The Synthesis and Structure of a Technetium Nitride Cation and Tetrabromotechnetate(II) Anion in $[TcBr(N)(bipy)_2]_2[TcBr_4]$ (bipy = 2,2′-bipyridyl)

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Reaction of $[TcNBr_4]^-$ with excess of 2,2′-bipyridyl (bipy) in methanol gives *cis*-$[TcBr(N)(bipy)_2]^+$; in ethanol the same cation is generated together with the novel tetrahedral Tc^{II} tetrabromo anion $[TcBr_4]^{2-}$.

The co-ordination chemistry of technetium is currently attracting considerable attention owing to the optimal properties of this element for radionuclide imaging.[1] Recent developments in technetium chemistry have led to the development of a series of clinically viable radiopharmaceutical reagents.[2]

Many of these agents contain TcO^{3+} or TcO_2^+ moieties[1—3] and there is in general a comparatively limited range of Tc precursor cores available. Future expansion of the range of technetium-based radiopharmaceuticals available will be facilitated by the prior development of new technetium cores.

We have been investigating the co-ordination chemistry of the technetium(V) nitride core with a wide range of ligand systems. Here we report the synthesis of the *cis*-$[TcBr(N)(bipy)_2]^+$ cation (bipy = 2,2′-bipyridyl) accompanied under certain conditions by the tetrahedral Tc^{II} anion $[TcBr_4]^{2-}$.

Thus reaction of $[Bu^n_4N][TcNBr_4]^-$ (ref. 4) with an excess of bipyridyl in methanol gives the orange cation *cis*-$[TcBr(N)(bipy)_2]^+$ isolated as a tetraphenylborate salt in good yield. Elemental analyses, and ^1H n.m.r. and i.r. [$\nu(Tc{\equiv}N)$

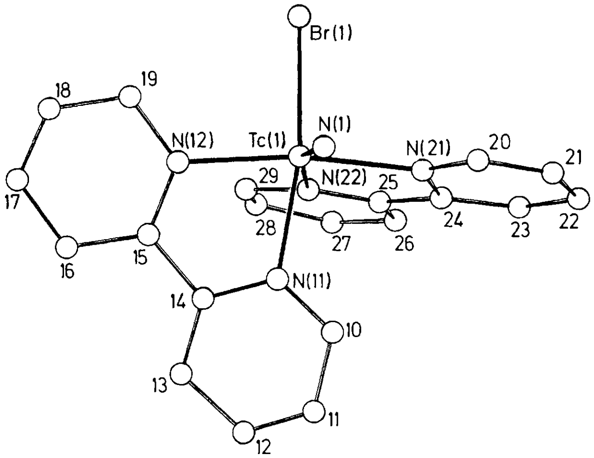

Figure 1. An ORTEP representation of the structure of one of the two virtually identical cations *cis*-$[TcBr(N)(bipy)_2]^+$ showing the atom-labelling scheme. Selected bond lengths (Å) and angles (°): Tc(1)–Br(1) 2.529(4); Tc(1)–N(1) 1.621(20); Tc(1)–N(11) 2.129(17); Tc(1)–N(2) 2.104(19); Tc(1)–N(21) 2.161(18); Tc(1)–N(22) 2.415(19); ∠N(1)–Tc(1)–Br(1) 102.2(7); N(11)–Tc(1)–N(1) 98.1(8); N(12)–Tc(1)–N(1) 103.8(9); N(21)–Tc(1)–Br(1) 91.6(5); N(21)–Tc(1)–N(11) 94.2(7); N(22)–Tc(1)–Br(1) 84.5(4); N(22)–Tc(1)–N(11) 78.1(6); N(22)–Tc(1)–N(21) 71.9(7); N(11)–Tc(1)–Br(1) 158.9(5); N(12)–Tc(1)–Br(1) 92.1(6); N(12)–Tc(1)–N(11) 77.1(7); N(21)–Tc(1)–N(1) 90.6(9); N(21)–Tc(1)–N(12) 164.0(7); N(22)–Tc(1)–N(1) 161.6(8); N(22)–Tc(1)–N(12) 93.0(7).

