

The Crystal Structure of MoOPO₄

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MoOPO₄ has a tetragonal unit cell containing two formula units and with the dimensions

$$\begin{aligned} a &= 6.1768 \pm 0.0003 \text{ \AA} \\ c &= 4.2932 \pm 0.0003 \text{ \AA} \\ V &= 163.8 \text{ \AA}^3 \end{aligned}$$

A structure has been derived on the basis of three-dimensional X-ray data with atomic positions in the space group No. 85, $P4/n$. The parameters were refined using the least-squares method. The crystals are built up of chains, parallel to the c -axis, formed by distorted MoO₆ octahedra linked together by sharing corners. The chains are then coupled together by PO₄ groups, so that every MoO₆ octahedron is sharing corners with four phosphate tetrahedra and every PO₄ tetrahedron with four MoO₆ octahedra, giving a three-dimensional network. The PO₄ tetrahedron is regular within experimental error, while the MoO₆ octahedron is so distorted that a description in terms of a square pyramidal arrangement is more appropriate. A discussion of the structure is given.

In connection with an X-ray investigation of phosphorus-oxygen compounds of molybdenum and wolfram undertaken at this Institute, reports on the crystal structure of several phases have been published and the results obtained are discussed in a review article.¹ Most of these crystalline compounds could be obtained at elevated temperatures from glasses with approximately the same composition as the crystals. In order to obtain more knowledge of the character of glasses in the system Mo—P—O, research work has been started using paperchromatographic methods and other techniques and the results obtained will be published later on.

During the preparative work on glasses use was made in some cases of commercial "molybdic acid" containing ammonium molybdate and here a crystalline phase with the composition Mo₂O₅·P₂O₅ was found. The compound was insoluble in water and very slightly soluble in dilute sodium hydroxide and hot concentrated acids. In solutions of the compound only orthophosphate could be detected and no other phosphate ions were found. According to this the compound should be written MoOPO₄ rather than the formula mentioned above. The building principle of the crystals according to the structure determination described below might also be expressed by the formula MoOPO₄.

This article will describe investigations on the structure of MoOPO₄.

EXPERIMENTAL

Preparation of the crystals. A viscous mixture of "molybdic acid" (13.2 g, "Baker Analyzed Reagent", 86.4 % MoO₃, 9.4 % NH₃) and concentrated (14.5 M) phosphoric acid (6 ml) was heated up to about 1000°C in a platinum crucible. The specimen was then maintained at this temperature for about 20 min. After cooling and washing with hot water the air dried sample contained yellowish crystals which under the microscope were found to be mostly rather thin plates.

Analysis. A sample was fused with sodium potassium carbonate in a platinum crucible. After dissolving in hot water the amounts of *molybdenum* and *phosphorus* were determined as described elsewhere.²

	Calculated for MoOPO ₄	Found
% MoO ₃	69.57	69.60 ± 0.05
% P ₂ O ₅	34.20	34.2 ± 0.1

Table 1. X-Ray powder data of MoOPO₄. CuKα₁ radiation. λ(CuKα₁) = 1.54050 Å.

<i>h k l</i>	10 ⁵ sin ² Θ _{obs}	10 ⁵ sin ² Θ _{calc}	10 ⁵ (sin ² Θ _{obs} - sin ² Θ _{calc})	<i>I</i> _{obs}
1 1 0	3105	3110	-5	st
0 0 1	—	3219	—	—
1 0 1	4768	4774	-6	vvst
2 0 0	6214	6220	-6	vvst
1 1 1	6327	6329	-2	vst
2 0 1	—	9439	—	—
2 1 1	10992	10994	-2	st
2 2 0	12437	12440	-3	st
0 0 2	12870	12876	-6	w
1 0 2	14437	14431	+6	vvw—
3 1 0	15556	15550	+6	vst
2 2 1	—	15659	—	—
1 1 2	15989	15986	+3	m
3 0 1	17214	17214	±0	vst
3 1 1	18781	18769	+12	m
2 0 2	19095	19096	-1	w
2 1 2	20644	20651	-7	st diff
3 2 1	23455	23434	+21	vst
4 0 0	24892	24880	+12	st
2 2 2	—	25316	—	—
3 0 2	—	26871	—	—
3 3 0	27999	27990	+9	w
4 0 1	—	28099	—	—
3 1 2	28433	28426	+7	vvst
0 0 3	28976	28971	+5	vvw diff
4 1 1	29660	29654	+6	m
1 0 3	—	30526	—	—
4 2 0	31123	31100	+23	st
3 3 1	—	31209	—	—
1 1 3	—	32081	—	—

The powder photograph was measured and interpreted to sin²Θ = 0.45. Reflections systematically absent in space group *P4/n* have been omitted.

