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The Crystal Structures of Two Oxyfluorides of Molybdenum*

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Single crystals of the compounds $MoO_{2.4}F_{0.6}$ and $Mo_4O_{11.2}F_{0.8}$ were prepared by reacting MoO_3 and powdered Mo metal in the presence of HF under hydrothermal conditions at $500°C$ and 2 kbar pressure. $Mo_4O_{11}.2F_{0.8}$ is orthorhombic with space group *Cmcm*, $Z=4$, cell dimensions $a=3·878\pm0·004$, $b=13·96\pm0·01$, $c=3·732\pm0·005$ Å. The measured and calculated densities are $d_m=4·6\pm0·1$ and $d_c=4·70$ g.cm⁻³. The intensity data were collected by the Weissenberg method and the structure refined by least-squares to a final R value of $9·1\%$ for 465 independent reflections. The structure is related to the MoO_3 structure with the Mo atom in a very distorted octahedral coordination. $MoO_{2.4}F_{0.6}$ is cubic with space group *Pm3m*, $Z=1$, cell dimension $a=3·842\pm0·003$ Å, measured and calculated densities of $d_m=4·1\pm0·1$ and $d_c=4·22$ g.cm⁻³. The intensities were measured by powder diffractometry and the R value based on intensities for 20 reflections was 12%. The structure is similar to the ReO_3 structure with the Mo atom in a normal octahedral coordination.

Introduction

Extensive studies on the structural chemistry of the molybdenum and tungsten oxide systems have been reviewed by Anderson & Magnéli (1950); Hägg & Magnéli (1954) and Kihlborg (1963). The structures of MoO_2 and MoO_3, as well as those of a number of intermediate oxides, have been established. The basic building unit for these structures is a distorted MoO_6 octahedron; however, the degree of distortion may be large

enough to alter significantly the number of neighbors nearest to the molybdenum atoms.

It was first suggested by Magnéli (1956) that an increase in the amount of reduced molybdenum present in the compound is accompanied by an increase in the coordination number of the molybdenum atoms. In the MoO_3 structure the molybdenum atoms have a strong tendency toward fourfold coordination. However, in $Mo_{18}O_{52}$ the average number of oxygen atom nearneighbors approaches five, and in Mo_4O_{11} the coordination number of the molybdenum atoms approaches six.

In addition, Wilhelmi (1969) has recently determined the structure of $Mo_4O_{10}(OH)_2$ and found it to be closely related to those of MoO_3 and $Mo_{18}O_{52}$. In the case of $Mo_4O_{10}(OH)_2$ reduced molybdenum has been intro-

duced into the structure while the anion to cation ratio remains 3:1. It has also been demonstrated by Sleight (1969) that compounds of the type $MoO_{3-x}F_x$ could be prepared.

The work of Wilhelmi (1969) indicated the possible existence of additional molybdenum oxyfluoride phases with structures related to the more distorted MoO_3 structure and containing smaller amounts of fluorine. Further investigation of the Mo–O–F system in this laboratory resulted in the preparation of single crystals of $Mo_4O_{11} \cdot 2F_{0 \cdot 8}$.

The work described here was undertaken in order to determine the structure of $Mo_4O_{11} \cdot 2F_{0 \cdot 8}$ and to verify the relationship between the ReO_3 structure and that of the cubic phases reported by Sleight (1969).

Experimental

Preparation and crystal growth

In order to prepare single crystals of $Mo_4O_{11} \cdot 2F_{0 \cdot 8}$, mixtures of MoO_3 and powdered molybdenum metal were weighed-out in mole ratios between 79:1 and 29:1. One gram of the mixed powder was then placed in an ampule formed by sealing one end of a 10 cm length of 5 mm (I.D.) gold tubing. Approximately 1 cc of 48% hydrofluoric acid was then added before the open end of the tube was crimped and melted to form a tight seal. The capsule was then placed in a pressure vessel and attached to hydrothermal pressure equipment available commercially.* The temperature, as measured with thermocouples attached to the outside of the pressure vessel, was brought rapidly to 515 °C while the pressure was held at 2 kbar. The vessel was then cooled at a rate of 5°hr^{-1} to 500 °C. The reaction was then allowed to proceed for 6 days at 500° under 2 kbar pressure before the vessel was slowly cooled to room temperature.

