
Positional Parameters and Their Estimated Standard
Deviations for CdMoO₂PO₄

Atom	x	y	z	B (\AA^2)
Cd	0.32727 (3)	0.15835 (1)	0.41551 (1)	0.610 (1)
Mo	0.01452 (3)	0.07669 (2)	0.10103 (1)	0.344 (2)
P	0.31131 (9)	0.43437 (5)	0.21002 (4)	0.349 (5)
O(1)	-0.2751 (3)	0.1963 (2)	0.0537 (2)	0.90 (2)
O(2)	-0.0543 (3)	0.0259 (2)	0.2717 (1)	0.65 (2)
O(3)	0.2566 (3)	0.2573 (2)	0.2164 (1)	0.65 (2)
O(4)	0.1537 (3)	0.1247 (2)	-0.0376 (1)	0.58 (1)
O(5)	0.4111 (3)	-0.0316 (2)	0.1855 (1)	0.71 (2)
O(6)	0.3328 (3)	0.0185 (2)	0.5838 (1)	0.68 (2)

Note. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B = 4/3 \sum_i \sum_j \mathbf{a}_i \cdot \mathbf{a}_j \cdot \beta_{ij}$.

Each Mo₂O₁₀ unit is connected to six tetrahedra: four of the same [Mo₂P₂O₁₄] $_{\infty}$ column and two of two other columns. On the other hand, each PO₄ tetrahedron is linked to three Mo₂O₁₀ units (two of them belong to the same [Mo₂P₂O₁₄] $_{\infty}$ column) and exhibits one free apex directed toward the center of the large tunnels (Fig. 1).

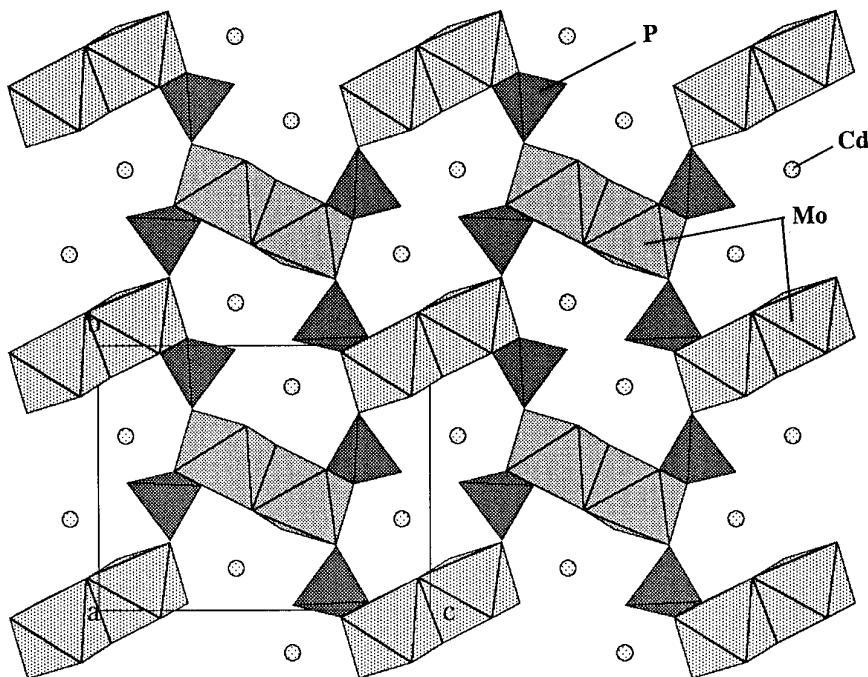


FIG. 1. Projection of the structure along a .

