Table 5. *Bond lengths* (Å) *and angles* (°) *involving hydrogen atoms in α-methyltetronic acid*

Parameters from the final Mo II data refinement.

C(22)–H(221)	0·9	C(2)—C(22)–H(221)	101
C(22)–H(222)	0·9	C(2)—C(22)–H(222)	111
C(22)–H(223)	0·9	C(2)—C(22)–H(223)	116
O(3)—H(3)	0·9	H(221)–C(22)–H(222)	108
C(4)—H(41)	1·0	H(221)–C(22)–H(222)	124
C(4)—H(42)	1·0	H(222)–C(22)–H(223)	99
O(4)—C(4)–H(41)	110	C(3)—C(4)—H(42)	113
O(4)—C(4)–H(42)	110	H(41)—C(4)—H(42)	103
C(3)—C(4)–H(41)	115	C(3)—O(3)—H(3)	108

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References

Andersen, E. K. (1971). *Experimentelle studier over strukturen af hydroxyquinoner og deres salte.* Dissertation, Odense Universitetsforlag.

Hvoslef, J. (1968). *Acta Cryst.* B**24**, 23–35.

International Tables for X-ray Crystallography (1962). Vol. III, pp. 201–209. Birmingham: Kynoch Press.

Lawrence, J. & MacDonald, S. G. G. (1969). *Acta Cryst.* B**25**, 1247–1251.

MacDonald, S. G. G. & Alleyne, A. B. (1963). *Acta Cryst.* **16**, 520–524.

Stewart, J. M., Kundell, F. A. & Baldwin, J. C. (1970). The X-RAY system. Univ. of Maryland, College Park, Maryland.

Stoicheff, B. P. (1962). *Tetrahedron*, **17**, 135–141.

Acta Cryst. (1975). B**31**, 398

The Structure of Fluorides. IX. The Orthorhombic Form of Molybdenum Hexafluoride

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The crystal structure of molybdenum hexafluoride at 193 K has been determined by powder neutron diffraction with the least-squares profile-fitting refinement technique, and a specially constructed cryostat. MoF_6 at 193 K is orthorhombic, space group *Pnma* (D_{2h}^{16}) with $a=9{\cdot}559$ (9), $b=8{\cdot}668$ (8), $c=5{\cdot}015$ (5) Å and $Z=4$, and is isostructural with UF_6. The refinement gave $R=\sum(|I_{oi}-I_{ci}|)/\sum I_{oi}=0{\cdot}11$. The fluorine layers are distorted from perfect hexagonal close packing by the Mo–F bonding. The MoF_6 octahedra are nearly regular, with Mo–F distances of 1·766 (12)–1·861 (29) Å and F–Mo–F angles of 82·3 (15)–95·4 (10)°. The F–F contacts in an octahedron are 2·39–2·67 Å, and external to the octahedron, 2·92–3·22 Å.

Introduction

The second and third-row transition metals Mo–Rh and W–Pt form a series of hexafluorides with melting points from 343 K for RhF_6 to 273 K for PtF_6 (Canterford & Colton, 1968). These hexafluorides all undergo a solid-state transformation from a low-temperature phase, which is probably orthorhombic, to a high-temperature phase of body-centred cubic symmetry. The transformation temperatures lie between 263·6 K for MoF_6 and 275·2 K for PtF_6 (Siegel & Northrop, 1966). Because this phase change occurs at 263·6 K for MoF_6, the sample had to be cooled below this temperature to study the orthorhombic phase.

Crystalline UF_6 was shown to be orthorhombic and its structure solved by Hoard & Stroupe (1958). Siegel & Northrop (1966) obtained X-ray powder photographs of the low- and high-temperature phases of all the above hexafluorides, and observed a similarity between the X-ray powder patterns of the low-temperature phases and that of UF_6. The X-ray patterns, however, were not suitable for detailed structural analysis, and single crystals of the hexafluorides could not be isolated. No crystallographic work other than the above appears to have been carried out on these hexafluorides.

The present structural investigation of MoF_6 was performed by the powder neutron-diffraction method. This technique has far more favourable atomic scattering factors than X-ray diffraction, while the effects of absorption and extinction are negligible.

Experimental

MoF_6 was prepared by direct fluorination of molybdenum (O'Donnell, 1956). The sample was distilled twice before use; it was handled using only vacuum and dry-box techniques appropriate to metal hexafluorides (O'Donnell & Stewart, 1966).

