Journal of Fluorine Chemistry, 23 (1983) 29–36

Received: October 14, 1982; accepted December 28, 1982

NEUTRON POWDER STRUCTURAL STUDIES OF UF_6, MoF_6 AND WF_6 AT 77 K

J.H. LEVY, J.C. TAYLOR* AND A.B. WAUGH

Chemical Technology Division, Australian Atomic Energy Commission Research Establishment, Private Mail Bag, Sutherland, NSW 2232 (Australia)

SUMMARY

The crystal structures of the hexafluorides UF_6, MoF_6 and WF_6 have been studied at 77 K by powder neutron diffraction. Profile refinements gave $R = \Sigma(|y_o|-|y_c|)/\Sigma y_o$ values of 6.9, 7.6 and 5.8% respectively, where y_o and y_c are the background - corrected pattern intensities. The structures are compared with the room-temperature structure of UF_6, the structures of MoF_6, WF_6 at 193K and with the plastic cubic structures of MoF_6, WF_6 and SF_6. The metal-fluorine bond lengths do not decrease significantly on cooling to 77 K but the octahedra pack more efficiently, and the atomic coordinates more closely approach the ideal coordinates based on perfect hexagonal close-packing of the fluorine atoms. Because of their shorter metal-fluorine bonds, the MoF_6 and WF_6 structures are more distorted from the ideal than UF_6. MoF_6, WF_6 and especially SF_6 are more compact and spherically-shaped molecules than UF_6; this explains the absence of a plastic cubic phase for UF_6, and the greater stability range of the SF_6 cubic phase. The existence of the orthorhombic Pnma phase for UF_6, MoF_6 and WF_6 down to 77 K is confirmed.

INTRODUCTION

This communication completes a series of neutron diffraction studies carried out of the Group VIa hexafluorides UF_6, MoF_6, WF_6 and SF_6 at different temperatures in this laboratory. UF_6 was studied at 293 and 193 K by neutron single crystal and powder diffraction [1,2], and MoF_6 and WF_6 at 193 K by neutron powder diffraction [3,4]. The high temperature plastic cubic phases of MoF_6, WF_6 and SF_6 were also studied with cubic harmonic refinements of neutron

* Present address : Division of Energy Chemistry, CSIRO, Lucas Heights Research Laboratories, Private Mail Bag 7, Sutherland, NSW 2232, Australia. Author to whom correspondence is addressed.

0022-1139/83/$3.00

powder data [5-7]. The present sets of 77 K data for UF_6, MoF_6 and WF_6 were collected to complete the study of structural changes on cooling, and to check the possibility of phase changes.

EXPERIMENTAL

UF_6, MoF_6 and WF_6 were distilled into 17 mm diameter Kel-F tubes, which were placed in a neutron cryostat. The melted samples were snap-frozen with liquid nitrogen to reduce preferred orientation. Neutron powder patterns were collected on the Australian Atomic Energy Commission research reactor HIFAR, with λ = 1.080 Å and step size 0.1° 2Θ. The 2Θ region below 13° was excluded because of the Kel-F diffraction peak. There were approximately 100 independent Bragg reflexions in each pattern. Profile refinements were carried out with the Rietveld-Hewat program [8]. The neutron scattering lengths were b(U) = 0.85, b(Mo) = 0.661, b(W) = 0.466 and b(F) = 0.566 fm.