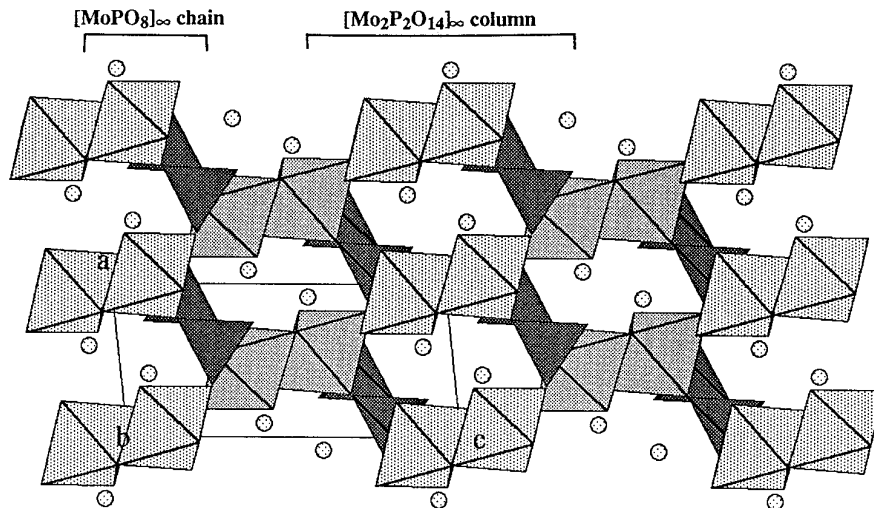


FIG. 2. Projection of the structure along **b**.

In the second description, cadmium, due to its octahedral coordination, forms with molybdenum an octahedral framework. This is illustrated by the projection of the structure along **a** (Fig. 4). Cadmium also forms Cd_2O_{10} bioctahedra built up of two edge-sharing CdO_6 octahedra. Along **c**, in the (001) plane two successive Cd_2O_{10} and Mo_2O_{10} bioctahedra share their edges forming $[\text{Mo}_2\text{Cd}_2\text{O}_{18}]_\infty$ ribbons waving along that direction (Fig. 4). along **b**, two successive $[\text{Mo}_2\text{Cd}_2\text{O}_{18}]_\infty$ ribbons are located at different x levels; each Cd_2O_{10} unit of one ribbon shares one apex with one MoO_6 octahedron of a second ribbon, and another

apex with two octahedra of a Mo_2O_{10} unit of a third ribbon. This rather close packed $[\text{MoCdO}_6]_\infty$ framework forms tetrahedral holes (Figs. 4 and 5) where the phosphorus atoms are located.

The PO_4 tetrahedron exhibits P–O distances ranging from 1.52 to 1.56 Å (Table 4), similar to those usually observed in monophosphates. The geometry of the MoO_6 octahedron is characteristic of Mo(V): it owns one free apex corresponding to a molybdenyl group with a short Mo–O bond of 1.69 Å (Table 4). But it must be noticed that, in contrast to the usual observed geometry of the $\text{Mo}^{\text{V}}\text{O}_6$ octahedra, the oxygen atom opposed to the free apex does not exhibit the longest Mo–O distance. The fact that this corner is shared with a PO_4 group whereas the equatorial oxygen atoms of the MoO_6 octahedra are triply bonded and linked to the cadmium can explain this difference. However, the pentavalent character of the molybdenum atom is confirmed by the valence calculations since values of 4.9 are obtained. As described above, two MoO_6 octahedra share one edge, forming an Mo_2O_{10} unit which was already observed in two Mo(V) phosphates: $\text{Na}_3\text{Mo}_2\text{P}_2\text{O}_{11}(\text{OH}) \cdot 2\text{H}_2\text{O}$ (2) and $\beta\text{-K}_2(\text{MoO}_2)_2\text{P}_2\text{O}_7$ (3). The short Mo–Mo distance in $\text{CdMoO}_2\text{PO}_4$ (2.62 Å) is comparable to those encountered in the other compounds; nevertheless, there exists a difference in the configuration of Mo_2O_{10} units, since the two free apices of one unit have a *cis* configuration with respect to the equatorial plane of the Mo_2O_{10} unit in $\text{Na}_3\text{Mo}_2\text{P}_2\text{O}_{11}(\text{OH}) \cdot 2\text{H}_2\text{O}$ and in $\beta\text{-K}_2(\text{MoO}_2)_2\text{P}_2\text{O}_7$, whereas they have a *trans* configuration in $\text{CdMoO}_2\text{PO}_4$. Another particular feature of this compound deals with the fact that the free apices of the MoO_6 octahedra are not pointing so clearly toward the center of the tunnels as in other Mo(V) phosphates.

