Crystal Structure of $[AsPh_4]_2[\{TcN(O_2)_2\}_2(ox)]\cdot 2Me_2CO$: An Oxalate-bridged Technetium(VII) Nitridoperoxo Dimer*

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Recrystallisation of $[AsPh_4]_2[\{TcN(O_2)_2\}_2(ox)]$ **1** (ox = oxalate(2−)] from acetone gives $[AsPh_4]_2[\{TcN(O_2)_2\}_2(ox)]\cdot 2Me_2CO$ **2**. Complex **2** crystallises in the monoclinic space group *C*2/*c* with cell parameters *a* = 34.49(1), *b* = 14.684(3), *c* = 22.776(6) Å, β = 107.18(3)° and *Z* = 8. The structure refined to a final *R* = 0.092 and *R*′ = 0.100 based on 2156 observed data. The structure is dimeric and consists of two $TcN(O_2)_2$ units bridged by a quadridentate sideways-bound oxalate. The geometry about each technetium atom is distorted pentagonal-bipyramidal with the nitrido ligand in an apical position.

We have recently reported the preparation of a variety of complexes containing the novel $Tc^{VII}N(O_2)_2$ core and the structural characterisation of $Cs[TcN(O_2)_2Cl]$.[1,2] These complexes are of particular interest since they are the first examples of technetium peroxo complexes, of transition-metal nitridoperoxo complexes and of peroxo complexes of a transition metal in the +7 oxidation state. Reaction of $[Tc^{VII}N(O_2)_2(OH_2)_2]$ with oxalic acid gave a pale yellow product which was formulated as $[AsPh_4]_2[\{TcN(O_2)_2\}_2(ox)]$ **1** [ox = oxalate(2−)] on the basis of microanalytical and spectral data.[2] The nature of the bridging oxalate, *i.e.* bidentate or quadridentate ('end on', four-membered ring, or 'sideways', five-membered ring, chelation)[3] could not be determined. We now report the X-ray structure determination of $[AsPh_4]_2[\{TcN(O_2)_2\}_2(ox)]\cdot 2Me_2CO$ **2**, the acetone solvate of **1**, which establishes the presence of a sideways-bound oxalate bridge. Complex **2** is only the second structurally characterised example of a nitridoperoxo complex.

Experimental

The preparation of **1** has been described previously.[2]

Crystallography.—Crystals of the acetone solvate **2** were grown by the slow evaporation of an acetone solution of **1**. Several crystals were studied by Weissenberg photography and, in preliminary attempts at data collection, on the diffractometer. Severe difficulties were encountered due to small crystal size, few observable reflections, all of which were relatively weak, and decomposition in the X-ray beam. The paucity and low quality of the data were indicative of poor crystallinity, and disorder within the lattice was suspected. Nevertheless, due to the significant nature of the compound it was decided to proceed with the structure analysis, accepting that only the gross geometry may be determined. The crystal chosen for data collection was from a freshly prepared batch of compound, and had dimensions 0.12 × 0.09 × 0.07 mm. Unit-cell parameters were obtained on a diffractometer at 23 °C with Cu-Kα radiation for 17 reflections well separated in reciprocal space with 15 ⩽ θ ⩽ 20°.

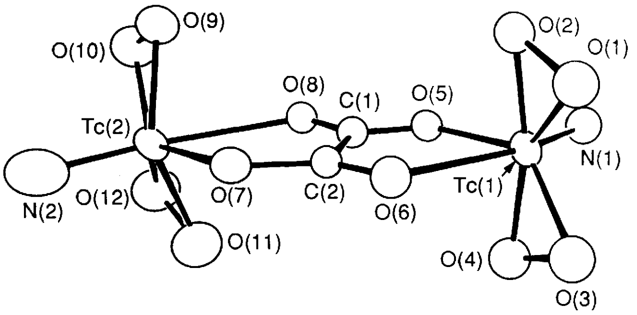

Fig. 1 A perspective view of the $[\{TcN(O_2)_2\}_2(ox)]^{2-}$ anion in **2**

Crystal data. $C_{50}H_{40}As_2N_2O_{12}Tc_2\cdot 2C_3H_6O$, *M* = 1324.7, monoclinic, space group *C*2/*c*, *a* = 34.49(1), *b* = 14.684(3), *c* = 22.776(6) Å, β = 107.18(3)°, *U* = 11 020.3 Å^3, *Z* = 8, D_c = 1.60 g cm^{-3}, *F*(000) = 5328, μ(Cu-Kα) = 56.03 cm^{-1}, λ(Cu-Kα) = 1.5418 Å.

