Fluoride Crystal Structures. Part XXIII.[1] *catena*-Di-μ-fluoro-(dimethyl sulphoxide)dioxouranium(VI)

By **John C. Dewan, Anthony J. Edwards,* and David R. Slim,** Chemistry Department, University of Birmingham, P.O. Box 363, Birmingham B15 2TT

Jacques E. Guerchais and René Kergoat, Laboratoire de Chimie Minérale, Université de Bretagne Occidentale, 29283 Brest-Cedex, France

The structure of the title compound has been determined by the heavy-atom method from 530 reflections, measured with a diffractometer, and refined by full-matrix least-squares methods to R 0.046. Crystals are orthorhombic, space group $Ama2$, a = 7.36(1), b = 14.77(2), c = 6.88(1) Å. In the structure uranium atoms are linked by di-μ-fluoro-bridges into zigzag chains with U–F 2.33 Å. The pentagonal bipyramidal co-ordination of the metal atoms is completed by two oxygen atoms in apical positions (U–O 1.74 Å) and by the oxygen atom of the dimethyl sulphoxide ligand (U–O 2.35 Å) in the fifth equatorial position.

THE linear uranyl group, UO_2, has been shown to exhibit co-ordination numbers in the plane perpendicular to itself of four,[2] five,[3-15] and six,[16-18] with the pentagonal bipyramidal arrangement the most common. These co-ordination arrangements are achieved in many

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cases [7-9,14-16] by a variety of types of bridging between uranium atoms.

In the present investigation, elemental analysis and i.r. studies provided no insight as to the co-ordination number in the plane perpendicular to the uranyl group or to the degree of polymerisation involved. Since this is the first example of a uranyl difluoride co-ordination compound, a full structure determination was undertaken.

EXPERIMENTAL

The complex was prepared in powder form by the dissolution of UO_2F_2 in 40% aqueous hydrofluoric acid and addition of dimethyl sulphoxide (dmso) to the solution. Excess of solvent was removed by evaporation. Yellow stable crystals were obtained by recrystallisation from aqueous HF (Found: C, 6.45; H, 1.55; F, 10.35; S, 8.00. $C_2H_6F_2O_3SU$ requires C, 6.22; H, 1.57; F, 9.84; S, 8.30%). Unit-cell and space-group data were obtained photographically and intensity data with a diffractometer.

TABLE 1

Atomic positional and thermal (× 10^3) parameters, with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
U	$\frac{1}{4}$	0.0425(1)	$\frac{1}{2}$	27.0(3)	22.6(4)	33.6(4)	0	0	3(1)
S	$\frac{1}{4}$	0.2810(6)	0.4299(14)	54(4)	36(4)	37(4)	0	0	−4(3)
F	−0.0576(12)	0.0800(7)	0.5316(41)	33(3)	27(4)	39(14)	−0.4(30)	0.3(50)	−4(7)
O(1)	$\frac{1}{4}$	0.1987(15)	0.5663(48)	45(9)	33(10)	84(25)	0	0	0.1(13)
O(2)	$\frac{1}{4}$	0.0425(27)	0.2513(57)	148(42)	102(35)	23(14)	0	0	−27(18)
O(3)	$\frac{1}{4}$	0.0436(31)	0.7554(65)	150(42)	124(40)	53(21)	0	0	−81(26)
C	0.0750(46)	0.3477(22)	0.4862(12)	83(18)	60(15)	90(38)	38(13)	−42(29)	−10(25)

Crystal Data.—$C_2H_6F_2O_3SU$, $M = 386$, Orthorhombic, $a = 7.36(1)$, $b = 14.77(2)$, $c = 6.88(1)$ Å, $U = 748$ Å^3, $D_m = 3.6$, $Z = 4$, $D_c = 3.42$, $F(000) = 672$. Space group $Ama2$ (C_{2v}^{16}, No. 40), $A2_1am$ (C_{2v}^{12}, No. 36, in a non-standard setting), or $Amam$ (C_{2h}^{17}, No. 63, in a non-standard setting) from systematic absences: hkl when $k + l \neq 2n$ and $h0l$ when $h \neq 2n$. $Ama2$ was confirmed from the subsequent successful refinement. Mo-K_α radiation, $\lambda = 0.7107$ Å; μ(Mo-K_α) = 327 cm^{-1}. Single-crystal precession and Weissenberg photographs and diffractometer data.

Structure Determination.—Intensity data were collected about the a axis (layers 0—8kl) with a Stoe two-circle computer-controlled diffractometer, by use of graphite monochromated Mo-K_α radiation. The stationary-counter–moving-crystal method was used, with an ω scan range of 1·2° on the lower levels, counting for 1 s at 0.01° intervals. For reflections on the third and higher layers ($\mu > 7°$) a variable range was scanned, with $\Delta\omega$ defined by ($A + B \sin \mu/\tan \nu$) where $A = 1.0$ and $B = 0.5$. Stationary-background counts were measured at the extremities of each scan for 10 s. Within the range $0.1 < \sin \theta/\lambda \leqslant 0.65$ 530 independent reflections having $I > 3\sigma(I)$ were obtained and considered observed. In converting intensities to structure amplitudes the polarisation factor appropriate to monochromated radiation was used. No absorption corrections were applied since the crystal was small and approximated to a needle of uniform cross-section elongated parallel to the a axis.

