

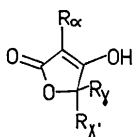
**$\alpha$ -Methyltetronic Acid. A Refinement of the Structure Based on New Experimental Data**

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The refinement was based on three-dimensional data collected with Cu and Mo radiation (Cu data 424 reflexions  $> 2\sigma$ , final  $R=0.053$ ; Mo data 919 reflexions  $> 2\sigma$ , final  $R=0.050$ ). The hydrogen atoms have been located. Most of the carbon and oxygen atoms of the molecule are coplanar. The hetero atom and an adjacent carbon atom are displaced from this plane (by up to 0.02 Å).

$\alpha$ -Methyltetronic acid ( $R_\alpha = \text{CH}_3$ ,  $R_\gamma = R_{\gamma'} = \text{H}$  in formula I) is the simplest tetronic acid derivative whose structure has been determined (MacDonald & Alleyne, 1963).



The structure of  $\alpha,\gamma$ -dimethyltetronic acid ( $R_\alpha = R_\gamma = \text{CH}_3$ ,  $R_{\gamma'} = \text{H}$ ) has been determined by Lawrence & MacDonald (1969), and that of ascorbic acid ( $R_\alpha = \text{OH}$ ,  $R_\gamma = -\text{CHOHCH}_2\text{OH}$ ,  $R_{\gamma'} = \text{H}$ ) by Hvoslef (1968). The results of these determinations are compared in the concluding section with the results of the present study.

The reinvestigation of the crystal structure of  $\alpha$ -methyltetronic acid was made for the following reasons:

1. The molecular structures of tetronic acids are important in connexion with our attempts to find correlations between structure and acidic strength (Andersen, 1971).

2. The original determination by MacDonald & Alleyne, although correct, is rather inaccurate (mainly due to the poor crystal material available to them).

3. Only a limited number of observed structure factors were used in MacDonald & Alleyne's refinement of the structure.

### Experimental

Density measurements (by flotation), lattice constants determination (by quartz-calibrated Guinier-Hägg diagrams) and single-crystal diagrams provided data in excellent agreement with MacDonald & Alleyne's findings. These data are recorded in Table 1.

The intensity data were collected on an automatic diffractometer (scintillation counter and pulse-height discriminator). Nickel-filtered Cu  $K\alpha$  and zirconium-filtered Mo  $K\alpha$  radiation was used. Intensities were recorded in the  $\omega$  scanning mode (scan angle  $1.4^\circ$ , scanning speed  $1.25^\circ \text{ min}^{-1}$ ). Background measure-

Table 1. *Crystal data for  $\alpha$ -methyltetronic acid*

Values in parentheses are standard deviations. Values in square brackets are from MacDonald & Alleyne (1963).

$\text{C}_5\text{H}_6\text{O}_3$	F.W. 114.10
$Z=4$	$F(000)$ 240
Monoclinic	Systematic absences
$a=3.998(0.001)$ [4.00(0.01)] Å	$hkl$ : no absences
$b=21.577(0.005)$ [21.57(0.03)]	$h0l$ : $l$ odd
$c=6.287(0.001)$ [6.30(0.01)]	$0k0$ : $k$ odd
$\beta=107.32(0.02)$ [107.6(0.3)]°	$P2_1/c$ assumed
$\mu(\text{Mo } K\alpha)=1.318 \text{ cm}^{-1}$	
$\mu(\text{Cu } K\alpha)=10.63 \text{ cm}^{-1}$	
$D_o=1.448(0.002)$ [1.460] $\text{g cm}^{-3}$ ; $D_c=1.464$ [1.461] $\text{g cm}^{-3}$	
Dimensions of crystal used for Cu $K\alpha$ data:	$0.1 \times 0.19 \times 0.26 \text{ mm}$
Dimensions of crystal used for Mo $K\alpha$ data:	$0.2 \times 0.6 \times 0.75 \text{ mm}$

ments were made for half the scan time at each end of the scanning interval. The 080 reflexion was measured every 15 reflexions. These measurements enabled the calculation of scale factors for each group of 15 reflexions. These factors were in the range 0.99–1.04.