The same procedure was followed in the synthesis of $MoO_2 \cdot 4F_{0 \cdot 6}$; however, the initial mole ratio of MoO_3:Mo was between 13:1 and 14:1.

Analyses

Samples of $Mo_4O_{11} \cdot 2F_{0 \cdot 8}$ were decomposed in $2N$ NaOH, brought to pH 5 with $2N$ HCl, and diluted to 100 ml. Fluorine was then determined with a specific ion electrode.† The total molybdenum in the sample was determined by passing the solution through a silver reductor and titrating the resulting Mo^{5+} with ceric sulfate.

Samples of $MoO_2 \cdot 4F_{0 \cdot 6}$ were decomposed in $2N$ HCl to which a trace of HNO_3 had been added. The solution was brought to pH 5 with $2N$ NaOH and subjected to the same fluorine and molybdenum determinations described above.

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* A model HR-2C-2 hydrothermal bench was used in conjunction with modified LRA-150 pressure vessels. Tem-Pres Research Inc., State College, Pennsylvania.

† Fluoride Ion Activity Electrode Model 94-09. Orion Research Inc., Cambridge, Massachusetts.

The total reducing power of both materials was determined by dissolving them in acid V^{5+} sulfate solution and titrating the resulting V^{4+} potentiometrically with ceric sulfate solution. The results were: calculated, for $Mo_4O_{11} \cdot 2F_{0 \cdot 8}$: Mo, 66·40; F, 2·37; Mo_{red} (as Mo^{5+}), 11·95; found: Mo, 66·0; F, 2·4; Mo_{red}, 13·1. Calculated for $MoO_2 \cdot 4F_{0 \cdot 6}$: Mo, 65·82; F, 7·95; Mo red, 40·16, found: Mo, 65·5; F, 7·9; Mo_{red}, 42·8.

Structure determination of $Mo_4O_{11} \cdot 2F_{0 \cdot 8}$

Powdered samples were prepared from the single crystals and examined using a Norelco diffractometer with monochromatic radiation (AMR-202 focusing monochromator) and a high intensity copper source $[\lambda(Cu\ K\alpha_1) = 1 \cdot 5405\ Å)]$, with a focal spot size of $1 \cdot 2 \times 3$ mm for 6° take-off angle. Powder diffraction data on $MoO_2 \cdot 8F_{0 \cdot 2}$ at 25° were indexed on the basis of an orthorhombic cell with $a = 3 \cdot 878 \pm 0 \cdot 005$, $b = 13 \cdot 96 \pm 0 \cdot 01$, and $c = 3 \cdot 732 \pm 0 \cdot 005$ Å. In addition, lattice constants were determined from single-crystal rotation and Weissenberg photographs, $a = 3 \cdot 874 \pm 0 \cdot 007$, $b = 13 \cdot 96 \pm 0 \cdot 01$ and $c = 3 \cdot 738 \pm 0 \cdot 007$ Å, using molybdenum radiation $[\lambda(Mo\ K\alpha_1) = 0 \cdot 70926\ Å]$ and focal spot size of 1×1 mm. The pycnometrically measured density was $d_m = 4 \cdot 6 \pm 0 \cdot 1$ g.cm^{-3} which indicated a cell containing four $MoO_2 \cdot 8F_{0 \cdot 2}$ units. The calculated density $d_c = 4 \cdot 70$ g.cm^{-3}. The reported errors for both the powder and single-crystal cell parameters represent the average deviations in the observed cell constants.

