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Structure of the Trivalent Molybdenum Metaphosphate $Mo(PO_3)_3$

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Crystals of the molybdenum(III) metaphosphate $Mo(PO_3)_3$ were grown by chemical vapor transport with iodine (1173 K → 1073 K). The structure was determined by single crystal X-ray diffraction. $Mo(PO_3)_3$ crystallizes in the monoclinic space group *Ia*, with a = 10.819(1) Å, b = 19.515(3) Å, c = 9.609(1) Å, β = 97.74(1)°, and Z = 12. $Mo(PO_3)_3$, and has a structure consisting of infinite chains of corner-sharing PO_4 tetrahedra running along [001], bridged by isolated MoO_6 octahedra. The octahedra are regular, with an average Mo–O distance of 2.084 Å. The structure can also be viewed as containing infinite MoP_3O_{14} chains along [102], which are linked so as to define small tunnels running in the same direction.

INTRODUCTION

The very rich chemistry of transition metal oxides is due to the ability of the transition elements to adopt several oxidation states with various coordination geometries. Among them, molybdenum is a very interesting element owing to its various oxidation states: III, IV, V, VI, and possible mixed valence. Nevertheless, until recently, trivalent molybdenum was considered unusual. It has in fact been observed over recent years in ternary phosphates (1–7), showing its close similarity with other trivalent transition elements such as Fe(III), V(III), or Ti(III).

In the Mo–P–O system, the compound $Mo(PO_3)_3$ is the only trivalent molybdenum phosphate which has been isolated until now (8), but its structure has not been established. The present paper reports the crystal growth and the structure determination of this Mo(III) metaphosphate, which is shown to be isostructural with $V(PO_3)_3$ (9).

SYNTHESIS AND CRYSTAL GROWTH

Microcrystalline $Mo(PO_3)_3$ was prepared from a high-temperature melt, as described in detail elsewhere (10). This preparation gives essentially pure material as indicated by X-ray powder diffraction and elemental analysis, although the samples used for crystal growth were sieved through 0.2-mm nylon mesh to remove occasional dark impurity particles.

Larger crystals of $Mo(PO_3)_3$ were grown by chemical vapor transport (CVT) with iodine, analogous with recent work on tungsten phosphates (11). CVT experiments were conducted in closed silica ampoules in a two-zone furnace (12), and yielded products mainly in the form of polycrystalline aggregates. For the run which produced the crystal used in the structure determination, 0.64 g of $Mo(PO_3)_3$ and ~10 mg of I_2 were sealed under vacuum in an ampoule 15 cm long and 8 mm in bore. The ampoule was heated for 10 days with a source temperature of 1173 K and a sink temperature of 1073 K, resulting in the transport of ~25 mg of material. Residual I_2 was removed from the transported product under dynamic vacuum at room temperature. The infrared spectrum of a KBr pellet prepared from crushed CVT crystals proved identical to that of the microcrystalline $Mo(PO_3)_3$ starting material (10).

STRUCTURE DETERMINATION

A yellow crystal 0.154 × 0.103 × 0.077 mm was selected for the structure determination. The cell parameters reported in Table 1 were determined 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 on a CAD 4 Enraf–Nonius diffractometer with the data collection parameters reported in Table 1. The reflections were corrected for Lorentz, polarization, and secondary extinction effects. No absorption corrections were performed. The systematic absences $h + k + l = 2n + 1$ for all reflections and $h = 2n + 1$ for $h\,0\,l$ are consistent with the space groups *I*2/*a* and *Ia*, in agreement with the cell previously determined by Douglas and Staritzky (8). The structure was solved by the heavy atom method. The structure refinement was successful only with the noncentrosymmetric group *Ia*. The refinement of the atomic coordinates and their anisotropic thermal factors lead to R = 0.024 and R_w = 0.024, and to the atomic parameters of Table 2.

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TABLE 1
Summary of Crystal Data Intensity, Measurements, and Structure Refinement Parameters for $Mo(PO_3)_3$

Crystal data	
Space group	*Ia*
Cell dimensions	a = 10.819(1) Å
	b = 19.515(3) Å β = 97.74(1)°
	c = 9.609(1) Å
Volume	2010(3) Å^3
Z	12
Intensity measurements	
λ (Mo$K\alpha$)	0.71073 Å
Scan mode	$\omega + 2/3\theta$
Scan width (°)	$1 + 0.35 \tan\theta$
Slit aperture (mm)	$1 + \tan\theta$
Max θ(°)	45
Standard reflections	3 (every 3000 s)
Reflections with $I > 3\sigma$	5049
μ (mm^{-1})	2.64
Structure solution and refinement	
Parameters refined	351
Agreement factors	R = 0.024 R_w = 0.024
Weighting scheme	$w = f(\sin\theta/\lambda)$
Δ/σ_{max}	<0.01
$\Delta\rho$ (eÅ^{-3})	<0.5