All reflexions (459) within the range  $0.04 \leq \sin \theta/\lambda \leq 0.47$  were measured with Cu radiation. 35 had intensities less than twice the standard deviation of the measurement and were discarded. The remaining 424 were corrected for Lorentz and polarization factors and converted into structure factors (Cu I data set). Data were also collected with Mo  $K\alpha$  radiation. All

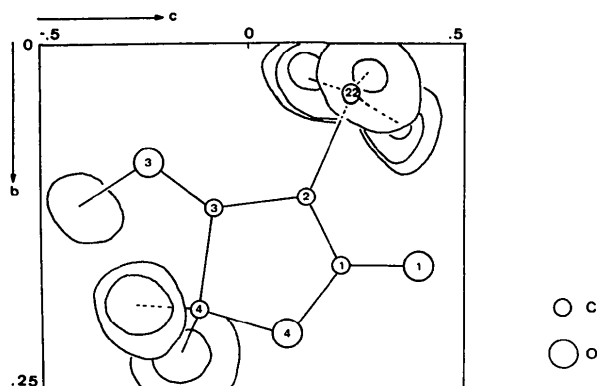


Fig. 1. Difference synthesis showing hydrogen atom peaks.

reflexions (1121) within the range  $0.08 \leq \sin \theta/\lambda \leq 0.64$  were measured. 202 had intensities less than twice the standard deviation of the measurement and were discarded. The remaining 919 were corrected for Lorentz and polarization factors and converted into structure factors (Mo II data set).

### Structure refinement

Structure-factor calculations based on MacDonald & Alleyne's parameters gave, when compared with the Cu I data set,  $R=0.27$ , which showed that the structure determination was correct (although probably not very accurate).

The structure was refined by full-matrix least-squares calculations with the *ORFLS* program of the X-RAY 70 calculating system (Stewart, Kundell & Baldwin, 1970). The quantity minimized was  $\sum w(F_o - F_c)^2$ . Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Unit weights were initially used and the subsequent weighting scheme was  $w=(a+F_o+bF_o^2)^{-1}$ . Finally, unit weights were again used. These gave mean values of  $w(F_o - F_c)^2$  almost independent of  $\sin \theta$  and magnitude of  $F_o$ . In the first calculations isotropic temperature factors were used (resulting  $R=0.16$ ); later anisotropic temperature factors were used (resulting  $R=0.099$ ). From a difference synthesis calculated at this stage the hydrogen atoms were located and included in the least-squares calculations with fixed parameters. Parameters from the final calculations are given in Table 2. The average ratio parameter shift/standard deviation was 0.61. The  $R$  index was 0.053.

The refinement based on the Mo II data set followed a similar course. The weighting scheme was  $w=(a+F_o+bF_o^2)^{-1}$ . With  $a=1.68$  and  $b=0.024$  this gave average  $w(F_o - F_c)^2$  values nearly independent of  $\theta$  and magnitude of  $F_o$ . Two cycles of least-squares calculations with starting parameters for the carbon and oxygen

atoms from the refinement based on the Cu I data set were followed by the calculation of three-dimensional difference electron-density maps. Fig. 1 is a composite diagram of these maps showing the hydrogen-atom peaks. The difference Fourier map provided positional parameters for the six hydrogen atoms in the asymmetric unit. Finally two cycles of least-squares refinement were performed in which all parameters except the

Table 2. *Final atomic parameters and standard deviations*

For the numbering of atoms see Fig. 3. The first line gives the parameters obtained from the Cu I data, the second those from the Mo II data.

