Preparation and Crystal Structures of Bis(tetraphenylarsonium) Tris(oxalato)technetate(IV), and Tetraphenylarsonium Tris(benzene-1,2-dithiolato)technetate(V): Octahedral *versus* Trigonal-prismatic Geometry for Tris-bidentate Complexes of Technetium†

Silvano F. Colmanet* and Geoffrey A. Williams
Australian Radiation Laboratory, Lower Plenty Road, Yallambie, Victoria 3085, Australia
Maureen F. Mackay
Department of Chemistry, La Trobe University, Bundoora, Victoria 3083, Australia

The addition of $[NH_4]_2[TcBr_6]$ to an aqueous solution of oxalic acid yields the complex $[AsPh_4]_2[Tc(ox)_3]$ (**1**), and the reaction of benzene-1,2-dithiol (H_2bdt) with $[AsPh_4][TcNCl_4]$ in acetone yields crystals of $[AsPh_4][Tc(bdt)_3]$ (**2**). The syntheses and crystal structures of the two compounds are reported. $[AsPh_4]_2[Tc(ox)_3]$ crystallises in the monoclinic space group $C2/c$ with cell parameters a = 23.164(2), b = 13.507(2), c = 16.047(1) Å, and β = 104.90(5)°, with Z = 4. Refinement on 3 223 non-zero data measured with Cu-K_α radiation converged to R = 0.054. The co-ordination geometry of the technetium(IV) atom and the six co-ordinated oxygen atoms is distorted octahedral and of pseudo-D_3 symmetry. Crystals of (**2**) are monoclinic, space group $P2_1/n$ with a = 12.966(1), b = 12.746(1), c = 23.233(1), and β = 92.27(8)° with Z = 4. Refinement on 5 395 non-zero data measured with Cu-K_α radiation converged to R = 0.048. The technetium(V) atom is co-ordinated to six sulphur atoms in close to ideal trigonal-prismatic geometry. The complex is distorted from ideal D_{3h} symmetry by the bending of SC_6H_4S ligand planes from the relevant TcS_2 planes by 4.1, 1.7, and 1.1°. Factors affecting octahedral *versus* trigonal-prismatic geometries in these two tris-bidentate complexes are discussed.

The chemistry of technetium has been studied extensively in recent years, mainly due to both the widespread use of technetium-99m ($t_{\frac{1}{2}}$ = 6 h) in diagnostic nuclear medicine[1,2] and the ready availability of macroscopic quantities of the long-lived technetium-99 isotope ($t_{\frac{1}{2}}$ = 2.12 × 10^5 years). Although a large number of technetium compounds have been synthesised and characterised by conventional methods,[3] very few complexes of the type $[Tc(L\text{–}L)_3]^{n-}$ (L–L = bidentate ligand) have been reported and even fewer of these tris-complexes have been characterised by single-crystal *X*-ray diffraction. Complexes reported which have a technetium atom co-ordinated to three bidentate ligands are $[Tc(acac)_3]$ (acac = acetylacetonate),[4] $[Tc(tdt)_3]$ (tdt = toluene-3,4-dithiolate),[5] $[Tc(NHC_6H_4S\text{-}o)_3]$,[6] and $[Tc_2(bdt)_4]$ (bdt = benzene-1,2-dithiolate).[7a] In the last two complexes, characterised by *X*-ray structure analyses, the co-ordination geometries are essentially trigonal prismatic.

A large number of tris-bidentate complexes of other transition metals have been characterised with co-ordination geometries ranging from octahedral to trigonal prismatic.[8] In the present paper we report the isolation, characterisation, and *X*-ray crystal structures of two tris-bidentate complexes of technetium. In one complex, $[AsPh_4]_2[Tc(ox)_3]$ (**1**) (ox = oxalate), prepared by the reaction of oxalic acid with $[NH_4]_2[TcBr_6]$, an octahedral geometry is observed. This is the first report of this geometry observed in a tris-bidentate complex of technetium. However, in the other complex, $[AsPh_4][Tc(bdt)_3]$ (**2**), unexpectedly prepared by the reduction of $[AsPh_4][TcNCl_4]$ in the presence of benzene-1,2-dithiol, trigonal-prismatic co-ordination geometry is observed. The latter preparation, involving the removal of the nitrogen atom from $[TcNCl_4]^-$, is surprising since it has been shown that the Tc≡N bond in such complexes is exceptionally stable.[9a,b]

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. Microanalyses were performed by the Australian Microanalytical Service, Melbourne. Tetraphenylarsonium tetrachloro(nitrido)technetate(VI) was prepared according to the method of Baldas *et al.*,[9a] and ammonium hexachlorotechnetate(IV) was prepared by a modification of the method of Dalziel *et al.*[10] for the preparation of $K_2[TcCl_6]$.

