Preparation and Crystal Structures of $[AsPh_4]_4[Tc_4N_4O_2(ox)_6]$ and $[AsPh_4]_2[TcO(ox)_2(Hox)]\cdot3H_2O$: Technetium Complexes containing Quadridentate or Unidentate Oxalato Ligands†

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The reaction of oxalic acid (H_2ox) with $[AsPh_4][TcNCl_4]$ and $[NBu_4][TcOCl_4]$ in aqueous acetone yields crystals of $[AsPh_4]_4[Tc_4N_4O_2(ox)_6]$ (**1**) and, after precipitation with $AsPh_4Cl$, $[AsPh_4]_2[TcO(ox)_2(Hox)]\cdot3H_2O$ (**2**) respectively. Complex (**1**) crystallises in the monoclinic space group $P2_1/n$ with cell parameters $a = 14.433(1)$, $b = 13.229(1)$, $c = 27.020(1)$ Å, $\beta = 92.90(1)°$, and $Z = 4$. Refinement with data measured with Cu-K_α radiation converged at $R = 0.069$ for 3 076 observed reflections. The anion in (**1**) is a cyclic tetranuclear complex, $[Tc_4N_4O_2(ox)_6]^{4-}$, with C_i point symmetry. Each technetium(VI) atom is co-ordinated by five oxygen atoms and one nitrogen atom to give a distorted octahedron. In each half of the anion, a quadridentate oxalato ligand forms a bridge between the two octahedra, each of which is also linked to an adjacent octahedron by the corner sharing of an oxo ligand. Two oxygen atoms of a bidentate oxalato ligand and a nitrido nitrogen complete the octahedral co-ordination in each polyhedron. The Tc ··· Tc spacings of 3.586(2) and 5.756(3) Å preclude any Tc–Tc bonding. The monoclinic crystals of complex (**2**) belong to the space group $P2_1/c$ with $a = 16.495(3)$, $b = 14.802(2)$, $c = 21.805(4)$ Å, $\beta = 98.76(1)°$, and $Z = 4$. Refinement with 5 099 observed data measured with Mo-K_α radiation converged at $R = 0.059$. The technetium(V) atom is co-ordinated by six oxygen atoms to give a distorted octahedron. The structure of the anion is unusual in that it contains a protonated unidentate oxalato ligand and that there is no appreciable lengthening of the Tc–O bond *trans* to the oxo ligand.

The preparation and chemistry of oxalato complexes of transition metals have been extensively studied. Complexes of the type $[M(ox)_3]^{n-}$ [ox = oxalate(2−)] have been prepared and structurally characterised for many transition metals.[1] Complexes where oxalate behaves either as a quadridentate[2–4] or unidentate[5,6] ligand are also known. Recently, we have reported the preparation and *X*-ray structure of $[AsPh_4]_2[Tc(ox)_3]$, the first example of a technetium oxalato complex.[7] This complex was prepared by the reaction of $[NH_4]_2[TcBr_6]$ with oxalic acid. We now report the reactions of oxalic acid with $[AsPh_4][TcNCl_4]$ and $[NBu_4][TcOCl_4]$ which give tetraphenylarsonium *cyclo*-bis{μ-(oxalato-*O,O′,O″,O‴*)-μ-oxo-bis-[nitrido-oxalatotechnetate(VI)]}, $[AsPh_4]_4[Tc_4N_4O_2(ox)_6]$ (**1**) and tetraphenylarsonium hydrogenoxalatobis(oxalato)oxotechnetate(V), $[AsPh_4]_2[TcO(ox)_2(Hox)]\cdot3H_2O$ (**2**) (after precipitation with $AsPh_4Cl$) respectively.

The *X*-ray analyses have established a number of unique co-ordination features. Complex (**1**), one of the few examples of a technetium(VI) complex anion, is tetrameric and has both bridging oxo and bridging quadridentate oxalato groups. Complex (**2**) is a rare example of co-ordination by a unidentate oxalato ligand and is, as far as we are aware, the first example where the non-bonding carboxylate group of the oxalato ligand exists in the protonated form.

Experimental

Ammonium [^{99}Tc]pertechnetate (31.7 mg Tc cm^{-3} in 0.1 mol dm^{-3} NH_3 solution) was supplied by Amersham International plc. I.r. spectra were determined for KBr discs on a Perkin-Elmer 197 spectrophotometer. Room-temperature magnetic susceptibility measurements were performed by the Faraday method. Microanalyses were performed by the Australian Microanalytical Service, Melbourne. Tetraphenylarsonium tetrachloronitridotechnetate(VI) was prepared according to the method of Baldas *et al.*,[8] and tetrabutylammonium tetrachloro-oxotechnetate(V) according to the method of Davison *et al.*[9]

Tetraphenylarsonium cyclo-*bis*{μ-(*oxalato*-O,O′,O″,O‴)-μ-*oxo-bis*[*nitrido-oxalatotechnetate*(VI)]} (**1**).—Oxalic acid dihydrate (110 mg, 870 μmol) dissolved in water (2 cm^3) was added to a solution of $[AsPh_4][TcNCl_4]$ (38 mg, 60 μmol) in acetone (2 cm^3). After a few minutes the solution turned red-brown, and on standing red-brown crystals formed. The crystals were collected by filtration and dried (yield 14 mg, 38% based on Tc), m.p. (decomp.) *ca.* 250—255 °C (Found: C, 51.8; H, 3.4; N, 2.5. $C_{108}H_{80}As_4N_4O_{26}Tc_4$ requires C, 51.0; H, 3.2; N, 2.2%). The i.r. spectrum showed peaks at 1 731s, 1 712vs, 1 660vs, 1 438s, 1 326vs, 1 080m, 1 050s (Tc≡N), 995m, 809m, 795s, 740s, and 688s cm^{-1}.