1062 cm^{-1}] spectra were consistent with the formulation $[TcBr(N)(bipy)_2][BPh_4]$ (**1**). However, when the reaction is carried out in absolute ethanol a deep red product (**2**) is produced [*i.r.*, ν(Tc≡N) 1050 cm^{-1}], which consistently failed to analyse as $[TcBr(N)(bipy)_2]Br$. Accordingly, a crystal structure determination was undertaken on suitable dark red crystals obtained from dichloromethane–methanol.†

The crystal structure revealed complex (**2**) to be *cis*-$[TcBr(N)(bipy)_2]_2[TcBr_4]\cdot0.5MeOH$. An ORTEP view of the structure of the two virtually identical cations and the anion are shown in Figures 1 and 2 together with selected bond lengths and angles.

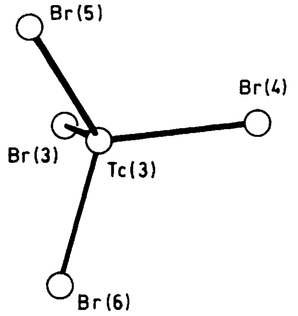

Figure 2. An ORTEP representation of the structure of $[TcBr_4]^{2-}$ showing the atom labelling. Selected bond lengths (Å) and angles (°): Tc(3)–Br(3) 2.399(4); Tc(3)–Br(4) 2.401(5); Tc(3)–Br(5) 2.417(4); Tc(3)–Br(6) 2.388(4); ∠Br(4)–Tc(3)–Br(3) 109.9(2); Br(5)–Tc(3)–Br(4) 106.1(2); Br(6)–Tc(3)–Br(4) 106.9(2); Br(5)–Tc(3)–Br(3) 112.1(2); Br(6)–Tc(3)–Br(3) 109.6(2); Br(6)–Tc(3)–Br(5) = 111.9(2).

The nitride cation exhibits distorted octahedral co-ordination about technetium, with the surprising feature that the nitride and bromide ligands are *cis*. This contrasts with the *trans* geometry found in the related complexes $[MNX(Ph_2PCH_2CH_2PPh_2)_2]^5$ and may reflect both the smaller bite angle exerted by the bipyridyl ligand and the steric difficulties of accomodating two bipyridyl ligands in the same place. The Tc≡N bond distances in the two independent cations are the same within experimental error at 1.609(20) Å. This lies within the range found for other Tc^V nitrido-complexes, *e.g.* $[TcN(S_2CNEt_2)_2]$ (1.604 Å),[6] $[TcNCl_4]^-$ [1.581(5) Å],[7] and $[TcN(MeCN)(SCN)_2(PPh_3)_2]$ (1.629 Å).[8] The two bipyridyl ligands are folded towards one another with a mean dihedral angle between the plane of the ligands of 70.8°. The strong *trans*-influence of nitride is reflected in lengthening of the Tc–N bond *trans* to the nitride ligand. Thus Tc(1)–N(22) is 2.415(19) Å compared to the other Tc–N distances for the bidentate ligands which lie in the range 2.106—2.159(18) Å.

The most unusual feature of the structure is the presence of the previously unreported tetrahedral $[TcBr_4]^{2-}$ counter-anion. The geometry is virtually completely regular tetrahedral with the Br–Tc–Br angles varying between 106.1(2) and 112.1(2)° [average value 109.4(2)°]. The Tc–Br bond lengths in the anion do not differ significantly from their mean value of 2.401(4) Å. This ion is isoelectronic and isostructural with the well known first row d^5 tetrahedral tetrahalometallate anions $[MnX_4]^{2-}$ and $[FeX_4]^-$ (X = halide). Second row transition metal analogues do not appear to have been previously structurally characterised. The mechanism of formation of the Tc^{II} anion is unclear and is at present under investigation together with the synthesis of other nitride-based technetium cations.

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† *Crystal data* for complex (**2**): monoclinic, space group $P2_1/c$, a = 9.143(2), b = 35.014(7), c = 15.581(3) Å, β = 105.96(2)°, U = 4795.7 Å^3, $F(000)$ = 2760, Z = 4, D_c = 1.590 g cm^{-3}, R = 0.0666. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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