Initial refinements showed discrepancies between observed and calculated intensities for UF_6 and MoF_6; profile factor values of R_1 (profile) = $= \Sigma(|y_o|-|y_c|)/\Sigma|y_o|$ were about 10% higher than R_2 (expected), where R_2 (expected) $= ((N-P)/\Sigma w y_o^2)^{\frac{1}{2}}$, N-P being the number of degrees of freedom. It was thought that this could be due to a phase change, but refinements with different symmetries gave no improvement. The largest (y_o-y_c) values (y_o and y_c being the background-corrected pattern intensities) were in the region of 26° 2Θ, where the (400) reflexion occurred. This suggested a preferred orientation correction G with [100] the orientation vector. Refinements in the original Pnma space group gave significant values of G, and the R_1 factors approached more closely the R_2 factors (Table 1), i.e. the agreement between observed and calculated patterns became nearly as good as that predicted from the counting statistics. An X-ray powder pattern of UF_6 at 77 K taken in a Guinier-Simon camera showed shifts in line positions due to the cooling, but no phase change capable of producing the effects observed in the refinements with no preferred orientation correction.

The R_1 and R_2 factors are shown in Table 1 together with the values of R_3 (Bragg) $= \Sigma|I_o-I_c|/\Sigma I_o$, where I is the integrated intensity of a Bragg reflexion. Halfwidth and preferred orientation parameters are given in Table 2. The halfwidth H is given by $H^2 = U \tan^2 \Theta + V \tan \Theta + W$. The unit cell dimensions found at 77 K and unit cell volumes are given in Table 3, and atomic positions and thermal parameters at 77 K in Table 4. The observed and calculated neutron powder profiles are given in Figure 1.

TABLE 1.

R-FACTORS IN THE NEUTRON PROFILE REFINEMENTS OF THE 77 K DATA FOR UF_6, MoF_6 AND WF_6. THE FACTORS R_1, R_2 AND R_3 ARE DEFINED IN THE TEXT.

Compound	R_1 (pattern)	R_2 (expected)	R_3 (Bragg)	Residual*	N†
UF_6, 77 K	0.069	0.037	0.055	5.1	97
MoF_6, 77 K	0.076	0.061	0.053	2.3	92
WF_6, 77 K	0.058	0.045	0.028	2.2	111

* Residual = $\Sigma\, w[y_o - y_c]^2/(NO-NV)$

† N = number of independent Bragg reflexions in refinement.

TABLE 2.

HALFWIDTH PARAMETERS U,V,W AND PREFERRED ORIENTATION PARAMETERS,G.*

Compound	U	V	W	G*
UF_6, 77 K	70(5)	-36(3)	6.6(4)	0.15(1)
MoF_6, 77 K	63(5)	-32(3)	6.1(4)	0.23(1)
WF_6, 77 K	64(4)	-33(2)	6.4(3)	0.15(1)

* $I_{corr} = I_{obs} \exp(-G\,\alpha^2)$ where α is the acute angle between the scattering vector and the preferred orientation direction.

TABLE 3.

UNIT CELL DIMENSIONS OF UF_6, MoF_6 AND WF_6 AT 77 K

Compound	a	b	c	U' (77 K)*	U' (193 K)	U' (293 K)
UF_6, 77 K	9.654(3)	8.776(4)	5.084(3)	430.7(3)	454.2(8)	461.9
MoF_6, 77 K	9.387(3)	8.530(3)	4.953(3)	399.9(3)	415.5	
WF_6, 77 K	9.422(2)	8.569(2)	4.980(2)	402.1(2)	422.0	

* U' = unit cell volume

TABLE 4.

(a) POSITIONAL PARAMETERS IN UF_6, MoF_6 AND WF_6 AT 77 K FROM THE NEUTRON PROFILE REFINEMENTS (MULTIPLIED BY 10^4).PARAMETE FOR PERFECT HEXAGONAL CLOSE-PACKING ARE ALSO SHOWN.
(b) ISOTROPIC DEBYE-WALLER FACTORS.