Reaction of Complex (**1**) *with Thionyl Chloride.*—Thionyl chloride (5 cm^3) was added to complex (**1**) (20 mg) and the mixture gently warmed. A clear orange solution formed and the thionyl chloride was removed in a rotary evaporator. The residue was extracted with dichloromethane, the orange solution evaporated to dryness, and the product recrystallised

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† Tetraphenylarsonium *cyclo*-bis{μ-(oxalato-*O,O′,O″,O‴*)-μ-oxo-bis[nitrido-oxalatotechnetate(VI)]} and tetraphenylarsonium hydrogenoxalatobis(oxalato)oxotechnetate(V) trihydrate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue pp. xvii—xx.

Table 1. Crystallographic data and summary of intensity data collection and structure refinement of complexes (**1**) and (**2**)

	$[AsPh_4]_4[Tc_4N_4O_2(ox)_6]$	$[AsPh_4]_2[TcO(ox)_2(Hox)]\cdot 3H_2O$
Formula	$C_{108}H_{80}As_4N_4O_{26}Tc_4$	$C_{54}H_{47}As_2O_{16}Tc$
M	2 545.12	1 200.70
Crystal dimensions/mm	0.75 × 0.13 × 0.06	0.64 × 0.43 × 0.29
Colour	Red-brown	Emerald green
Space group	$P2_1/n$	$P2_1/c$
a/Å	14.433(1)	16.495(3)
b/Å	13.229(1)	14.802(2)
c/Å	27.020(1)	21.805(4)
α/°	90	90
β/°	92.90(1)	98.76(1)
γ/°	90	90
U/Å^3	5 152(1)	5 262(3)
Z	4	4
D_m/g cm^{-3}	1.65(1)	1.51(1)
D_c/g cm^{-3}	1.64	1.52
F(000)	2 536	2 432
μ/cm^{-1}	60.37 (Cu-K_α)	15.49 (Mo-K_α)
Temperature/°C	15(1)	24(1)
Absorption correction factors	1.44—2.80	1.53—1.93
$2\theta_{max.}$/°	130	50
Scan rate ($\Delta\omega$)/° min^{-1}	2	Variable*
Scan range/°	$1.2 + 0.5 \tan\theta$	$0.8 + 0.35 \tan\theta$
Unique non-zero data used	5 293	9 238
Final no. parameters refined	400	407
Goodness of fit for last cycle	1.64	2.28
Residual electron density/e Å^{-3}	+1.00 and −1.81	+0.82 and −1.78
Max. shift/error for last cycle	0.06	0.01

* Prescan: 20° min^{-1}. Final scan 60 s (max.).

from acetonitrile–benzene (1:1) to give orange-red needles shown by the m.p. and i.r. spectrum to be identical with $[AsPh_4][TcNCl_4]$.

Tetraphenylarsonium Hydrogenoxalatobis(oxalato)oxotechnetate(V) *Trihydrate* (**2**).—Oxalic acid dihydrate (1 g, 7.9 mmol) dissolved in water (5 cm^3) was added to a solution of $[NBu_4][TcOCl_4]$ (300 mg, 0.6 mmol) in acetone (5 cm^3). The mixture immediately turned aquamarine. Tetraphenylarsonium chloride (250 mg, 0.6 mmol) dissolved in water (1 cm^3) was added and the solution allowed to stand at room temperature. A pale green microcrystalline product slowly formed and was collected by filtration (in some preparations yellow-green clumps formed and these were redissolved by addition of acetone and heating). The crystals were washed with a small amount of cold acetone and dried (yield 360 mg), m.p. (decomp.) 245—255 °C (Found: C, 52.1; H, 3.6%). The i.r. spectrum showed peaks at 1 732vs, 1 702vs, 1 673vs, 1 480m, 1 438m, 1 346s, 1 307m, 1 079s, 996s, 963vs (Tc=O), 803m, 781m, 740vs, and 688vs cm^{-1}. Attempted recrystallisation from water, acetone, dichloromethane, acetonitrile, methanol, and ethanol resulted in decomposition. The pale green crystals, however, dissolved without decomposition in acetone–water (1:1) containing a 20-fold molar excess of oxalic acid. Slow evaporation of this solution resulted in the deposition of emerald-green hexagonal pillars of (**2**), m.p. (decomp.) *ca.* 180 °C. The i.r. spectrum showed peaks at 1 740vs, 1 698vs, 1 675vs, 1 482vs, 1 438vs, 1 330vs, 1 081vs, 995m, 985vs (Tc=O), 810m, 788m, 740vs, and 688vs cm^{-1}.

