Crystal and Molecular Structure of Molybdenum Tetrachloride Oxide by Neutron and *X*-Ray Diffraction

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The crystal and molecular structure of $MoOCl_4$ has been determined by neutron and *X*-ray diffraction at 293 K and 77 K. A model, derived from consideration of the cubic close-packing together with an *X*-ray Patterson synthesis with Weissenberg data, was refined by the neutron powder profile-fitting technique to $R = \Sigma|y_o - y_c|/\Sigma y_o = 0.094$ (293 K) and 0.081 (77 K). The compound $MoOCl_4$ is triclinic, space group $P\bar{1}$, with unit-cell dimensions $a = 6.255(4)$, $b = 7.236(3)$, $c = 7.134(3)$ Å, $\alpha = 103.49(3)$, $\beta = 107.02(6)$, and $\gamma = 92.82(4)°$ at 293 K. There are no large changes in the structure on cooling to 77 K. The Mo atoms occur in adjacent octahedral holes (Mo–Mo = 4.12 Å) but there is no dimer formation as in $MoCl_5$. The configuration around Mo is a square pyramid, with four basal chlorine atoms and an apical oxygen atom [Mo–Cl (av.) = 2.32 Å, Mo–O = 1.7 Å]. The Mo atom is 0.41 Å above the basal plane. There is a longer Mo · · · Cl interaction of 2.9 Å in the octahedral position through the basal plane; if this were stronger (*ca.* 2.3 Å), then the structure would consist of dimers. The structure is in agreement with a gas electron-diffraction study, which found a C_{4v} square pyramid with Mo–O = 1.658(5) and Mo–Cl = 2.279(3) Å. It is also in agreement with the structures of $WOCl_4$, $ReOCl_4$, $WSCl_4$, and $WSBr_4$ where similar square pyramids are observed, but associated with different crystal symmetries.

ALTHOUGH many second- and third-row transition-metal oxide tetrachlorides have been reported, only $WOCl_4$ [1] and $ReOCl_4$ [2] have known solid-state structures. The compound $WOCl_4$ is tetragonal, with $WOCl_4$ square pyramids weakly associated through a W · · · Cl interaction through the basal plane into chains. The compound $ReOCl_4$ is a more complex structure based on $ReOCl_4$ square pyramids linked by weak Re · · · Cl interactions (3.5 Å) through the basal plane into chains and incipient dimers. Similarly, $WSCl_4$ [3] and $WSBr_4$ [3] have square-pyramidal units weakly associated into dimers by W · · · X interactions through the basal plane. Although the basic unit of these structures is a square pyramid, so far no members of the series have been found to be isostructural.

The compound $MoOCl_4$ melts at 102 °C (*cf.* m.p. of $ReOCl_4$ 30 °C and $WOCl_4$ 209 °C), is monomeric in the vapour,[4] and has been shown to be square pyramidal in the gaseous state by electron diffraction.[5] The crystal structure of $MoOCl_4$ was investigated in order to see whether it fitted into the pattern created by the above structural studies of the oxide tetrachlorides.

EXPERIMENTAL

The compound $MoOCl_4$ was prepared by refluxing MoO_3 in thionyl chloride [4] followed by vacuum sublimation. The compound is moisture sensitive, so all manipulations were carried out in dry-box conditions. Attempts to prepare single crystals resulted in fibrous crystals which gave poor diffraction patterns, so the structural study was commenced with powders. *X*-Ray powder data were taken with 114.6 and 200.0 mm Debye–Scherrer cameras (Cu-K_α radiation) and also on a sample in a capillary rotated on a four-circle diffractometer (Cu-K_β radiation). Neutron powder data were collected from a sample in a Kel-F tube at 293 K and 77 K on HIFAR, the A.A.E.C. research reactor, with $\lambda = 1.083$ Å using the elastic diffraction technique.[6]

The compound $MoOCl_4$ was shown to be based on a cubic-close-packed (c.c.p.) anion array by comparison of the neutron patterns with a theoretical pattern for a simple c.c.p. structure. Application of standard indexing programs [7,8] to the *X*-ray and neutron powder data, however, failed to produce the unit-cell dimensions, but indicated the symmetry was low-monoclinic or triclinic. Further attention was then given to single-crystal growth, and it was found that the quality of the crystals could be improved by sublimation at 90 °C in a slight gradient, but it was difficult to obtain separated single crystals. Weissenberg photographs of a crystal dominating a cluster showed triclinic symmetry, and 150 intensities were estimated visually and used in a Patterson synthesis. The Patterson synthesis confirmed the c.c.p. lattice and indicated the probable Mo–Mo vector which was superposed on Cl–Cl vectors.