TABLE 2
Positional Parameters and Their Estimated Standard Deviations

Atom	x	y	z	B(A2)
Mo(1)	0	0.17096(1)	0	0.472(3)
Mo(2)	0.50301(3)	0.16133(1)	0.00075(4)	0.471(3)
Mo(3)	0.48049(2)	−0.00578(1)	0.51493(3)	0.498(3)
P(1)	0.13457(8)	0.11402(4)	0.32050(9)	0.53(1)
P(2)	0.34401(8)	0.11293(4)	0.69318(9)	0.58(1)
P(3)	0.13263(8)	0.05395(4)	0.82716(9)	0.56(1)
P(4)	0.72401(8)	0.10814(5)	0.5176(1)	0.59(1)
P(5)	0.34834(8)	0.05238(4)	0.19737(9)	0.54(1)
P(6)	0.64779(8)	0.22342(4)	0.31077(9)	0.55(1)
P(7)	0.85918(8)	0.21809(4)	0.6848(1)	0.61(1)
P(8)	0.26594(8)	0.22652(4)	0.4909(1)	0.59(1)
P(9)	0.75198(9)	0.06020(5)	−0.0035(1)	0.61(1)
O(1)	−0.1094(2)	0.2532(1)	0.0504(3)	0.78(3)
O(2)	−0.0341(3)	0.1943(1)	−0.2116(3)	0.88(4)
O(3)	−0.1621(3)	0.1130(2)	−0.0451(3)	1.00(4)
O(4)	0.1043(3)	0.0851(2)	−0.0401(3)	1.02(4)
O(5)	0.1528(3)	0.2380(2)	0.0247(4)	1.60(5)
O(6)	0.0362(3)	0.1427(2)	0.2132(3)	1.08(4)
O(7)	0.5501(3)	0.2149(2)	0.1877(3)	1.21(4)
O(8)	0.3670(3)	0.2328(2)	−0.0583(3)	1.05(4)
O(9)	0.6321(3)	0.2191(2)	−0.0925(3)	1.02(4)
O(10)	0.6346(3)	0.0826(2)	0.0476(4)	1.18(4)
O(11)	0.3702(3)	0.1083(2)	0.0999(3)	1.22(4)
O(12)	0.4491(3)	0.1138(2)	−0.1910(3)	1.01(4)
O(13)	0.6278(3)	0.0623(2)	0.5629(4)	1.25(4)
O(14)	0.4462(3)	0.0395(2)	0.3182(3)	1.10(4)
O(15)	0.5224(3)	−0.0364(2)	0.7248(3)	1.08(4)
O(16)	0.5926(3)	−0.0818(2)	0.4456(3)	1.01(4)
O(17)	0.3520(3)	0.0619(2)	0.5803(3)	1.08(4)
O(18)	0.3382(3)	−0.0782(2)	0.4736(4)	1.37(4)
O(19)	0.2163(3)	0.0604(2)	0.2492(3)	1.10(4)
O(20)	0.2354(3)	0.1710(2)	0.3725(3)	1.18(4)
O(21)	0.3251(3)	0.1866(2)	0.6279(3)	1.11(4)
O(22)	0.2165(3)	0.1048(2)	0.7544(4)	1.52(4)
O(23)	0.2226(3)	−0.0102(2)	0.8662(3)	1.30(4)
O(24)	0.6582(3)	0.1538(2)	0.3944(4)	1.13(4)
O(25)	0.7585(3)	0.1599(1)	0.6473(3)	0.96(4)
O(26)	0.3303(3)	−0.0174(2)	0.1161(3)	1.19(4)
O(27)	0.7810(2)	0.2728(1)	0.7586(3)	0.92(3)

Note. Anisotropically refined atoms are given in the isotropic equivalent displacement parameter defined as: $B = \frac{4}{3}[\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab\cos\gamma + \beta_{13}ac\cos\beta + \beta_{23}bc\cos\alpha]$.