The sample was cooled using the cryostat shown in Fig. 1. The cryostat design was such that the outer jacket and the heat shield were sufficiently large in diameter to prevent diffraction lines from aluminum appearing in the collected pattern. The inner jacket was fitted with a brass base-plate to aid thermal conduction to the sample. The cryostat was rotated at about 2π rad s^{-1}, since rotation increased the observed intensity by a factor of 3 to 4.

The sample was distilled into the Kel–F tube using normal vacuum techniques. The MoF_6 was cooled to 77 K, and the Kel–F sample tube was then fitted to the cryostat inner jacket using dry-bag techniques.

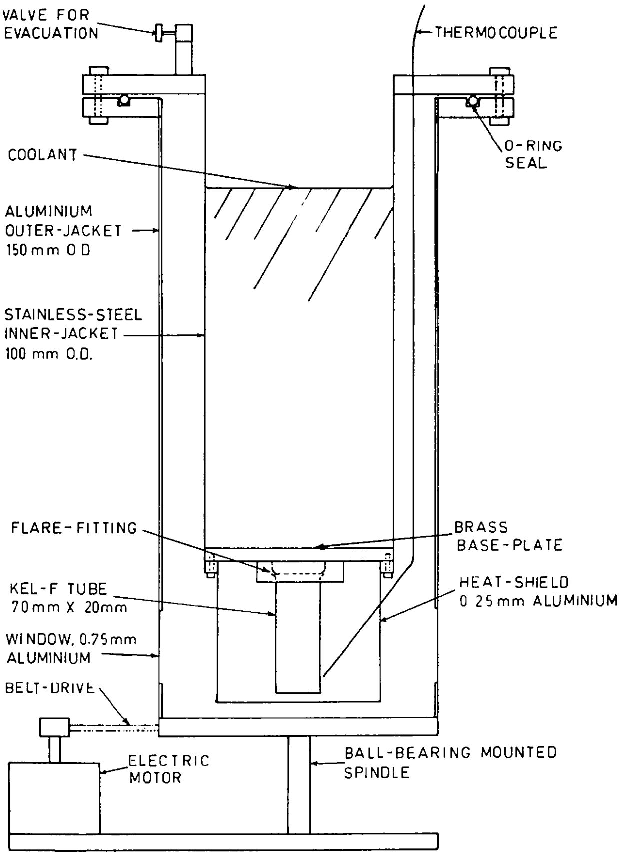

Fig. 1. The neutron-diffraction cryostat.

It was important to randomize the orientation of the crystallites for the powder neutron-diffraction study. This was done by snap-freezing the remelted MoF_6 using liquid nitrogen. The sample was then allowed to warm to the temperature selected for the investigation.

Since the pattern required approximately 50 h for collection, it was important that no change occurred in the sample during this period. If the vapour pressure of the sample was high the crystallites tended to sinter, dramatically altering the pattern obtained. At 263·6 K (just below the solid-phase transition temperature) the vapour pressure is about 13 kPa; at 213 K it is still about 130 Pa. Consequently, the temperature selected for the investigation was 193 K since this was sufficiently low to prevent sintering, and was conveniently obtained using an acetone/dry ice slush bath. During the experiment, a thermocouple, placed near the warmer end of the sample, indicated a temperature of 196 K.

The neutron-diffraction pattern of MoF_6 was collected to $2\theta = 45°$ with $\lambda = 1{\cdot}083$ Å by the elastic diffraction technique (Caglioti, 1970) on the AAEC research reactor HIFAR. The 2θ positions of the lines were consistent with an orthorhombic unit cell of the UF_6 type, and a least-squares refinement gave the unit-cell con-

Table 1. *Crystal data for molybdenum hexafluoride at* 193 K

MoF_6, M.W. 209·93: orthorhombic, space group $Pnma$ (D_{2h}^{16}) $a = 9{\cdot}559(9)$, $b = 8{\cdot}668(8)$, $c = 5{\cdot}015(5)$ Å, $U = 415{\cdot}5$ Å^3, $Z = 4$ $D_m = 3{\cdot}27$ g cm^{-3} at 227 K,* $D_x = 3{\cdot}35$ g cm^{-3} at 196 K, neutron wavelength = 1·083 Å

* Osborne, Schreiner, Malm, Selig & Rochester (1966).