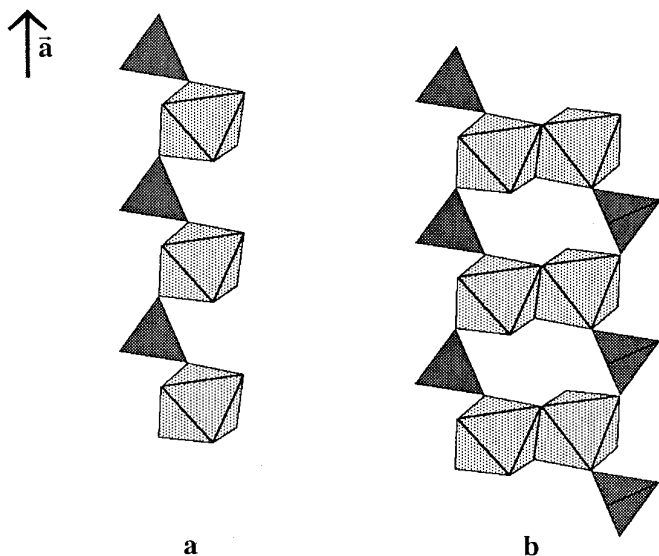


FIG. 3. (a) $[\text{MoPO}_8]_\infty$ chain running along **a**. (b) $[\text{Mo}_2\text{P}_2\text{O}_{14}]_\infty$ column resulting from the assemblage of two $[\text{MoPO}_8]_\infty$ chains.

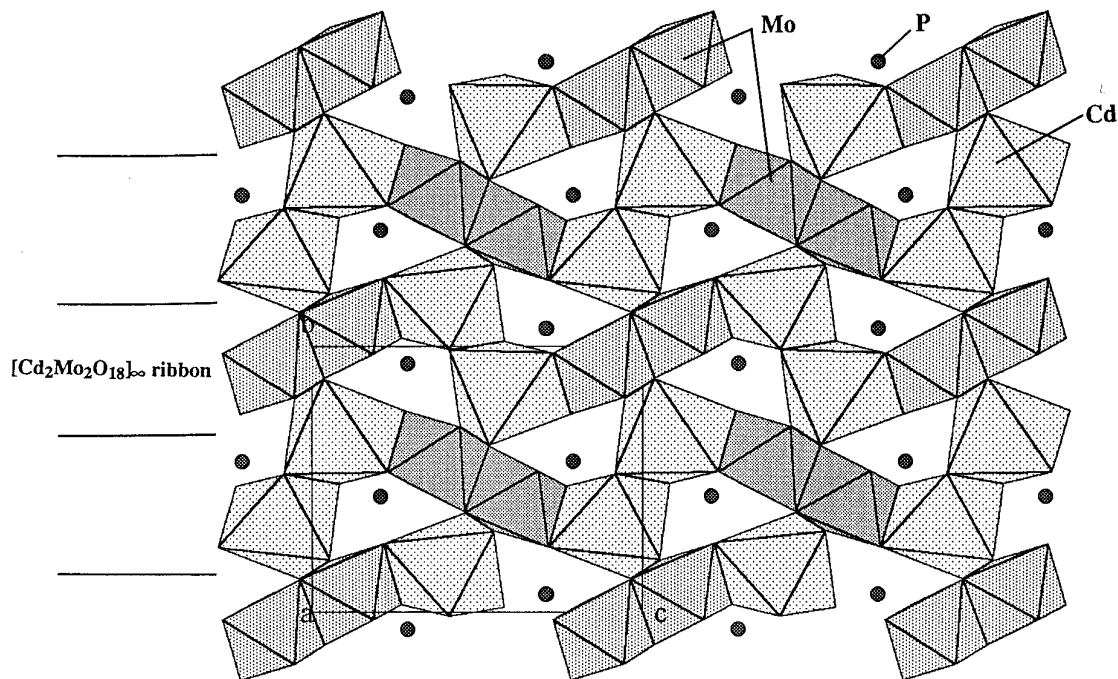


FIG. 4. Projection of the octahedral framework along *a*, showing $[\text{Cd}_2\text{Mo}_2\text{O}_{18}]_\infty$ ribbons.