Crystallography.—Single crystals suitable for *X*-ray diffraction studies were grown by slow evaporation of an acetone–water (1:2) solution of $[AsPh_4]_4[Tc_4N_4O_2(ox)_6]$ (**1**); slow evaporation of an acetone–water (1:1) solution of the pale green crystals containing oxalic acid (1:20) gave crystals of (**2**). Crystal densities were measured by flotation in aqueous $CdCl_2$ solutions. Oscillation and Weissenberg photographs showed the crystals to be monoclinic and the space groups were determined as $P2_1/n$ for (**1**) and $P2_1/c$ for (**2**) from systematic absences. Accurate unit-cell parameters for (**1**) were determined at 15 °C by least-squares fits of the 2θ values for 25 independent reflections ($35 < 2\theta < 80°$) measured with Cu-K_α radiation. Integrated intensities were measured on a Rigaku AFC four-circle diffractometer with Cu-K_α radiation (graphite-crystal monochromator, $\bar{\lambda} = 1.5418$ Å) at 15 °C and recorded by an ω—2θ scan with 10 s stationary background counts to a maximum $(\sin\theta)/\lambda = 0.588$ Å^{-1}. Three reflections ($2\,\bar{5}\,5$, $6\,0\,4$, and $\bar{1}\,1\,12$) monitored every 50 reflections showed a gradual 10% decrease in intensities during data collection; the intensity data were scaled accordingly. Intensity data for complex (**2**) were measured on an Enraf-Nonius CAD-4F four-circle diffractometer with Mo-K_α (graphite monochromatised) radiation ($\bar{\lambda} = 0.710\,69$ Å) and recorded by an ω—2θ scan. Accurate unit-cell dimensions were determined at 24 °C from the setting angles of 25 reflections ($30 < 2\theta < 46°$) by a least-squares procedure. Reflections to a maximum $(\sin\theta)/\lambda = 0.595$ Å^{-1} were measured. The intensities of four standard reflections ($1\,2\,13$, $1\,2\,11$, $\bar{2}\,8\,\bar{3}$, and $7\,3\,3$) measured every 4 500 s of exposure time during data collection indicated that no significant crystal decomposition had occurred during the intensity measurements. Intensity data for both (**1**) and (**2**) were corrected for Lorentz and polarisation effects and for absorption.[10]

Structure determination and refinement. The sites of the Tc and As atoms in complex (**1**) were determined from an *E* map generated by the SHELX-76 program system,[11] whereas for (**2**) an *E* map generated by SHELXS 86[12] revealed the sites of the Tc and As and most of the non-hydrogen atoms. For both structures, the remaining non-hydrogen atoms were located by difference, apart from those of a phenyl group of one of the $AsPh_4$ cations in (**1**) which was disordered. To approximate for this, the C atoms of this phenyl ring were included in the

Table 2. Fractional co-ordinates for $[AsPh_4]_4[Tc_4N_4O_2(ox)_6]$ (**1**)

Atom	10^4x	10^4y	10^4z
Tc(1)	3 417(1)	5 798(1)	5 724(1)
Tc(2)	4 349(1)	3 010(1)	4 191(1)
As(1)	3 827(1)	2 908(1)	790(1)
As(2)	4 338(1)	1 564(1)	7 067(1)
O(1)	3 380(12)	5 396(12)	6 433(5)
O(2)	2 217(10)	4 972(13)	5 721(6)
O(3)	3 960(9)	4 103(8)	5 588(4)
O(4)	3 379(10)	5 572(10)	4 963(4)
O(5)	4 229(10)	3 083(10)	4 947(4)
O(6)	3 496(9)	4 503(9)	4 334(4)
O(7)	3 989(11)	3 334(10)	3 469(4)
O(8)	3 005(10)	2 426(10)	4 144(6)
O(9)	4 669(9)	6 068(9)	5 769(4)
O(10)	2 591(13)	4 523(16)	6 954(7)
O(11)	1 406(12)	3 961(15)	6 185(8)
O(12)	2 772(12)	3 409(12)	2 941(6)
O(13)	1 861(14)	2 169(15)	3 607(6)
N(1)	2 980(13)	6 941(13)	5 696(7)
N(2)	4 924(13)	1 972(12)	4 176(6)
C(1)	2 698(23)	4 814(22)	6 549(11)
C(2)	2 016(18)	4 549(21)	6 111(10)
C(3)	3 950(14)	3 912(15)	5 136(7)
C(4)	3 572(14)	4 728(15)	4 787(7)
C(5)	3 089(21)	3 144(18)	3 342(10)
C(6)	2 630(20)	2 537(17)	3 724(10)
C(7)	2 598(14)	3 430(15)	726(7)
C(8)	2 472(16)	4 491(17)	767(8)
C(9)	1 570(16)	4 853(18)	690(8)
C(10)	860(18)	4 229(19)	545(8)
C(11)	962(18)	3 194(19)	512(8)
C(12)	1 864(15)	2 764(17)	584(7)
C(13)	4 470(13)	3 250(13)	216(6)
C(14)	4 062(16)	3 912(16)	−134(8)
C(15)	4 518(16)	4 147(17)	−564(8)
C(16)	5 338(16)	3 717(16)	−633(8)
C(17)	5 761(15)	3 079(16)	−296(7)
C(18)	5 320(13)	2 823(14)	129(7)
C(19)	4 424(14)	3 518(14)	1 365(7)
C(20)	3 906(17)	3 807(16)	1 752(8)
C(21)	4 345(17)	4 261(17)	2 182(9)
C(22)	5 240(19)	4 390(19)	2 175(10)
C(23)	5 829(22)	4 137(22)	1 790(10)
C(24)	5 356(17)	3 661(17)	1 381(9)
C(25)	3 857(13)	1 504(15)	829(7)
C(26)	3 858(14)	1 024(16)	1 294(8)
C(27)	3 889(15)	−26(17)	1 336(8)
C(28)	3 976(15)	−553(19)	915(8)
C(29)	3 956(16)	−154(19)	460(9)
C(30)	3 894(14)	891(16)	416(7)
C(31)	4 910(13)	317(13)	7 246(6)
C(32)	5 707(14)	58(15)	7 032(7)
C(33)	6 072(15)	−945(16)	7 101(7)
C(34)	5 600(15)	−1 583(17)	7 384(7)
C(35)	4 817(15)	−1 337(16)	7 597(7)
C(36)	4 414(15)	−345(15)	7 531(7)
C(37)	3 595(13)	1 300(14)	6 463(7)
C(38)	3 702(14)	378(15)	6 230(7)
C(39)	3 263(16)	228(19)	5 763(9)
C(40)	2 734(15)	980(18)	5 546(8)
C(41)	2 626(16)	1 903(18)	5 786(8)
C(42)	3 066(14)	2 068(17)	6 259(7)
C(43)	5 246(14)	2 506(15)	6 945(7)
C(44)	5 114(17)	3 235(17)	6 566(8)
C(45)	5 787(17)	3 994(18)	6 518(9)
C(46)	6 573(19)	4 038(20)	6 794(9)
C(47)	6 696(18)	3 387(18)	7 172(9)
C(48)	6 045(16)	2 577(18)	7 275(9)
C(49)	3 661	2 054	7 592
C(50)	4 139	2 368	8 027
C(51)	3 654	2 771	8 415
C(52)	2 690	2 859	8 368
C(53)	2 212	2 545	7 933
C(54)	2 697	2 142	7 546