(a) POSITIONAL PARAMETERS

Atom	x,y,z	UF_6	MoF_6	WF_6	Ideal
M	x	1306(7)	1285(11)	1278(10)	1250
	z	750(17)	912(26)	856(28)	833
F(1)	x	54(13)	76(13)	115(9)	0
	z	-2417(20)	-2033(28)	-2086(19)	-2500
F(2)	x	2518(13)	2441(18)	2432(11)	2500
	z	3915(52)	3933(59)	3695(26)	4167
F(3)	x	49(9)	170(10)	177(6)	0
	y	854(10)	993(10)	979(7)	0833
	z	2326(14)	2423(16)	2381(12)	2500
F(4)	x	2508(8)	2375(10)	2387(6)	2500
	y	851(18)	1047(21)	932(14)	833
	z	-758(57)	-706(35)	-624(23)	-833

(b) THERMAL PARAMETERS, B ($\mathring{A}^2$)

	UF_6	MoF_6	WF_6
B(M)	1.53(14)	0.69(21)	1.38(21)
B(F)	2.02(13)	1.90(15)	1.76(8)

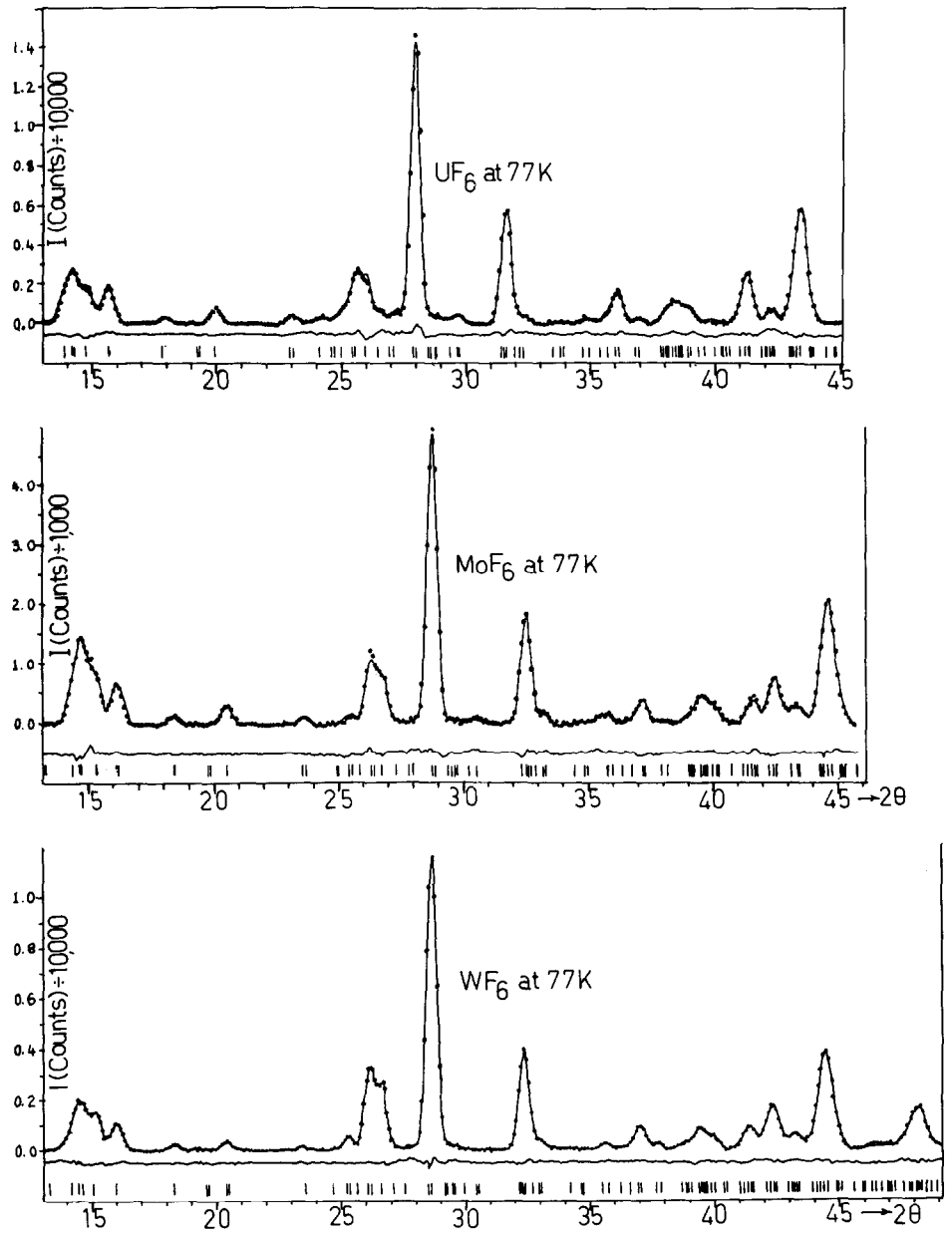

Figure 1. Observed (dots) and calculated (line) neutron powder diffraction profiles for UF_6, MoF_6 and WF_6 at 77 K. A difference plot is given immediately below each pattern. Markers below the difference plot indicate the positions of the (hkl) reflexions.

DISCUSSION

The M-F bonds measured at 77 K by powder neutron diffraction are accurate to 0.02 Å. At this level of accuracy, differences in the bond lengths in the octahedra are not observable. The average M-F bond lengths are given for the three structures in Table 5. A correction of + 0.003 Å has been added to the bond lengths at 77 and 193 K to correct for thermal motion [9]. The single-crystal neutron value for UF_6 at 293 K and the cubic harmonic values are corrected for thermal motion. Table 5 shows that the bond lengths in the structures do not change significantly on cooling; rather, the unit cell contractions (Table 3) are due to improved packing of the octahedra. The MoF_6 and WF_6 bond lengths agree with values from the cubic harmonic refinements of the b.c.c. phases [6,7]. As the metal-fluorine bond lengths are 0.1 Å less than the ionic radius sums, the structures are molecular, rather than a close-packed ionic array.