X-Ray diffraction data and computing methods. The powder pattern was easily interpreted assuming a tetragonal unit cell. Values for the cell dimensions were calculated from a photograph taken with strictly monochromatized CuK α_1 radiation in a Guinier type focusing camera. Potassium chloride was used as an internal standard (see Table 1). The unit-cell dimensions are:

$$\begin{aligned} a &= 6.1768 \pm 0.0003 \text{ (\AA)} \\ c &= 4.2932 \pm 0.0003 \text{ (\AA)} \\ V &= 163.8 \text{ (\AA}^3\text{)} \end{aligned}$$

The value 4.06 for the density found from the apparent loss of weight in benzene gives $1.96 \approx 2$ formula units in the unit cell.

From rotation and Weissenberg photographs ($hk0-hk2$, $0kl-3kl$) of a single crystal — a well shaped plate with dimensions 0.058 mm (in the direction of the a axis) \times 0.058 mm (b) \times 0.018 mm (c) — taken with CuK radiation, it was concluded that the crystals have the Laue symmetry $4/m$. The reflections systematically absent are $hk0$ with $h+k = \text{odd}$, which is characteristic of the space group $P4/n$.

The reflections were recorded photographically with the multiple-film technique and the relative intensities were estimated visually by comparison with an intensity scale obtained by photographing a reflection with different exposure times.

Practically all the computational work involved in this study, including refinement of the lattice constants (Program No. 6018), absorption correction (No. 6019), Lorentz-polarization correction (No. 6024), Fourier summations (No. 6015), least-squares refinement (No. 6023) and calculation of interatomic distances (No. 6016), were performed on the electronic computers FACIT EDB and BESK. The figures are referred to the list of crystallographic computer programs.³

When determining the F^2 values, the linear absorption coefficient, $\mu = 364.5 \text{ cm}^{-1}$, derived from the atomic absorption coefficients given in the International Tables,⁴ was used for the calculation of the absorption factors. These factors are included in a document⁵ which may be obtained from the secretary of this Institute.

THE STRUCTURE DETERMINATION

In the Patterson projection $P(pvw)$ (Fig. 1) there is a high peak (besides the origin maximum) at $v = \frac{1}{2}$, $w = 0.39_0$, and this maximum certainly

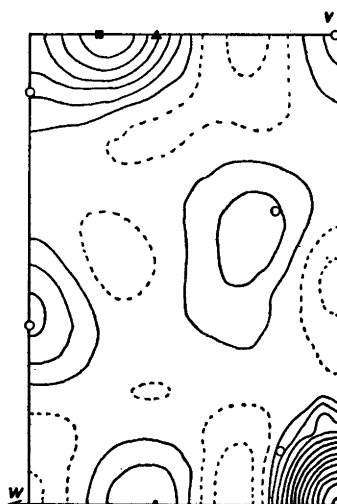


Fig. 1. The Patterson projection $P(pvw)$ for MoOPO₄. The Mo—Mo (■), Mo—P (▲) and Mo—O (○) vectors have been indicated for the final structure. Dashed lines indicate negative values.

corresponds to the Mo—Mo vector in the half cell. The two molybdenum atoms thus must occupy the point position 2 (c): $(0, \frac{1}{2}, z)$; $(\frac{1}{2}, 0, \bar{z})$, as the other twofold point positions, 2 (a)—(b), would require the Mo—Mo vector to have $w = 0$. Thus, from the coordinates given above we get $z_{\text{Mo}} \approx 0.19_5$.

The electron density projection $\rho(pyz)$ was then calculated, using the signs of F_{obs} obtained from the molybdenum contributions only. At this and subsequent calculations atomic scattering curves for un-ionized atoms were used. The real part of the anomalous dispersion correction (Dauben and Templeton ⁶) was applied to the scattering curves. From the electron density projection, $\rho(pyz)$, the position of the phosphorus atoms could easily be obtained — 2 P in 2(b) — and in addition to the maxima corresponding to the molybdenum and phosphorus positions there were peaks which could correspond to oxygen positions. By introducing three-dimensional calculations of the Patterson and the electron density functions using all the observed reflections, the positions of the ten oxygen atoms — found to be situated in 2(c) and 8(g) — in the unit cell could be determined with moderate accuracy.

