Fluoride Crystal Structures. Part 29.[1] Tetraethylammonium Tetrafluoro(2-methylpyridine *N*-oxide)peroxotantalate(v): An Example of Pentagonal Bipyramidal Seven-co-ordination

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The structure of the title compound has been determined by the heavy-atom method from 1 676 reflections, measured with a diffractometer, and refined by full-matrix least-squares methods to *R* 0.061. Crystals are monoclinic, space group *Cc*, $a = 10.04$ (2), $b = 13.76(2)$, $c = 28.49(3)$ Å, $\beta = 102.4(3)°$, $Z = 8$. In the two crystallographically independent anions of the structure, which have the $[\text{Metal(bidentate)(unidentate)}_5]^{x\pm}$ stoicheiometry, a seven-co-ordinate tantalum atom is at the centre of a pentagonal bipyramid; the pentagonal plane comprises two fluorine atoms (mean Ta–F 1.95 Å), the peroxo-group (mean Ta–O 1.92 Å), and the ligand oxygen atom (mean Ta–O 2.20 Å). The two capping positions are occupied by fluorine atoms (mean Ta–F 1.94 Å). The two independent cations were refined as rigid-groups and are not disordered.

CRYSTAL structures of seven-co-ordinate complexes with stoicheiometry $[\text{Metal(bidentate)(unidentate)}_5]^{x\pm}$ are rare,[2] especially where the bidentate ligand is of small bite. Accordingly, we have undertaken a full structure determination of the present complex, the first to be performed on a tantalum fluoride co-ordination compound, and have compared the results with ligand–ligand repulsion-energy calculations for the $[\text{Mbu}_5]^{x\pm}$ stoicheiometry.[2]

EXPERIMENTAL

The complex was prepared by dissolution of $[\text{NEt}_4][\text{Ta(O}_2)\text{F}_4(\text{H}_2\text{O})]$ (ref. 3) and a slight excess of 2-methylpyridine *N*-oxide in cold acetonitrile. Hygroscopic, colourless single crystals of the complex, obtained by further cooling or evaporation of the solution at 30—40 °C, were washed with ethanol and dried in a desiccator (Found: C, 31.9; H, 5.15; F, 14.3; N, 5.35. $\text{C}_{14}\text{H}_{27}\text{F}_4\text{N}_2\text{O}_3\text{Ta}$ requires C, 31.9; H, 5.15; F, 14.4; N, 5.3%). The crystal used for data collection was coated in nail-varnish to prevent decomposition. Unit-cell and space-group data were obtained photographically and intensity data with a diffractometer.

Crystal Data.—$\text{C}_{14}\text{H}_{27}\text{F}_4\text{N}_2\text{O}_3\text{Ta}$, $M = 528$, Monoclinic, $a = 10.04(2)$, $b = 13.76(2)$, $c = 28.49(3)$ Å, $\beta = 102.4(3)°$, $U = 3\,845$ Å^3, $D_m = 1.83$, $Z = 8$, $D_c = 1.82$, $F(000) = 2\,064$. Space group $Cc(C_s^4$, No. 9) or $C2/c$ (C_{2h}^6, No. 15) from systematic absences: hkl when $h + k \neq 2n$ and $h0l$ when $l \neq 2n$, the former confirmed by the successful structure refinement. Mo-K_α radiation ($\lambda = 0.7107$ Å; $\mu = 55$ cm^{-1}). Single-crystal precession and Weissenberg photographs and diffractometer data.

Structure Determination.—Intensity data were collected about the *b* axis (layers $h0$—$12l$) with a Stoe two-circle computer-controlled diffractometer as previously described.[4] Within the range $0.1 < \sin\theta/\lambda \leqslant 0.65$, 1 676 independent reflections having $I > 3\sigma(I)$ were observed. Data were corrected for Lorentz and polarization factors but not for absorption.

