

The Adduct XeF<sub>2</sub>·WOF<sub>4</sub>

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**Abstract.** XeF<sub>2</sub>·WOF<sub>4</sub>,  $M=445.2$ , monoclinic, space group  $P2_1/c$ ,  $a=5.44$  (1),  $b=9.97$  (1),  $c=12.17$  (2) Å,  $\beta=92.0$  (2)°,  $U=659.4$  Å<sup>3</sup>,  $Z=4$ ,  $D_c=4.50$  g cm<sup>-3</sup>. The atomic positions have been determined by block-diagonal least-squares refinement of counter intensities, the final  $R$  being 0.081 for 817 reflexions. Mean bond lengths are W–F(terminal) 1.79, W–F(bridging) 2.18, W–O 1.65, Xe–F(terminal) 1.89 and Xe–F(bridging) 2.04 Å. The geometry of the fluorine bridge is related to the degree of covalency of the adduct.

**Introduction.** Clear colourless crystals, prepared as described by Holloway, Schrobilgen & Taylor (1974), were mounted under vacuum in Pyrex glass capillaries. The cell dimensions were determined from an oscillation photograph about  $a$  and from optimized counter angles for zero and upper-layer reflexions on a Weissenberg diffractometer. The intensities of reflexions with  $\sin \theta/\lambda < 0.7$  Å<sup>-1</sup> were collected at 22–25°C on a Stoe Weissenberg diffractometer with monochromatic Mo  $K\alpha$  radiation and an  $\omega$  scan technique. The intensities were corrected for Lorentz and polarization effects. The irregular shape of the crystal was approximated by a parallelepiped of dimensions  $0.042 \times 0.026 \times 0.017$  cm bounded by the forms  $\{100\}$ ,  $\{032\}$  and  $\{01\bar{3}\}$ . An absorption correction was applied [ $\mu(\text{Mo } K\alpha)=238.1$  cm<sup>-1</sup>] to the 817 reflexions with significant [ $I > 2\sigma(I)$ ] intensities (de Meulenaer & Tompa, 1965).

Scattering factors were taken from Cromer & Waber (1965). The positions of the W and Xe atoms were deduced from a Patterson synthesis and the positions of the remaining atoms found from a subsequent difference synthesis. The structure was refined by block-diagonal least-squares calculations. Corrections for the anomalous dispersion of W and Xe were included

(Cromer, 1965). All light atoms were initially treated as fluorine; the chosen position of the oxygen atom was based on the molecular geometry and is discussed later. Anisotropic temperature factors were refined for all atoms. The function minimized was  $\sum w(|F_o| - |F_c|)^2$  where  $w = (11.50 - 0.015|F_o| + 0.012|F_o|^2)^{-1}$ . The final  $R$  was 0.081 ( $R_w = \sum w(|F_o| - |F_c|) / \sum w|F_o| = 0.098$ ) for 817 reflections with a maximum shift in the final cycle of  $0.5\sigma$ . The final atomic parameters are given in Table 1.\*

**Discussion.** We were interested in the structure of the 1:1 adduct obtained when XeF<sub>2</sub> reacts with WOF<sub>4</sub> because initial Raman data indicated that the structure was essentially fluorine-bridged (Holloway, Schrobilgen & Taylor, 1974). We wished to determine which of the alternative formulations of the adduct, namely an ionic salt [XeF]<sup>+</sup>[WOF<sub>3</sub>]<sup>-</sup> or a covalent fluorine-bridged adduct, is the more appropriate. The molecular geometry and atom numbering are shown in Fig. 1 and the molecular packing in Fig. 2. Bond lengths and angles are listed in Table 2.

The distinction between O and F atoms on the basis of this work is not entirely unambiguous. The W–O length is shorter than the smallest W–F length only at a 97% level of confidence. However the mean O–W–F angle is larger, at a 99.9% confidence level, than the mean F(bridging)–W–F angle, as would be expected on the basis of the greater steric effect of the formal W–O bond order of 2. Further, considering the five terminal bonds to W, only for the W–O bond is the length different from the mean of the other four at the 99.9%

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30770 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Thermal parameters and final atomic positions with standard deviations derived from the least-squares refinement

Temperature factors are in the form  $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$ .