A refinement of the coordinates so obtained was then performed by means of the least-squares program mentioned above. The starting values of the individual isotropic temperature factors used in this program, were zero for all of the atoms. Initially all 171 of the independent reflections measured were included in the calculations, but after a few cycles five strong, low-angle reflections were omitted as suffering from extinction. The refinement was considered as complete when the parameter shifts were less than five per cent of the standard deviations, at which stage the discrepancy index

$$R = \sum ||F_{\text{obs}}(hkl)| - |F_{\text{calc}}(hkl)|| : \sum |F_{\text{obs}}(hkl)|, \text{ was down to } 0.082.$$

Hughes' weighting function $w = 1/h^2|F_{\text{obs}, \text{min}}|^2$ for $|F_{\text{obs}}| \leq h|F_{\text{obs}, \text{min}}|$ and $w = 1/|F_{\text{obs}}|^2$ for $|F_{\text{obs}}| > |F_{\text{obs}, \text{min}}|$ with $h = 4$ was used in the refinement. A weight analysis obtained in the last cycle is given in Table 2.

Table 2. Weight analysis obtained in the final cycle of the least-squares refinement of MoOPO_4 .

$$w = \text{weighting factor, } \Delta = ||F_{\text{obs}}| - |F_{\text{calc}}||$$

Interval $\sin \Theta$	Number of independent reflections	$\overline{w\Delta^2}$	Interval F_{obs}	Number of independent reflections	$\overline{w\Delta^2}$
0.00—0.46	20	1.30	0—6	2	0.94
0.46—0.58	21	0.98	6—12	10	0.68
0.58—0.67	23	0.76	12—18	29	0.45
0.67—0.74	17	0.72	18—24	37	0.74
0.74—0.79	18	0.54	24—30	33	1.07
0.79—0.84	16	0.80	30—36	19	2.63
0.84—0.89	12	1.59	36—42	8	1.16
0.89—0.93	19	1.00	42—48	9	1.09
0.93—0.97	14	1.66	48—54	9	0.69
0.97—1.00	6	0.99	54—60	10	0.61

Table 3. The structure of MoOPO₄.Space group: No. 85, *P4/n*.Unit-cell dimensions: *a* = 6.1768 ± 0.0003 Å*c* = 4.2932 ± 0.0003 ÅCell content: 2 MoOPO₄2 Mo and 2 O₁ in 2 × 2(c): (0, ½, *z*); (½, 0, \bar{z})

2 P in 2(b): (0, 0, ½); (½, ½, ½)

8 O₂ in 8(g): (*x*, *y*, *z*); (\bar{x} , \bar{y} , *z*); (½ + *x*, ½ + *y*, \bar{z}); (½ - *x*, ½ - *y*, \bar{z}); (\bar{y} , *x*, \bar{z}); (*y*, \bar{x} , \bar{z}); (½ - *y*, ½ + *x*, *z*); (½ + *y*, ½ - *x*, *z*)

Atom	<i>x</i> ± σ(<i>x</i>)	<i>y</i> ± σ(<i>y</i>)	<i>z</i> ± σ(<i>z</i>)	<i>B</i> ± σ(<i>B</i>) Å ²
Mo	0	½	0.1975 ± 0.0007	1.00 ± 0.04
P	0	0	½	1.2 ± 0.1
O ₁	0	½	0.8102 ± 0.0059	1.7 ± 0.4
O ₂	0.0625 ± 0.0037	0.1946 ± 0.0038	0.2994 ± 0.0045	2.0 ± 0.3

A list of the observed and calculated structure factors is included in the document⁵ mentioned above.

A subsequent three-dimensional difference synthesis calculated over the unique part of the unit cell at points spaced 0.2 Å apart showed very small maxima and minima. The largest maximum in this synthesis has a magnitude of about 20 % of the heights of the oxygen peaks in the electron density functions. Thus, from this calculation as well as from a computation of the interatomic distances, which were found to be within the normal range (*cf.* p. 2223), further evidence was obtained that the atomic parameters arrived at in the last cycle and listed in Table 3 should present an adequate description of the structure.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The crystals of MoOPO₄ are built up of chains, parallel to the *c*-axis, formed by distorted MoO₆ octahedra linked together by sharing corners. The chains are then coupled together by PO₄ groups, so that every MoO₆ octahedron shares corners with four phosphate tetrahedra, each one of which shares corners with four octahedra, giving a three-dimensional network. Schematic drawings showing the links between the octahedra and tetrahedra are given in Figs. 2 and 3.

