Evidence for the Technetium(VI) Aquanitrido Cation $[\{TcN(OH_2)_3\}_2(\mu\text{-}O)_2]^{2+}$ in Solution: Preparation and Structure of $[\{TcN(S_2CNEt_2)\}_2(\mu\text{-}O)_2]$

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Electrophoretic and spectroscopic data together with the isolation and structural characterisation of $[\{TcN(S_2CNEt_2)\}_2(\mu\text{-}O)_2]$ provide evidence for the formation of the Tc^{VI} aquanitrido dimer $[\{TcN(OH_2)_3\}_2(\mu\text{-}O)_2]^{2+}$ in solutions of weakly co-ordinating acids.

The diamagnetic Mo^V aquaoxo cation $[MoO(OH_2)_3(\mu\text{-}O)_2MoO(OH_2)_3]^{2+}$ (abbreviated as $[Mo_2O_4]^{2+}$) is well established and has been the subject of many substitution studies.[1,2] Numerous complexes containing the $[Mo_2O_4]^{2+}$ core, and its thio analogues, have been prepared and structurally characterised.[3] The preparation and properties of the dimeric W^V aquaoxo cation, $[W_2O_4(OH_2)_6]^{2+}$, have recently been reported.[4] We now report evidence for the formation of the isoelectronic $Tc^{VI}N$ analogue, $[TcN(OH_2)_3(\mu\text{-}O)_2\text{-}TcN(OH_2)_3]^{2+}$ (abbreviated as $[Tc_2N_2O_2]^{2+}$), in solutions of

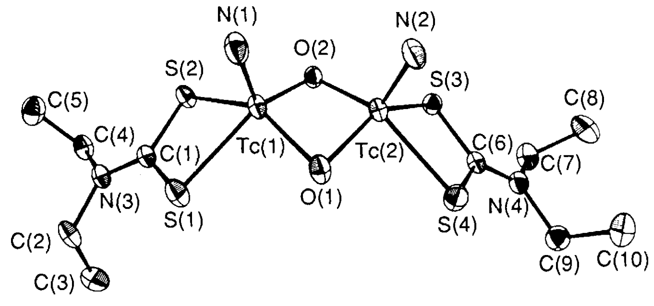


Figure 1. ORTEP diagram for [{TcN(S_2CNEt_2)}$_2$(μ-O)$_2$] (**2**) showing the 30% probability thermal ellipsoids. Distances (Å): Tc–Tc, 2.543(1); Tc(1)–S(1), 2.433(1); Tc(1)–S(2), 2.436(1); Tc(1)–N(1), 1.623(4); Tc(1)–O(1), 1.942(3); Tc(1)–O(2), 1.935(3); Tc(2)–S(3), 2.433(1); Tc(2)–S(4), 2.428(1); Tc(2)–N(2), 1.624(4); Tc(2)–O(1), 1.942(3); Tc(2)–O(2), 1.936(3). Angles (°): Tc(1)–O(1)–Tc(2), 81.8(1); Tc(1)–O(2)–Tc(2), 82.1(1); O(1)–Tc(1)–O(2), 94.7(1); O(1)–Tc(2)–O(2), 94.6(1); S(1)–Tc(1)–S(2), 72.2(1); S(3)–Tc(2)–S(4), 72.2(1).

weakly co-ordinating acids. The $[Tc_2N_2O_2]^{2+}$ ion is the first example of a transition metal nitrido cation containing only additional water and oxo ligands and is a further indication of the particular stability of the TcN core.

Substitution reactions of $[TcNCl_4]^-$ have generally resulted in reduction and the isolation of $Tc^{V}N$ complexes.[5] The $[Tc_2N_2O_2]^{2+}$ ion provides a general route for the preparation of $Tc^{VI}N$ complexes with a variety of ligands.

In a previous paper, we reported the hydrolysis of $Cs_2[TcNCl_5]$ to give a chloride-free brown precipitate of 'nitridotechnetic(VI) acid' (**1**).[6] Dissolution of (**1**) in 1 M toluene-*p*-sulphonic acid (Hpts), CF_3SO_3H, or $MeSO_3H$ gave, on standing for *ca.* 1/2 h, air-stable yellow solutions. Paper electrophoresis (600 V for 30 min, 0.5 M acid as the electrolyte) showed the presence of a single cationic species and the absence of neutral and anionic species. The yellow solutions in 1 M Hpts, CF_3SO_3H, or $MeSO_3H$ ([Tc] = 2 × 10^{-3} M) exhibited no ESR signals when frozen to 130 K. Addition of conc. HCl (1 : 1) to these solutions resulted in the appearance of signals due to $[TcNCl_4]^-$ and corresponding to all of the Tc present.