Bis(tetraphenylarsonium) Tris(oxalato)technetate(IV).—$[NH_4]_2[TcBr_6]$ (42 mg, 68 μmol) was added to an aqueous solution of oxalic acid (500 mg, 5.6 mmol). The solution was heated and turned brown in colour. Addition of $AsPh_4Cl$ (63 mg, 0.15 mmol) to the mixture gave a yellow precipitate which was filtered off, washed first with water then ethanol (99.9%), and dried. Yield: 44 mg, 57% based on $[NH_4]_2[TcBr_6]$. The complex was recrystallised from ethanol–acetonitrile (1:1 v/v) to give pale yellow crystals, m.p. *ca.* 260 °C (decomp.) (Found: C, 58.8; H, 3.7. $C_{54}H_{40}As_2O_{12}Tc$ requires C, 59.4; H, 3.6%). The i.r. spectrum showed peaks at 1 712vs, 1 670m, 1 439s, 1 335s, 1 081m, 998m, 794m, 741vs, and 690s cm^{-1}.

*Tetraphenylarsonium Tris(benzene-*1,2*-dithiolato)technetate*(V).—Benzene-1,2-dithiol (33 mm^3, 265 μmol) in acetone (5 cm^3) was added to a solution of $[AsPh_4][TcNCl_4]$ (66 mg, 103 μmol) dissolved in acetone (10 cm^3). After a few minutes the solution turned dark brown in colour, and after 24 h dark brown crystals formed. The crystals were collected and washed with acetone. Yield: 20 mg, 21% based on $[AsPh_4][TcNCl_4]$; m.p. *ca.* 280 °C (decomp.) (Found: C, 55.1; H, 3.4; S, 19.4. $C_{42}H_{32}AsS_6Tc$ requires C, 55.8; H, 3.6; S, 21.3%). The i.r. spectrum showed peaks at 1 439s, 1 298s, 1 082m, 995m, 750s, 738s, and 688m cm^{-1}.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

X-Ray Crystallography.—Single crystals suitable for *X*-ray diffraction studies were grown by slow evaporation of an acetonitrile–ethanol (1:1 v/v) solution of $[AsPh_4]_2[Tc(ox)_3]$ (**1**) and by slow evaporation of an acetone–water solution of $[AsPh_4][Tc(bdt)_3]$ (**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 $C2/c$ for (**1**) and $P2_1/n$ for (**2**) from systematic extinctions. Accurate unit-cell parameters were determined at 288(1) K by least-squares fits of the 2θ values measured on a Rigaku–AFC four-circle diffractometer with Cu-K_α radiation for 25 independent reflections ($35 < 2\theta < 80°$). Integrated intensities were measured on the diffractometer with Cu-K_α radiation (graphite-crystal monochromator, $\bar{\lambda} = 1.5418$ Å) at 288(1) K and recorded by an ω–2θ scan with 10-s stationary background counts. In each case, three reflections (224, $\bar{5}33$, 621, and $3\bar{3}0$, 071, $1\bar{1}7$ for (**1**) and (**2**) respectively) monitored every 50 reflections showed no significant variations in intensities during the data collections. Data to a maximum $\sin\theta/\lambda = 0.588$ Å^{-1} were recorded. Crystal data and a summary of data collection conditions are given in Table 1. Intensity data were corrected for Lorentz and polarisation effects and for absorption.[11]

Structure Determination and Refinement.—The structures were solved by the heavy-atom method, the positions of the technetium and arsenic atoms being determined from Patterson maps. Subsequent difference Fourier syntheses revealed the sites of the remaining non-hydrogen atoms. The hydrogen atoms were included in the analyses at calculated positions (C–H 1.08 Å) and assigned a variable overall isotropic thermal parameter. The structures were refined by the full-matrix least-squares method with anisotropic thermal parameters given to the non-hydrogen atoms. The function minimised 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 $m = 5 \times 10^{-4}$ for (**1**) and 1×10^{-4} for (**2**). An empirical isotropic extinction parameter, g, where $F_c = F[1 - (gF^2/\sin\theta)]$ was applied to the calculated structure amplitudes of (**2**).

During the refinement of (**1**), based on 3 317 non-zero data, it was observed that 94 of the weakest intensity reflections exhibited relatively poor agreement with the calculated structure factors, and in all cases $F_o \gg F_c$. As this effect was clearly systematic, it was decided to omit these low-intensity data from further refinement cycles and the remaining 3 223 data were used [$I_o \geqslant \sigma(I_o)$]. The refinement of (**2**) was based on 5 395 terms for which $I_o \geqslant 2\sigma(I_o)$. The largest peaks on the final difference maps for (**1**) and (**2**) (Table 1) were close to the technetium atoms. Final atomic positional parameters for 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 refs. 12(*a*) and 12(*b*) respectively; those for hydrogen were taken from ref. 13. Real and imaginary anomalous dispersion corrections were applied to the non-hydrogen atoms.[11] The major calculations were made with the SHELX 76[14] program and the molecular plots have been prepared from the output of ORTEP.[15]

Table 1. Crystallographic data at 288(1) K and summary of intensity data collection and structure refinement of (**1**) and (**2**)*