The U-F distance is greater than the fluorine diameter $/\sqrt{2}$, 1.91 Å; thusthere is no distortion of the UF_6 molecule from overcrowding of the fluorine atoms [10]. Slight distortions observed in the UF_6 octahedra in the single crystal neutron study of UF_6 were caused by cation repulsions [1]. The Mo-F and W-F distances are less than 1.91 Å, but intrinsic distortion due to anion overcrowding was not observed in these octahedra at the level of accuracy of the profile refinements.

The Mo-F and W-F bonds have approximately the same length (≈1.83 Å) but the U-F bonds are much longer (≈2.00 Å). Thus the MoF_6 and WF_6 molecules have a more spherical shape than the UF_6 molecule. Molecular librations are thus greater in MoF_6 and WF_6 than in UF_6, since their molecules have less of a tendency to interlock. This is the reason why MoF_6 and WF_6 have a high-temperature plastic cubic phase, but UF_6 does not. A very small S-F bond length is observed in SF_6 [7] (1.542(4)Å); the SF_6 molecule is so compact that its disordered cubic phase exists over the range 93-222 K, a much greater range than the cubic range for MoF_6 (263.4-290.6 K) or WF_6 (264.7-275.1 K). The molecular librations have been studied in the UF_6 structure at 293 K [1]; at this temperature the UF_6 molecule has hindered librations as a rigid body with an amplitude of 4½°, illustrating the damping effect of the longer U-F bonds on the librations.

Table 6 gives the displacements in Å between the ideal (Table 4) and observed positional parameters for the three structures between 77 and 293 K. The directions of displacement in all three structures are similar and correspond to movements of fluorine atoms into occupied and away from unoccupied

TABLE 5.

MEAN BOND LENGTHS $\overline{M\text{-}F}$ IN UF_6, MoF_6 AND WF_6 AT 77, 193 AND 293 K

Compound	$\overline{M\text{-}F}$, 77 K	$\overline{M\text{-}F}$, 193 K	$\overline{M\text{-}F}$, 293 K	Gas e.d.†	Cubic Harmonic*
UF_6	2.023(6)	1.983(6)	1.995(2)	1.996	
MoF_6	1.824(7)	1.812(8)			1.802(14) (266 K)
WF_6	1.834(5)	1.815(6)		1.829	1.838(8) (266 K)

* From cubic harmonic refinement of plastic cubic phase.