refinement at positions chosen to correspond to a regular hexagon of side 1.40 Å. The hydrogens for both structures were included at idealised positions (C–H 1.08 Å) and were assigned common isotropic thermal parameters. The structures were refined by the full-matrix least-squares method and, because of the many parameters, anisotropic thermal parameters were assigned to the non-hydrogen atoms of the anions only. The function minimized was $\Sigma w(\Delta F)^2$ where $\Delta F = (|F_o| - |F_c|)$ with the terms weighted according to $w = (\sigma^2|F_o| + m|F_o|^2)^{-1}$ with $m = 1 \times 10^{-3}$ for (**1**) and 5×10^{-4} for (**2**). Refinement of (**1**), based on 3 076 unique non-zero data $[I_o \geqslant 3\sigma I_o]$ converged with $R = 0.069$ and $R' = 0.081$. The refinement of (**2**) based on 5 099 terms for which $I_o \geqslant 2\sigma(I_o)$ converged with $R = 0.059$ and $R' = 0.077$. The largest peaks on the final difference maps (Table 1) were close to the disordered phenyl ring and technetium atoms in (**1**) and to the technetium atom in (**2**).

The R indices are defined as $R = \Sigma\Delta F/\Sigma|F_o|$, $R' = [\Sigma w(\Delta F)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ and the 'goodness of fit' is given by $[\Sigma w(\Delta F)^2/(n - m)]^{\frac{1}{2}}$ where n is the number of reflections used in the refinement and m is the number of variables. Final atomic positional parameters of the non-hydrogen atoms are given in Tables 2 and 3 for (**1**) and (**2**) respectively. Neutral atom scattering factors for technetium and other non-hydrogen atoms were taken from ref. 13*a* and 13*b* respectively, whereas those for hydrogen were taken from ref. 14. Real and imaginary anomalous dispersion corrections were applied to the non-hydrogen atoms. The Figures have been prepared from the output of ORTEP.[15]

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

Results and Discussion

Substitution reactions of $[Tc^{V}OX_4]^-$ or $[Tc^{IV}X_6]^{2-}$ (X = Cl or Br) provide a major route to complexes of Tc^{V} and Tc^{IV}.[16] More recently, substitution reactions of $[Tc^{VI}NCl_4]^-$ have provided a convenient method for the preparation of technetium complexes containing the Tc≡N core.[17] The reaction of $[AsPh_4][TcNCl_4]$ with oxalic acid resulted in the formation of the tetrameric $[AsPh_4]_4[Tc_4N_4O_2(ox)_6]$ (**1**) in moderate yield. The i.r. spectrum of (**1**) indicated the presence of two types of oxalato ligands chelated to the technetium atoms. There were three intense CO stretches at 1 731, 1 712, and 1 660 cm^{-1} and two peaks at 809 and 795 cm^{-1} [δ(O–C=O)].[18] The salt $[AsPh_4]_2[Tc(ox)_3]$, where all the oxalato ligands are equivalent, showed an intense CO stretch at 1 711 cm^{-1} together with a weaker peak at 1 670 cm^{-1} and only one sharp peak at 793 cm^{-1}.[7] The presence of a Tc≡N group was confirmed by a strong band at 1 050 cm^{-1}. The position of the Tc≡N band indicated the presence of a *trans* ligand.[17]

The *X*-ray crystal structure of complex (**1**) indicated that the technetium atoms are in the +VI oxidation state. This was confirmed by a calculated magnetic moment of 1.64 B.M. (1 B.M. ≈ 9.27×10^{-24} J T^{-1}) per technetium atom, a value consistent with the presence of an unpaired 4*d* electron. The

Table 3. Fractional co-ordinates for $[AsPh_4]_2[TcO(ox)_2(Hox)]{\cdot}3H_2O$ (**2**)