Intensity data were recorded at 23 ± 1 °C on an automated Siemens AED diffractometer with nickel-filtered Cu-Kα radiation. Because of the need to collect data quickly, an initial point count was performed at each reflection position and only those reflections with significant intensity were scanned. Initially, data were collected within θ ⩽ 50°. A total of 12 259 reflections were screened in the above manner, of which 5226 were scanned. During this process, three reflections, which were monitored every 50 reflections, showed a decrease of *ca.* 20% in intensity and data were scaled accordingly. A further screening of data in the range 50 ⩽ θ ⩽ 65° yielded only a few hundred extra reflections with intensities significant at the $2\sigma(I_o)$ level. The intensities were corrected for Lorentz and polarisation effects and for absorption.[4]

The sites of the Tc and As atoms were determined by use of a combined Patterson–structure-expansion method using SHELXS 86.[5] The $[\{TcN(O_2)_2\}_2(ox)]^{2-}$ anions and one $AsPh_4^+$ cation lie on eight-fold general positions, whereas two additional $AsPh_4^+$ cations lie on crystallographic two-fold axes, and were therefore included with a site occupancy of 0.5. Subsequent difference syntheses using SHELX 76[6] revealed the sites of all the remaining atoms of the anion, whereas, due to severe disorder, the phenyl rings of the $AsPh_4^+$ cations were included in the refinement at positions chosen to correspond to regular hexagons of side 1.40 Å. Hydrogen atoms were included at idealised positions (C–H 1.08 Å) and were assigned a common isotropic thermal parameter. The solvent

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* Bis(tetraphenylarsonium) μ-oxalato-κ^2*O*^{1},*O*^{2}; κ^2*O*^{1}, *O*$^{2'}$-bis[nitridodi(peroxo-κ^2*O*,*O*′)technetate (1−)]-acetone (1/2).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Atomic positional coordinates, with estimated standard deviations in parentheses, for $[AsPh_4]_2[\{TcN(O_2)_2\}_2(ox)]\cdot 2Me_2CO$

