Fluoride Crystal Structures. Part 28.[1] Bis(tetraethylammonium) μ-Oxo-bis[pentafluorotantalate(V)]

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The structure of the title compound has been determined by the heavy-atom method from 1 267 reflections, measured with a diffractometer, and refined by full-matrix least-squares methods to R 0.069. Crystals are monoclinic, space group $P2_1/n$, $a = 8.57(1)$, $b = 13.68(2)$, $c = 11.79(2)$ Å, $\beta = 96.1(1)°$, $Z = 2$. In the structure two tetraethylammonium ions counterbalance each $[Ta_2OF_{10}]^{2-}$ complex anion in which the two tantalum atoms are bridged by an oxygen atom (Ta–O 1.875 Å; Ta–O–Ta 180° by symmetry); the five remaining octahedral sites around each tantalum atom are occupied by fluorine atoms (mean Ta–F 1.90 Å).

THE action of hydrogen peroxide on a solution of $[NEt_4][TaF_6]$ produces a mixture of unchanged fluoride as well as $[NEt_4][Ta(O_2)F_5]$, $[NEt_4][Ta(O_2)F_4(H_2O)]$, and a small amount of an unidentified product: the compound $[NEt_4][Ta(O_2)F_4(H_2O)]$ has been used to prepare a series of compounds of the type $[NEt_4][Ta(O_2)F_3(\beta\text{-ketoenolate})]$.[2] The n.m.r. spectrum of the unidentified material was of a different AX_5 type from the AX_5 spectra which we have observed previously for peroxofluorotantalates and elemental analysis gave an $NEt_4 : F$ ratio of 1 : 5. A dimeric species was suggested, $[NEt_4]_2[F_5Ta(O{-}O)TaF_5]$, but the alternative of an oxygen atom in place of the peroxo-group could not be excluded. A full X-ray structure determination was therefore undertaken in order to elucidate the nature of this group. While the structure determination was in progress,

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[1] Part 27, J. C. Dewan and A. J. Edwards, *J.C.S. Dalton*, 1976, 2433.

[2] J. Y. Calves and J. E. Guerchais, *J. Fluorine Chem.*, 1974, **4**, 47.

identical crystals were obtained from a solution containing no hydrogen peroxide, confirming the oxygen-bridge formulation.

EXPERIMENTAL

Air-stable colourless crystals, obtained by recrystallization from acetonitrile, were invariably twinned but a single crystal fragment was eventually obtained and used for data collection (Found: C, 23.45,23.6; H, 4.9,4.95; F, 22.5,22.5; N, 3.25,3.35. $C_{16}H_{40}F_{10}N_2OTa_2$ requires C, 23.20; H, 4.87; F, 22.93; N, 3.38%). Unit-cell and space-group data were obtained photographically and intensity data with a diffractometer.

Crystal Data.—$C_{16}H_{40}F_{10}N_2OTa_2$, $M = 828$, Monoclinic, $a = 8.57(1)$, $b = 13.68(2)$, $c = 11.79(2)$ Å, $\beta = 96.1(1)°$, $U = 1\,374$ Å^3, $D_m = 2.03$, $Z = 2$, $D_c = 2.00$, $F(000) = 788$. Space group $P2_1/n$ (C^5_{2h}, No. 14, in a non-standard setting) from systematic absences: $h0l$ when $h + l \neq 2n$ and $0k0$ when $k \neq 2n$. Mo-K_α radiation ($\lambda = 0.7107$ Å; $\mu = 77$ cm^{-1}). Single-crystal precession and Weissenberg photographs and diffractometer data.

Structure Determination.—Intensity data were collected about the b axis (layers $h0$—$14l$) with a Stoe two-circle computer-controlled diffractometer as previously described.[3] Within the range $0.1 < \sin\theta/\lambda \leqslant 0.65$, 1 276 independent reflections having $I > 3\sigma(I)$ were observed. Data were corrected for Lorentz and polarization factors but not for absorption.