The distances between neighbouring atoms in MoOPO₄ are given in Table 4. From the table we can see that all distances are within the normal range, and it is also obvious that the lattice is well stabilized by O—O contacts, as each one of the oxygen atoms is surrounded by twelve oxygen atoms at distances of 2.5—3.0 Å. The oxygen volume (in Å³) — derived by dividing the unit-cell volume by the number of oxygen atoms in the unit cell — is 16.4,

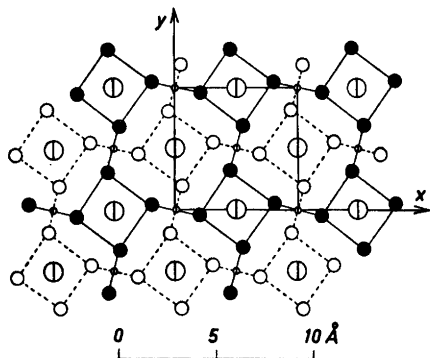


Fig. 2. Schematic drawing showing the links between PO_4 tetrahedra and MoO_6 octahedra viewed along $[001]$ in the structure of MoOPO_4 . Open and full large circles denote oxygen atoms in two separate planes, 1.72 \AA apart. Lined open circles denote oxygen atoms shared between MoO_6 octahedra as shown in Fig. 3. Small lined circles denote phosphorus atoms. The molybdenum atoms have not been indicated.

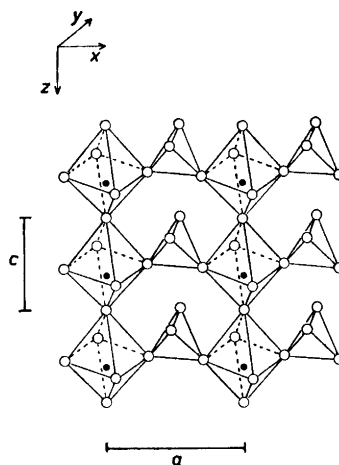


Fig. 3. The structure of MoOPO_4 . Schematic drawing showing the chains formed by MoO_6 octahedra linked together by sharing corners and also showing the links between PO_4 tetrahedra and MoO_6 octahedra. Full circles denote molybdenum atoms and open ones oxygen atoms. The phosphorus atoms have not been indicated. The two remaining oxygens in each PO_4 tetrahedron are shared — as shown in Fig. 2 — with two further MoO_6 octahedra which have not been indicated.

which quantity is in close agreement with the values 16.3 and 16.9 found in two molybdenum oxides MoO_2 and MoO_3 .

The P—O distances within the phosphate group are $1.53 \pm 0.02 \text{ \AA}$ and the O—O distances are $2.48 \pm 0.03 \text{ \AA}$ (four distances) and $2.53 \pm 0.03 \text{ \AA}$ (two distances), from which an average angle O—P—O = 109.5° is calculated. These values are close to those given by Furberg⁷ in H_3PO_4 (average values 1.56 \AA and 109.9°) and also to those found by Cruickshank⁸ in the refinement of a series of phosphate structures.

As mentioned above, the coordination polyhedron around the molybdenum atoms could be described as a distorted octahedron, formed by six oxygen atoms. However, the distortion is so pronounced that a description in terms of five coordination, *viz.* as a square pyramidal arrangement of oxygen atoms around the molybdenum atoms is more adequate (*cf.* Fig. 4a). It is striking how this arrangement is similar to the coordination around the vanadium atoms in vanadyl bisacetylacetonate, $\text{VO}(\text{C}_5\text{H}_7\text{O}_2)_2$ ⁹ (Fig. 4b). As we can see from the figures, the coordination polyhedra, although being more regular around the molybdenum atom, are very much alike.

Table 4. Interatomic distances and estimated standard deviations (in Å) in MoOPO₄.

Mo—O	Mo—2 O ₁ (O ₁ —2 Mo) = 1.663 ± 0.026; 2.630 ± 0.026
	Mo—4 O ₂ (O ₂ —Mo) = 1.974 ± 0.023
P—O	P—4 O ₂ (O ₂ —P) = 1.528 ± 0.022
O—O	O ₁ —12 O ₂ = 4 × (2.850 ± 0.028)
	= 4 × (2.918 ± 0.028)
	= 4 × (2.995 ± 0.023)
	(O ₂ —6 O ₁) = 2 × (2.85; 2.92; 2.99)
	O ₂ —6 O ₂ = 2 × (2.481 ± 0.030) (*)
	= 2.526 ± 0.033 (*)
	= 2 × (2.723 ± 0.033)
	= 2.966 ± 0.031

* Denote O—O distances within the PO₄ group.