The structure was solved by conventional Patterson–Fourier techniques, the uranyl oxygen atoms being assigned on geometrical considerations, since they could not be distinguished from fluorine atoms by X-ray methods, in the presence of the heavy uranium atom. Scattering factors employed were those for neutral atoms,[19] with corrections for the effects of anomalous dispersion ($\Delta f'$ and $\Delta f''$) [20] applied to those of uranium and sulphur. Refinement by full-matrix least-squares, with layer scale factors refined separately, and all atoms vibrating isotropically gave R 0.065. Refinement was continued with the layer scale factors held constant and the introduction of anisotropic thermal parameters of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. In the later stages of refinement the weighting scheme [21] $w = [\sigma^2(F_o) + (0.04|F_o|)^2]^{-1}$ was found appropriate, giving a satisfactory analysis of the variation of $w\Delta^2$ with increasing $\sin \theta/\lambda$ and with increasing fractions of $|F_o|$. At convergence no parameter shift was $>0.04\sigma$, apart from those for the uranyl oxygen atoms O(2) and O(3), where the largest shift-to-error ratio was 0.3. A final difference-Fourier map showed no significant features.

TABLE 2

Interatomic distances (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Distances

$U \cdots U^{I}$	3.889(1)	$F \cdots F^{I}$	2.51(1)
U–F	2.34(1)	$F^{I} \cdots F^{III}$	2.83(1)
U–F^{I}	2.31(1)	$F \cdots O(1)$	2.87(2)
U–O(1)	2.35(2)	$F \cdots C^{VI}$	3.31(9)
U–O(2)	1.71(4)	$O(2) \cdots O(3^{V})$	3.41(6)
U–O(3)	1.76(4)	$O(2) \cdots C^{VII}$	3.42(6)
S–O(1)	1.54(3)	$O(3) \cdots C^{VI}$	3.29(6)
S–C	1.67(4)		

(*b*) Angles

$U^{I} \cdots U \cdots U^{II}$	142.3(1)	O(2)–U–O(1)	101(2)
O(2)–U–O(3)	180(2)	O(3)–U–O(1)	78(2)
F^{I}–U–F^{III}	75.7(3)	O(1)–S–C	109(2)
F–U–F^{I}	65.4(4)	C–S–C^{IV}	101(2)
F–U–F^{IV}	150.6(5)	U–F–U^{I}	113.5(5)
F–U–O(1)	75.5(3)	U–O(1)–S	131(2)

Roman numerals, as superscripts, refer to atoms in the positions:

I $-x, -y, z$
II $1 - x, -y, z$
III $\frac{1}{2} + x, -y, z$
IV $\frac{1}{2} - x, y, z$
V $x, y, -1 + z$
VI $-x, \frac{1}{2} - y, \frac{1}{2} + z$
VII $-x, \frac{1}{2} - y, -\frac{1}{2} + z$

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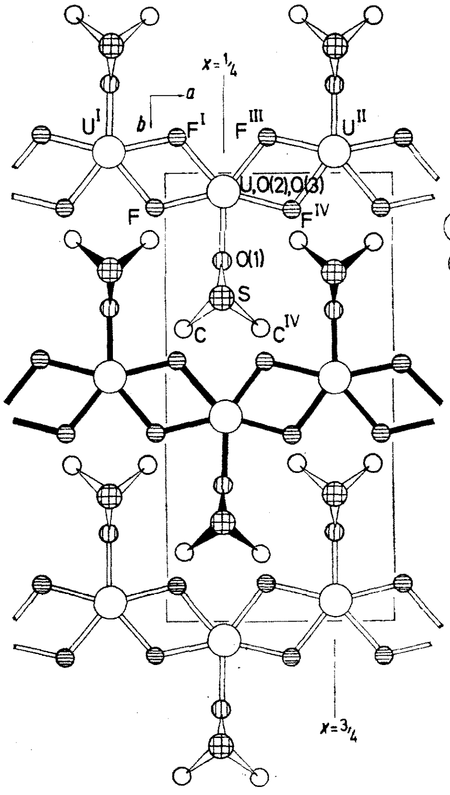
The final R was 0.046 and R' 0.058 $\{R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ for the preferred hand. Location of hydrogen atoms was not attempted. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21376 (3 pp., 1 microfiche),* and final positional parameters and anisotropic temperature factors, with their estimated standard deviations, in Table 1. Interatomic distances and angles are given in Table 2.