The position of the one crystallographically independent tantalum atom was obtained from a three-dimensional Patterson synthesis computed by use of all data. All light atom positions, apart from that of the bridging atom, were fairly simply located by the usual methods employing least-squares cycles of refinement and subsequent difference-Fourier maps. The nature of the bridging group remained in doubt, exacerbated perhaps by the fact that the mid-point of the two tantalum atoms was a point of $\bar{1}$ symmetry. An elongated region of electron density, not at right angles to the Ta $\cdots$ Ta direction, existed between the two tantalum atoms, peaking at the $\bar{1}$ position, but tailing off to *ca.* 1 Å from each tantalum. This could not be successfully interpreted in terms of either a symmetric or an asymmetric peroxo-bridge, and the fact that all O–Ta–F angles were $>90°$, leant weight to the assignment of an oxygen atom on the centre of symmetry. The preparation of identical crystals from a solution to which no hydrogen peroxide had been added confirmed our assignment of an oxo-bridge.

Scattering factors used were those for neutral atoms,[4] with corrections for the effects of anomalous dispersion [5] applied to those for tantalum. Initial refinement by full-matrix least-squares methods was with layer scale-factors refined separately, and all atoms vibrating isotropically. Refinement was continued with layer scale-factors held constant [6] and with the introduction of anisotropic thermal parameters, for all atoms, of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)]$. In the final stages of refinement the weighting scheme [7] $w = [\sigma^2(F_o) + (0.06|F_o|)^2]^{-1}$ 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 $>0.001\sigma$. A final difference-Fourier map contained two peaks *ca.* 3.5 eÅ^3 in height at (0.391, 0.501, 0.716) and (0.511, 0.501, 0.589). The first was 0.97 Å from the tantalum atom and the second was 0.94 from the tantalum and 1.03 Å from the oxygen atom. Neither of these peaks could be successfully included in the present model, nor in a model wherein a peroxo-group bridged the two tantalum atoms either symmetrically or asymmetrically, and they were therefore assumed to arise from absorption errors. The remainder of the map was featureless. The final R was 0.069 and R' $\{=[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ 0.086. Most of the calculations were carried out on a CDC 7600 at the University of Manchester Regional Computer Centre using SHEL-X.[8] Observed and calculated structure factors and anisotropic thermal parameters are listed in Supplementary Publication No.

TABLE 1

Atomic positional parameters, with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Ta	0.452 0(1)	0.507 1(1)	0.651 3(1)
O	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
F(1)	0.233(2)	0.520(1)	0.607(2)
F(2)	0.405(3)	0.514(1)	0.804(1)
F(3)	0.663(2)	0.489(1)	0.713(2)
F(4)	0.424(2)	0.370(1)	0.659(1)
F(5)	0.479(2)	0.645(1)	0.653(1)
N	0.027(2)	0.247(1)	0.485(2)
C(1)	0.115(4)	0.157(2)	0.454(2)
C(2)	0.060(4)	0.264(2)	0.613(2)
C(3)	−0.144(4)	0.233(2)	0.444(3)
C(4)	0.086(4)	0.339(2)	0.429(2)
C(5)	0.292(5)	0.161(3)	0.483(4)
C(6)	−0.039(4)	0.345(3)	0.660(4)
C(7)	−0.224(4)	0.153(2)	0.509(3)
C(8)	0.055(5)	0.333(2)	0.297(3)

In the non-standard setting of the space group general equivalent positions are: x,y,z; $\bar{x},\bar{y},\bar{z}$; $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.

TABLE 2

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

(*a*) Distances

Ta–O	1.875(1)	N–C(2)	1.53(3)
Ta–F(1)	1.90(2)	N–C(3)	1.50(4)
Ta–F(2)	1.89(2)	N–C(4)	1.53(3)
Ta–F(3)	1.89(2)	C(1)–C(5)	1.52(5)
Ta–F(4)	1.90(1)	C(2)–C(6)	1.54(5)
Ta–F(5)	1.90(2)	C(3)–C(7)	1.54(5)
Ta $\cdots$ Ta^{I}	3.750(1)	C(4)–C(8)	1.55(4)
N–C(1)	1.51(3)		