An unmodified three-dimensional Patterson synthesis, computed by use of all data, could only be solved for the tantalum atom positions in the non-centrosymmetric space group. Structure solution was continued by the usual trial-and-error methods with the choice of space group being vindicated by the eventual successful structure solution and refinement. Scattering factors employed were those for neutral atoms,[5] with corrections for the effects of anomalous dispersion ($\Delta f'$ and $\Delta f''$)[6] 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 the layer scale-factors held constant and with the introduction of anisotropic thermal parameters, for the tantalum atoms, of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)]$. Because of the paucity of observed reflections, and the large number of variables involved, the pyridine ring of each ligand and both tetraethylammonium cations were refined as rigid groups.[7] Within the pyridine rings [N(i1)–*C*(i5); $i = 1$ or 2], all angles were constrained to be 120° and all bond lengths were fixed at the aromatic C–C value of 1.395 Å.[8] In the tetraethylammonium cations [N(i1)–C(i8); $i = 3$ or 4] the C–N–C angles were fixed at the tetrahedral value of 109.5° and the C–C–C angles at 112°. The N–C bonds were fixed at 1.48 Å and C–C bonds at 1.54 Å.[8] Terminal carbon atoms C(i5)—(i8) were constrained to be equidistant from C(i1), C(i3); C(i1),C(i4); C(i2),C(i3); and C(i2),C(i4). There was no evidence for disorder of the cations. In all cases, the rigid-groups pivoted on their respective nitrogen atoms with individual isotropic temperature factors being refined for all atoms. In the final stages of refinement the weighting scheme[9] $w = [\sigma^2(F_o) + (0.06|F_o|)^2]^{-1}$ 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 $>0.3\sigma$ and a final difference-Fourier map showed no significant features. The final *R* was 0.061 and R' $\{= [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ was 0.078. Most of the calculations were carried out by use of SHELX-76[7] on an ICL 1906A at the University of Birmingham Computer Centre. Observed and calculated structure factors are listed in Supplementary Publication

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No. SUP 21942 (11 pp., 1 microfiche),* final positional and thermal parameters, with their estimated standard deviations, in Table 1, and interatomic distances and angles in Table 2. Atoms are numbered *e.g.* C(*ij*) with $i = 1$ or 2 for the anions and $i = 3$ or 4 for the cations.

TABLE 1

Atomic positional and isotropic thermal parameters ($\times 10^2$), with least-squares estimated standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*	*U*
(*a*) The anions; values for atoms with $i = 2$ follow those for $i = 1$				
Ta(*i*1)	1	0.078 5(2)	0	*
	0.374 3(2)	0.076 0(3)	0.242 4(1)	*
F(*i*1)	1.126(3)	0.031(2)	0.055(1)	4.8(8)
	0.227(4)	0.039(3)	0.189(1)	7.9(13)
F(*i*2)	0.838(4)	0.112(3)	−0.046(1)	8.0(11)
	0.520(3)	0.135(2)	0.290(1)	4.6(7)
F(*i*3)	0.915(4)	−0.044(3)	0.003(1)	8.0(14)
	0.492(3)	−0.036(3)	0.239(1)	6.8(11)
F(*i*4)	1.034(3)	0.211(2)	0.016(1)	5.8(9)
	0.316(3)	0.216(3)	0.221(1)	6.5(10)
O(*i*1)	0.889(3)	0.113(2)	0.054(1)	2.9(7)
	0.519(4)	0.090(3)	0.192(1)	7.8(13)
O(*i*2)	1.086(3)	−0.002(3)	−0.043(1)	4.9(7)
	0.354(6)	−0.018(5)	0.287(2)	14.2(21)
O(*i*3)	1.142(3)	0.113(2)	−0.036(1)	4.3(7)
	0.271(5)	0.066(4)	0.289(2)	11.3(16)
N(*i*1)	0.900(3)	0.176(2)	0.082(1)	5.3(15)
	0.481(4)	0.191(2)	0.162(1)	5.2(13)
C(*i*1)	1.004(3)	0.173(2)	0.123(1)	4.4(13)
	0.372(4)	0.175(2)	0.123(1)	10.5(31)
C(*i*2)	1.028(3)	0.254(2)	0.154(1)	8.1(21)
	0.337(4)	0.246(2)	0.087(1)	7.6(20)
C(*i*3)	0.948(3)	0.337(2)	0.143(1)	7.6(17)
	0.410(4)	0.333(2)	0.090(1)	8.7(19)
C(*i*4)	0.844(3)	0.340(2)	0.101(1)	3.8(10)
	0.518(4)	0.349(2)	0.129(1)	7.5(16)
C(*i*5)	0.820(3)	0.259(2)	0.071(1)	3.4(10)
	0.554(4)	0.278(2)	1.651(1)	6.7(16)
C(*i*6)	0.729(5)	0.262(4)	0.034(2)	5.9(14)
	0.698(5)	0.264(4)	0.216(2)	5.2(13)
(*b*) The cations: values for atoms with $i = 4$ follow those for $i = 3$				
N(*i*1)	0.398(2)	0.527(2)	0.795(1)	5.7(14)
	0.484(2)	0.038(1)	0.443(1)	7.1(17)
C(*i*1)	0.327(2)	0.435(2)	0.802(1)	11.6(21)
	0.581(2)	0.065(1)	0.413(1)	7.7(14)
C(*i*2)	0.463(2)	0.517(2)	0.754(1)	21.4(45)
	0.393(2)	0.121(1)	0.446(1)	5.6(11)
C(*i*3)	0.504(2)	0.548(2)	0.839(1)	13.8(27)
	0.402(2)	−0.046(1)	0.421(1)	6.3(12)
C(*i*4)	0.299(2)	0.607(2)	0.787(1)	15.8(31)
	0.561(2)	0.013(1)	0.492(1)	4.6(9)
C(*i*5)	0.229(2)	0.621(2)	0.830(1)	14.5(29)
	0.311(2)	0.151(1)	0.396(1)	9.6(22)
C(*i*6)	0.356(2)	0.495(2)	0.707(1)	16.3(35)
	0.494(2)	−0.135(1)	0.418(1)	12.2(25)
C(*i*7)	0.427(2)	0.349(2)	0.811(1)	12.6(25)
	0.464(2)	−0.016(1)	0.525(1)	11.0(21)
C(*i*8)	0.581(2)	0.643(2)	0.833(1)	8.5(18)
	0.699(2)	0.153(1)	0.434(1)	6.7(13)