Atom	$10^4\ x$	$10^4\ y$	$10^4\ z$
Tc(1)	2 271(0)	7 905(1)	207(0)
As(1)	4 798(1)	3 928(1)	2 495(0)
As(2)	106(1)	6 236(1)	2 507(0)
O(1)	1 207(4)	8 055(4)	−423(3)
O(2)	1 355(4)	7 571(4)	706(3)
O(3)	2 830(4)	8 335(5)	−472(3)
O(4)	2 135(4)	9 241(4)	334(3)
O(5)	2 174(4)	6 607(4)	−97(3)
O(6)	2 122(5)	4 742(5)	−78(4)
O(7)	2 634(6)	4 895(6)	−942(5)
O(8)	3 472(5)	6 357(5)	−193(5)
O(9)	−148(4)	7 864(4)	−570(3)
O(10)	25(4)	7 295(4)	666(3)
O(11)	2 630(4)	10 549(5)	62(3)
O(12)	3 228(6)	9 588(5)	−894(4)
O(13)	2 984(4)	7 709(5)	803(3)
OW(1)	8 368(4)	6 889(5)	303(4)
OW(2)	8 108(5)	8 101(5)	9 302(4)
OW(3) *	4 629(16)	4 839(18)	325(13)
OW(4) *	4 809(16)	9 687(16)	4 447(12)
C(1)	521(6)	7 843(6)	−251(4)
C(2)	626(6)	7 531(5)	432(4)
C(3)	2 895(6)	9 216(6)	−509(5)
C(4)	2 541(6)	9 730(6)	18(4)
C(5)	2 743(6)	6 147(6)	−226(5)
C(6)	2 487(6)	5 180(8)	−463(6)
C(7)	5 795(5)	4 600(5)	2 623(4)
C(8)	5 916(6)	5 189(6)	2 167(4)
C(9)	6 629(6)	5 711(6)	2 238(5)
C(10)	7 186(6)	5 663(6)	2 779(4)
C(11)	6 964(5)	5 072(5)	3 166(4)
C(12)	6 330(5)	4 522(6)	3 161(4)
C(13)	4 648(5)	3 326(6)	3 234(4)
C(14)	5 082(6)	2 506(6)	3 379(5)
C(15)	5 040(6)	2 050(8)	3 915(5)
C(16)	4 542(6)	2 388(8)	4 319(6)
C(17)	4 107(6)	3 185(8)	4 184(5)
C(18)	4 166(6)	3 679(6)	3 637(5)
C(19)	4 814(5)	3 060(6)	1 855(4)
C(20)	4 146(6)	2 507(6)	1 707(5)
C(21)	4 149(6)	1 865(8)	1 251(5)
C(22)	4 818(6)	1 775(6)	943(5)
C(23)	5 463(6)	2 350(6)	1 092(5)
C(24)	5 456(6)	3 002(6)	1 541(4)
C(25)	3 950(5)	4 801(6)	2 245(4)
C(26)	3 485(6)	4 759(6)	1 657(5)
C(27)	2 938(6)	5 492(6)	1 477(6)
C(28)	2 862(6)	6 156(8)	1 876(5)
C(29)	3 304(6)	6 204(6)	2 457(5)
C(30)	3 880(6)	5 517(6)	2 646(5)
C(31)	226(5)	5 460(5)	3 213(4)
C(32)	−372(5)	5 418(6)	3 600(4)
C(33)	−241(6)	4 847(6)	4 114(5)
C(34)	456(6)	4 367(6)	4 237(5)
C(35)	1 044(6)	4 377(6)	3 855(5)
C(36)	929(6)	4 942(6)	3 336(5)
C(37)	977(4)	7 109(5)	2 612(3)
C(38)	1 522(5)	7 140(5)	3 152(4)
C(39)	2 103(5)	7 817(6)	3 228(4)
C(40)	2 129(5)	8 441(6)	2 756(4)
C(41)	1 591(5)	8 395(6)	2 216(4)
C(42)	1 000(5)	7 724(5)	2 141(4)
C(43)	−882(5)	6 941(6)	2 430(4)
C(44)	−981(6)	7 517(6)	2 916(4)
C(45)	−1 645(6)	8 105(6)	2 854(5)
C(46)	−2 176(6)	8 096(6)	2 305(5)
C(47)	−2 083(6)	7 519(6)	1 823(5)
C(48)	−1 429(5)	6 931(6)	1 889(4)
C(49)	137(5)	5 497(5)	1 796(4)
C(50)	−413(6)	4 784(6)	1 690(5)
C(51)	−408(6)	4 250(6)	1 173(5)
C(52)	148(6)	4 387(6)	787(5)
C(53)	706(6)	5 082(6)	898(5)
C(54)	697(5)	5 640(6)	1 414(4)

* Occupancy factor of 0.5.

presence of the $Tc^{VI}{\equiv}N$ group in (**1**) was also confirmed by the reaction of (**1**) with thionyl chloride to produce $[AsPh_4][TcNCl_4]$. Technetium(VI) compounds are uncommon, $R[TcNX_4]$ ($R = AsPh_4$ or NBu_4, $X = Cl$ or Br),[8] $Cs_2[TcNX_5]$ ($X = Cl$ or Br),[17,19] and $[NMe_4]_2[TcO_4]$[20] being the only ionic complexes to have been isolated from solution. The $[TcNCl_4]^-$ anion is readily reduced and all its substitution reactions reported to date with phosphines and sulphur-containing ligands have resulted in reduction to the $Tc^{V}{\equiv}N$ core.[17] The formation of (**1**) in the presence of the reducing ligand oxalic acid was surprising. Oxalatonitrido complexes of transition metals have previously been reported only for osmium, where $Cs[OsN(ox)_2(H_2O)]$ and $K[OsN(ox)(H_2O)(OH)_2]$ have been prepared by the addition of oxalic acid or $KHC_2O_4{\cdot}H_2C_2O_4$ to $K[OsO_3N]$.[21]

Reaction of $[NBu_4][TcOCl_4]$ with oxalic acid in aqueous acetone and addition of $AsPh_4Cl$ gave a pale green crystalline product. Recrystallisation of this product from aqueous acetone containing added oxalic acid resulted in the formation of emerald-green hexagonal pillars which were shown to be $[AsPh_4]_2[Tc^{V}O(ox)_2(Hox)]{\cdot}3H_2O$ (**2**) by *X*-ray analysis. The magnetic susceptibility of the pale green crystals showed the absence of unpaired spins, which is consistent with the assigned oxidation state +V ($4d^2$) for Tc. An attempted *X*-ray analysis of the pale green crystals was unsuccessful because of decomposition in the beam. The i.r. spectra of the initial pale green crystals and the emerald green crystals were essentially identical except for the position of the Tc=O absorptions which occurred at 963 and 985 cm^{-1} respectively. The i.r. spectrum of (**2**) showed the presence of two types of oxalato ligand with CO stretching frequencies at 1 740, 1 698 and 1 675 cm^{-1} and two peaks for the δ(O–C=O) absorption at 810 and 788 cm^{-1}.