DESCRIPTION OF THE STRUCTURE

The metaphosphate $Mo(PO_3)_3$ is isotypic with $V(PO_3)_3$ (9). Its structure is built up from isolated MoO_6 octahedra linked through infinite $[PO_3]_\infty$ chains of PO_4 tetrahedra (Fig. 1). Each octahedron share its six apices with six different PO_4 tetrahedra. As shown in Table 3, the geometry of the octahedra is regular. The mean Mo–O distance is 2.084 Å, larger than that observed in more oxidized molybdenum phosphates. The electrostatic valence calculated by Zachariasen curves (13) of 3.23 is in agreement with the valence of sample III deduced from the formula $Mo(PO_3)_3$. The geometry of the tetrahedra is almost regular (Table 3). Each tetrahedron shares corners with two octahedra and two tetrahedra. Thus one observes two sets of P–O distances, one involving oxygens common to P and Mo, ranging from 1.479 to 1.489 Å, and the second involving oxygens bonded to two P atoms, ranging from 1.569 to 1.608 Å.

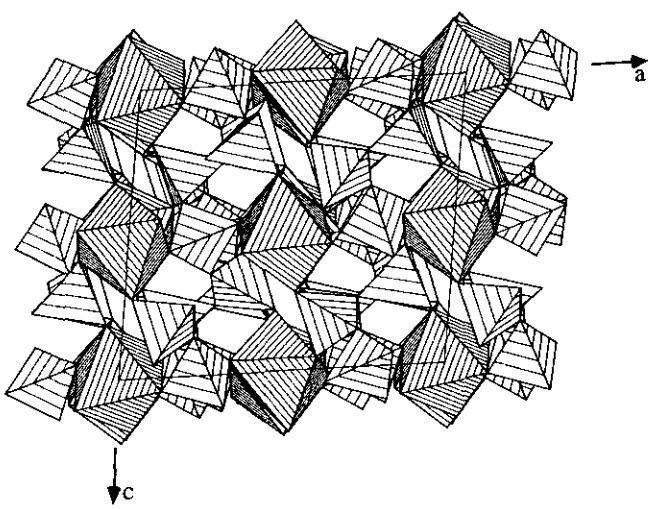

FIG. 1. Projection of the structure of $Mo(PO_3)_3$ along **b**.