	$x/a$	$y/b$	$z/c$	$B_{11}$	$B_{22}$	$B_{33}$	$B_{23}$	$B_{13}$	$B_{12}$
W	0.6000 (3)	0.5054 (2)	0.2723 (1)	4.30 (8)	3.04 (7)	3.57 (7)	0.31 (6)	0.27 (4)	0.17 (6)
Xe	0.9814 (5)	0.2530 (3)	0.4759 (2)	5.26 (12)	3.80 (10)	3.48 (9)	-0.08 (8)	-0.10 (8)	0.78 (12)
F(1)	0.366 (7)	0.396 (5)	0.311 (4)	6.3 (21)	12.5 (29)	13.8 (31)	4.7 (24)	3.0 (18)	-5.6 (19)
F(2)	0.505 (8)	0.614 (3)	0.378 (2)	15.5 (31)	7.1 (17)	3.3 (11)	-0.6 (11)	-0.8 (14)	5.8 (19)
F(3)	0.902 (6)	0.583 (4)	0.272 (4)	5.3 (18)	9.5 (25)	11.8 (25)	-0.6 (21)	-1.5 (16)	0.4 (17)
F(4)	0.785 (6)	0.370 (2)	0.202 (3)	7.0 (16)	3.5 (11)	8.0 (16)	-1.5 (11)	3.6 (12)	0.2 (10)
F(5)	0.779 (8)	0.410 (4)	0.416 (3)	13.5 (32)	9.7 (22)	5.8 (16)	3.6 (16)	-2.0 (17)	5.0 (22)
F(6)	1.172 (7)	0.114 (3)	0.541 (4)	7.4 (21)	4.4 (19)	14.6 (31)	0.0 (16)	2.5 (18)	1.8 (13)
O(1)	0.472 (7)	0.586 (3)	0.166 (3)	6.5 (19)	4.6 (16)	7.5 (20)	1.5 (14)	-1.9 (15)	-1.2 (14)

Table 2. Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

W-F(1)	1.75 (3)	F(1)-W-F(2)	87 (2)
W-F(2)	1.77 (3)	F(2)-W-F(3)	91 (2)
W-F(3)	1.82 (4)	F(3)-W-F(4)	83 (2)
W-F(4)	1.83 (2)	F(4)-W-F(1)	92 (2)
Mean	1.79 (2)		
W-O(1)	1.65 (3)	O(1)-W-F(1)	103 (2)
W-F(5)	2.18 (3)	O(1)-W-F(2)	98 (2)
Xe-F(5)	2.04 (3)	O(1)-W-F(3)	98 (2)
Xe-F(6)	1.89 (3)	O(1)-W-F(4)	101 (1)
		Mean	100.0 (8)
O(1)-W-F(5)	177 (2)	F(5)-W-F(1)	80 (2)
F(1)-W-F(3)	159 (2)	F(5)-W-F(2)	79 (2)
F(2)-W-F(4)	161 (1)	F(5)-W-F(3)	80 (2)
F(5)-Xe-F(6)	176 (2)	F(5)-W-F(4)	82 (2)
W-F(5)-Xe	147 (2)	Mean	80.3 (8)

confidence level. The assignment of oxygen *trans* to bridging fluorine is confirmed by the solution  $^{19}\text{F}$  n.m.r. spectrum (Holloway, Schrobilgen & Taylor, 1974).

The mean W-F length is short compared with the values of 1.826 Å in  $\text{WF}_6$  (Tables of Interatomic Distances and Configuration in Molecules and Ions, 1965) and 1.84 Å in  $\text{WOF}_4$  (Bennett, Haas & Purdham, 1972).