	$[AsPh_4]_2[Tc(ox)_3]$ (**1**)	$[AsPh_4][Tc(bdt)_3]$ (**2**)
Formula	$C_{54}H_{40}As_2O_{12}Tc$	$C_{42}H_{32}AsS_6Tc$
M	1 129.65	902.91
Crystal dimensions (mm)	0.19 × 0.15 × 0.06	0.54 × 0.28 × 0.09
Crystal colour	Pale yellow	Dark brown
Space group	$C2/c$	$P2_1/n$
a/Å	23.164(2)	12.966(1)
b/Å	13.507(2)	12.746(1)
c/Å	16.047(1)	23.233(1)
β/°	104.90(5)	92.27(8)
U/Å^3	4 852(1)	3 836.6(5)
Z	4	4
D_m/g cm^{-3}	1.54(1)	1.55(1)
D_c/g cm^{-3}	1.55	1.56
F(000)	2 276	1 824
μ(Cu-K_α)/cm^{-1}	42.13	69.94
λ/Å	1.5418	1.5418
Absorption correction factors	1.28—1.84	1.76—9.93
$2\theta_{max.}$/°	130	130
Scan rate (°/min^{-1})	4	2
Scan range (°)	1.2 + 0.5tanθ	1.2 + 0.5tanθ
Unique non-zero data used	3 317	5 781
Terms used for refinement	3 223	5 395
Final no. of parameters	313	237
R	0.054	0.048
R'	0.057	0.051
G.o.f. for last cycle	1.48	2.96
Residual density (e Å^{-3})	+1.95 and −0.93	+0.99 and −1.03
Max. Δ/σ for last cycle	0.008	0.006
Isotropic extinction parameter (g)		0.0029

* $R = \Sigma\Delta F/\Sigma|F_o|$, $R' = [\Sigma w(\Delta F)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$; 'goodness of fit' (g.o.f.) = $[\Sigma w(\Delta F)^2/(n - m)]^{\frac{1}{2}}$, where n is the number of reflections used in the refinement and m is the number of variables.

Discussion

Substitution reactions of $[Tc^VOX_4]^-$ or $[Tc^{IV}X_6]^{2-}$ (X = Cl or Br) provide a major route to Tc^V and Tc^{IV} complexes.[3,16] More recently, substitution reactions of $[Tc^{VI}NCl_4]^-$,[9] generally with the reduction of the technetium, have provided a convenient method for the formation of technetium complexes containing the $Tc^V{\equiv}N$ group.

Attempts to prepare a tris(oxalato)technetium complex by the reaction of $[TcCl_6]^{2-}$ or $[TcI_6]^{2-}$ with sodium oxalate have been reported.[17] In both cases no apparent reaction was observed in the cold but hydrolysis with formation of TcO_2 occurred on heating. Hydrolysis of $[TcX_6]^{2-}$ (X = Cl, Br, or I) occurs readily under neutral or basic conditions and therefore substitution reactions under acidic conditions may be required in order to compete favourably with hydrolysis. Acid conditions, however, reduce the concentration of oxalate anions and hence the rate of substitution of $[TcX_6]^{2-}$. We found that dissolution of $[NH_4]_2[TcBr_6]$ in aqueous oxalic acid and addition of $AsPh_4Cl$ resulted in the precipitation of $[AsPh_4]_2[Tc(ox)_3]$ in good yield. Under these conditions the concentration of oxalate anions was sufficient for the substitution reaction to be fast and hydrolysis to form TcO_2 was unimportant. Whereas oxalato complexes have been prepared and extensively studied for a wide variety of metals,[18,19] the tris(oxalato)technetium complex (**1**) reported here is the first such complex with technetium. It is also the first observation of a tris-bidentate complex of technetium exhibiting octahedral geometry.

The formation of $[AsPh_4][Tc(bdt)_3]$ (**2**) from the reaction of $[AsPh_4][TcNCl_4]$ with benzene-1,2-dithiol was totally unexpected. As the nitrido ligand (N^{3-}) is isoelectronic with the oxo ligand (O^{2-}), the Tc≡N group may be considered as the

Table 2. Fractional atomic co-ordinates (× 10^4) for $[AsPh_4]_2[Tc(ox)_3]$ (**1**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Tc	0	3 204(1)	2 500	C(11)	3 681(3)	2 128(6)	3 571(4)
As	3 385(1)	2 776(1)	1 825	C(12)	4 003(4)	2 150(6)	4 432(4)
O(1)	−757(2)	3 240(4)	1 557(2)	C(13)	4 442(3)	2 820(6)	4 709(4)
O(2)	−457(2)	4 176(4)	2 996(3)	C(14)	4 585(3)	3 475(6)	4 165(4)
O(3)	295(2)	2 080(4)	1 921(3)	C(15)	4 272(3)	3 474(5)	3 291(4)
O(4)	−1 677(2)	3 815(5)	1 223(4)	C(16)	3 195(3)	4 082(5)	1 362(3)
O(5)	−1 374(3)	4 773(5)	2 833(4)	C(17)	2 603(3)	4 400(6)	1 118(4)
O(6)	185(3)	486(5)	1 737(6)	C(18)	2 484(4)	5 337(6)	778(5)
C(1)	−1 190(3)	3 759(6)	1 706(4)	C(19)	2 945(5)	5 945(6)	688(5)
C(2)	−1 021(3)	4 299(6)	2 574(5)	C(20)	3 520(4)	5 613(6)	926(5)
C(3)	137(3)	1 236(6)	2 098(5)	C(21)	3 652(3)	4 680(6)	1 265(4)
C(4)	2 678(3)	2 016(5)	1 755(4)	C(22)	3 840(2)	2 139(4)	1 147(3)
C(5)	2 614(3)	1 108(5)	1 330(4)	C(23)	3 710(3)	2 306(6)	276(4)
C(6)	2 108(4)	549(6)	1 311(5)	C(24)	3 999(3)	1 782(6)	−232(4)
C(7)	1 688(3)	881(6)	1 713(5)	C(25)	4 427(3)	1 109(6)	138(5)
C(8)	1 768(3)	1 762(6)	2 148(5)	C(26)	4 569(3)	947(6)	1 012(5)
C(9)	2 261(3)	2 346(6)	2 180(4)	C(27)	4 272(3)	1 468(5)	1 522(4)
C(10)	3 819(3)	2 797(5)	3 010(3)				