TABLE 3
Distances (Å) and Angles (°) in Polyhedra

Mo(1)	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)
O(1)	2.089(4)	2.980(6)	2.917(6)	4.171(6)	2.895(6)	2.985(6)
O(2)	91.6(2)	2.068(4)	2.756(6)	2.972(6)	2.955(6)	4.173(6)
O(3)	88.7(2)	83.2(2)	2.083(4)	2.927(6)	4.170(6)	3.108(6)
O(4)	176.2(2)	91.4(2)	89.2(2)	2.084(4)	3.078(6)	2.865(6)
O(5)	87.5(2)	90.4(2)	172.5(2)	94.8(2)	2.096(4)	2.991(6)
O(6)	90.7(2)	177.5(2)	95.8(2)	86.3(2)	90.7(2)	2.106(4)
Mo(2)	O(7)	O(8)	O(9)	O(10)	O(11)	O(12)
O(7)	2.082(4)	2.894(6)	2.948(6)	3.106(6)	2.896(6)	4.154(6)
O(8)	88.9(2)	2.052(4)	2.944(6)	4.150(6)	2.865(6)	2.848(6)
O(9)	90.0(2)	90.6(2)	2.089(4)	2.984(6)	4.188(6)	2.922(6)
O(10)	95.9(2)	175.1(2)	90.8(2)	2.102(4)	3.012(6)	2.901(6)
O(11)	87.7(2)	87.2(2)	176.8(2)	91.6(2)	2.101(4)	3.033(6)
O(12)	176.0(2)	87.3(2)	89.1(2)	88.0(2)	93.2(2)	2.075(4)
Mo(3)	O(13)	O(14)	O(15)	O(16)	O(17)	O(18)
O(13)	2.078(4)	2.888(6)	2.812(6)	3.034(6)	3.011(6)	4.165(6)
O(14)	88.1(2)	2.075(4)	4.156(6)	3.015(6)	2.875(6)	3.057(6)
O(15)	84.8(2)	171.2(2)	2.093(4)	3.018(6)	2.885(6)	3.028(6)
O(16)	93.7(2)	93.0(2)	92.6(2)	2.082(4)	4.151(6)	2.803(6)
O(17)	92.3(2)	87.7(2)	87.6(2)	173.4(2)	2.076(4)	2.918(6)
O(18)	176.8(2)	94.5(2)	92.8(2)	84.5(2)	89.0(2)	2.089(4)
P(1)	O(6)	O(16^{i})	O(19)	O(20)		
O(6)	1.489(4)	2.531(6)	2.513(6)	2.530(6)		
O(16^{i})	117.0(3)	1.481(4)	2.492(6)	2.490(6)		
O(19)	109.7(3)	108.7(3)	1.584(4)	2.458(6)		
O(20)	110.5(3)	108.3(3)	101.5(3)	1.590(4)		
P(2)	O(12^{ii})	O(17)	O(21)	O(22)		
O(12^{ii})	1.480(4)	2.518(6)	2.493(6)	2.506(6)		
O(17)	116.3(3)	1.483(4)	2.499(6)	2.512(6)		
O(21)	109.6(3)	109.8(3)	1.570(4)	2.406(6)		
O(22)	110.0(3)	110.2(3)	99.6(3)	1.579(4)		
P(3)	O(4^{ii})	O(15^{i})	O(22)	O(23)		
O(4^{ii})	1.482(4)	2.501(6)	2.483(6)	2.495(6)		
O(15^{i})	115.2(3)	1.480(4)	2.472(6)	2.563(6)		
O(22)	108.8(3)	108.2(3)	1.571(4)	2.486(6)		
O(23)	108.1(3)	112.6(3)	103.3(3)	1.599(4)		
P(4)	O(13)	O(18^{iii})	O(24)	O(25)		
O(13)	1.482(4)	2.588(6)	2.462(6)	2.445(6)		
O(18^{iii})	119.5(3)	1.479(4)	2.479(6)	2.541(6)		
O(24)	107.4(3)	108.6(3)	1.573(4)	2.527(6)		
O(25)	104.5(3)	110.7(3)	105.1(3)	1.608(4)		
P(5)	O(11)	O(14)	O(19)	O(26)		
O(11)	1.477(4)	2.532(6)	2.519(6)	2.499(6)		
O(14)	117.6(3)	1.483(4)	2.519(6)	2.433(6)		
O(19)	110.8(3)	110.5(3)	1.582(4)	2.427(6)		
O(26)	110.2(3)	105.7(3)	100.7(3)	1.569(4)		
P(6)	O(7)	O(9^{iv})	O(24)	O(27^{v})		
O(7)	1.485(4)	2.530(6)	2.471(6)	2.511(6)		
O(9^{iv})	117.1(3)	1.481(4)	2.500(6)	2.522(6)		
O(24)	107.7(3)	109.8(3)	1.574(4)	2.446(6)		
O(27^{v})	109.4(3)	110.4(3)	101.2(3)	1.590(4)		
P(7)	O(1^{vi})	O(2^{vii})	O(25)	O(27)		
O(1^{vi})	1.489(4)	2.538(6)	2.479(6)	2.511(6)		
O(2^{vii})	116.6(3)	1.493(4)	2.551(6)	2.506(6)		
O(25)	107.7(3)	112.1(3)	1.581(4)	2.448(6)		
O(27)	109.4(3)	108.8(3)	101.1(3)	1.588(4)		

TABLE 3—*Continued*

Mo(1)	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)
P(8)	O(5^{iv})	O(8^{iv})	O(20)	O(21)		
O(5^{iv})	1.480(4)	2.552(6)	2.537(6)	2.475(6)		
O(8^{iv})	119.2(3)	1.479(4)	2.395(6)	2.470(6)		
O(20)	112.4(3)	103.3(3)	1.573(4)	2.532(6)		
O(21)	107.5(3)	107.2(3)	106.5(3)	1.588(4)		
P(9)	O(3^{viii})	O(10)	O(23^{ix})	O(26^{iii})		
O(3^{viii})	1.478(4)	2.552(6)	2.454(6)	2.433(6)		
O(10)	118.7(3)	1.488(4)	2.527(6)	2.482(6)		
O(23^{ix})	106.4(3)	110.6(3)	1.585(4)	2.528(6)		
O(26^{iii})	105.7(3)	108.3(3)	106.4(3)	1.573(4)		

Symmetry codes

i	$-\frac{1}{2} - x$	$-y$	z
ii	x	y	$1 + z$
iii	$\frac{1}{2} + x$	$-y$	z
iv	x	$\frac{1}{2} - y$	$\frac{1}{2} + z$
v	x	$\frac{1}{2} - y$	$-\frac{1}{2} + z$
vi	$1 + x$	$\frac{1}{2} - y$	$\frac{1}{2} + z$
vii	$1 + x$	y	$1 + z$
viii	$1 + x$	y	z
ix	$\frac{1}{2} + x$	$-y$	$-1 + z$

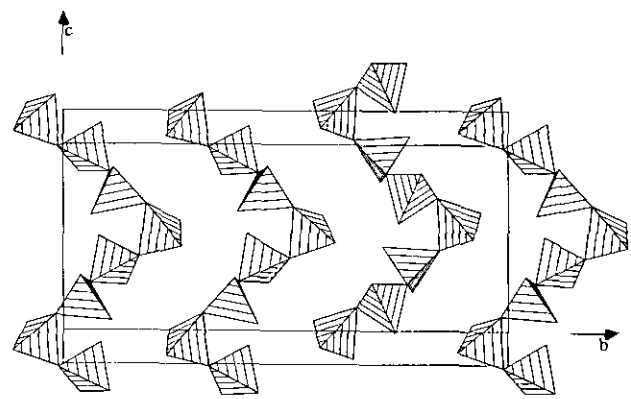

FIG. 2. The polyphosphate chain undulating along **c**.