The Laue symmetry was found to be mmm. Systematic extinctions, determined from zero- and upper-layer Weissenberg and precession photographs occurred only for hkl: $h + k = 2n + 1$ and $h0l$: $l = 2n + 1$. These extinctions are consistent with space groups $Cmcm$, $C2cm$ and $Cmc2_1$. Piezoelectric and pyroelectric measurements were not made on this material as it had been shown to be a semiconductor (Cady, 1929).

A single crystal of $Mo_4O_{11} \cdot 2F_{0 \cdot 8}$ in the form of a flattened needle was cleaved to give a sample approximately $0 \cdot 1 \times 0 \cdot 1 \times 0 \cdot 3$ mm. This was mounted about its c axis and data were taken for $l = 0 - 6$, using the multiple-film equi-inclination Weissenberg technique with Zr-filtered Mo radiation. The sample was then cut and remounted about its a axis and data were taken for $h = 0 - 6$. A total of 980 reflections were measured visually by comparison with a standard intensity scale. These data were scaled and average to give a total of 465 independent reflections. Corrections were applied to the data for extended spot-shape and Lorentz-polarization effects. The inter-film and inter-layer scaling was carried out by the usual scaling algorithms (Hamilton, Rollett & Sparks, 1965). No absorption or extinction corrections were applied. Before the averaging of equivalent reflections was made, lack of absorption correction caused an estimated maximum error of 10% in the intensities of some reflections.

Comparison of the powder patterns of MoO_3 and $Mo_4O_{11} \cdot 2F_{0 \cdot 8}$ indicated that the two structures were

closely related. In the three possible space groups the molybdenum, oxygen and fluorine atoms occupy positions 4(b) in C2cm, 4(c) in Cmcm, or 4(a) in Cmc2₁. These positions are analogous to the corresponding positions in the MoO₃ structure. The initial positional parameters for the refinement were assumed to be those observed for MoO_3 and shown in Table 1. It was assumed that the oxygen and fluorine atoms were randomly distributed among the three sets of oxygen positions. The refinement was carried out using a full-matrix least-squares algorithm (Busing, Martin & Levy, 1962), modified to make real and imaginary

Table 1. *Positional and thermal parameters*[*][†]

MoO_3 (Kihlborg, 1963)

Space group: *Pbnm*, Z = 4
4Mo and 12O in 4(c): $(x, y, \frac{1}{4}; \frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{4}; \frac{1}{2}+y, \frac{1}{2}-y, \frac{3}{4}; \bar{x}, \bar{y}, \frac{3}{4})$

	x	y	z	β_{11}	β_{22}	β_{33}[‡]
Mo	0·0867 (2)	0·1016 (1)	$\frac{1}{4}$	38	3	41
O(1)	0·5212 (18)	0·0866 (5)	$\frac{1}{4}$	104	8	113
O(2)	0·4994 (19)	0·4351 (5)	$\frac{1}{4}$	93	7	100
O(3)	0·0383 (19)	0·2214 (4)	$\frac{1}{4}$	158	12	171

$Mo_4O_{11}\cdot 2F_{0\cdot 8}$

Space group: *Cmcm*, Z = 4
4Mo and 12O in 4(c): $(0, y, \frac{1}{4}; \frac{1}{2}, \frac{1}{2}+y, \frac{1}{4}; \frac{1}{2}-y, \frac{3}{4}; 0, \bar{y}, \frac{3}{4})$

	x	y	z	β_{11}	β_{22}	β_{33}
Mo	0	0·1026 (0)	$\frac{1}{4}$	121 (5)	3·2 (0·2)	0 (1)
O(1)	$\frac{1}{2}$	0·0805 (11)	$\frac{1}{4}$	155 (55)	25 (5)	303 (78)
O(2)	$\frac{1}{2}$	0·4371 (4)	$\frac{1}{4}$	92 (31)	1 (0·6)	116 (34)
O(3)	0	0·2208 (8)	$\frac{1}{4}$	139 (47)	15 (3)	292 (68)

* The standard deviations, where available, are shown in parentheses and refer to the last decimal position of the respective values.