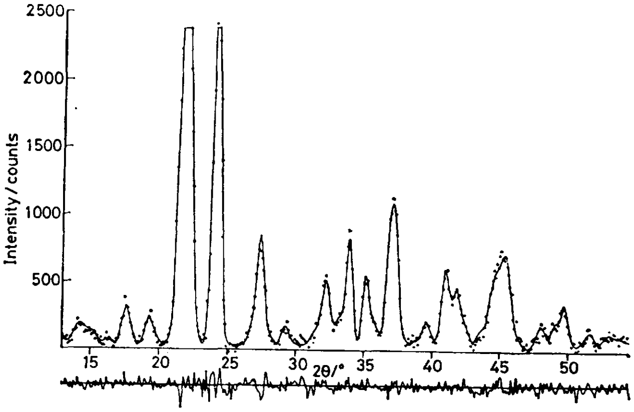

FIGURE 1 Observed (dots) and calculated (——) neutron powder diffraction profiles and their difference for $MoOCl_4$ at 293 K

Since co-ordinates from the Patterson map were found to be not sufficiently precise to allow refinement of the neutron powder data, the initial model was derived from an idealised c.c.p. lattice converted to the triclinic cell (see below for transformation matrices). This model refined with the neutron data by the profile refinement method [9] to $R = \Sigma(|y_o - y_c|)/\Sigma|y_o| = 0.094$ (293 K) and 0.081 (77 K), only slightly higher than the values expected from the statistics (0.082 and 0.067).

Unit-cell and crystal data are given in Table 1, and the final atomic co-ordinates at 293 K and 77 K in Table 2. Table 3 gives the final agreement factors and Table 4 the interatomic distances and angles. The observed and calculated neutron profiles and their differences are plotted in Figures 1 and 2.

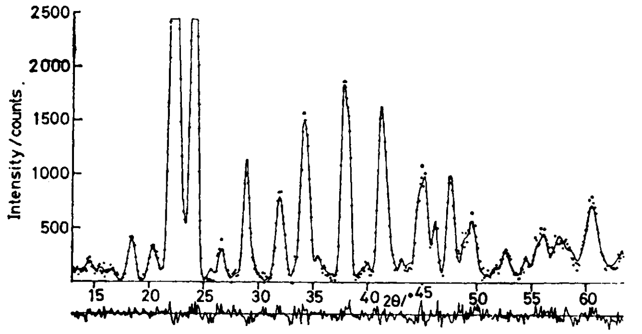

FIGURE 2 Observed (dots) and calculated (—) neutron powder diffraction profiles and their difference for $MoOCl_4$ at 77 K

DISCUSSION

The reduced triclinic unit cell is the only one which can be drawn in a cubic-close-packed array to enclose 10 anions. The structure of $MoOCl_4$ is best described in terms of the underlying cubic close-packing. A body-centred orthorhombic cell can be drawn in a c.c.p. array with dimensions $a' = c' \doteqdot 2\ r_{Cl} = 3.62$ Å and $b' \doteqdot 2\ r_{Cl}\sqrt{2} = 5.1$ Å. Transformation between this cell and the triclinic cell can be carried out with the matrices (*a*) and $(a)^{-1}$. The measured atomic co-ordinates are com-

$$(a) = \begin{pmatrix} \frac{3}{2} & -\frac{1}{2} & -\frac{1}{2} \\ \frac{1}{2} & \frac{3}{2} & -\frac{1}{2} \\ 0 & 0 & 2 \end{pmatrix} \qquad (a)^{-1} = \begin{pmatrix} \frac{3}{5} & \frac{1}{5} & \frac{1}{5} \\ -\frac{1}{5} & \frac{3}{5} & \frac{1}{10} \\ 0 & 0 & \frac{1}{2} \end{pmatrix}$$

pared in Table 2 with ' ideal ' co-ordinates for c.c.p. It can be seen that there are large deviations from the ideal, caused by contraction of anions about occupied octahedral holes, and the tendency of Mo atoms, in adjacent octahedral holes, to repel each other [*cf.* the large deviation of *y*(Mo) from the ideal].

The co-ordination polyhedron about Mo^{VI} is a square pyramid, with four basal Cl atoms (Mo–Cl = 2.2—2.4 Å) and an apical oxygen atom (Mo–O = 1.7 Å). The Mo atom lies 0.41 Å above the basal plane, and the O–Mo–Cl angles are 97—104°. The Mo–Cl distances are only slightly less than the sum of the ionic radii, 2.41 Å.[10] The

TABLE 1

Unit cell and crystal data for $MoOCl_4$[a]

Formula weight	253.8
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	6.205(3), 6.255(4)
b/Å	6.943(2), 7.236(3)
c/Å	7.249(2), 7.134(3)
α/°	104.13(2), 103.49(3)
β/°	107.53(4), 107.02(6)
γ/°	90.81(3), 92.82(4)
U/Å^3	287.5(2), 297.8(3)
D_c/g cm^{-3}	2.83 [b]
Z	2

[a] Where there are two values, the first is measured at 77 K, and the second at 293 K. [b] At 293 K.