* Anisotropic thermal parameters ($\times 10^3$)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ta(11)	35.9(11)	35.2(8)	34.6(10)	22.7(13)	7.0(9)	2.1(14)
Ta(21)	62.1(22)	61.1(12)	60.0(20)	9.2(15)	5.9(17)	−14.0(17)

DISCUSSION

The structure consists of discrete $[Ta(O_2)F_4(C_6H_7NO)]^-$ anions and $[NEt_4]^+$ cations. In each of the two crystallographically independent anions (Figure 1), a seven-co-ordinate tantalum atom lies at the centre of a pentagonal bipyramid, the pentagonal plane of which [plane (*a*) Table 3] comprises the peroxo-group [O(*i*2), O(*i*3)], two fluorine atoms [F(*i*3), F(*i*4)], and the oxygen atom of the organic ligand [O(*i*1)] which is opposite to the bidentate ligand; the two capping positions are occupied by fluorine atoms [F(*i*1), F(*i*2)]. The Ta–F distances (mean 1.94 Å) agree with those in the recent structure determinations of $K_2[Ta(O_2)F_5]\cdot KHF_2$ (mean

TABLE 2

Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses. Only values obtained from non-rigid group refinement are presented; values of fixed bond lengths and angles are to be found in the Experimental section. Values for atoms with $i = 2$ follow those for $i = 1$

(*a*) Distances

Ta(*i*1)–F(*i*1)	1.91(3)	Ta(*i*1)–O(*i*2)	1.98(3)
	1.96(4)		1.84(6)
Ta(*i*1)–F(*i*2)	1.91(3)	Ta(*i*1)–O(*i*3)	1.99(3)
	1.94(2)		1.85(6)
Ta(*i*1)–F(*i*3)	1.89(4)	O(*i*2)–O(*i*3)	1.67(5)
	1.95(4)		1.43(8)
Ta(*i*1)–F(*i*4)	1.89(3)	O(*i*1)–N(*i*1)	1.17(4)
	2.06(3)		1.64(5)
Ta(*i*1)–O(*i*1)	2.14(3)	C(*i*5)–C(*i*6)	1.25(5)
	2.26(4)		1.82(5)