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
As(1)	0.5	0.3433(4)	0.75	C(21)	0.0043(8)	0.0798(15)	0.3199(11)
As(2)	0.5	0.1564(4)	0.25	C(22)	−0.0218(8)	0.0913(15)	0.3559(11)
As(3)	0.2488(1)	0.4095(3)	0.2433(2)	C(23)	−0.0205(8)	0.0305(15)	0.4035(11)
Tc(1)	0.1714(2)	0.4730(2)	0.9788(2)	C(24)	0.0069(8)	−0.0419(15)	0.4151(11)
Tc(2)	0.0780(1)	0.7915(2)	1.0222(2)	C(25)	0.0330(8)	−0.0534(15)	0.3791(11)
N(1)	0.1667(11)	0.3606(23)	0.9920(15)	C(26)	0.0317(8)	0.0074(15)	0.3315(11)
N(2)	0.0827(11)	0.8991(24)	1.0132(16)	C(27)	0.2534(9)	0.3358(15)	0.3134(11)
O(1)	0.1754(10)	0.4771(19)	0.8970(14)	C(28)	0.2839(9)	0.2701(15)	0.3251(11)
O(2)	0.1335(9)	0.4803(16)	0.8944(12)	C(29)	0.2901(9)	0.2124(15)	0.3757(11)
O(3)	0.2298(10)	0.4942(18)	1.0129(12)	C(30)	0.2657(9)	0.2205(15)	0.4146(11)
O(4)	0.2079(9)	0.5071(17)	1.0576(12)	C(31)	0.2351(9)	0.2863(15)	0.4028(11)
O(5)	0.1239(7)	0.5134(16)	1.0125(10)	C(32)	0.2290(9)	0.3439(15)	0.3522(11)
O(6)	0.1651(8)	0.6356(15)	0.9679(11)	C(33)	0.2047(7)	0.4884(14)	0.2333(12)
O(7)	0.1247(7)	0.7510(16)	0.9855(10)	C(34)	0.1717(7)	0.4806(14)	0.1805(12)
O(8)	0.0839(8)	0.6238(15)	1.0290(10)	C(35)	0.1385(7)	0.5388(14)	0.1717(12)
O(9)	0.0396(8)	0.7521(17)	0.9436(12)	C(36)	0.1383(7)	0.6047(14)	0.2157(12)
O(10)	0.0200(11)	0.7685(18)	0.9918(13)	C(37)	0.1713(7)	0.6125(14)	0.2685(12)
O(11)	0.1167(11)	0.7741(19)	1.1053(14)	C(38)	0.2045(7)	0.5543(14)	0.2773(12)
O(12)	0.0728(11)	0.7860(19)	1.1011(14)	C(39)	0.2427(10)	0.3311(16)	0.1733(12)
C(1)	0.1130(13)	0.5999(24)	1.0131(15)	C(40)	0.2684(10)	0.3365(16)	0.1362(12)
C(2)	0.1378(12)	0.6667(13)	0.9873(14)	C(41)	0.2645(10)	0.2741(16)	0.0886(12)
C(3)	0.4969(8)	0.0807(13)	0.1815(10)	C(42)	0.2349(10)	0.2062(16)	0.0782(12)
C(4)	0.5211(8)	0.0983(13)	0.1433(10)	C(43)	0.2093(10)	0.2007(16)	0.1154(12)
C(5)	0.5199(8)	0.0398(13)	0.0946(10)	C(44)	0.2132(10)	0.2631(16)	0.1629(12)
C(6)	0.4945(8)	−0.0362(13)	0.0839(10)	C(45)	0.2935(6)	0.4857(14)	0.2558(11)
C(7)	0.4703(8)	−0.0538(13)	0.1220(10)	C(46)	0.2924(6)	0.5577(14)	0.2153(11)
C(8)	0.4715(8)	0.0047(13)	0.1708(10)	C(47)	0.3250(6)	0.6181(14)	0.2262(11)
C(9)	0.4515(8)	0.2322(14)	0.2286(13)	C(48)	0.3587(6)	0.6065(14)	0.2775(11)
C(10)	0.4509(8)	0.3024(14)	0.2696(13)	C(49)	0.3599(6)	0.5345(14)	0.3180(11)
C(11)	0.4176(8)	0.3610(14)	0.2577(13)	C(50)	0.3273(6)	0.4741(14)	0.3071(11)
C(12)	0.3850(8)	0.3494(14)	0.2049(13)	C(51)*	0.4198(16)	0.2314(31)	0.9820(26)
C(13)	0.3855(8)	0.2792(14)	0.1639(13)	C(52)*	0.0785(18)	0.3241(41)	0.0480(27)
C(14)	0.4188(8)	0.2206(14)	0.1757(13)	C(53)*	0.0908(20)	0.2323(46)	0.0822(31)
C(15)	0.0476(8)	0.2339(15)	0.2648(14)	C(54)*	0.0934(26)	0.1803(57)	0.0244(38)
C(16)	0.0475(8)	0.2967(15)	0.2188(14)	C(55)*	0.3332(10)	0.5788(24)	0.5434(14)
C(17)	0.0788(8)	0.3599(15)	0.2277(14)	C(56)*	0.3311(9)	0.5003(19)	0.5370(13)
C(18)	0.1104(8)	0.3603(15)	0.2826(14)	C(57)*	0.3151(14)	0.4668(26)	0.4717(22)
C(19)	0.1106(8)	0.2975(15)	0.3287(14)	C(58)*	0.3457(18)	0.4465(34)	0.5847(27)
C(20)	0.0792(8)	0.2343(15)	0.3198(14)				

* Atoms C(51)–C(58) are those of the solvent acetone molecules; disorder within the solvent precluded the unequivocal assignment of the oxygen atoms.