Table 3. Fractional atomic co-ordinates (× 10^4) for $[AsPh_4][Tc(bdt)_3]$ (**2**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Tc	2 038(1)	2 115(1)	786(1)	C(18)	4 372(4)	2 032(5)	202(2)
As	2 535(1)	1 512(1)	7 091(1)	C(19)	1 293(4)	2 055(4)	7 383(2)
S(1)	891(1)	3 461(1)	533(1)	C(20)	408(5)	2 077(5)	7 028(2)
S(2)	965(1)	1 180(1)	148(1)	C(21)	−479(5)	2 536(6)	7 213(3)
S(3)	1 691(1)	2 794(1)	1 696(1)	C(22)	−496(5)	2 986(6)	7 750(3)
S(4)	2 147(1)	546(1)	1 305(1)	C(23)	378(5)	2 982(6)	8 104(3)
S(5)	3 253(1)	3 459(1)	757(1)	C(24)	1 283(5)	2 537(6)	7 919(3)
S(6)	3 304(1)	1 228(1)	262(1)	C(25)	3 158(4)	2 619(4)	6 684(2)
C(1)	−11(4)	3 032(4)	18(2)	C(26)	2 791(6)	2 823(6)	6 120(3)
C(2)	−756(4)	3 715(5)	−227(2)	C(27)	3 172(6)	3 703(6)	5 843(3)
C(3)	−1 436(4)	3 359(5)	−651(2)	C(28)	3 894(6)	4 327(6)	6 105(4)
C(4)	−1 393(4)	2 313(5)	−830(2)	C(29)	4 258(5)	4 113(6)	6 652(4)
C(5)	−680(4)	1 642(5)	−588(2)	C(30)	3 894(4)	3 249(5)	6 950(3)
C(6)	36(4)	1 997(4)	−165(2)	C(31)	3 482(5)	1 012(5)	7 678(2)
C(7)	1 716(4)	1 795(4)	2 198(2)	C(32)	4 507(5)	873(5)	7 533(3)
C(8)	1 513(4)	1 992(5)	2 783(2)	C(33)	5 195(6)	427(6)	7 933(4)
C(9)	1 502(5)	1 173(6)	3 167(2)	C(34)	4 879(6)	143(6)	8 456(4)
C(10)	1 666(5)	161(6)	2 983(3)	C(35)	3 868(6)	272(8)	8 606(4)
C(11)	1 870(5)	−51(6)	2 421(3)	C(36)	3 158(6)	716(6)	8 212(3)
C(12)	1 900(4)	776(4)	2 021(2)	C(37)	2 240(4)	359(5)	6 586(2)
C(13)	4 332(4)	3 052(5)	415(2)	C(38)	2 915(6)	143(6)	6 153(2)
C(14)	5 176(5)	3 735(6)	334(2)	C(39)	2 747(6)	−752(6)	5 820(3)
C(15)	6 019(6)	3 383(9)	37(3)	C(40)	1 934(6)	−1 392(6)	5 908(3)
C(16)	6 044(6)	2 382(9)	−175(4)	C(41)	1 265(6)	−1 184(6)	6 338(3)
C(17)	5 239(5)	1 683(6)	−89(3)	C(42)	1 414(5)	−293(5)	6 679(3)

nitrogen analogue of the Tc=O group. Therefore, the product expected was $[Tc^VN(bdt)_2]^{2-}$, the nitrogen analogue of $[Tc^VO(bdt)_2]^-$.[7b] As the Tc≡N group has been shown to be exceptionally stable under a wide range of reaction conditions,[9a,9b] the loss of the nitrido atom was therefore unexpected. It may, however, be noted that the facile cleavage of the Tc=O bond in $[TcOCl_4]^-$ by the bidentate morpholine-*N*-carbodithioate ($CH_2CH_2OCH_2CH_2NCS_2^-$, mcdt) to give the eight-co-ordinate complex $[Tc^{IV}(mcdt)_4]$ has been reported.[20] We have also attempted the preparation of $[Tc(bdt)_3]^-$ by a more conventional method, *i.e.*, the reaction of $[TcO_4]^-$ with benzene-1,2-dithiol. However, this resulted in the formation of the dimeric complex $[Tc_2(bdt)_4]$ which shows novel trigonal-prismatic geometry.[7a]

For six-co-ordinate complexes of the type $[M(L\text{-}L)_3]^{n-}$ there are two limiting co-ordination geometries, *viz.* trigonal prismatic and octahedral.[8] These geometries may be characterised by the normalised bite (the ratio of intraligand distance to