TABLE 2

Final atomic co-ordinates and profile parameters in $MoOCl_4$ with estimated standard deviations in parentheses

Atom	Structure	10^3x	10^3y	10^3z	B(Å^2)†
Mo	293 K	080(4)	267(2)	202(3)	2.3(4)
	77 K	078(4)	269(2)	214(3)	2.1(3)
	ideal *	100	200	200	
O	293 K	−001(6)	488(4)	262(5)	3.1(8)
	77 K	006(5)	516(4)	283(3)	0.7(4)
	ideal	000	500	250	
Cl(1)	293 K	364(4)	277(3)	515(4)	5.5(8)
	77 K	372(3)	272(2)	515(3)	1.2(3)
	ideal	400	300	550	
Cl(2)	293 K	345(4)	313(2)	065(4)	4.4(7)
	77 K	336(3)	314(2)	065(3)	3.8(5)
	ideal	400	300	050	
Cl(3)	293 K	−186(4)	137(2)	−120(3)	1.7(4)
	77 K	−192(3)	139(2)	−113(3)	1.7(3)
	ideal	−200	100	−150	
Cl(4)	293 K	−165(5)	108(3)	328(4)	5.8(8)
	77 K	−174(3)	116(3)	331(3)	3.0(4)
	ideal	−200	100	350	

* Idealised co-ordinates for a perfect cubic-close-packed lattice.
† Overall isotropic Debye–Waller factor.

TABLE 3

R Factors *

	293 K	77 K
$R(\text{profile}) = \Sigma(\lvert y_o - y_c\rvert)/\Sigma y_o$	0.094	0.081
$R(\text{expected}) = [(\text{NO} - \text{NV})/\Sigma w y_o^2]^{\frac{1}{2}}$	0.082	0.069
$R(\text{nuclear}) = \Sigma(\lvert F_o^2 - F_c^2\rvert)/\Sigma F_o^2$	0.034	0.041
$x^2 = \Sigma w(y_o - y_c)^2/(\text{NO} - \text{NV})$	1.3	1.6

* NO = Number of observations; NV = number of variables.

TABLE 4

Interatomic distances (Å) and angles (°) in $MoOCl_4$*

	293 K	77 K		293 K	77 K
Mo=O	1.69	1.77	O–Mo–Cl(1)	99.9	98.6
Mo–Cl(1)	2.39	2.38	O–Mo–Cl(2)	103.5	100.7
Mo–Cl(2)	2.21	2.24	O–Mo–Cl(3)	100.4	102.5
Mo–Cl(3)	2.35	2.40	O–Mo–Cl(4)	96.9	97.4
Mo–Cl(4)	2.36	2.34	Cl(1)–Mo–Cl(2)	89.8	90.6
Cl(1)–Cl(2)	3.25	3.29	Cl(1)–Mo–Cl(4)	85.8	88.8
Cl(2)–Cl(3)	3.26	3.23	Cl(3)–Mo–Cl(2)	91.2	88.2
Cl(3)–Cl(4)	3.22	3.23	Cl(4)–Mo–Cl(3)	86.0	85.9
Cl(4)–Cl(1)	3.24	3.30			
Mo–Mo	4.12	4.12			
Mo · · · Cl(3)	2.90	2.90			
O · · · Cl(1)		3.17			
O · · · Cl(2)		3.10			
O · · · Cl(3)		3.27			
O · · · Cl(4)		3.11			

* Errors in interatomic distances and angles ±0.04 Å and ±1.5° respectively.

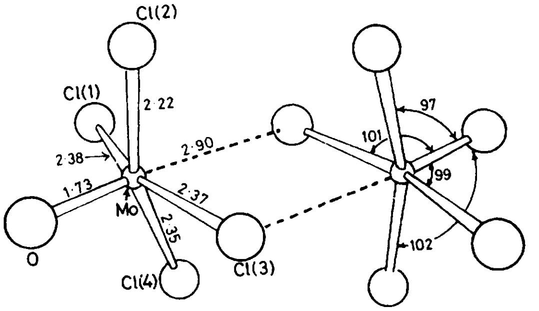

FIGURE 3 Perspective view of two adjacent square-pyramidal $MoOCl_4$ units, showing the longer interactions (dashed lines) from chlorine atoms in octahedral positions giving rise to pseudo dimers. Distances are the average of the 293 K and 77 K refinements

Cl $\cdots$ Cl contacts around the base, 3.2—3.3 Å, are less than the ionic radius sum, 3.62 Å, indicating some distortion of the Cl density from a spherical distribution. There is a weak Mo $\cdots$ Cl interaction of 2.90 Å through the base of the pyramid, corresponding to van der Waals contact with the basal chlorines, suggesting incipient dimer formation, as the Mo atoms are in adjacent octahedral holes.