† The temperature factor expression used was $\exp[-10^{-4}(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. Constraints placed on the β_{ij} values are: for all atoms $\beta_{12} = \beta_{13} = \beta_{23} = 0$.

‡ These anisotropic temperature factors have been calculated by the authors from the respective isotropic temperature factors for the purpose of comparison.

Table 2. *Selected distances and bond angles for* $Mo_4O_{11}\cdot 2F_{0\cdot 8}$

The standard deviations shown in parentheses include the errors in the cell parameters.

	Distance	Atoms (central atom is vertex)	Angle
O(1)—Mo	1·963 (3) Å	O(1)–Mo–O(1′)	161·9 (0·8)°
O(1′)–Mo	1·963 (3)	O(2)–Mo–O(2″)	146·9 (0·3)
O(2)—Mo	1·947 (2)	O(3)–Mo–O(2′)	180
O(2′)–Mo	2·311 (6)	O(1)–Mo–O(3)	99·4 (0·4)
O(2″)–Mo	1·947 (2)	O(1)–Mo–O(2)	87·4 (0·1)
O(3)—Mo	1·650 (11)	O(2)–Mo–O(3)	106·5 (0·2)
Mo—Mo′	3·419 (2)	O(2)–Mo–O(2′)	73·5 (0·2)

Table 3. *Observed and calculated structure factors for* $Mo_4O_{11}\cdot 2F_{0\cdot 8}$

anomalous dispersion corrections. The atomic scattering factors for oxygen, fluorine and molybdenum were taken from *International Tables for X-ray Crystallography* (1962). The necessary parameters used for the anomalous dispersion were those given by Dauben & Templeton (1962). Weights were assigned to each reflection according to the scheme of Cruickshank & Pilling (1961), *i.e.* $w = (A + BF_o + CF_o^2)^{-1}$, with $A = 2F_{min}$, $B = 1 \cdot 0$, and $C = 2/F_{max}$ ($F_{max} = 410$, $F_{min} = 25$).

The function $\sum w(|F_o| - |F_c|)^2$ was minimized where F_o and F_c are the observed and calculated structure amplitudes and w is the weight defined above. For the refinement procedure one overall scale factor was used. Initially the refinement was carried out in the non-centrosymmetric space group, *C2cm*. In the course of several cycles of isotropic refinement in the non-centrosymmetric space group, the x parameters of all the atoms were observed to oscillate across a mirror plane consistent with the centrosymmetric space group *Cmcm*.

It was then decided to refine the structure in the centrosymmetric space group. Three cycles of isotropic least-squares refinement led to the following R indices:

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} = 0 \cdot 119$$

$$wR = \left[\frac{\sum w (|F_o| - |F_c|)^2}{\sum w |F_o|^2} \right]^{1/2} = 0 \cdot 133 .$$

The refinement was then continued with several anisotropic calculations. The final values of R and wR were 0·091 and 0·117 respectively. The final positional and thermal parameters of this refinement are given in Table 1. Interatomic distances, bond angles, and the standard deviations of these parameters were calculated using the Busing, Martin & Levy (1964) *ORFFE* program and are shown in Table 2. The final structure factors are given in Table 3 for observed reflections only. Those reflections too weak to observe had, at the end, calculated structure factors whose magnitude did not exceed the minimum observable value in nearby regions of reciprocal space.
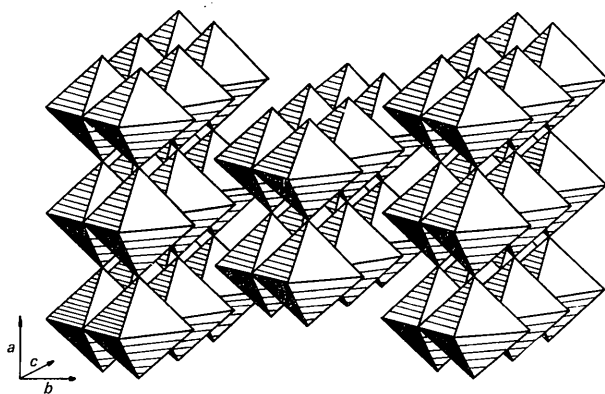

Fig. 1. The structure of $Mo_4O_{11} \cdot 2F_{0 \cdot 8}$ showing layers of distorted MoX_6 octahedra sharing edges and corners.