Table 2 Selected bond distances (Å) and angles (°) for the $[\{TcN(O_2)_2\}_2(ox)]^{2-}$ anion in **2**

Tc(1)–N(1)	1.69(3)	Tc(2)–N(2)	1.61(4)
Tc(1)–O(1)	1.91(3)	Tc(2)–O(9)	1.97(3)
Tc(1)–O(2)	1.98(3)	Tc(2)–O(10)	1.94(4)
Tc(1)–O(3)	1.96(3)	Tc(2)–O(11)	1.98(3)
Tc(1)–O(4)	1.93(3)	Tc(2)–O(12)	1.86(3)
Tc(1)–O(5)	2.09(2)	Tc(2)–O(7)	2.11(2)
Tc(1)–O(6)	2.40(2)	Tc(2)–O(8)	2.47(2)
O(1)–O(2)	1.43(4)	O(9)–O(10)	1.47(4)
O(3)–O(4)	1.45(3)	O(11)–O(12)	1.50(4)
C(1)–O(5)	1.33(4)	C(2)–O(7)	1.31(3)
C(1)–O(8)	1.22(4)	C(2)–O(6)	1.24(4)
C(1)–C(2)	1.53(4)		
N(1)–Tc(1)–O(1)	104(1)	N(2)–Tc(2)–O(9)	104(2)
N(1)–Tc(1)–O(2)	99(1)	N(2)–Tc(2)–O(10)	105(2)
N(1)–Tc(1)–O(3)	103(1)	N(2)–Tc(2)–O(11)	101(2)
N(1)–Tc(1)–O(4)	99(1)	N(2)–Tc(2)–O(12)	102(2)
N(1)–Tc(1)–O(5)	95(1)	N(2)–Tc(2)–O(7)	96(2)
N(1)–Tc(1)–O(6)	167(1)	N(2)–Tc(2)–O(8)	168(2)

acetone molecules were poorly defined in general lattice positions. There were no significant interactions between the solvent and other ions of the compound. The structure was refined by the full-matrix least-squares method and, because of the paucity of data and many parameters, anisotropic thermal parameters were assigned to the technetium and arsenic atoms only. The function minimised was $\Sigma w(\Delta F^2)$ with $w = 9.3 \times 10^{-4}$. Refinement of **2** based on 2156 unique non-zero data $[I_o > 2\sigma(I_o)]$ converged with $R = 0.092$ and $R' = 0.100$. Attempts at refinements in the alternative non-centrosymmetric space group and in *C*2/*m* were unsuccessful.

Final atomic positional parameters of the non-hydrogen atoms are given in Table 1 and selected bond lengths and angles are given in Table 2. Fig. 1 has been prepared from the output of ORTEP.[7] Neutral atom-scattering factors for non-hydrogen atoms were taken from ref. 8(*a*) with the exceptions of arsenic and technetium, which were taken from ref. 8(*b*); those for hydrogen were taken from ref. 9. Real and imaginary anomalous dispersion corrections were applied to the non-hydrogen atoms.[4]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Recrystallisation of **1** from acetonitrile gave large well defined crystals shown by the IR spectrum to contain acetonitrile. However, these crystals rapidly became opaque in the absence of solvent and were unsuitable for X-ray analysis. Complex **1** was less soluble in acetone, but gave small crystals of the acetone solvate **2** as shown by the presence of a strong ν(C=O) absorption at 1713 cm^{-1} in the IR spectrum. Other absorptions were ν(Tc≡N) 1062, ν(O–O) 900 and ν(TcO_2) 658 cm^{-1}, with absorptions due to oxalate at 1665 ν(C=O), 1277 and 801 cm^{-1}.[10] The mode of oxalate bridging could not, however, be established from the IR spectrum.