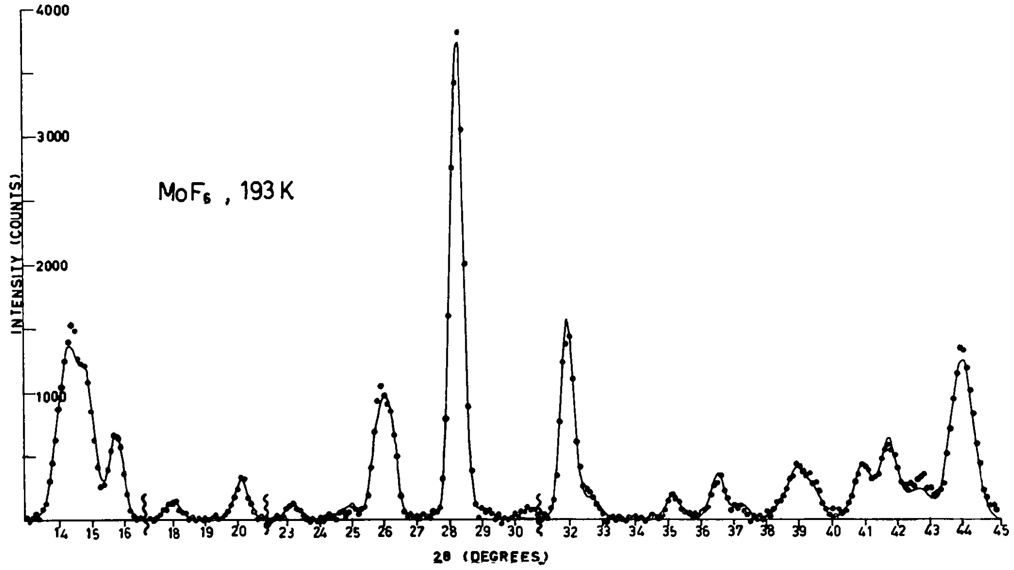

Fig. 2. Observed and calculated powder neutron-diffraction profiles for MoF_6 at 193 K.

stants: $a=9{\cdot}559$ (9), $b=8{\cdot}668$ (8) and $c=5{\cdot}015$ (5) Å. The neutron-diffraction pattern is shown in Fig. 2, and the various crystal data for MoF_6 are given in Table 1.

As the low-temperature MoF_6 neutron-diffraction pattern was similar to the previously collected UF_6 pattern at 293 K (Taylor, Wilson & Kelly, 1973), it appeared that the two compounds were isostructural. The UF_6 coordinates were therefore used as the starting point of a least-squares refinement with the MoF_6 neutron-diffraction data, using the profile-fitting technique described by Rietveld (1967). The neutron scattering factors used were $b_{Mo}=6{\cdot}9$ fm and $b_F=5{\cdot}6$ fm (Neutron Diffraction Commission, 1972), and an overall isotropic Debye–Waller temperature factor was assumed. A satisfactory refinement was achieved, with final values of

$$R=\sum(|I_{o_i}-I_{c_i}|)/\sum I_{o_i}=0{\cdot}11\,,$$

where I_{o_i} is one of the 298 observed background-corrected intensities in the pattern, and

$$\chi=[\sum w(I_{o_i}-I_{c_i})^2/(NO-NV)]^{1/2}=1{\cdot}27\,.$$

The observed and calculated neutron-diffraction pattern profiles are shown in Fig. 2, and the final neutron-diffraction parameters in Table 2.

Table 2. *Positional parameters for molybdenum hexafluoride at* 193 K ($\times 10^4$), *compared with the ideal values of Hoard & Stroupe* (1958) *for a perfect hexagonal close-packed structure*

Overall Debye–Waller factor $\bar{B}=2{\cdot}5$ (1) Å^2.

	Parameter*	Value	Ideal
Mo	x	1224 (12)	1250
Mo	z	1043 (35)	833
F(1)	x	155 (14)	0
F(1)	z	−1978 (30)	−2500
F(2)	x	2559 (17)	2500
F(2)	z	3744 (71)	4167
F(3)	x	221 (11)	0
F(3)	y	993 (11)	833
F(3)	z	2446 (20)	2500
F(4)	x	2320 (10)	2500
F(4)	y	1120 (21)	833
F(4)	z	−711 (42)	−833

* Where a y parameter is not given, $y=0{\cdot}25$.

Discussion

The present analysis has shown that orthorhombic MoF_6 at 193 K is isostructural with UF_6 at 293 K and, in addition, has provided the first measured structural parameters for MoF_6. The good agreement between the observed and calculated profiles, Fig. 2, suggests that the parameters are reliable.