Structure determination of $MoO_{2 \cdot 4}F_{0 \cdot 6}$

Powder diffraction patterns and single-crystal precession photographs indicated that this phase was cubic with a cell constant $a = 3 \cdot 842 \pm 0 \cdot 003$ Å. The pycnometrically determined density was $d_m = 4 \cdot 1 \pm 0 \cdot 1$ g.cm^{-3} indicating a cell containing one formula unit. The calculated density was $d_c = 4 \cdot 22$ g.cm^{-3}.

The Laue symmetry was found to be *m3m*. No systematic extinctions were observed. Three space groups are therefore possible: *P*432, *P$\bar{4}$3m*, and *Pm3m*. The space group *Pm3m* was assumed for this material. This space group is consistent with that assigned to the ReO_3 structure.

A powdered sample was mixed with Canada balsam in order to alleviate preferred orientation effects and integrated intensity data were collected with a Norelco diffractometer.

Parthé's[*] program was used to calculate intensities based on the ReO_3 structure with oxygen and fluorine atoms distributed randomly in the positions $3(d)$, $(\frac{1}{2}00)$, and the molybdenum atom at position $1(a)$, (000), of space group *Pm3m*. The occupancy factors for oxygen and fluorine were adjusted to comply with the observed stoichiometry. The isotropic temperature factor was set at 1·00 based on temperature factors observed for other molybdenum oxides. The data were corrected for Lorentz–polarization effects. The results are shown in Table 4. The reliability index based on intensity was found to be:

$$R_{I_o} = \frac{\sum |I_o - I_c|}{\sum |I_o|} = 0 \cdot 12 .$$

Table 4. *Powder diffraction data for* $MoO_{2 \cdot 4}F_{0 \cdot 6}$

h k l	d_{hkl}	I(obs)	I(calc)
1 0 0	3·842	810	1000
1 1 0	2·717	278	283
1 1 1	2·218	32	22
2 0 0	1·921	176	200
2 1 0	1·718	296	296
2 1 1	1·568	101	101
2 2 0	1·358	90	94
3 0 0 } 2 2 1 }	1·281	108	113
3 1 0	1·215	45	40
3 1 1	1·158	17	15
2 2 2	1·109	28	27
3 2 0	1·066	41	45
3 2 1	1·0268	47	47
4 0 0	0·9605	12	14
4 1 0 } 3 2 2 }	0·9318	66	69
4 1 1 } 3 3 0 }	0·9056	27	31

Results and discussion

The structure of $Mo_4O_{11} \cdot 2F_{0 \cdot 8}$ is similar to that of the parent oxide MoO_3 (Kihlborg, 1963) and isostructural

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[*] W. Jeitschko & E. Parthé, *A Fortran* IV *Program for the Intensity Calculation of Powder Patterns*. Univ of Pennsylvania Press.

Table 5. *Comparison between interatomic distances in* MoO_3 *and* $Mo_4O_{10}(OH)_2$
and the corresponding distances in $MoO_{2\cdot8}F_{0\cdot2}$

[(*cf.* Fig. 3 (*a*), (*b*) and (*c*))]