(a) Positional parameters ( $\times 10^4$ )

		<i>x</i>	<i>y</i>	<i>z</i>
O(1)	Cu I	9067 (11)	1628 (2)	4191 (7)
	Mo II	9077 (7)	1625 (1)	4182 (4)
O(3)		635 (10)	932 (2)	-2272 (6)
		624 (6)	932 (1)	-2274 (4)
O(4)		6777 (9)	2046 (2)	852 (6)
		6792 (6)	2045 (1)	849 (4)
C(1)		7012 (15)	1574 (3)	2311 (11)
		7020 (9)	1574 (2)	2320 (5)
C(2)		4691 (14)	1074 (2)	1331 (9)
		4684 (8)	1078 (1)	1323 (5)
C(3)		3023 (14)	1258 (2)	-750 (9)
		3014 (8)	1254 (1)	-760 (5)
C(4)		4151 (14)	1890 (2)	-1217 (8)
		4186 (9)	1885 (2)	-1197 (5)
C(22)		4363 (16)	485 (2)	2511 (9)
		4389 (10)	488 (2)	2530 (6)
H(3)		9750	1170	-3120
		9824 (92)	1173 (16)	6419 (56)
H(41)		5670	1900	-2560
		5196 (96)	1913 (18)	7506 (56)
H(42)		2150	2340	-1700
		2193 (101)	2206 (17)	8418 (61)
H(221)		6500	120	3160
		6408 (110)	280 (18)	2513 (69)
H(222)		2660	190	1440
		2322 (111)	240 (17)	1696 (70)
H(223)		3890	650	3640
		3667 (108)	528 (18)	3732 (70)

Table 2 (cont.)

(b) Thermal parameters in the form  $-\frac{1}{4}\{\sum \sum B_{ij}h_i h_j a_i^* a_j^*\}$

	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
O(1)	5.92 (23)	5.00 (21)	3.21 (21)	-0.13 (17)	-0.54 (19)	-0.17 (17)
	5.70 (09)	4.60 (08)	3.43 (07)	-0.12 (07)	-0.20 (06)	-0.17 (06)
O(3)	5.22 (21)	4.72 (20)	3.81 (19)	-0.47 (18)	-0.36 (17)	0.39 (16)
	4.71 (08)	4.41 (07)	3.76 (07)	-0.73 (06)	0.02 (06)	0.06 (06)
O(4)	5.05 (20)	3.48 (18)	3.62 (19)	-0.40 (16)	0.32 (17)	0.41 (17)
	4.85 (08)	3.12 (06)	4.10 (07)	-0.33 (06)	0.52 (06)	0.34 (05)
C(1)	4.17 (30)	3.68 (30)	3.43 (32)	0.35 (26)	0.87 (27)	-0.06 (28)
	4.06 (10)	3.50 (09)	3.36 (09)	0.41 (07)	0.93 (07)	0.02 (07)
C(2)	3.90 (27)	3.57 (28)	2.85 (30)	0.27 (24)	0.72 (23)	0.05 (23)
	3.69 (09)	3.12 (08)	3.14 (08)	0.24 (07)	1.10 (07)	0.17 (06)
C(3)	3.61 (27)	4.09 (30)	3.04 (31)	0.09 (24)	0.66 (24)	-0.35 (24)
	3.42 (09)	3.52 (08)	3.24 (08)	0.12 (07)	1.00 (07)	0.02 (07)
C(4)	4.36 (30)	3.51 (27)	3.27 (29)	-0.36 (22)	0.29 (25)	0.48 (20)
	4.18 (10)	3.70 (09)	3.18 (09)	0.24 (08)	0.42 (07)	0.61 (07)
C(22)	6.19 (36)	3.70 (28)	3.89 (29)	-0.40 (25)	0.82 (25)	0.64 (22)
	5.37 (12)	4.16 (10)	4.32 (10)	-0.31 (09)	1.88 (09)	0.74 (08)

In the Cu I refinement the  $B_{iso}$  for the hydrogen atoms were H(3) 3.79; H(41) and H(42) 3.09; H(221), H(222) and H(223) 3.89. In the Mo II refinement the  $B_{iso}$  for the hydrogen atoms were H(3) 4.29; H(41) and H(42) 3.69; H(221), H(222) and H(223) 4.62.