(*b*) Angles

F(*i*1)–Ta(*i*1)–F(*i*2)	164(2)	F(*i*3)–Ta(*i*1)–O(*i*3)	128(2)
	170(2)		114(2)
F(*i*1)–Ta(*i*1)–F(*i*3)	83(2)	F(*i*4)–Ta(*i*1)–O(*i*1)	73(1)
	97(2)		85(1)
F(*i*1)–Ta(*i*1)–F(*i*4)	94(1)	F(*i*4)–Ta(*i*1)–O(*i*2)	128(1)
	84(1)		142(2)
F(*i*1)–Ta(*i*1)–O(*i*1)	81(1)	F(*i*4)–Ta(*i*1)–O(*i*3)	78(1)
	91(2)		96(2)
F(*i*1)–Ta(*i*1)–O(*i*2)	91(1)	O(*i*1)–Ta(*i*1)–O(*i*2)	159(1)
	100(2)		133(2)
F(*i*1)–Ta(*i*1)–O(*i*3)	95(1)	O(*i*1)–Ta(*i*1)–O(*i*3)	150(1)
	95(2)		174(2)
F(*i*2)–Ta(*i*1)–F(*i*3)	86(2)	O(*i*2)–Ta(*i*1)–O(*i*3)	50(1)
	89(1)		45(3)
F(*i*2)–Ta(*i*1)–F(*i*4)	91(1)	Ta(*i*1)–O(*i*2)–O(*i*3)	65(2)
	86(1)		68(3)
F(*i*2)–Ta(*i*1)–O(*i*1)	87(1)	Ta(*i*1)–O(*i*3)–O(*i*2)	65(1)
	85(1)		67(3)
F(*i*2)–Ta(*i*1)–O(*i*2)	98(1)	Ta(*i*1)–O(*i*1)–N(*i*1)	132(3)
	90(2)		107(3)
F(*i*2)–Ta(*i*1)–O(*i*3)	101(1)	O(*i*1)–N(*i*1)–C(*i*1)	120(3)
	89(2)		110(3)
F(*i*3)–Ta(*i*1)–F(*i*4)	154(2)	O(*i*1)–N(*i*1)–C(*i*5)	120(3)
	149(1)		129(3)
F(*i*3)–Ta(*i*1)–O(*i*1)	82(2)	C(*i*6)–C(*i*5)–N(*i*1)	120(4)
	64(2)		106(3)
F(*i*3)–Ta(*i*1)–O(*i*2)	78(2)	C(*i*6)–C(*i*5)–C(*i*4)	120(4)
	69(2)		134(3)

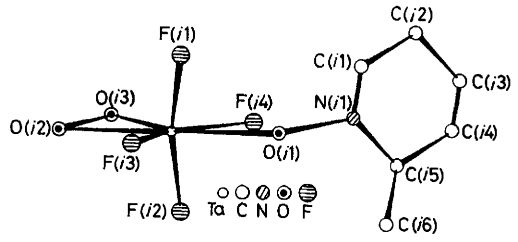

FIGURE 1 The pentagonal bipyramidal $[Ta(O_2)F_4(C_6H_7NO)]^-$ anion showing atom numbering; $i = 1$ or 2

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

1.92 Å)[10] and $[NEt_4]_2[Ta_2OF_{10}]$ (mean 1.90 Å).[1] Within experimental error, the Ta–O(peroxo) distances (mean 1.92 Å) and O–O distances of the peroxo-group (mean 1.55 Å) agree with those in the $[Ta(O_2)F_5]^-$ anion (mean 2.04 and 1.64 Å). The Ta–O distances to the organic ligand (mean 2.20 Å) appear to be the first reported.

TABLE 3

(*a*) Equations of least-squares planes in the form $Ax + By + Cz = D$, where x, y, z are the fractional co-ordinates of the defining atoms (italicized) in the direct cell. Atomic distances (Å) from each plane are in square brackets. Values for atoms with $i = 2$ follow those for $i = 1$

Plane (*a*): F(i3), F(i4), O(i1)—(i3)

$$6.02x - 3.76y + 12.28z = 5.79$$
$$5.90x \quad 5.32y \quad 16.19z = 6.62$$

[*F*(i3) −0.06, −0.04; *F*(i4) −0.07, −0.02; *O*(i1) 0.07, 0.03; *O*(i2) 0.02, 0.02; *O*(i3) 0.04, 0.01; Ta(i1) −0.06, −0.08; *F*(i1) 1.83, −2.02; *F*(i2) −1.95, 1.85; N(i1) 0.38, −0.14; C(i1) 1.73, −1.50; C(i2) 2.10, −1.91; C(i3) 1.11, −0.97; C(i4) −0.23, 0.39; C(i5) −0.60, 0.80; C(i6) −1.81, 2.40; σ 0.06, 0.03]

Plane (*b*):* N(i1), C(i1)—(i5)

$$-7.78x - 4.90y + 19.27z = 6.28$$
$$-7.56x + 5.69y + 18.83z = 0.050$$

[O(i1) −0.15, −0.29]

Plane (*c*): Ta, O(i1), N(i1)

$$5.09x - 7.63y + 15.28z = 4.49$$
$$5.07x + 6.87y + 16.52z = 6.42$$

(*b*) Angles (°) between planes: (*b*)–(*c*) 87,79

* Constrained to be planar by rigid-group refinement.