Crystal Structure of $[AsPh_4]_4[Tc_4N_4O_2(ox)_6]$ (**1**).—The structure consists of $[AsPh_4]^+$ cations and $[Tc_4N_4O_2(ox)_6]^{4-}$ anions. A perspective view of the anion which includes the atom numbering is shown in Figure 1, and selected interatomic distances and angles are given in Table 4.

The anion is a cyclic tetranuclear complex $[Tc_4N_4O_2(ox)_6]^{4-}$ with C_i point symmetry. Each technetium(VI) atom is co-ordinated by five oxygen atoms and one nitrogen atom to give a distorted octahedron. In each half of the anion, a quadridentate oxalato ligand forms a bridge between two octahedra each of which is also linked to an adjacent octahedron by a bridging oxo ligand. Two oxygen atoms of a bidentate oxalato ligand and a nitrido nitrogen atom complete the octahedral co-ordination in each polyhedron. In general, the O–Tc–O angles for both adjacent and *trans* oxygen atoms deviate considerably (Table 4) from the respective values of 90 and 180° expected for a regular octahedron. In addition to these distortions there is a strong

Table 4. Selected interatomic distances (Å) and angles (°) for $[AsPh_4]_4[Tc_4N_4O_2(ox)_6]$ (**1**)

Tc(1)–O(1)	1.991(14)	O(4)–C(4)	1.251(24)
Tc(1)–O(2)	2.048(15)	O(5)–C(3)	1.283(24)
Tc(1)–O(4)	2.076(11)	O(6)–C(4)	1.259(22)
Tc(1)–O(9)	1.840(13)	O(7)–C(5)	1.350(33)
Tc(1)–N(1)	1.639(17)	O(8)–C(6)	1.241(31)
Tc(2)–O(5)	2.061(11)	O(10)–C(1)	1.178(36)
Tc(2)–O(7)	2.039(11)	O(11)–C(2)	1.199(33)
Tc(2)–O(8)	2.086(14)	O(12)–C(5)	1.207(31)
Tc(2)–O(9′)	1.869(13)	O(13)–C(6)	1.238(34)
Tc(2)–N(2)	1.606(17)	C(1)–C(2)	1.541(40)
O(1)–C(1)	1.300(36)	C(3)–C(4)	1.517(27)
O(2)–C(2)	1.240(32)	C(5)–C(6)	1.489(38)
O(3)–C(3)	1.247(22)		
O(1)–Tc(1)–O(2)	78.3(7)	O(4)–Tc(1)–N(1)	95.5(8)
O(1)–Tc(1)–O(4)	156.0(7)	O(9)–Tc(1)–N(1)	101.4(7)
O(1)–Tc(1)–O(9)	93.6(7)	O(5)–Tc(2)–O(7)	155.3(6)
O(1)–Tc(1)–N(1)	105.2(8)	O(5)–Tc(2)–O(8)	87.3(7)
O(2)–Tc(1)–O(4)	86.5(7)	O(5)–Tc(2)–O(9′)	90.8(6)
O(2)–Tc(1)–O(9)	158.7(7)	O(5)–Tc(2)–N(2)	97.7(7)
O(2)–Tc(1)–N(1)	99.7(8)	O(7)–Tc(2)–O(8)	80.1(7)
O(4)–Tc(1)–O(9)	94.0(6)	O(7)–Tc(2)–O(9′)	94.2(6)
O(8)–Tc(2)–N(2)	99.3(8)	O(8)–Tc(2)–O(9′)	161.0(6)
O(9′)–Tc(2)–N(2)	99.7(7)		

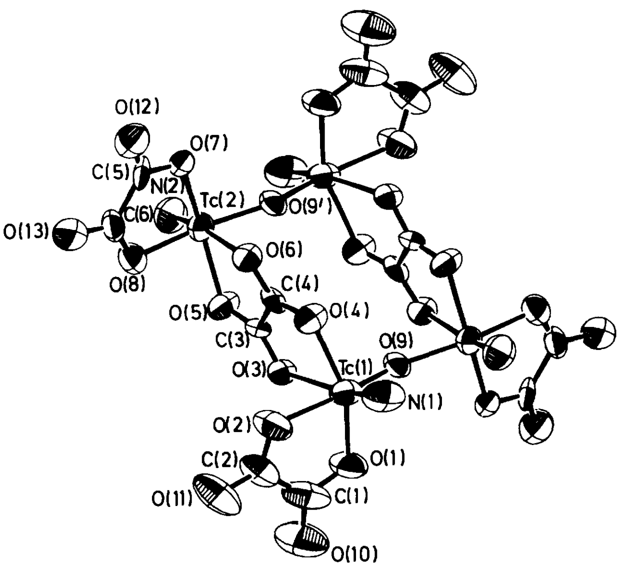

Figure 1. A perspective view of the $[Tc_4N_4O_2(ox)_6]^{4-}$ anion in $[AsPh_4]_4[Tc_4N_4O_2(ox)_6]$ showing the numbering scheme. Thermal ellipsoids are drawn at the 50% probability level

trans effect exerted by the nitrido ligand.[22] This effect is manifested by the displacement of the technetium atoms above the plane of the four oxygen atoms by 0.36(1) Å for Tc(1) [O(1), O(2), O(4), O(9)] and 0.37(1) Å for Tc(2) [O(5), O(7), O(8), O(9′)]. Also the strong *trans* effect results in the marked asymmetry of the Tc–O bond distances in the bridging quadridentate oxalato ligand. The *trans* Tc(1)–O(3) and Tc(2)–O(6) distances of 2.410(11) and 2.369(12) Å are much longer than the Tc(1)–O(4) and Tc(2)–O(5) distances of 2.076(11) and 2.061(11) Å. Asymmetry of μ_4-oxalato ligands has been observed in dimeric complexes of a variety of transition metals.[2] The technetium nitrido bond lengths of 1.639(17) and 1.606(17) Å for Tc(1)–N(1) and Tc(2)–N(2) respectively are similar to those observed in other nitrido complexes