The general tendency for the octahedral environment of the molybdenum atom to be irregular has been discussed in several papers. Thus, Magnéli¹⁰ concluded from his observation that molybdenum is able to replace wolfram only to a very limited extent in wolfram trioxide, that molybdenum seems to have a preference to enter into five-coordination by directing five of the six oxygen atoms surrounding it towards a square pyramidal arrangement. It has also been suggested by Orgel¹¹ that distorted octahedral structures occur for metal ions such as molybdenum, which are too small to form regular octahedrally coordinated oxides, but are not small enough to be restricted to tetrahedrally coordinated structures. The metal ions are said to "rattle" inside an octahedron of oxide ions. Now, very few structural data are available relating to oxide compounds containing pentavalent molybdenum. However, the square pyramidal arrangement of oxygen atoms around the molybdenum atoms, observed in MoOPO₄, seems understandable if the general tendency of the molybdenum atoms to distortion is recalled.

Regarding the Mo—O distances found (*cf.* Table 4 and Fig. 4a), it is tempting to assume double-bonding between molybdenum and one oxygen — the apex of the square pyramid — and single bonds between molybdenum and the oxygen atoms belonging to the PO₄ groups. The bonds should then be directed towards the five corners of the pyramid, which with the unpaired electron of the Mo(V)-atom would form an octahedron. But, this assumption is only based on the distances determined and further experimental data certainly have to be determined in order to make possible a calculation of the electronic energy levels and a further discussion of the bond conditions. Magnetic and spectral measurements should in this case be of considerable interest.

As mentioned above, there seem to exist some similarities between the oxygen arrangement around molybdenum in MoOPO₄ and around vanadium in VO(C₅H₇O₂)₂. A comparison between Mo(V) compounds and further com-

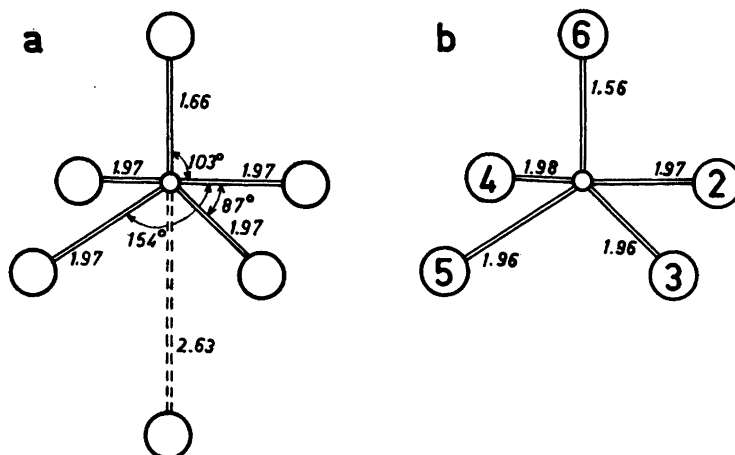


Fig. 4. a) The coordination of oxygen atoms (large circles) around the molybdenum atom (small circle) in MoOPO₄. Angles related to the others by symmetry have not been indicated. b) The coordination of oxygen atoms (large circles) around vanadium (small circle) in VO(C₆H₇O₃)₃. The oxygen atoms have been numbered as in Ref.⁹ The bond angles (°) within the triclinic structure are

O ₂ -V-O ₃ = 87.2	O ₂ -V-O ₅ = 149.8
O ₄ -V-O ₅ = 87.9	O ₃ -V-O ₄ = 145.5
O ₂ -V-O ₄ = 83.8	O ₂ -V-O ₆ = 104.5
O ₃ -V-O ₅ = 83.5	O ₃ -V-O ₆ = 106.3
	O ₄ -V-O ₆ = 108.2
	O ₅ -V-O ₆ = 105.6

pounds containing transition metal ions isoelectronic with pentavalent molybdenum, *viz.* (nd)¹-ions, is thus likely to be rewarding. Unfortunately, such structural data are very meagre, which may be due to experimental difficulties in handling such compounds, which are mostly unstable in air. On the other hand, extensive information is available about, *e.g.*, optical and magnetic properties of transition metal compounds and in particular such containing 3d elements. Such studies have been performed in order to describe and characterize the bonding between the central ion and the ligands in terms of some electronic theory. Thus by application of ligand field theory¹² it has been possible to understand characteristic variations in magnetic susceptibility, stability, ionic radii, and absorption spectra.

This study forms part of a research program intended to provide accurate structural data and information about other physical properties appropriate for the elucidation of the bonding conditions in transition metal compounds of simple stoichiometry.

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