Addition of 1.5 equivalents of $NaS_2CNEt_2 \cdot 3H_2O$ in 1 M K_2HPO_4 to the yellow solution of (**1**) in 1 M Hpts, extraction with CH_2Cl_2, and silica gel chromatography with CH_2Cl_2 as eluent, gave the yellow dimer [{$Tc^{VI}N$(S_2CNEt_2)}$_2$(μ-O)$_2$] (**2**) (37% yield) together with the known [$Tc^{V}N$(S_2CNEt_2)$_2$] (15% yield). Elemental analysis and the IR spectrum [1061 vs and 1053 m (Tc≡N) and 703 m cm^{-1} (*asym* Tc–O–Tc)] were consistent with the di-(μ-O) structure (**2**), which was confirmed by a single-crystal *X*-ray structure determination.†

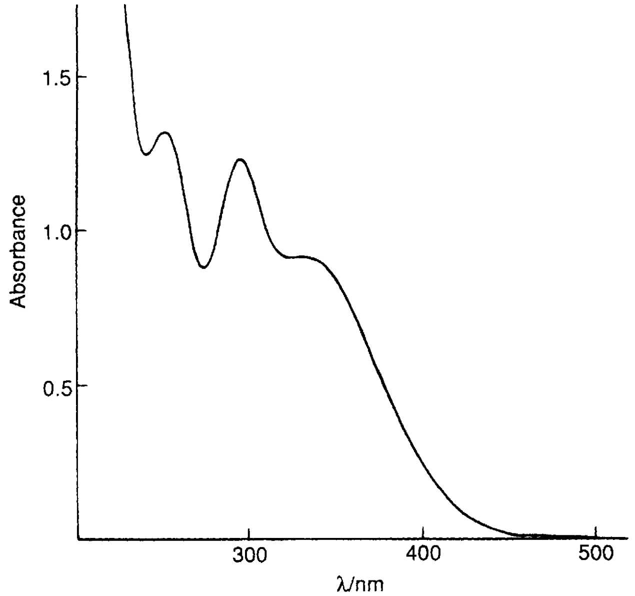
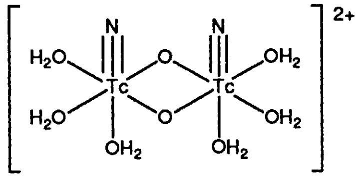


Figure 2. UV-VIS spectrum of 5 × 10^{-4} M [{TcN(OH_2)$_3$}$_2$(μ-O)$_2$]$^{2+}$ in 1 M CF_3SO_3H.



(4)

Complex (**2**) (Figure 1) is isostructural with the $Mo^{V}O$ analogue, [{MoO(S_2CNEt_2)}$_2$(μ-O)$_2$] (**3**)[7] and the geometry is best described as two square pyramids sharing an edge. The Tc≡N distances are identical at 1.623(4) and 1.624(4) Å and the Tc–Tc distance of 2.543(1) Å is similar to the Mo–Mo distance of 2.580(1) Å in (**3**). The short Tc–Tc distance and the acute Tc(1)–O(1)–Tc(2) and Tc(1)–O(2)–Tc(2) angles of 81.8(1) and 82.1(1)° indicate a direct metal–metal interaction. Complex (**2**) is the *syn*-isomer, with a dihedral angle of 150.8(3)° between the O(1), Tc(1), O(2) and O(1), Tc(2), O(2) planes. The Tc atoms are situated 0.65 Å above the corresponding S_2O_2 basal planes.

The isolation of (**2**) and the absence of ESR signals from solutions of (**1**) in the 1 M weakly co-ordinating acids are consistent with the diamagnetic di-(μ-oxo) structure (**4**) for $[Tc_2N_2O_2]^{2+}$. In view of the strong *trans*-influence of the nitrido ligand, it is likely that the *trans* water ligands are only weakly bound. The UV-VIS spectrum of $[Tc_2N_2O_2]^{2+}$ in 1 M CF_3SO_3H (Figure 2) shows maxima at λ 295 nm (ε = 250 mol^{-1} m^2 per dimer) and 251 (266) which correspond closely to the absorptions at λ 295 (ε 355) and 255 (432) reported for $[Mo_2O_4]^{2+}$.[8]

We note the analogy of $Mo^{V}O$ cores with the isoelectronic $Tc^{VI}N$ cores as exemplified by $[Mo_2O_4]^{2+}$ and $[Tc_2N_2O_2]^{2+}$. The $[Tc^{VI}N\text{–}O\text{–}Tc^{VI}N]^{4+}$ analogue of the $[Mo^{V}{}_2O_3]^{4+}$ core has been established crystallographically in the cyclic tetramer $(AsPh_4)_4[Tc_4N_4(O)_2(ox)_6]$ (ox = oxalate).[9] Recently, the Tc^{VII} nitridoperoxo complexes $AsPh_4[TcN(O_2)_2X]$ (X = Cl or Br) and [TcN(O_2)$_2$(LL)] (LL = 2,2′-bipyridyl or 1,10-phen-

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† *Crystal data* for (**2**): $C_{10}H_{20}N_4O_2S_4Tc_2$, *M* = 554.35, triclinic, space group $P\bar{1}$, *a* = 8.069(2), *b* = 9.224(2), *c* = 14.017(3), α = 107.77(2), β = 102.05(2), γ = 93.80(2)°, *U* = 962.1 $Å^3$, *Z* = 2. Intensity data were measured at 296(1) K with nickel-filtered Cu-K_α radiation (λ = 1.5418 Å) on an automatic Siemens AED diffractometer. The crystal had well developed faces of type (100), (001), and (010) with perpendicular distances between faces of 0.304, 0.126, and 0.168 mm, respectively. The structure was solved by the heavy-atom method, and full-matrix least-squares refinement with SHELX-76 converged with *R* = 2.81 and R_W = 3.45 for 3117 observed terms [$I > 2\sigma(I)$]. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Data Centre. See Notice to Authors, Issue No. 1.

anthroline) have been prepared, which are isoelectronic (or pseudo-isoelectronic) with the corresponding $M^{VI}O(O_2)_2$ (M = Cr, Mo, W) complexes.[10]

We are currently investigating substitution reactions of $[Tc_2N_2O_2]^{2+}$ with a variety of ligands.

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