thermal parameters of the hydrogen atoms were allowed to vary. In the last cycle the average ratio parameter shift/standard deviation was 0.27. The final parameters from this calculation are listed in Table 2, where the parameters based on the Cu I data set are also shown. The final  $R$  value was 0.050 (unobserved structure factors were not included in the calculations).\*

### The crystal structure

The methyltetronic acid molecules are linked by hydrogen bonds to form infinite ribbons. One of these ribbons is represented by the three molecules connected by dashed lines in the upper part of Fig. 2. The molecule in the middle is the reference molecule with the coordinates  $(x_1, y_1, z_1)$  given in Table 2. The other molecules belonging to the ribbon have coordinates  $(x_1 \pm n_i, y_1, z_1 \pm n_i)$  ( $n_i$  integers  $1 \rightarrow \infty$ ). The hydrogen bonds are between O(3)–H(3) groups and the O(1) atoms. They are rather short with  $O(3) \cdots O(1) = 2.600$  Å. O(3)–H(3) is about 0.9 Å and H(3)  $\cdots$  O(1) about 1.7 Å. The hydrogen atom is situated near the line connecting O(3) and O(1) [ $O(3)–H(3) \cdots O(1) = 171^\circ$ ]. Besides the hydrogen bond there are short contacts within the ribbons, between C(4) and O(1) (3.065 Å), and between C(3) and O(1) (3.202 Å). All other intermolecular contacts involving carbon and oxygen atoms are longer than 3.4 Å.

There are short hydrogen–hydrogen and heavy atom–hydrogen contacts between atoms belonging to different molecules. The shortest of these is 2.56 Å between H(222) and H(221) and 2.59 Å between two H(222) atoms. The only other distance shorter than 2.7 Å is 2.64 Å between O(4) and H(41).

### The molecular structure

The perpendicular distances from the atoms to a plane through the  $\alpha$ -methyltetronic acid molecule are given in Table 3. From this table one concludes that the ring is slightly buckled. The major part of the molecule is

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30639 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. Deviations (Å) of atoms for the plane through the  $\alpha$ -methyltetronic acid molecule

Equation of plane in monoclinic space

$$-3.406x + 9.014y + 3.491z = -0.1645$$

(a) Deviations of atoms included in calculating the plane

O(1)	-0.001;	O(3)	-0.002;	C(1)	0.000
C(2)	0.001;	C(3)	0.002;	C(22)	0.000

(b) Deviations of atoms not included in calculating the plane

C(4)	0.025;	O(4)	-0.009;	H(3)	0.007
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planar (within the limits of accuracy) but C(4) and O(4) deviate significantly from the plane and in opposite directions.

Details about the molecular structure are given in Fig. 3 and in Table 4 the bond lengths and angles are compared with those for other tetronic acids. The structures of these compounds are very similar. Bond lengths and angles agree well (except for a few bonds in the MacDonald & Alleyne work).

According to the classical valence structure there are three carbon–carbon single bonds and one carbon–carbon double bond in methyltetronic acid. This is also

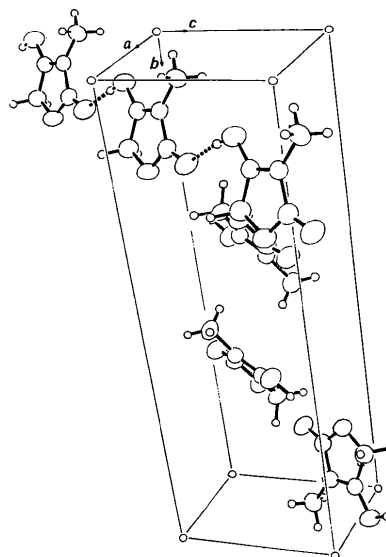


Fig. 2. The molecular packing in  $\alpha$ -methyltetronic acid. The molecules in two unit cells are shown. In addition two molecules in adjacent cells are shown. Atoms may be identified by the hydrogen atoms [one at O(3), two at C(4) and three at C(22)].