(*b*) Angles

O–Ta–F(1)	92.9(7)	F(3)–Ta–F(5)	90.7(7)
O–Ta–F(2)	179.6(6)	F(4)–Ta–F(5)	176.6(6)
O–Ta–F(3)	93.6(8)	Ta–O–Ta^{I}	180
O–Ta–F(4)	92.2(5)	C(1)–N–C(2)	109(2)
O–Ta–F(5)	91.1(5)	C(1)–N–C(3)	108(2)
F(1)–Ta–F(2)	87(1)	C(1)–N–C(4)	112(2)
F(1)–Ta–F(3)	173(1)	C(2)–N–C(3)	114(2)
F(1)–Ta–F(4)	88.8(8)	C(2)–N–C(4)	106(2)
F(1)–Ta–F(5)	91.7(7)	C(3)–N–C(4)	109(2)
F(2)–Ta–F(3)	86(1)	N–C(1)–C(5)	115(2)
F(2)–Ta–F(4)	87.7(6)	N–C(2)–C(6)	115(3)
F(2)–Ta–F(5)	89.0(6)	N–C(3)–C(7)	113(2)
F(3)–Ta–F(4)	88.5(7)	N–C(4)–C(8)	111(2)

Roman numeral superscripts refer to atoms in the following equivalent positions: I $1 - x, 1 - y, 1 - z$.

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[3] J. C. Dewan, A. J. Edwards, D. R. Slim, J. E. Guerchais, and R. Kergoat, *J.C.S. Dalton*, 1975, 2171.

[4] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[5] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[6] E. C. Lingafelter and J. Donohue, *Acta Cryst.*, 1966, **20**, 321.

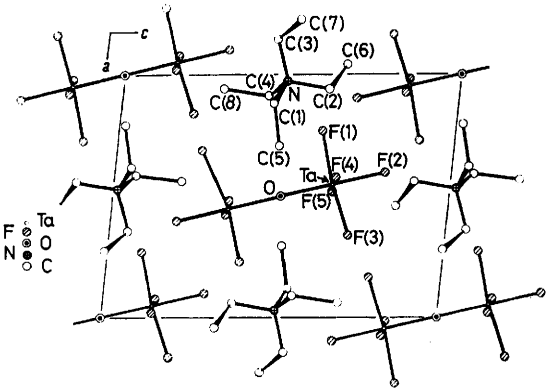
[7] G. H. Stout and L. H. Jensen, '*X*-Ray Structure Determination,' Macmillan, London, 1969, p. 456.

[8] SHEL-X, 'Program for Crystal Structure Determination,' G. M. Sheldrick, University of Cambridge, 1975.

SUP 21943 (10 pp., 1 microfiche),* final positional parameters with their estimated standard deviations in Table 1, and interatomic distances and angles in Table 2.

DISCUSSION

The structure, illustrated in the Figure, consists of discrete $[Ta_2OF_{10}]^{2-}$ anions and $[N(C_2H_5)_4]^+$ cations. In the anion two tantalum atoms are bridged by an oxygen atom, which lies on a centre of symmetry, thus constraining the Ta–O–Ta angle to 180° and the overall symmetry of the anion to approximately D_{4h}. The octahedral coordination of the tantalum atom is completed by five fluorine atoms with mean Ta–F 1.90 Å, slightly larger than the Ta–O distance of 1.875 Å. Deviations of atoms from the plane of four of the fluorine atoms are listed in Table 3.



Projection of the structure down [010]

TABLE 3

Deviations (Å) of atoms from the least-squares plane

$$-2.78\,X + 0.84\,Y + 11.47\,Z = 6.72$$

Plane: F(1), F(3)—(5)

F(1) 0.03, F(3) 0.03, F(4) −0.03, F(5) −0.03, Ta −0.08, O −1.96, F(2) 1.81

The Ta–F distance is normal for tantalum(v) and is essentially the same as corresponding distances in the $[Ta(O_2)F_5]^{2-}$ (ref. 9) and $[TaF_6]^-$ (ref. 10) anions. Although the $[Ta_2F_{11}]^-$ ion has not been crystallographically characterised, a useful comparison can be made with the $[Nb_2F_{11}]^-$ ion,[11] since the compounds NbF_5 (ref. 12) and TaF_5 (ref. 10) and $[SeF_3][NbF_6]$ and $[SeF_3][TaF_6]$ have been shown to be structurally identical.