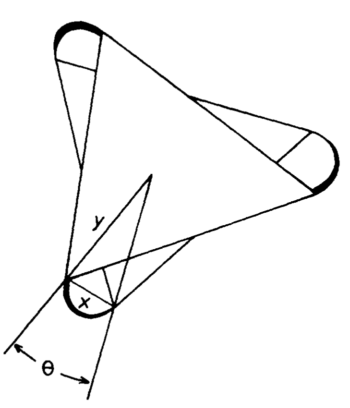

Figure 1. Trigonal twist angle (θ) projected perpendicular to the molecular three-fold axis. The 'normalised bite', $b = x/y$

Table 4. Selected interatomic distances (Å) and angles (°) for $[AsPh_4]_2[Tc(ox)_3]$ (**1**)*

Tc–O(1)	2.001(4)	O(2) ··· O(3′)	2.854(8)
Tc–O(2)	1.978(5)	O(3) ··· O(3′)	2.574(7)
Tc–O(3)	1.990(5)	O(4) ··· O(5)	2.812(9)
C(1)–O(1)	1.295(9)	O(6) ··· O(6′)	2.795(14)
C(1)–O(4)	1.196(9)	O(1)–Tc–O(1′)	177.2(2)
C(2)–O(2)	1.318(9)	O(1)–Tc–O(2)	80.4(2)
C(2)–O(5)	1.194(10)	O(1)–Tc–O(2′)	97.8(2)
C(3)–O(3)	1.252(10)	O(1)–Tc–O(3)	90.3(2)
C(3)–O(6)	1.186(11)	O(1)–Tc–O(3′)	91.9(2)
C(1)–C(2)	1.531(10)	O(2)–Tc–O(2′)	96.8(2)
C(3)–C(3′)	1.578(10)	O(2)–Tc–O(3)	167.9(2)
O(1) ··· O(2)	2.567(6)	O(2)–Tc–O(3′)	92.0(2)
O(2) ··· O(2′)	2.958(7)	O(3)–Tc–O(3′)	80.6(2)

* Primed atoms are related to the corresponding unprimed atoms by the two-fold axis.

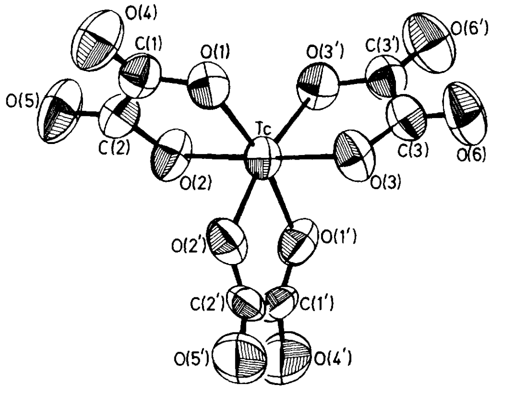

Figure 2. A perspective view of the $[Tc(ox)_3]^{2-}$ anion in $[AsPh_4]_2[Tc(ox)_3]$ showing the atom numbering scheme. Thermal ellipsoids are drawn at the 50% level

the metal–ligand distance), and the angle of twist, θ, between the upper and lower triangular faces (Figure 1). For a regular octahedron the triangular faces are staggered with θ = 60°, whereas the trigonal prism is the eclipsed arrangement with θ = 0°. Of the two tris-bidentate complexes of technetium whose structures are reported here, one complex shows octahedral geometry while the other shows trigonal-prismatic geometry.

Crystal Structure of $[AsPh_4]_2[Tc(ox)_3]$ (**1**).—The structure consists of $[Tc(ox)_3]^{2-}$ anions and $[AsPh_4]^+$ cations. A perspective view of the anion which includes the atom numbering scheme is shown in Figure 2, and selected interatomic distances and angles are given in Table 4. The $[AsPh_4]^+$ cations occupy general positions in the unit cell and the $[Tc(ox)_3]^{2-}$ anions lie on crystallographic two-fold axes with the technetium atoms occupying the four(*e*) special positions.

In $[Tc(ox)_3]^{2-}$ the technetium atom is co-ordinated to six oxygen atoms in a distorted octahedral array. In general, the angles O–Tc–O for both adjacent and *trans* oxygens deviate considerably from the respective values of 90 and 180° expected for a regular octahedron. For adjacent oxygen atoms the values range from 80.4(2) to 80.6(2)° (intraligand) and 90.3(2) to 97.8(2)° (interligand), while for *trans* atoms across Tc the angles are 167.9(2) and 177.2(2)°. However, for the intraligand O–Tc–O angle of *ca.* 81°, when the geometric constraint of the oxalato group is taken into account, a corrected *trans* O–Tc–O angle of 171° is obtained for the octahedron.* Thus the *trans* angles in (**1**) are close to the corrected values. The other measure of distortion from octahedral geometry is the chelate twist angle (θ) between the triangular faces O(1),O(2′),O(3) and O(1′),O(2),O(3′). These faces are nearly parallel, the dihedral angle between their normals being only 1.6°, whereas the individual twist angles for the three oxalato ligands are θ_1 = 47.9° and $\theta_2 = \theta_{2'}$ = 50.2° (average θ ≃ 49°). When taking into account the constraint of the ligand bite (*b* = 1.29; see Figure 1) and minimising interligand repulsions, the corrected octahedral twist is *ca.* 49°.[8] It is, therefore, clear that the oxalato ligands have attained the octahedral limit for chelate twist.