TABLE 4

Angular co-ordinates for compounds of structure B *

	b	ϕ_A	ϕ_C	θ_C	ϕ_D	θ_D	ϕ_E	θ_E	ϕ_F	θ_F	ϕ_G	θ_G
	0.7	20.5	100	0	93	90	100	180	93	270	180	*a*
	0.8	23.6	102	0	92	90	102	180	92	270	180	
	0.9	26.7	103	0	92	90	103	180	92	270	180	
	1.2	36.9	108	0	90	90	108	180	90	270	180	
(I) $[NH_4]_3[Mo(O_2)OF_4]F$ [b,d]	0.71	20.9	97	4	86	86	100	168	102	264	165	82
(II) $K_2[Mo(O_2)OF_4]\cdot H_2O$ [b,e]	0.74	21.8	102	6	86	90	98	171	103	270	165	104
(III) $[NEt_4][Ta(O_2)F_4(C_6H_7NO)]$ [c,f,g]	0.81	23.8	98	0	95	88	111	180	96	267	164	74
(IV) $K_2[Ta(O_2)F_5]\cdot KHF_2$ [h]	0.81	24.0	105	1	88	92	90	164	107	279	170	101
(V) $[W\{C_6H_4(AsMe_2)_2\}OCl_4]$ [b,i]	1.18	36.3	104	0	80	89	103	175	84	272	180	

* Calculated values obtained from Table 4 of ref. 2.

[a] θ_G has no meaning when ϕ_G 180°. [b] Unidentate oxygen occupies F (or D) site. [c] Unidentate oxygen occupies G site. [d] Ref. 12. [e] Ref. 13. [f] This work. [g] Mean of values for the two anions. [h] Ref. 10. [i] Ref. 14.

The geometry of the ligands is, in general, the same as reported elsewhere[11] but is inaccurately determined and further comment is not warranted. The pyridine rings were refined as rigid groups but the effect of the nitrogen atom on the ring geometry was not taken into account.

The cations are not disordered and were refined as rigid groups. All interionic contacts are >3.2 Å.

Ligand–ligand repulsion energy calculations have previously been performed[2] for compounds of stoicheiometry $[\text{Metal(bidentate)(unidentate)}_5]^{x\pm}$ and reveal that for normalized bites of the chelating bidentate ligand ranging from 0.7 to 1.1 there are two minima of comparable energy on the potential–energy surface, and for normalized bites from 1.2 to 1.4 there are four minima, again of comparable energy. The stereochemistries corresponding to these minima, and the method of calculation, have been explained in detail in ref. 2 and were designated as A, B, C, and D.

The ' normalized bite ' of a bidentate ligand is defined as $b = AB/MA = AB/MB$ (Figure 2).

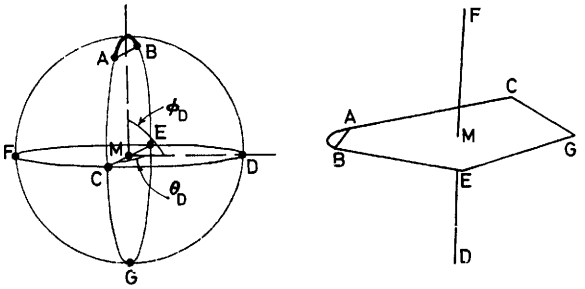

FIGURE 2 Axes used to define stereochemistry B (the pentagonal bipyramid) as discussed in ref. 2

The pentagonal bipyramid, stereochemistry B (Figure 2), was found to exist for all values of the normalized bite. The anions of the present compound (with an average normalized bite of 0.81) are found to have this stereochemistry and a detailed comparison of the angular parameters of the known compounds, having stereochemistry B, with the theoretical angles for this stereochemistry, is given in Table 4. The agreement in the angular co-ordinates is reasonable considering that each compound has at least two different types of donor atom, that the *R* factors for compounds (I),[12] (II),[13] and (V)[14] (Table 4) are high (0.129, 0.136, and 0.10), and that the two recent structure determinations [(III) and (IV)[10]] are of limited accuracy because of poor data as a result of the air-sensitive nature of the tantalum species.

[6/1427 *Received, 21st July, 1976*]

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