Table 5. Selected interatomic distances (Å) and angles (°) for $[AsPh_4]_2[TcO(ox)_2(Hox)]\cdot 3H_2O$ (**2**)

Tc(1)–O(1)	2.069(6)	O(6)–C(6)	1.281(16)
Tc(1)–O(2)	2.052(7)	O(7)–C(6)	1.185(17)
Tc(1)–O(3)	1.966(7)	O(8)–C(5)	1.233(14)
Tc(1)–O(4)	2.014(6)	O(9)–C(1)	1.212(11)
Tc(1)–O(5)	2.031(6)	O(10)–C(2)	1.233(12)
Tc(1)–O(13)	1.640(6)	O(11)–C(4)	1.223(13)
O(1)–C(1)	1.284(12)	O(12)–C(3)	1.204(15)
O(2)–C(2)	1.260(11)	C(1)–C(2)	1.544(12)
O(3)–C(3)	1.312(13)	C(3)–C(4)	1.564(15)
O(4)–C(4)	1.260(12)	C(5)–C(6)	1.558(16)
O(5)–C(5)	1.226(13)		
O(1)–Tc(1)–O(2)	76.1(3)	Tc(1)–O(5)–C(5)	125.1(6)
O(1)–Tc(1)–O(3)	85.0(3)	O(3)–Tc(1)–O(13)	107.0(3)
O(1)–Tc(1)–O(4)	83.4(3)	O(4)–Tc(1)–O(5)	165.7(3)
O(1)–Tc(1)–O(5)	82.4(3)	O(4)–Tc(1)–O(13)	98.4(3)
O(1)–Tc(1)–O(13)	168.0(3)	O(5)–Tc(1)–O(13)	95.9(3)
O(2)–Tc(1)–O(3)	160.9(3)	O(5)–C(5)–O(8)	128.3(7)
O(2)–Tc(1)–O(4)	93.3(3)	O(5)–C(5)–C(6)	114.1(8)
O(2)–Tc(1)–O(5)	85.3(3)	O(8)–C(5)–C(6)	117.6(8)
O(2)–Tc(1)–O(13)	92.0(3)	O(6)–C(6)–O(7)	125.2(8)
O(3)–Tc(1)–O(4)	82.0(3)	O(6)–C(6)–C(5)	112.2(8)
O(3)–Tc(1)–O(5)	94.8(3)	O(7)–C(6)–C(5)	122.5(9)

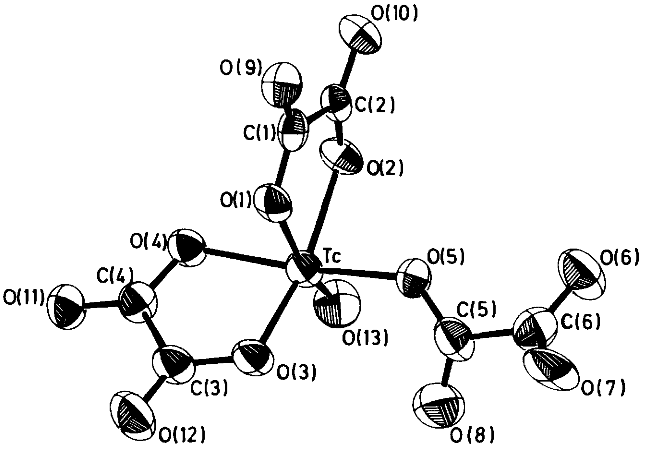

Figure 2. A perspective view of the $[TcO(ox)_2(Hox)]^{2-}$ anion in $[AsPh_4]_2[TcO(ox)_2(Hox)]\cdot 3H_2O$ showing the numbering scheme. Thermal ellipsoids are drawn at the 40% probability level

of technetium.[17,23,24] The Tc···Tc spacings of 3.586(2) [Tc(1)···Tc(2′)] and 5.756(3) Å [Tc(1)···Tc(2)] preclude any Tc–Tc bonding.

The bridging and terminal oxalato ligands in complex (**1**) are essentially planar: O(1), O(2), O(10), O(11), C(1), C(2) [root mean square deviation (r.m.s.d.) 0.03(1) Å, $\delta_{max.}$ = 0.04(1) Å]; O(7), O(8), O(12), O(13), C(5), C(6) [r.m.s.d. 0.08(1) Å, $\delta_{max.}$ = 0.11(1) Å]; and O(3), O(4), O(5), O(6), C(3), C(4) [r.m.s.d. 0.05(1) Å, $\delta_{max.}$ = 0.06(1) Å]. Also, the two basal planes comprising O(1), O(2), O(4), O(9) [r.m.s.d. 0.01(1) Å, $\delta_{max.}$ = 0.01(1) Å] and O(5), O(7), O(8), O(9′) [r.m.s.d. 0.04(1) Å, $\delta_{max.}$ = 0.04(1) Å] are essentially planar.