Distance	MoO_3 (Kihlborg, 1963)	$Mo_4O_{10}(OH)_2$ (Wilhelmi, 1969)	$Mo_4O_{11\cdot2}F_{0\cdot8}$
Mo–Mo across shared edges	3·438 Å	3·427 Å	3·462 Å
Mo–Mo along [100]	3·963	3·888	3·878
Mo–Mo along [001]	3·696	3·734	3·732
Mo–O(2)	2·332	2·33	2·31
Mo–O(2′)	1·948	1·96	1·95
Mo–O(2″)	1·948	1·96	1·95
Mo–O(1)	1·734	1·96	1·96
Mo–O(1′)	2·251	1·96	1·96
Mo–O(3)	1·671	1·69	1·65

with $Mo_4O_{10}(OH)_2$ (Wilhelmi, 1969). All three structures are composed of distorted MoX_6 octahedra linked as shown in Fig. 1. The octahedra are joined by edges to form zigzag-shaped rows which are mutually connected by corners to form layers. The layers are placed side by side so that adjacent layers have no atoms in common. In this way three of the six anions surrounding each molybdenum atom are common to three MoX_6 octahedra and two of them are shared by two octahedra. The sixth anion is unshared and Wilhelmi (1969) asserts on the basis of observed bond lengths that hydrogen bonds between pairs of these anions in adjacent layers account for the observed stoichiometry of $Mo_4O_{10}(OH)_2$.

Fig. 2 shows the structure viewed down the c axis and illustrates the major difference between the structure of MoO_3 [Fig. (2*a*)] and the structures of $Mo_4O_{10}(OH)_2$ and $Mo_4O_{11\cdot2}F_{0\cdot8}$ [Fig. (2*b*)]. Fig. 3(*a*), (*b*) and (*c*) illustrates the coordination of anions about the molybdenum atoms for MoO_3, $Mo_4O_{10}(OH)_2$ and

$Mo_4O_{11\cdot2}F_{0\cdot8}$ respectively. Interatomic distances are presented for comparison in Table 5.

Kihlborg (1963) has shown that MoO_3 represents a transitional stage between octahedral and tetrahedral coordination with a strong tendency toward fourfold coordination. In the structure common to $Mo_4O_{10}(OH)_2$ and $Mo_4O_{11\cdot2}F_{0\cdot8}$ the tendency towards a more ideal octahedral coordination around the molybdenum atoms is obvious.

The structure of the cubic phase, $MoO_{2\cdot4}F_{0\cdot6}$, consists of a three-dimensional array of regular MoX_6 octahedra joined by sharing corners as shown in Fig. 4. In this case octahedral coordination has been attained.

It can be seen from Table 6 that the structures of the oxyfluorides are consistent with the predictions of Magnéli (1956), namely that as the amount of reduced molybdenum in the compound increases, the coordination number of molybdenum approaches a maximum.

Table 6. *Formal oxidation state and coordination number of molybdenum in compounds with stoichiometries approaching* MoX_3

Compound	Oxidation State	Coordination No.
MoO_3	6·00	4
$Mo_4O_{11\cdot2}F_{0\cdot8}$	5·80	5
$Mo_{18}O_{52}$	5·78	5
Mo_4O_{11}	5·50	6
$MoO_{2\cdot4}F_{0\cdot6}$	5·40	6
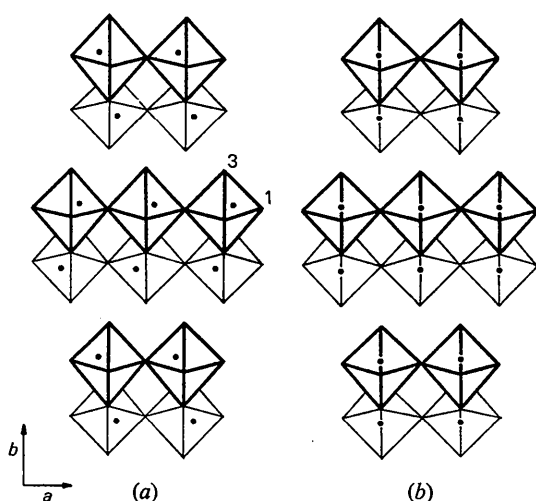
Fig. 2. The crystal structure of (*a*) MoO_3 and (*b*) $Mo_4O_{11\cdot2}F_{0\cdot8}$ in terms of octahedra. Heavy lines indicate the octahedra above, and light lines octahedra below. The black dot indicates the position of the molybdenum atom in the octahedra.
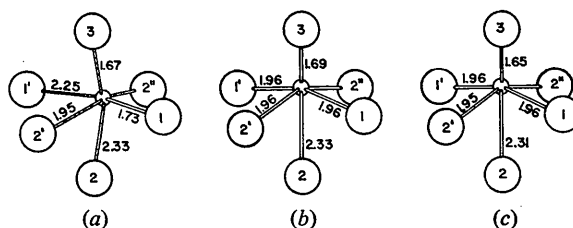