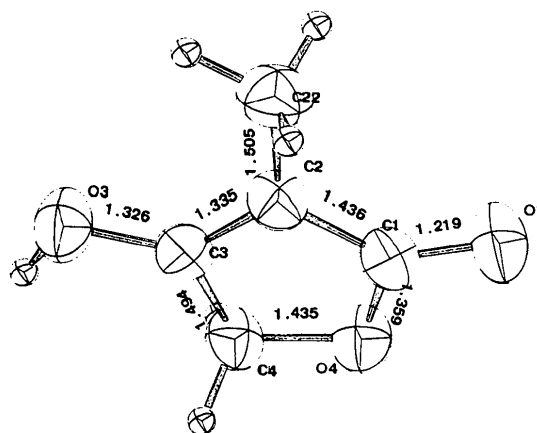


Fig. 3. Perspective drawing of one molecule of  $\alpha$ -methyltetronic acid. Atoms are represented by ellipsoids enclosing 50% of thermal displacements. Parameters from Mo data refinement.

Table 4. Bond lengths (Å) and angles (°) involving carbon and oxygen atoms in  $\alpha$ -methyltetronic acid and similar molecules

	Ascorbic acid (Hvoslef, 1968)	$\alpha,\gamma$ -Dimethyl- tetronic acid (Lawrence & MacDonald 1969)	$\alpha$ -Methyltetronic acid		
			This work Mo II data	This work Cu I data	MacDonald & Alleyne (1963)
	R( $\alpha$ )=OH R( $\gamma$ )= CHOHCH <sub>2</sub> OH	R( $\alpha$ )=CH <sub>3</sub> R( $\gamma$ )=CH <sub>3</sub>	R( $\alpha$ )=CH <sub>3</sub> R( $\gamma$ )=H	R( $\alpha$ )=CH <sub>3</sub> R( $\gamma$ )=H	R( $\alpha$ )=CH <sub>3</sub> R( $\gamma$ )=H
C(1)-O(1)	1.216 (2)	1.22*	1.219 (3)	1.228 (7)	1.21 (2)
C(2)-R( $\alpha$ )	1.361 (2)	1.52	1.505 (4)	1.497 (7)	1.57 (2)
C(3)-O(3)	1.326 (3)	1.30	1.326 (3)	1.334 (7)	1.24 (2)
C(4)-R( $\gamma$ )	1.521 (4)	1.52	-	-	-
C(1)-C(2)	1.452 (3)	1.45	1.436 (3)	1.438 (7)	1.47 (2)
C(2)-C(3)	1.338 (2)	1.34	1.335 (3)	1.341 (7)	1.37 (2)
C(3)-C(4)	1.493 (3)	1.53	1.494 (4)	1.492 (7)	1.59 (2)
C(4)-O(4)	1.444 (2)	1.43	1.435 (3)	1.447 (7)	1.41 (2)
O(4)-C(1)	1.355 (2)	1.34	1.359 (3)	1.355 (7)	1.36 (2)
O(4)-C(1)-C(2)	109.5 (2)	111	110.9 (2)	111.6 (5)	111 (1)
O(4)-C(1)-O(1)	121.4 (3)	121	118.4 (2)	118.2 (5)	121 (1)
O(1)-C(1)-C(2)	129.1 (2)	128	130.7 (2)	130.2 (5)	128 (1)
C(1)-C(2)-C(3)	107.8 (2)	105	106.7 (2)	105.4 (5)	106 (1)
C(1)-C(2)-R( $\alpha$ )	124.6 (2)	124	123.3 (2)	124.5 (5)	127 (1)
R( $\alpha$ )-C(2)-C(3)	127.5 (2)	131	129.9 (2)	130.1 (5)	127 (1)
C(2)-C(3)-C(4)	109.5 (2)	111	110.2 (2)	111.8 (5)	109 (1)
C(2)-C(3)-O(3)	133.5 (2)	126	126.8 (2)	125.8 (5)	127 (1)
O(3)-C(3)-C(4)	117.1 (2)	122	122.9 (2)	122.4 (5)	124 (1)
C(3)-C(4)-O(4)	104.0 (2)	102	103.8 (2)	102.5 (5)	102 (1)
C(3)-C(4)-R( $\gamma$ )	114.8 (2)	115	-	-	-
O(4)-C(4)-R( $\gamma$ )	110.4 (2)	110	-	-	-
C(1)-O(4)-C(4)	109.1 (2)	111	108.3 (2)	108.6 (5)	112 (1)