† Gas electron diffraction.

TABLE 6.

DISPLACEMENTS IN Å BETWEEN IDEAL AND OBSERVED
POSITIONAL PARAMETERS IN UF_6, MoF_6 AND WF_6 ($\times 10^3$)

Atom	Parameter	UF_6			MoF_6		WF_6	
		77K	193 K	293 K	77 K	193 K	77 K	193 K
M	x	-54(7)	-29(6)	-45(2)	-33(11)	6(11)	-26(9)	3(12)
	z	42(9)	17(8)	18(2)	-39(13)	-105(18)	-11(14)	-84(17)
F(1)	x	-52(13)	-116(9)	-125(4)	-71(12)	-148(13)	-108(8)	-139(10)
	z	-42(10)	-122(8)	-110(4)	-231(14)	-262(15)	-206(10)	-276(12)
F(2)	x	-17(13)	12(11)	29(4)	55(17)	-56(16)	64(10)	46(12)
	z	128(27)	104(21)	142(4)	116(30)	212(36)	235(13)	227(23)
F(3)	x	-47(9)	-159(7)	-142(3)	-160(9)	-211(11)	-167(6)	-204(7)
	y	-18(9)	-71(7)	-102(4)	-136(9)	-139(10)	-125(6)	-117(7)
	z	88(7)	74(6)	64(3)	38(8)	27(10)	59(6)	86(8)
F(4)	x	-8(8)	47(7)	58(3)	117(9)	172(10)	106(6)	137(7)
	y	-16(16)	-126(21)	-93(4)	-183(18)	-249(18)	-85(12)	-211(16)
	z	-38(29)	-18(25)	-38(3)	-63(18)	-61(21)	-104(11)	-105(20)
$\overline{\Delta}$ *		0.046(4)	0.075(4)	0.081(1)	0.104(4)	0.137(5)	0.108(3)	0.136(4)

$\overline{\Delta}$ * = mean displacement (Å)

octahedral holes. The movements are greater for the WF_6 and MoF_6 structures since the shorter M-F bonds give greater distortion of the h.c.p. fluorine framework (mean displacements in Table 6 for WF_6 and MoF_6 are twice those for UF_6). Also, as a structure is cooled, the coordinates approach the ideal values when the octahedra pack more efficiently.

The present neutron studies of UF_6, MoF_6 and WF_6 at 77 K confirm the existence of the orthorhombic Pnma phase for UF_6, MoF_6 and WF_6 down to 77 K.

REFERENCES

1 J.H. Levy, J.C. Taylor and P.W. Wilson, J. Chem. Soc. (Dalton), 1976, 219.

2 J.C. Taylor and P.W. Wilson, J. Solid State Chem., 14, 378 (1975).

3 J.H. Levy, J.C. Taylor and P.W. Wilson, Acta Cryst., B31, 398 (1975).

4 J.H. Levy, J.C. Taylor and P.W. Wilson, J. Solid State Chem., 15, 360 (1975).

5 J.H. Levy, P.L. Sanger, J.C. Taylor and P.W. Wilson, Acta. Cryst., B31, 1065 (1975).

6 J.H. Levy, J.C. Taylor and P.W. Wilson, J. Less Common Metals, 45, 155 (1976).

7 J.C. Taylor and A.B. Waugh, J. Solid State Chem., 18, 241 (1976).

8 A.W. Hewat, A.E.R.E. Report R7350 (1973).

9 W.R. Busing and H.A. Levy, Acta Cryst., 17, 142 (1964).

10 H.D. Megaw, Acta Cryst., B24, 149 (1968).