The tetrameric complexes containing oxalato and bridging oxo groups which have been structurally characterised are $[NH_4]_4[Ti_4O_4(ox)_8]\cdot 4H_2O$,[25] $K_4[V_4O_8(ox)_4(H_2O)_2]$,[26] and $K_6[\{Mo_2O_3S(ox)_2\}_2ox]\cdot 10H_2O$.[27] However, only the molybdenum complex contains a quadridentate oxalato ligand and is unusual in that this ligand co-ordinates to the four molybdenum atoms, *i.e.* it acts as a bridge between two dimeric units. The complexes of Ti and V contain only bridging oxo ligands and both have eight-membered macrocyclic rings. Complex (**1**) represents a new oxalate-containing tetrameric co-ordination type with a twelve-membered macrocyclic ring. The oxo ligands in (**1**) have Tc–O distances of 1.840(13) and 1.869(13) Å and a Tc(1)–O(9)–Tc(2′) angle of 150.4(8)°. The bond angle is similar to those of the titanium tetramer [Ti–O–Ti 152.1(5) and 139.2(4)°] but different to that observed for the vanadium tetramer [V–O–V 136.3(6)°]. The alternative possibility of hydroxyl bridging has been discarded on the basis of the short Tc–O–Tc bond distances [in (**1**) mean value 1.854(9) Å] which are similar to those observed for other technetium μ-oxo complexes.[28,29] Hydroxo-bridged species are usually strongly bent and exhibit M–O bond distances similar to those of single bonds,[29] *ca.* 2.0 Å for Tc–O.[30]

Crystal Structure of $[AsPh_4]_2[TcO(ox)_2(Hox)]\cdot3H_2O$ (**2**).—The crystal structure consists of discrete $[AsPh_4]^+$ cations and $[TcO(ox)_2(Hox)]^{2-}$ anions. A perspective view of the anion which includes the atom numbering is shown in Figure 2, and selected interatomic distances and angles are given in Table 5.

The technetium(v) atom is co-ordinated by six oxygen atoms to give a distorted octahedron. As found for (**1**), the O–Tc–O angles in (**2**) deviate considerably from the values expected for a regular octahedron. The oxo ligand is expected to exert a similar *trans* effect to that exerted by the nitrido ligand. The technetium atom in (**2**) is displaced by 0.25(1) Å above the plane of the four oxygen atoms [O(2), O(3), O(4), O(5)]. However, there is no appreciable lengthening of the Tc–O bond *trans* to the oxo ligand [Tc–O(1) 2.069(6) Å, *cf.* mean 2.016(7) Å for Tc–O(2—5)]. This non-lengthening of the bond is reflected in the 'bite' angle of 76.1(3)° for the oxalato ligand [O(1)–Tc–O(2)] compared to that of 82.0(3)° for O(3)–Tc–O(4).

The anion in complex (**2**) is unusual in that it contains a unidentate oxalato group. This oxalato group exists in the protonated form, Hox, as evidenced by the asymmetric C–O bond lengths [C(6)–O(6) 1.281(16) and C(6)–O(7) 1.185(17) Å] at the non-chelating end and the diamagnetism of the pale green crystals initially formed by the reaction of $[Tc^{V}OCl_4]^-$ with oxalic acid. The site of the hydrogen atom on the monodentate oxalato ligand was not determined in the analysis. However, the hydrogen atom most likely resides at O(6) since the C(6)–O(6) and C(6)–O(7) bond lengths are similar to those found in other hydrogenoxalates, *i.e.* $[M][HC_2O_4]$ (M = Li, Na, K, or NH_4).[31] The unidentate group is co-ordinated to the technetium atom *via* the oxygen atom O(5) [Tc–O(5) 2.031(6) Å], the adjacent O(8) is not co-ordinated, since the Tc ··· O(8) spacing is 3.234(9) Å. The C–O distances at the chelating end are not significantly different, C(5)–O(5) 1.226(13) and C(5)–O(8) 1.233(14) Å. The unidentate oxalato group exhibits a similar geometry to that observed in non-co-ordinated hydrogenoxalates.[31]

Although hydrogenoxalates of the type $[M][HC_2O_4]$ (M = Li, Na, K, or NH_4) have been extensively studied by *X*-ray analysis, only two examples of co-ordinated unidentate oxalato ligands have been reported, $K_4[Pt(ox)_2(SCN)_2]\cdot4H_2O$[5] and *trans*-$[Co(en)_2(ox)(H_2O)][CF_3SO_3]\cdot2H_2O$ (en = ethylenediamine).[6] However, the unidentate oxalato groups in these two complexes are not in the protonated form but as the anion and therefore do not show the asymmetry in the C–O bond lengths found in (**2**).

Although the two bidentate oxalato ligands in complex (**2**) are essentially planar {O(1), O(2), O(9), O(10), C(1), C(2) [r.m.s.d. 0.01(1) Å, $\delta_{max.}$ = 0.02(1) Å] and O(3), O(4), O(11), O(12), C(3), C(4) [r.m.s.d. 0.06(1) Å, $\delta_{max.}$ = 0.08(1) Å]}, the unidentate oxalato ligand is severely distorted from planarity. The distortion arises from a twisting about the C(5)–C(6) bond, resulting in an angle of 50° between the O(6), C(6), O(7) and O(5), C(5), O(8) planes. A similar but smaller distortion of 5.3 and 13° was also observed in the cobalt and platinum complexes containing unidentate oxalato ligands.[5,6] These distortions have been ascribed to dissimilar interactions involving the oxygen atoms of the anion.

The six-co-ordinate structure of complex (**2**) was unexpected in view of the preference of the TcO core to form square-pyramidal complexes of the type $[TcO(L-L)_2]^{n-}$ with bidentate oxygen and sulphur ligands.[30,32] Structure (**2**) represents a new structural type closely related to $[NH_4]_3[NbO(ox)_3]\cdot H_2O$ which is seven-co-ordinate.[33] An example of a seven-co-ordinate technetium complex containing the Tc=O core is $Ba[TcO(edta)]_2$ (edta = ethylenediaminetetra-acetate).[32] The reason why six-co-ordination with a pendant oxalate is preferred for (**2**) rather than the five- or seven-co-ordinate complexes with all oxalato ligands bidentate is unclear.

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