Fig. 3. Coordination of anions around the molybdenum atom for (*a*) MoO_3, (*b*) $Mo_4O_{10}(OH)_2$ and (*c*) $Mo_4O_{11\cdot2}F_{0\cdot8}$.

and for all the facilities put at their disposal. They are also much indebted to Professor G. B. Carpenter for his helpful comments during the completion of the work. They also wish to thank the Brown University Computing Centre for providing them with ample time for the calculations.
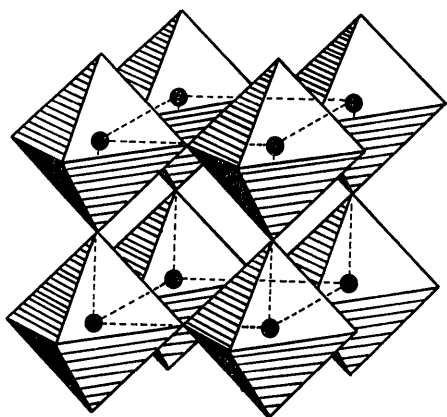
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Fig. 4. The structure of $MoO_{2\cdot4}F_{0\cdot6}$ showing a three-dimensional array of regular MoX_6 octahedra sharing corners.

X-ray Crystallography of the Diphosphatriazines.
I. The Crystal of Structure of 6-Methyl-2,2,4,4-tetraphenyldiphospha-1,3,5-triazine

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The crystal structure of 6-methyl-2,2,4,4-tetraphenyldiphospha-1,3,5-triazine has been determined from Patterson and Fourier syntheses, and has been refined by least-squares to an R index of 0·067 for 4832 observed reflexions. The unit cell is triclinic, $P\bar{1}$, of dimensions $a=13\cdot585$, $b=18\cdot007$, $c=10\cdot838$ Å, $\alpha=79\cdot42$, $\beta=112\cdot97$, $\gamma=109\cdot58°$, and has two molecules in the asymmetric unit. The diphosphatriazine ring is non-planar, has a skewed boat form and approximate twofold symmetry, and its atoms are within $-0\cdot07$ and $+0\cdot10$ Å from the mean plane. The weighted mean bond lengths are: P–N in P–N–P segments, 1·597; P–N in P–N–C segments, 1·620; P–C, 1·801; N–C, 1·335; C–CH$_3$, 1·508 Å. The weighted mean angles are: N–P–N, 116·5; P–N–P, 115·4; P–N–C, 119·9; N–C–N, 129·1; C–P–C, 105·4; N–C–CH$_3$, 115·4°. One of the phenyl rings is disordered and has two possible orientations.

Introduction

The six-membered diphosphatriazine ring, CP_2N_3, is intermediate between the aromatic and planar triazine ring, C_3N_3, and the cyclotriphosphazene ring, P_3N_3,

which has been found to be planar only in $F_6P_3N_3$ and non-planar in other compounds by varying amounts depending on the ligands. In order to examine the planarity of the CP_2N_3 ring, its bond lengths and valency angles and their dependence on the ligands, two compounds have been chosen for X-ray analysis, namely: (I) the 6-methyl-, and (II) the 6-dimethyl-

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