DISCUSSION

In the atomic arrangement shown in the Figure endless zigzag chains of uranium atoms, linked by di-μ-fluoro-bridges, run parallel to the a axis. Each uranium atom thus has the seven-co-ordinate pentagonal bipyramid arrangement, with the two uranyl oxygen atoms [O(2) and O(3)] at the apices. The pentagonal plane, which is almost perpendicular to [001], is composed of the four bridging fluorine atoms and O(1) from the dmso ligand. The uranyl group and the oxygen and sulphur atoms of the dmso ligand lie on the mirror planes at $x = \frac{1}{4}$ and $\frac{3}{4}$, bisecting each pentagonal bipyramid. The linear UO_2 group [O–U–O 180(2)°] is almost perpendicular to the plane of the pentagon [the angle between the normal to the least-squares plane (Table 3) through the equatorial atoms and the O · · · U · · · O vector is 2.5°].



Projection of the structure down [001]. O(2) Lies above and O(3) below each uranium atom. Filled bonds are for uranium atoms at $z = 0$, those unfilled at $z = \frac{1}{2}$

TABLE 3

Deviations (Å) of atoms from the least-squares plane through the equatorial atoms, $0.00\ X - 0.66Y + 6.87Z = 3.68$. Atoms defining the plane are italicised

F, −0.07, *F*^{I} 0.03, *F*^{III} 0.03, *F*^{IV} −0.07, *O*(1) 0.09, U −0.27, S −0.91, O(2) −1.98, O(3) 1.49, C −0.56, U^{I} −0.21

In all other examples of fluorine-containing pentagonal bipyramidal uranyl species the uranyl oxygen atoms occupy the apical positions. The $[UO_2F_5]^{3-}$ anion in the $M_3[UO_2F_5]$ compounds ($M = NH_4$,[3] Rb,[4] Cs,[5] and K[6]) is monomeric. The $[(UO_2)_2F_9]^{5-}$ anion in $K_5[(UO_2)_2F_9]$ is dimeric [7] and consists of two pentagonal bipyramids linked by a single fluorine bridge. The $[U_2O_4F_8]^{4-}$ anion in the $X_2[UO_2F_4]\cdot H_2O$ compounds ($X = Rb$[8] or Cs[9]) is also dimeric, and consists of two pentagonal bipyramids bridged by two fluorine atoms. The present complex is the first to have pentagonal bipyramids linked by pairs of bridging fluorine atoms into a polymeric chain.

The U · · · U distance (3.889 Å) in the chain arrangement is significantly shorter than those in the $[U_2O_4F_8]^{2-}$ anions (4.043 and 4.005 Å for the Cs[9] and Rb[8] salts respectively). The two independent U–F distances (2.31 and 2.34 Å) are not significantly different from each other or from the U–F bridging or terminal distances in either the di-μ-bridged $[U_2O_4F_8]^{4-}$ anions [U–F(br) 2.4 and 2.34, U–F(term) 2.2 and 2.16 in the Cs[9] and Rb[8] salts] or the singly bridged $[U_2O_4F_9]^{-}$ anion [U–F(br) 2.35, U–F(term) 2.28 Å in the K[7] compound]. The uranyl U–O distances (1.71 and 1.76 Å) are also not significantly different, and comparable to such distances in other compounds.[3-13] The U–O(1) distance (2.35 Å) to the dmso ligand is the first reported example and is very close to those found for other U–O(ligand) distances in the pentagonal plane.[15]

The geometry of the dmso ligand is as expected (see *e.g.* Table 3 of ref. 22). The sulphur atom lies 0.61 Å above the plane of O(1), C, and C^{IV} and has a pyramidal co-ordination. Short interchain contacts (<3.5 Å) are between uranyl oxygen atoms, and between uranyl oxygen atoms and carbon atoms of dmso ligands (Table 2).

The pentagonal bipyramidal arrangement about the uranium atom appears to be the favoured configuration for fluorine-containing uranyl compounds. The oxygen atoms of the rigid linear uranyl group force the arrangement [23] and take up the two apical positions. The remaining ligands, which can be regarded as two bidentate UF_2 groups and one unidentate dmso ligand, position themselves in the equatorial plane so as to reduce ligand–ligand repulsions. This description of the arrangement in the pentagon is supported by the

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue (items less than 10 pp. are supplied as full-size copies).

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short F $\cdots$ F^{I} distance (2.51 Å) in the di-μ-fluoro-bridge, compared with the equivalence (within experimental error) of the long F^{I} $\cdots$ F^{III} (2.83 Å) and the F $\cdots$ O(1) distances (2.87 Å). The repulsions between the fluorine atoms in the 'bidentate chelates' are constant and can thus be disregarded.[24]

We thank the S.R.C. for financial support (to J. C. D. and D. R. S.). Most of the calculations were carried out on the University of Manchester Regional Computer Centre's CDC 7 600 with the '*X*-Ray '72' system [25] and we thank the staff at Birmingham University Computer Centre for their assistance.

[5/289 *Received, 12th February,* 1975]

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