Table 5. Comparative structural data for some $[M(ox)_3]^{n-}$ complexes*

Complex	M–O/Å	O–M–O (bite)/°	O–M–O (*trans*)/°	Chelate twist (θ)/°	Ref.
$[Tc(ox)_3]^{2-}$	1.991(7)	80.5(1)	172.5(1)	49.4	This work
$[Al(ox)_3]^{3-}$	1.893(7)	83.6(1)	169.7(5)	47.4	21
$[Cr(ox)_3]^{3-}$	1.970(5)	82.3(1)	169.9(6)	47.9	21
$[Rh(ox)_3]^{3-}$	2.021(5)	83.2(3)	174.9(8)		22
$[Mn(ox)_3]^{3-}$	2.000(30)	80(1)	167(2)		23

* Bond distances and angles given are weighted mean values, with the variance of the mean in parentheses.

Although one oxalato ligand in (**1**), comprising atoms C(1), C(2), O(1), O(2), O(4), and O(5), is almost planar [root mean square deviation (r.m.s.d.) 0.02(1) Å; maximum deviation, $\delta_{max.}$ = 0.03(1) Å for O(1)], the other ligand, comprising atoms C(3), C(3′), O(3), O(3′), O(6), and O(6′), is considerably distorted from planarity [r.m.s.d. 0.13(1) Å; $\delta_{max.}$ = 0.17(1) Å for O(3)]. The non-planarity of oxalato ligands has also been observed in other tris(oxalato) complexes.[21–23]

Selected dimensions of the co-ordination spheres in some $[M(ox)_3]^{n-}$ complexes which have been characterised by *X*-ray crystallography are listed in Table 5; the values determined for the co-ordination sphere of $[Tc(ox)_3]^{2-}$ correspond closely with those reported for the other complexes. The Tc^{IV}–O bond lengths observed in (**1**), which range from 1.978(5) to 2.001(4) Å, are similar to the Tc^{IV}–O distances of 1.98(2) and 2.04(2) Å in $[PPh_4][TcCl_4(OC_6H_4CHO\text{-}o)]$[24] and 2.034(3) and 2.072(2) Å in $Na_2[\{TcN(CH_2COO)_3\}_2(\mu\text{-}O)_2]$.[25]

The conformation of the $[AsPh_4]^+$ cation is typical of that observed in other structures,[26,27] with only slight distortions from regular tetrahedral geometry about the arsenic atom. There are no unusually short interionic contacts in the structure.

Crystal Structure of $[AsPh_4][Tc(bdt)_3]$ (**2**).—The crystal structure of (**2**) consists of discrete $[AsPh_4]^+$ cations and $[Tc(bdt)_3]^-$ anions. A perspective view of the anion with the atom numbering scheme is shown in Figure 3. Selected interatomic distances and angles are given in Table 6.

The technetium(V) atom in $[Tc(bdt)_3]^-$ is co-ordinated by a trigonal-prismatic array of six sulphur atoms. The dithiolato ligands radiate out from the technetium atom in the 'paddle wheel' arrangement shown in Figure 4, similar to that observed in other trigonal-prismatic complexes containing 1,2-dithiols.[28] Although the S_6 polyhedron is distinctly trigonal prismatic, there is some distortion from the ideal geometry. The two triangular faces S(1),S(3),S(5) and S(2),S(4),S(6) are nearly parallel, with a dihedral angle between their normals of 0.6°. The dihedral angles between the mean planes of the triangular S_3 faces and the three TcS_2 planes formed by the metal atom and the two donor atoms of each ligand are 88.8, 82.0, and 93.8°. These values are closer to the trigonal-prismatic ideal of 90° than to the value of 54.7° for the octahedral limit.[29] The chelate twist angles (θ) for the three dithiolato ligands of 1.1, 16.3, and 5.8° are close to the ideal trigonal-prismatic value of zero. Other

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* The complement of the chelate bite angle equals the supplement of the *trans* angle.

Table 6. Selected interatomic distances (Å) and angles (°) for $[AsPh_4][Tc(bdt)_3]$ (**2**)

Tc–S(1)	2.331(1)	Tc–S(1)–C(1)	110.4(2)
Tc–S(2)	2.322(2)	Tc–S(2)–C(6)	110.4(2)
Tc–S(3)	2.345(2)	Tc–S(3)–C(7)	109.8(2)
Tc–S(4)	2.337(2)	Tc–S(4)–C(12)	110.0(2)
Tc–S(5)	2.330(1)	Tc–S(5)–C(13)	110.8(2)
Tc–S(6)	2.369(2)	Tc–S(6)–C(18)	109.4(2)
S(1) ··· S(2)	3.044(2)	S(1)–Tc–S(2)	81.75(6)
S(1) ··· S(3)	2.979(3)	S(1)–Tc–S(3)	79.18(6)
S(1) ··· S(5)	3.086(2)	S(1)–Tc–S(4)	141.73(6)
S(2) ··· S(4)	3.147(3)	S(1)–Tc–S(5)	82.93(6)
S(2) ··· S(6)	3.034(2)	S(1)–Tc–S(6)	132.06(6)
S(3) ··· S(4)	3.070(2)	S(2)–Tc–S(3)	129.32(6)
S(3) ··· S(5)	3.151(3)	S(2)–Tc–S(4)	84.98(6)
S(4) ··· S(6)	3.028(3)	S(2)–Tc–S(5)	138.39(6)
S(5) ··· S(6)	3.069(2)	S(2)–Tc–S(6)	80.61(6)
S(1)–C(1)	1.728(5)	S(3)–Tc–S(4)	81.98(6)
S(2)–C(6)	1.731(5)	S(3)–Tc–S(5)	84.77(6)
S(3)–C(7)	1.726(5)	S(3)–Tc–S(6)	143.24(6)
S(4)–C(12)	1.731(5)	S(4)–Tc–S(5)	128.10(6)
S(5)–C(13)	1.716(5)	S(4)–Tc–S(6)	80.08(6)
S(6)–C(18)	1.733(6)	S(5)–Tc–S(6)	81.55(6)