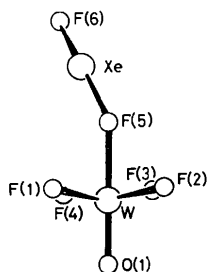
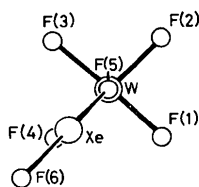


Fig. 1. Molecular geometry and atom numbering. (a) Projected onto the F(1)-F(2)-F(3)-F(4) plane. (b) Projected onto the plane defined by O(1), F(5) and the midpoints of the F(2)-F(3) and F(1)-F(4) vectors.

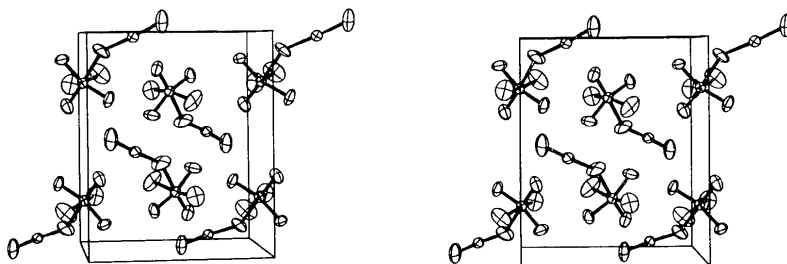


Fig. 2. A stereoscopic drawing of the molecular packing looking along *a*. Thermal ellipsoids are scaled to include 40% probability.

This may be because no correction has been made for libration effects. The large standard deviations of the F thermal parameters make the nature of the libration ambiguous, although the smaller W-F(terminal) lengths are to those F atoms with the largest r.m.s. amplitudes of vibration. The W=O length is shorter than in  $\text{WO}_4^{2-}$  (1.78 Å; Koster, Kools & Rieck, 1969) but similar to the value in  $\text{WOF}_4$ . The latter length of 1.66 Å is thought to be an average of W=O and W-F bonds (Bennett, Haas & Purdham, 1972). The W-F(bridging) length compares well with the value of 2.19 Å for the longer of the bridging bonds in  $\text{WOF}_4$  (Bennett, Haas & Purdham, 1972).

The length of the Xe-F(bridging) bond is rather short and approaches the values reported for Xe-F bonds in the, essentially discrete,  $\text{XeF}_2$  molecule in the complexes  $\text{XeF}_2 \cdot \text{IF}_5$  (2.018 Å; Jones, Burbank & Bartlett, 1970) and  $\text{XeF}_2 \cdot \text{XeF}_4$  (2.010 Å; Burns, Ellison & Levy, 1965). It is also shorter than the bridging bonds in the  $[\text{Xe}_2\text{F}_3^+]$  ion (2.14 Å; Bartlett, De Boer, Hollander, Sladky, Templeton & Zalkin, 1974). The Xe-F(bridging) lengths in the series of compounds  $\text{XeF}_2 \cdot \text{A}$  (A =  $\text{WOF}_4$ , 2.04 Å; A =  $\text{RuF}_5$ , 2.182 Å; Bartlett, Gennis, Gibler, Morrell & Zalkin, 1973; A =  $2\text{SbF}_5$ , 2.35 Å; Burgess, Fraser, McRae, Peacock & Russell, 1975) indicate an increasing tendency towards the formalism  $[\text{XeF}^+][\text{AF}^-]$ .

The terminal Xe-F length is shorter than in  $\text{XeF}_2$  (2.00 Å, Levy & Agron, 1963) but is not significantly different from those in  $[\text{Xe}_2\text{F}_3^+][\text{AsF}_6^-]$  (1.90 Å; Bartlett *et al.*, 1974),  $\text{XeF}_2 \cdot \text{RuF}_5$  (1.872 Å; Bartlett *et al.*, 1973) and  $\text{XeF}_2 \cdot 2\text{SbF}_5$  (1.84 Å; Burgess *et al.*, 1974). In view of the variation in bridging bond lengths in these compounds a reciprocal variation in the terminal bond lengths might be expected; unfortunately the errors in the structure determinations are of the same order as these differences.