The structure of UF_6 has been previously described (Taylor, Wilson & Kelly, 1973) and is based on hexagonal close-packed fluorine layers stacked perpendicular to the a axis. The layers at $x=0$ and $x=\frac{1}{4}$ in MoF_6 are shown in Fig. 3. The only molybdenum atom between these layers (in an octahedral hole) is shown and the faces of the octahedron are shaded. The fluorine atoms are contracted around Mo to form a nearly regular octahedron, while the hexagonal close packing around vacant octahedral holes is expanded and greatly distorted.

Hoard & Stroupe (1958) derived idealized coordinates for the UF_6 structure-type based on perfect hexagonal close packing of the anions. The measured coordinates for MoF_6 are compared with these idealized coordinates in Table 2. It is seen that there is considerable distortion from the ideal structure due to the strong Mo–F bonding. The deviations from ideality are greater than in the case of UF_6, since Mo^{VI} is the smaller cation, and shorter M–F bonds are formed.

The ionic radii of Mo^{VI} and U^{VI} for six-coordination are 0·60 and 0·75 Å (Shannon & Prewitt, 1969). For ionic structures, the M–F bond lengths in MoF_6 and UF_6 should thus be 1·95 and 2·10 Å. The observed mean M–F distances in MoF_6 and UF_6, 1·81 and 1·98 Å, are shorter than the ionic separations, indicating covalent bonding. In Fig. 4, the packing of MoF_6 is again illustrated, the circles being drawn to represent the ionic radii. The contraction about the occupied hole and expansion about the vacant holes is evident.

According to Megaw (1968), the observed Mo–F distances should be less than $1/\sqrt{2}$ times the fluorine diameter (1·91 Å) for intrinsic distortion of the MoF_6 octahedron to occur. Since the mean Mo–F distance

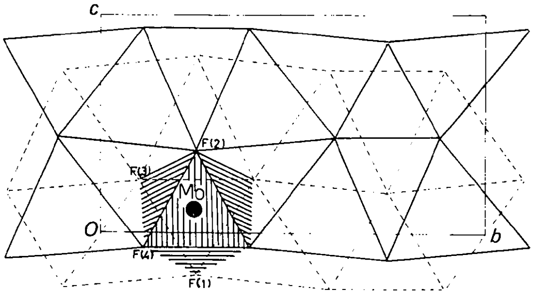

Fig. 3. The fluorine layers at $x=0$ and $x=\frac{1}{4}$ in MoF_6 at 193 K, illustrating the distortions from hexagonal close packing.

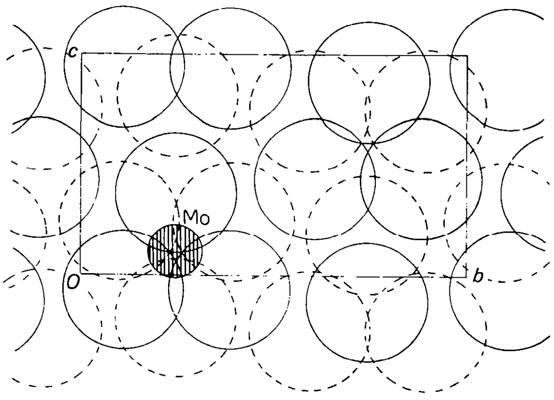

Fig. 4. The packing of the fluorine layers at $x=0$ and $x=\frac{1}{4}$ in MoF_6 at 193 K. The circles correspond to the ionic radii.

observed is less than 1·91 Å, departures from regularity in the octahedron due to this effect are possible. Slight differences in the Mo–F distances appear to be present (Table 3); the bond Mo–F(2) is probably slightly longer than the other Mo–F distances. This mode of distortion is predictable from the metal–metal repulsions (Taylor, Wilson & Kelly, 1973). Thus, effects external to the octahedron may outweigh the effect of the intrinsic instability within the octahedron in MoF_6.

Table 3. *Interatomic distances* (Å) *and angles* (°) *in* MoF_6 *at* 193 K

(*a*) In the octahedron

Mo–F(1)	1·827 (17)	F(3)–Mo–F(4)	91·1 (7) (2×)
Mo–F(2)	1·861 (29)	F(3)–Mo–F(1)	91·5 (6) (2×)
Mo–F(3)	1·766 (12) (2×)	F(3)–Mo–F(2)	94·7 (10) (2×)
Mo–F(4)	1·817 (20) (2×)	F(3)–Mo–F(3)	95·4 (10)
F(3)–F(3)	2·61 (2)	F(4)–Mo–F(4)	82·3 (15)
F(2)–F(3)	2·67 (2) (2×)	F(4)–Mo–F(1)	85·5 (11) (2×)
F(1)–F(3)	2·58 (2) (2×)	F(4)–Mo–F(2)	87·5 (9) (2×)
F(3)–F(4)	2·56 (2) (2×)	F(2)–Mo–F(1)	170·7 (17)
F(4)–F(4)	2·39 (4)	F(4)–Mo–F(3)	173·0 (12) (2×)
F(2)–F(4)	2·55 (2) (2×)		
F(1)–F(4)	2·47 (2) (2×)		