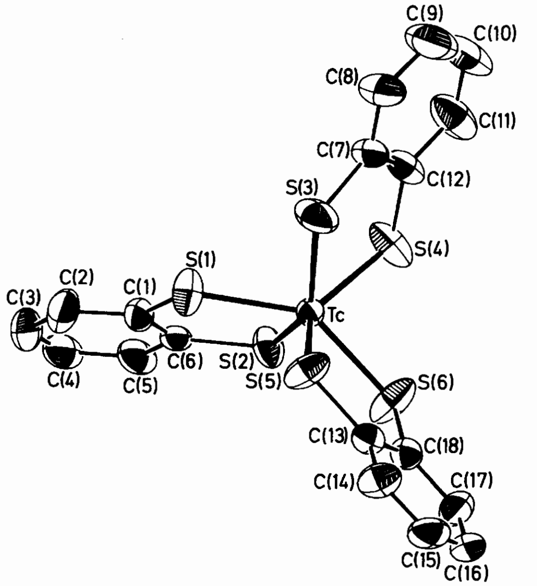

Figure 3. A perspective view of the $[Tc(bdt)_3]^-$ anion in $[AsPh_4][Tc(bdt)_3]$ showing the atom numbering scheme. Thermal ellipsoids are drawn at the 50% level

indications that the co-ordination about the technetium atom approaches regular trigonal-prismatic geometry are the S–Tc–S angles involving pseudo-*trans* sulphur atoms and the angles between TcS_2 planes (Table 7). The average value of 135(3)° for S–Tc–S angles [ranging from 128.1(1) to 143.2(1)°] is close to the average value of 136° found for other trigonal-prismatic complexes,[30] while the average angle between TcS_2 planes of 119.4° is close to the expected value of 120°. The mean intraligand bite angle of 81.8(1)° is similar to values found for this angle in other tris(benzene-1,2-dithiolato) complexes (Table 8).

The Tc^V–S bond lengths of 2.322(1)—2.369(2) Å are similar to M–S distances found in other tris(1,2-dithiolato) complexes (Table 8).[8] They also agree well with Tc–S bond distances in the two other known trigonal-prismatic complexes of technetium, *viz.* $[Tc(NHC_6H_4S\text{-}o)_3]$[6] with Tc^{VI}–S distances in the range 2.339(3)—2.359(3) Å, and the dimer $[Tc_2(bdt)_4]$[7a] with Tc^{IV}–S distances of 2.291(7)—2.416(8) Å. Tc^V–S distances in some square-pyramidal 1,2-dithiol complexes are somewhat shorter than those found in (**2**). In $[AsPh_4][TcO(SCH_2CH_2S)_2]$[31] the four Tc^V–S distances range from 2.283(4) to 2.313(4) Å, in $[NEt_4][TcO\{SCH(CO_2Me)CH(CO_2Me)S\}_2]$[32] they lie between 2.306(3) and 2.322(2) Å, and in $[AsPh_4][TcO(bdt)_2]$[7b] they lie within the range 2.310(2)—2.319(2) Å. The small increase in the Tc^V–S bond length in the 1,2-dithiol complexes on going from square-pyramidal to trigonal-prismatic geometry is possibly a manifestation of greater inter-ligand repulsions in the trigonal prism. Alternatively, the effect may be electronic in origin and simply a result of weaker technetium–sulphur π interactions or of a smaller proportion of metal *s*-orbital character in the σ-bonding framework of the trigonal prism.

Table 7. Selected dihedral angles for $[AsPh_4][Tc(bdt)_3]$ (**2**)

Atoms in plane 1	Atoms in plane 2	Angle (°) between planes 1—2
S(1), S(3), S(5)	S(2), S(4), S(6)	0.6
Tc, S(1), S(2)	Tc, S(3), S(4)	119.4
Tc, S(1), S(2)	Tc, S(5), S(6)	119.4
Tc, S(3), S(4)	Tc, S(5), S(6)	119.3
Tc, S(1), S(2)	C(1)—C(6), S(1), S(2)	4.1
Tc, S(3), S(4)	C(7)—C(12), S(3), S(4)	1.7
Tc, S(5), S(6)	C(13)—C(18), S(5), S(6)	1.1