Complex **1** was prepared by substituting oxalate into $[TcN(O_2)_2(OH_2)_2]$. Complexes containing the $Tc^{VII}N(O_2)_2$ core have also been prepared previously from $Tc^{VI}N$ precursors such as $[AsPh_4][TcNX_4]$ (X = Cl or Br).[2] Reaction of the $Tc^{V}N$ complexes $[NEt_4]_2[TcN(NCS)_4(MeCN)]$[11] and $[TcN(tu)_4Cl]Cl$[12] (tu = thiourea) with 10% H_2O_2, and addition of $AsPh_4Cl$, has now been shown to give also $[AsPh_4][TcN(O_2)_2Cl]$ in high yield.

Crystal Structure of **2**.—The paucity and poor quality of the diffraction data resulted in a poor structure refinement. However, the geometry of the anion is well defined. The structure is dimeric and consists of two $TcN(O_2)_2$ units bridged by a quadridentate sideways-bound oxalate (Fig. 1). The geometry about each technetium atom is distorted pentagonal-bipyramidal with the nitrido ligand in an apical position and the peroxo ligands in equatorial positions. The Tc≡N bond distances of 1.69(3) and 1.61(4) Å are in the range found for TcN complexes.[13] The O–O distances of 1.43(4)–1.50(4) Å are in the range characteristic of sideways-bound (η^2) peroxide.[14] The Tc–O distances are in the range 1.91(3)–1.98(3) Å except for Tc(2)–O(12) which is 1.86(3) Å. The nitrido ligand is known to exert a strong *trans* influence[13] and this effect is evident in the Tc–O(oxalate) distances for **2**. The Tc(1)–O(5) and Tc(2)–O(7) distances of 2.09(2) and 2.11(2) Å are markedly shorter than the Tc(1)–O(6) and Tc(2)–O(8) distances of 2.40(2) and 2.47(2) Å. The *trans* influence of the nitrido ligand also results in N≡Tc–O(peroxo) angles of 99(1)–105(2)° and N≡Tc–O_{eq}(oxalate) angles of 95(1)–96(2)°. The N≡Tc–O_{ax}(oxalate) angles of 167(1) and 168(2)° are only approximately linear.

The structures of the Mo^{VI} and W^{VI} monomeric analogues of **2**, $K_2[MO(O_2)_2(ox)]$ (M = Mo or W), have been reported[15,16] and show a similar pentagonal-bipyramidal geometry. The M=O group exerts a similar *trans* influence to the Tc≡N group in **2** with M–O_{eq}(oxalate) of 2.051(1) (Mo) and 2.033(6) (W) Å, and M–O_{ax}(oxalate) of 2.269(1) (Mo) and 2.245(6) (W) Å. It is pertinent to note that whilst the $Mo^{VI}O(O_2)_2$ core gives the monomeric oxalato complex, the isoelectronic $Tc^{VII}N(O_2)_2$ core evidently prefers the oxalate-bridged dimeric structure even though the reaction is performed in the presence of an excess of oxalic acid.[2] Quadridentate sideways-bound oxalato ligands have previously been shown to join two $[Tc^{VI}N(ox)–O–Tc^{VI}N(ox)]$ units in the cyclic tetramer $[AsPh_4]_4[Tc_4N_4(O)_2(ox)_6]$.[17] The less common quadridentate oxalate end-on chelation has been observed in $K_6[\{Mo_2O_3S(ox)_2\}_2(ox)]\cdot10H_2O$.[18]

Structurally characterised peroxo complexes are rare for the Group 7 metals Mn and Re. Two examples are $[Mn_2L_2(\mu\text{-}O)_2(\mu\text{-}O_2)][ClO_4]_2$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane),[19] where the peroxo ligand bridges the two Mn atoms, and $[ReCl_2(PPh_3)_2(NNCO_2Me)(O_2)]$.[20] The O–O distances in these complexes are 1.46(3) and 1.26(3) Å, respectively.

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