(*b*) External to the octahedron

Intralayer F–F contacts		Interlayer F–F contacts	
F(1)–F(3)	3·09 (2)	F(4)–F(3)	3·16 (2)
F(1)–F(3)	3·06 (1)	F(4)–F(1)	3·18 (2)
F(3)–F(3)	3·03 (2)	F(4)–F(3)	3·22 (2)
F(3)–F(3)	3·12 (2)	F(4)–F(3)	3·12 (2)
F(2)–F(4)	3·15 (2)	F(3)–F(2)	2·92 (2)
F(2)–F(4)	3·04 (4)	F(2)–F(1)	2·96 (3)
F(4)–F(4)	3·19 (2)	F(2)–F(1)	3·14 (3)

Mo–Mo separations

In mirror plane	Between mirror planes
5·00 (1), 5·015 (5), 5·96 (2)	5·57 (1), 5·04 (1), 6·33 (3)

Table 3 lists the observed distances and angles in MoF_6. A corresponding table with compatible nomenclature occurs in the previous publication on UF_6 (Taylor, Wilson & Kelly, 1973). The atoms can be located in the unit cell with the aid of Figs. 3, 4 and 5 of the earlier paper. Despite the large distortions of the h.c.p. fluorine layers, the MoF_6 octahedron does not deviate markedly from regularity. The Mo–F distances lie between 1·766 (12) and 1·861 (32) Å. The F–F distances within the octahedron, 2·39–2·67 Å (Table 3), are slightly smaller than the fluorine ionic diameter, 2·70 Å, while the F–F distances external to the octahedron, 2·92–3·22 Å, are about 0·6 Å larger. The F–Mo–F angles deviate slightly from 90° and the F–Mo–F diameters from 180°. The MoF_6 (orthorhombic) structure may alternatively be described as an array of interlocking MoF_6 molecules.

In MoF_5 (Edwards, Peacock & Small, 1962), the five terminal Mo–F bonds in the octahedron of the tetrameric unit lie between 1·66 and 1·89 Å, with a mean value of 1·76 Å. In $MoOF_4$ (Edwards & Steventon, 1968) the mean Mo–F distance for the terminal bonds is 1·83 Å. The mean Mo–F distance found in the octahedron of MoF_6 in the present study is in agreement with previously measured Mo–F distances in the above hexavalent molybdenum fluorides.

References

CAGLIOTI, G. (1970). *Thermal Neutron Diffraction*, edited by B. T. M. WILLIS, chap. 2. Oxford Univ. Press.

CANTERFORD, J. H. & COLTON, R. (1968). *Halides of the Second and Third Row Transition Metals*, chap. 6. New York: John Wiley.

EDWARDS, A. J., PEACOCK, R. D. & SMALL, R. W. H. (1962). *J. Chem. Soc.* (*A*), pp. 4486–4491.

EDWARDS, A. J. & STEVENTON, B. R. (1968). *J. Chem. Soc.* (*A*), pp. 2503–2510.

HOARD, J. L. & STROUPE, J. D. (1958). *USAEC Report TID*-5290, Paper 45.

MEGAW, H. D. (1968). *Acta Cryst.* B**24**, 149–153.

NEUTRON DIFFRACTION COMMISSION (1972). *Acta Cryst.* A**28**, 357–358.

O'DONNELL, T. A. (1956). *J. Chem. Soc.* pp. 4681–4682.

O'DONNELL, T. A. & STEWART, D. F. (1966). *Inorg. Chem.* **5**, 1434–1437.

OSBORNE, D. W., SCHREINER, F., MALM, J. G., SELIG, H. & ROCHESTER, L. (1966). *J. Chem. Phys.* **44**, 2802–2809.

RIETVELD, H. M. (1967). *Acta Cryst.* **22**, 151–152.

SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* B**25**, 925–946.

SIEGEL, S. & NORTHROP, D. A. (1966). *Inorg. Chem.* **5**, 2187–2188.

TAYLOR, J. C., WILSON, P. W. & KELLY, J. W. (1973). *Acta Cryst.* B**29**, 7–12.