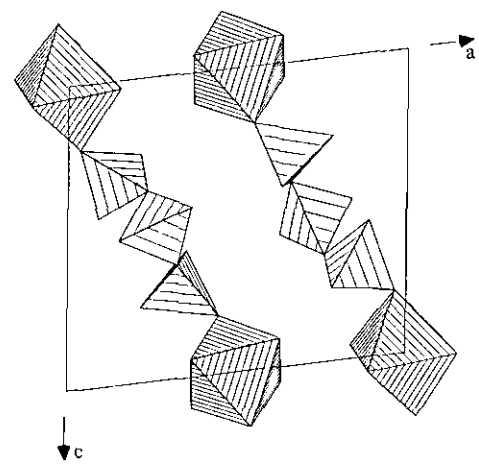

FIG. 3. $[MoP_3O_{14}]_\infty$ chains.

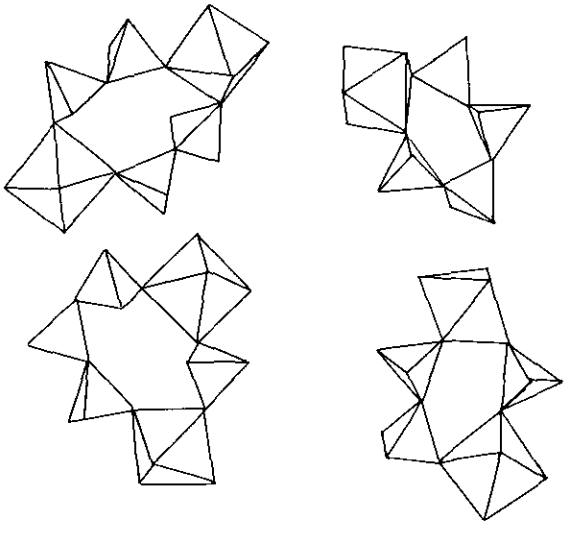

FIG. 4. The six-sided windows and five-sided windows.

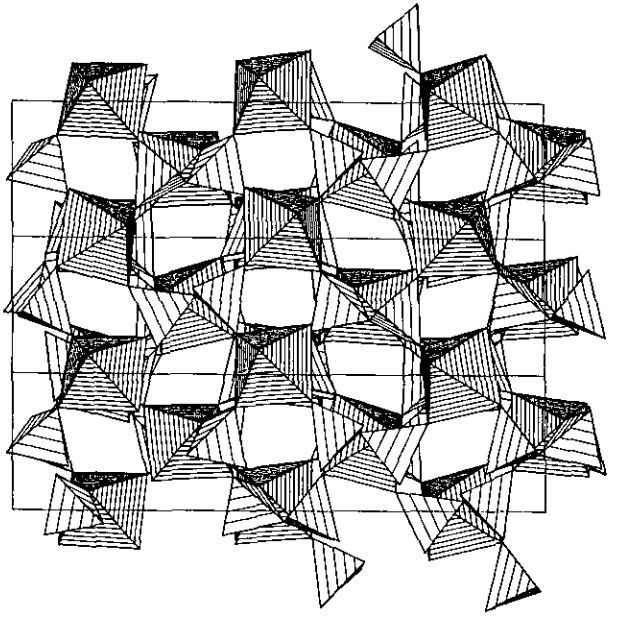

FIG. 5. A view along [102] showing the tunnels.

The PO_4 tetrahedra form infinite $[PO_3]_\infty$ chains snaking through the structure along **c** (Fig. 2). These infinite chains are linked together by isolated octahedra.

Another description is possible. One observes infinite MoP_3O_{14} chains running along [102] (Fig. 3). Each chain shares corners of its polyhedra with four adjacent chains to form the three-dimensional framework. This connectivity defines two kinds of six-sided window, built up from two octahedra and four tetrahedra, and two kinds of five-sided window, also built up from octahedra and tetrahedra (Fig. 4). This framework delimits small five-sided tunnels running along [102] (Fig. 5).

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