TABLE 5

Comparison of the known structures in the second- and third-row transition-metal oxide or sulphide tetrahalide series

Compound	Crystal system	Packing	Co-ordination polyhedron	Δ(Å) [a]	Unit cell volume (Å^3)	Z
$WOCl_4$	Tetragonal	Cubic	Square pyramid	0.32	287	2
$ReOCl_4$	Monoclinic	Hexagonal	Square pyramid	0.60	1 214	8
$MoOCl_4$	Triclinic	Cubic	Square pyramid	0.41	298	2
$WSCl_4$	Triclinic	h.c.p. [b]	Square pyramid	0.43	315	2
$WSBr_4$	Monoclinic	h.c.p.	Square pyramid	0.41	701	4

[a] Δ = Deviation of metal atom from basal plane. [b] h.c.p. = Hexagonal-close-packed.

No great changes in the deviations of the atoms from the ideal co-ordinates were found on cooling to 77 K, Table 2. The expected collapse into vacant octahedral holes did not occur. Thus, the 77 K refinement is essentially a confirmation of the room-temperature structure, and, since the changes in the molecular dimensions are probably negligible on cooling, better dimensions may be obtained by averaging the 293 and 77 K results.

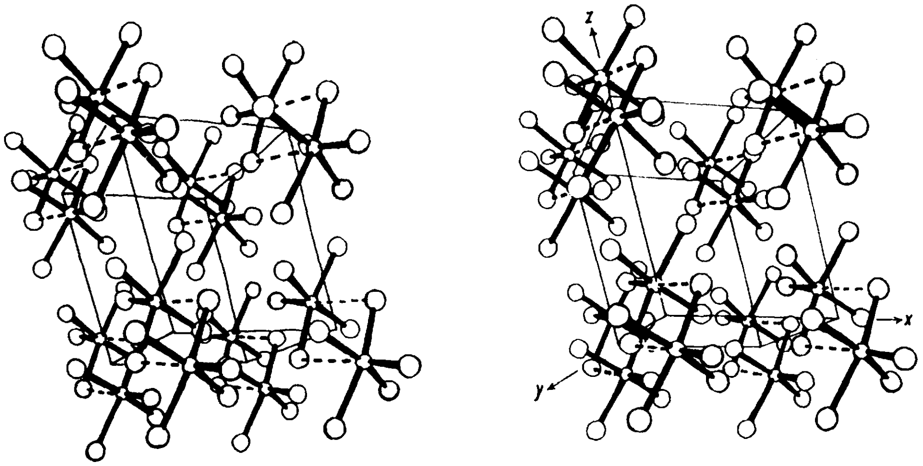

FIGURE 4 Stereoview of $MoOCl_4$ structure

Two adjacent square pyramidal $MoOCl_4$ units are illustrated in Figure 3, while Figure 4 shows a stereoview of the overall structure. The cubic packing can be seen from Figure 4.

The present structure is in good agreement with an electron diffraction study of gaseous $MoOCl_4$.[5] In the vapour, $MoOCl_4$ is monomeric, a C_{4v} square pyramid, with Mo–O = 1.658(5), Mo–Cl = 2.279(3), Cl $\cdots$ Cl = 3.142(8) Å, and O–Mo–Cl = 102.8(7)°. The transition to the vapour-state structure is thus readily explained.

The tendency towards dimerisation in solid $MoOCl_4$ is very weak, in contrast to the solid pentahalides such as $MoCl_5$,[11] α- and β- UCl_5,[12,13] or UBr_5.[14] In the vapour, $MoCl_5$ is a trigonal bipyramid.[11] However, all the oxide or sulphide tetrachlorides so far studied in the solid state are like $MoOCl_4$ and have square-pyramidal co-ordination, with only a slight tendency towards dimerisation. Table 5 summarises the crystallography of those members so far studied; it is interesting that, although they are all based on close packing and square pyramids, so far none has been found isostructural, the crystal symmetry varying from tetragonal to triclinic. Similar square-pyramidal units are also found in $MoOCl_3$,[15] which associate weakly into infinite chains.

The present structural studies of $MoOCl_4$ at 293 K and 77 K thus show that the structure determined fits well into the pattern so far established by previous studies of other second- and third-row transition-metal oxide tetrachlorides.

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