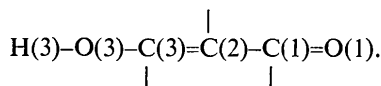
\* Standard deviations are not given by Lawrence & MacDonald; for bond lengths they are probably about 0.02 Å.

the general conclusion to be drawn from the structure determination. Some of the bonds, however, are modified in a way which is common to all the compounds listed in Table 4.

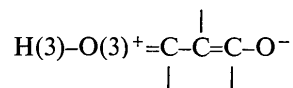
The best base for comparing C-C bonds has been given by Stoicheff (1962). Stoicheff's summary of bonds (henceforth called standard bonds) will be used in the following discussion, although it is based on open-chain molecules.

In the tetronic acids three types of C-C bonds are present. The length of bond type  $\text{>C=C<} [C(2)-C(3)]$  is 1.34 Å in close agreement with Stoicheff's standard bonds (e.g. 1.344 Å in acrolein and 1.336 Å in propylene). The length of bond type  $\text{>C-C<} [C(1)-C(2)]$  is definitely shorter (1.44 Å) than the standards for this type of bond (e.g. 1.472 Å in acrolein and 1.476 Å in butadiene). The third type of bond in tetronic acids is the  $\text{>C-C<}^+$  species. Bonds belonging to this type [C(2)-C(22) and C(3)-C(4)] are of same length (1.50 Å) as the standard bonds given by Stoicheff (e.g. in propylene, 1.501 Å).

The most interesting part of the structure from a chemical point of view is the chain



The lengths of C-(OH) bonds at  $sp^2$ -hybridized carbon atoms are usually found to be in the range 1.3-1.4 Å. It has been found (Andersen, 1971) that there is an inverse proportionality between C-(OH) bond lengths and acidic strength (acid dissociation constants). It is therefore not surprising that the tetronic acids (with dissociation constants around  $10^{-4}$ ) have C-(OH) bond lengths at the lower end of the above-mentioned range. The shortness of the O(3)-C(3) and C(2)-C(1) bonds and the acidic strength of the tetronic acids suggest that the following structure contributes to the ground state of the tetronic acid structure:



in which the net positive charge on O(3) should enhance the release of the proton.

The C-O bonds in the lactone ring have, as usual, different lengths.

Table 5 contains bond lengths and angles involving the hydrogen atoms.

It is a pleasure to thank Dr Per M. Boll of Odense University for providing the crystal material (in a suitable form) used in this investigation. All calculations were performed at NEUCC Lyngby, Denmark. We

Table 5. Bond lengths (Å) and angles (°) involving hydrogen atoms in  $\alpha$ -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

wish to thank the Carlsberg Foundation for financial support.

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## 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<sub>6</sub> at 193 K is orthorhombic, space group *Pnma* ( $D_{2h}^{10}$ ) with  $a = 9.559$  (9),  $b = 8.668$  (8),  $c = 5.015$  (5) Å and  $Z = 4$ , and is isostructural with UF<sub>6</sub>. The refinement gave  $R = \sum(|I_{oi} - I_{ci}|) / \sum I_{oi} = 0.11$ . The fluorine layers are distorted from perfect hexagonal close packing by the Mo–F bonding. The MoF<sub>6</sub> 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<sub>6</sub> to 273 K for PtF<sub>6</sub> (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<sub>6</sub> and 275.2 K for PtF<sub>6</sub> (Siegel & Northrop, 1966). Because this phase change occurs at 263.6 K for MoF<sub>6</sub>, the sample had to be cooled below this temperature to study the orthorhombic phase.

Crystalline UF<sub>6</sub> 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<sub>6</sub>. 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<sub>6</sub> 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<sub>6</sub> 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