TABLE 4
Distances (Å) and Angles (°) in the Polyhedra

Mo	O(1)	O(2)	O(3)	O(4)	O(4 ⁱ)	O(5)
O(1)	1.693 (2)	2.779 (2)	2.716 (2)	2.714 (2)	2.828 (2)	3.759 (3)
O(2)	92.57 (8)	2.130 (2)	2.700 (2)	4.076 (3)	2.860 (2)	2.819 (2)
O(3)	90.04 (8)	78.82 (6)	2.123 (1)	2.998 (2)	4.025 (3)	2.643 (2)
O(4)	95.55 (8)	169.37 (6)	94.29 (6)	1.964 (1)	2.904 (3)	2.851 (2)
O(4 ⁱ)	101.84 (8)	89.07 (6)	163.45 (6)	95.95 (6)	1.944 (1)	2.785 (2)
O(5)	167.69 (8)	83.86 (6)	77.73 (6)	89.90 (7)	86.78 (6)	2.088 (2)
	P	O(2 ⁱⁱ)	O(3)	O(5 ⁱⁱⁱ)	O(6 ^{iv})	
O(2 ⁱⁱ)		1.559 (2)	2.525 (2)	2.537 (2)	2.496 (2)	
O(3)		108.92 (9)	1.544 (2)	2.446 (2)	2.546 (2)	
O(5 ⁱⁱⁱ)		111.05 (9)	106.06 (9)	1.518 (2)	2.521 (2)	
O(6 ^{iv})		107.68 (9)	111.67 (9)	111.47 (9)	1.533 (2)	
Cd	O(1 ^{vi})	O(2)	O(3)	O(4 ^{vii})	O(6 ^v)	O(6)
O(1 ^{vi})	2.415 (2)	4.754 (3)	3.803 (3)	2.728 (2)	3.137 (2)	3.198 (2)
O(2)	176.57 (6)	2.341 (2)	2.700 (2)	3.640 (3)	3.410 (3)	3.446 (3)
O(3)	106.15 (6)	70.43 (6)	2.342 (2)	3.178 (2)	3.438 (3)	4.569 (3)
O(4 ^{vii})	72.60 (6)	107.15 (6)	89.18 (6)	2.181 (1)	4.346 (3)	3.347 (3)
O(6 ^v)	86.33 (6)	95.82 (6)	96.82 (6)	156.94 (6)	2.254 (2)	2.924 (2)
O(6)	84.35 (6)	97.09 (6)	167.09 (6)	97.92 (6)	80.83 (6)	2.256 (2)

Symmetry code

- | | |
|---------------------------------|--------------------------------|
| (i) $-x, -y, -z$ | (iv) $x, 1/2 - y, z - 1/2$ |
| (ii) $-x, 1/2 + y, 1/2 - z$ | (v) $1 - x, -y, 1 - z$ |
| (iii) $1 - x, 1/2 + y, 1/2 - z$ | (vi) $1 + x, 1/2 - y, 1/2 + z$ |
| | (vii) $x, 1/2 - y, 1/2 + z$ |

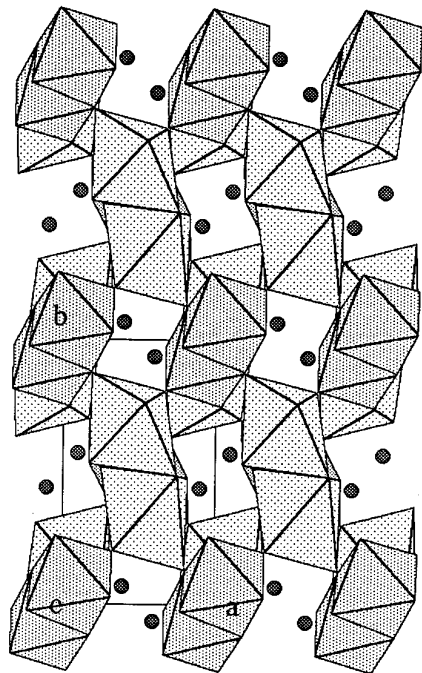


FIG. 5. Projection of the octahedral framework along *c*.

The geometry of the CdO_6 octahedron, with Cd–O distances ranging from 2.18 to 2.42 Å (Table 4), shows a significant distortion. It suggests a rather large flexibility of cadmium, which may be promising for the generation of new mixed frameworks.

CONCLUDING REMARKS

A molybdenum(V) phosphate involving cadmium has been synthesized for the first time. The main feature deals with the great ability of Mo(V) and cadmium to form a rather close packed octahedral framework. This study opens the route to the research of ternary or pseudo-ternary oxides involving Mo(V) and cadmium, in which the presence of phosphate groups may not be necessary.

REFERENCES

1. G. Costentin, A. Leclaire, M. M. Borel, A. Grandin, and B. Raveau, *Rev. Inorg. Chem.* **13**, 77 (1993).
2. L. A. Mundi and R. Haushalter, *Inorg. Chem.* **29**, 2879 (1990).
3. A. Guesdon, A. Leclaire, M. M. Borel, A. Grandin, and B. Raveau, *J. Solid State Chem.* **114**, 481 (1995).