The angles at W are as expected on the basis of a larger repulsive effect of the W=O bond. The F-Xe-F grouping has an eclipsed orientation with respect to the W octahedron (Fig. 1); a similar orientation is observed in  $\text{XeF}_2 \cdot \text{RuF}_5$  (Bartlett *et al.*, 1973) and  $\text{XeF}_2 \cdot 2\text{SbF}_5$  (Burgess *et al.*, 1975). The angle at the bridging fluorine atom (147°) compares with values of 137° in  $\text{XeF}_2 \cdot \text{RuF}_5$ , 149° in  $\text{XeF}_2 \cdot 2\text{SbF}_5$  and 151° in the  $[\text{XeF}_3^+]$  ion; no correlation with other structural parameters is apparent.

The two shortest Xe...F non-bonded contacts,

Xe...F(1<sup>I</sup>) 3.27 Å and Xe...F(4<sup>II</sup>) 3.26 Å, where I and II refer to atoms symmetry-related to those in Table 1 by the operations  $(1+x, y, z)$  and  $(x, \frac{1}{2}-y, \frac{1}{2}+z)$  respectively, are only slightly shorter than the non-bonded Xe...F contact in XeF<sub>2</sub> (3.42 Å; Levy & Agron, 1963). The crystal structure therefore consists of fluorine-bridged molecules with weak intermolecular forces rather than of ions.

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## Calcium Tetrantalate

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**Abstract.** CaTa<sub>4</sub>O<sub>11</sub>, hexagonal,  $P6_322$ ,  $a=6.2173$  (3),  $c=12.271$  (2) Å,  $Z=2$ ,  $D_x=7.60$  g cm<sup>-3</sup>. Colourless transparent crystals of CaTa<sub>4</sub>O<sub>11</sub> were synthesized from a 1:2 mixture of CaCO<sub>3</sub> and Ta<sub>2</sub>O<sub>5</sub> by the floating-zone technique [Akashi, Matsumi, Okada & Mizutani. *IEEE Trans. Mag.* (1969). **5**, 285–289]. One of the two independent Ta atoms is surrounded by seven oxygen atoms in the form of a pentagonal bipyramid with the average distance 2.06 Å. The remaining Ta and Ca atoms are coordinated to six and eight oxygen atoms with average distances 1.97 and 2.52 Å, respectively.

**Introduction.** The systematic absence observed on Weissenberg photographs was  $00l$  for  $l$  odd. The space group was uniquely determined to be  $P6_322$  from the systematic absence and the Laue symmetry of  $6/mmm$ . Cell dimensions were determined by the least-squares method from 11 reflexion data. For intensity measurements, a specimen was roughly ground into a sphere with average radius 0.04 mm. Intensities were collected on an automated four-circle diffractometer with Mo  $K\alpha$  radiation monochromated by a graphite plate. The  $\omega$ - $2\theta$  scan technique was employed with a scanning speed of  $0.5^\circ$  min<sup>-1</sup> in  $\omega$ . In all, 291 independent re-

flexion data, whose  $|F|$ 's were larger than  $3\sigma(|F|)$ , were obtained within the range  $2\theta \leq 75^\circ$ . The intensities were corrected for Lorentz, polarization and absorption factors.

The structure was solved by the heavy-atom method. The positions of the Ta atoms were obtained from the Patterson maps. Those of the remaining atoms were found on Fourier maps phased with the Ta atoms. The structure was refined with the full-matrix least-squares program *LINUS* (Coppens & Hamilton, 1970) by assuming anisotropic temperature factors for Ta and Ca atoms and isotropic for oxygen atoms. At the final stage of the refinement, the isotropic secondary-extinction parameter was included in the calculation. The final  $R$  value was 0.032 for the 291 observed reflexions.\* Unit weight was given to all the reflexions. The atomic scattering factors used were those given by Tokonami (1965) and Cromer & Waber (1965) for O<sup>2-</sup> and Ta<sup>5+</sup>,

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30782 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.