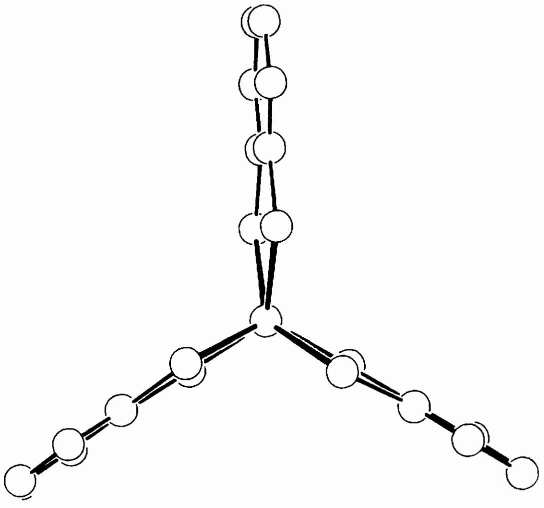

Figure 4. View of $[Tc(bdt)_3]^-$ projected down the approximate three-fold axis showing the 'paddle-wheel' arrangement

The C–S bond lengths in (**2**) [mean 1.727(3) Å] are similar to those in other trigonal-prismatic complexes (Table 8),[30] and are consistent with considerable C=S double bond character. While there is obviously a significant contribution from the dithiolene form of the ligands, it is reasonable, considering the reaction which yields the $[Tc(bdt)_3]^-$ complex, to assign a formal oxidation state of +5 to technetium.

The dithiol ligand and associated TcS_2 planes are essentially coplanar (dihedral angles 4.1, 1.7, and 1.1°, Table 7). This is a significant result as previously all dithiol prisms with ligands $SC_2H_2S^{2-}$ and $SC_6H_4S^{2-}$ have been found to have considerable (*ca.* 20°) folding between MS_2 and ligand planes.[28,33] The only coplanar examples have been observed for the $S_2C_2Ph_2{}^{2-}$ ligand.[34,35] These observations led Cowie and Bennett[28,30,33] to postulate that folding about the S ··· S axes enables the dithiol ligands to achieve a more stabilising π interaction with the metal *d* orbitals, with the anomalous coplanar $S_2C_2Ph_2{}^{2-}$ complexes being explained by invoking steric interactions

Table 8. Selected distances (Å) and angles (°) for some $[M(L\text{–}L)_3]^{n-}$ (L–L = dithiolate) complexes

Complex	M–S	S···S (intra)	S···S (inter)	S–C	ψ*	S–M–S (bite)	Ref.
$[Tc(bdt)_3]^-$	2.336(5)	3.061(9)	3.07(2)	1.727(3)	2.3	81.8(1)	This work
$[Mo(bdt)_3]$	2.367(4)	3.110(5)	3.09(1)	1.73(1)	21.4	82.1(3)	33
$[Nb(bdt)_3]^-$	2.441(5)	3.150(5)	3.23(2)	1.74(1)	22.4	80.4(1)	28
$[V(S_2C_2Ph_2)_3]$	2.337(3)	3.059(5)	3.07(7)	1.69(1)	0	81.6(1)	34
$[Re(S_2C_2Ph_2)_3]$	2.32(1)	3.032(10)	3.05(1)	1.69(2)	0	81.5(3)	35

* ψ = Mean dihedral angle between the normals to the MS_2 and ligand planes.

between the bulky phenyl groups. The present observation of coplanarity in the presence of $SC_6H_4S^{2-}$ ligands, and incidentally in the trigonal-prismatic complex $[Tc(NHC_6H_4\text{-}S\text{-}o)_3]$[6] with a mean TcNS and $NHC_6H_4S^{2-}$ dihedral angle of 4.4°, indicates that the bent ligand configuration is not necessarily a significant factor in stabilising trigonal-prismatic geometry.

The interligand S···S distances (Table 6) are in the range 2.979(3)—3.151(3) Å [mean 3.07(2) Å] and are significantly less than the sum of the van der Waals radii (3.7 Å).[36] These distances are similar to those found in other trigonal-prismatic complexes (Table 8), and such close contacts have been taken to indicate the presence of inter-donor-atom bonding forces which help stabilise trigonal-prismatic co-ordination over the alternative octahedral geometry.[37]

There are no unusually short interionic contacts in the structure, and the $[AsPh_4]^+$ cation has the conformation generally observed in other structures.[26,27]

Conclusions

Of the two tris-bidentate complexes reported here, the $[Tc(ox)_3]^{2-}$ anion has the more usual distorted octahedral geometry, while the $[Tc(bdt)_3]^-$ anion has the less common trigonal-prismatic co-ordination. Apart from three unusual complexes,[8] all known trigonal-prismatic structures contain sulphur (or selenium) donor atoms.[8,30] Also all the known doubly charged anionic tris-bidentate complexes are either octahedral or twisted between the two limiting geometries due to significant ligand–ligand repulsions.[8,30] Therefore, it is not surprising that $[Tc(ox)_3]^{2-}$ is as close to the ideal octahedral configuration as the ligand constraints allow. We note that this is the first report of octahedral geometry observed in a tris-bidentate complex of technetium.

In the case of $[Tc(bdt)_3]^-$, the observation of near-perfect trigonal-prismatic geometry is also consistent with known metal tris(dithiolato) structures.[8,30] However, considering the coplanar arrangement of ligand and MS_2 planes, the reasons why trigonal-prismatic geometry is preferred over the less sterically strained octahedral geometry remain elusive.

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