In the $[Nb_2F_{11}]^-$ ion, the bridge is not linear, the angle Nb–F–Nb being 166°, but the two octahedra are in a very similar eclipsed configuration to that of the present oxo-anion.

The Nb–F(br) distance (2.05 Å) is 0.21 Å longer than the mean terminal Nb–F distance (1.84 Å). The F(br)–Nb–F angles average 83.5° (for the fluorine atoms approximately at right angles to the bridge), significantly less than 90°. In comparison the Ta–O(br) distance is 0.025 Å less than the Ta–F(term) distance and the corresponding mean O–Ta–F angle is 92.4°, significantly greater than 90°.

Thus the replacement of fluorine by oxygen in the bridging position causes a shortening of the bridge bonds and a characteristic change in the angles in the octahedron.

Although this is the first example of an $[M_2OF_{10}]^{2-}$ ion for a transition metal, there are several crystallographically characterised examples [13-16] for arsenic and antimony. In these anions the bridge angle is close to 135°, and the As–O or Sb–O distances are slightly longer than the corresponding As–F or Sb–F distances. These differences may reflect a stronger π-bonding interaction in the linear-bridge system, since the $[Ta_2OF_{10}]^{2-}$ anion is very similar to the linear-bridged ions $[M_2OCl_{10}]^{4-}$ (M = Ru [17] and Re [18]) where the bonding system has been discussed in detail,[19] and π-bonding is considered important.

For the $[Sb_2OF_{10}]^{2-}$ ions, in the rubidium [13] and caesium [14] salts, the two octahedra take on different configurations with respect to one another, giving the overall symmetry for the anion C_1 and C_2 respectively. For the $[As_2OF_{10}]^{2-}$ ion, in the caesium,[15] hydrated rubidium,[16] and hydrated potassium [16] salts, the symmetry is C_s with the molecule lying on a mirror plane.

The D_4 arrangement, with eclipsed fluorine atoms, in the present case, may be due to the steric effects of π-bonding in the bridge system. With the large $[NEt_4]^+$ cations, the linear-bridge system cannot be correlated with a cubic close-packing of fluorine and oxygen atoms, as it is in the structures of niobium,[12] tantalum,[12] molybdenum,[20] and tungsten [21] pentafluorides, and tungsten tetrafluoride oxide.[22]

The cations occupy general positions in the unit-cell. Their geometry agrees with that found in previous structure determinations [23,24] as do the bond lengths. They are not disordered. Interionic contacts are between fluorine and carbon atoms and are all >3.34 Å.

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue.

[9] Z. Ruzic-Toros, B. Kojic-Prodic, and M. Sljukic, *Acta Cryst.*, 1976, **B32**, 1096.

[10] A. J. Edwards and G. R. Jones, *J. Chem. Soc.* (*A*), 1970, 1891.

[11] A. J. Edwards and G. R. Jones, *J. Chem. Soc.* (*A*), 1970, 1491.

[12] A. J. Edwards, *J. Chem. Soc.*, 1964, 3714.

[13] W. Haase, *Acta Cryst.*, 1974, **B30**, 2508.

[14] W. Haase, *Chem. Ber.*, 1973, **106**, 41.

[15] W. Haase, *Z. anorg. Chem.*, 1973, **397**, 258.

[16] W. Haase, *Acta Cryst.*, 1974, **B30**, 1722.

[17] A. M. Mathieson, D. P. Mellor, and N. C. Stephenson, *Acta Cryst.*, 1952, **5**, 185.

[18] J. C. Morrow, *Acta Cryst.*, 1962, **15**, 851.

[19] J. D. Dunitz and L. E. Orgel, *J. Chem. Soc.*, 1953, 2594.

[20] A. J. Edwards, R. D. Peacock, and R. W. H. Small, *J. Chem. Soc.*, 1962, 4486.

[21] A. J. Edwards, *J. Chem. Soc.* (*A*), 1969, 909.

[22] A. J. Edwards and G. R. Jones, *J. Chem. Soc.* (*A*), 1968, 2074.

[23] A. J. Edwards and D. R. Slim, unpublished data.

[24] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, p. 276.