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A Dissymmetric μ-oxo Technetium Complex

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While oxo-bridged binuclear complexes are fairly common 'thermodynamic sinks' in the chemistry of transition metal ions, they usually form spontaneously in a symmetric fashion [1]. In developing the chemistry of technetium with a view toward improved radio-imaging agents for diagnostic use [2, 3], we have uncovered a family of stable, dissymetric, neutral complexes, which form upon allowing common technetium starting materials to stand for long periods in neat solutions of common pyridine derivatives.

We have recently reported on a series of Tc^V compounds with amine [4], imidazole [5] and pyridine [6] ligands, which generally yield complexes of the type, *trans*-$[O_2L_4Tc]^+$, where L is a sterically unhindered nitrogen ligand. When pyridine derivatives with electron-withdrawing substituents are used in alcoholic solvents, compounds with the general formulation *trans*-$[O(RO)X_2(pyr)_2Tc]$ result, where X = Cl or Br and RO = $-OCH_3$ or $-OCH_2CH_3$ [7]. In this work the synthesis of $[Cl(Pic)_4Tc-O-Tc(Pic)Cl_4]\cdot H_2O$* is reported together with a crystal and molecular structure determination. The solid state infrared spectra, magnetic properties and electrochemical and spectroscopic behavior of this complex in solution are also described.

Results

The compound, $[Cl(Pic)_4Tc-O-TcCl_4Pic]\cdot H_2O$, could be readily synthesized from almost any common technetium starting material including: $(NH_4)TcO_4$ with $NaBH_4$, $(NH_4)_2TcCl_6$, $[(n\text{-}Bu)_4N](TcOCl_4)$, and $[O_2(Pic)_4Tc]Cl$ by refluxing in neat picoline. The reaction proceeds with the production of *trans*-$[O_2(pic)_4Tc]^+$, which may be an intermediate. Upon continued heating a mixture of neutral complexes appears with $[Cl(Pic)_4Tc-O-TcCl_4Pic]\cdot H_2O$ eventually predominating. Precipitation was effected by addition of water and crystals were obtained from chloroform. *Anal.* for $Tc_2O_2C_{30}H_{37}N_5Cl_5$. Calc. (found): C, 41.19(42.71); H, 4.26(4.51); N, 8.01(7.75); Cl, 20.3(20.5); Tc, 22.6(22.5).

The compound was insoluble in water but soluble in common organic solvents. Conductance measurements in acetone (see Fig. 1) revealed conductivities substantially below those of the comparison compound, sodium tetraphenylborate, and only slightly above those of the nonionic ferrocene or the solvent alone. Solutions of the complex in ethanol passed quickly through both cation (Biorex 70 and Sephadex CM 25) and anion (Sephadex DEAE) ion exchange columns. Dissolution in DMF did not alter the pH of the solution.

The compound appeared stable in the various organic solvents and exhibited no spectral change

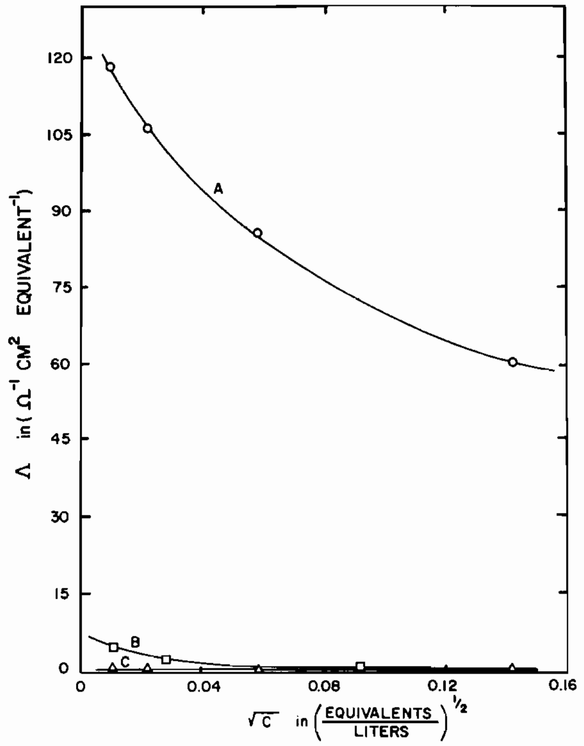

Fig. 1. Conductance measurements of: (a) sodium tetraphenylborate, (b) $[Cl(Pic)_4Tc-O-TcCl_4(Pic)]$, and (c) ferrocene.

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*aghij-pentachloro-μ-oxo-*bcdek*-pentakis(4-methylpyridine)ditechnetium monohydrate.

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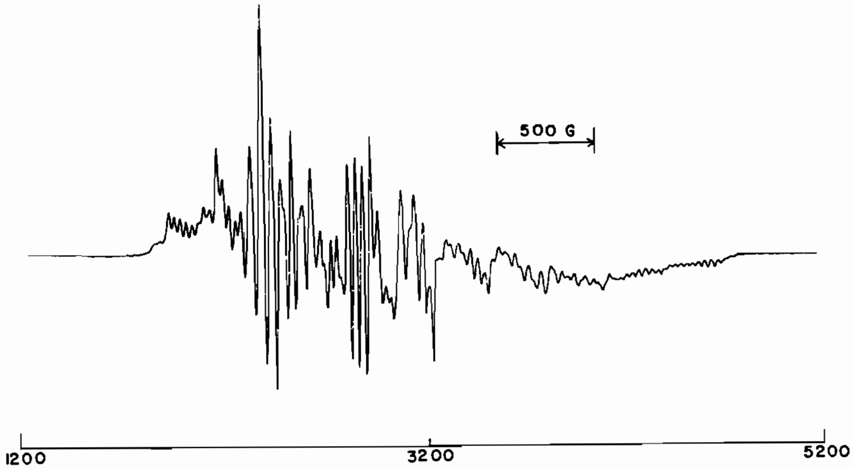

Fig. 2. EPR spectrum of $[Cl(Pic)_4Tc{-}O{-}TcCl_4(Pic)]$ in $CHCl_3$ at −173 °C.

in ethanol over a period of hours. Its spectra in ethanol is (λ,ϵ): 251 nm (2.5×10^4 M^{-1} cm^{-1}); 360 nm (1.3×10^4 M^{-1} cm^{-1}); 406 nm (2.3×10^4 M^{-1} cm^{-1}); 505 nm (0.37×10^4 M^{-1} cm^{-1}). The compound exhibits Tc–Cl stretching modes at 319 cm^{-1} and 306 cm^{-1} and a probable Tc–O–Tc stretch at 699 cm^{-1}.

Magnetic susceptibility measurements yielded an effective magnetic moment around 1.1 β, when corrected for the diamagnetic contributions of the metal core electrons and ligands. Solid state EPR signals were severely broadened and barely observable at room temperature, while at −170 °C the signal remained broad, but was easily observable. An ESR spectrum of the compound in a frozen $CHCl_3$ matrix (Fig. 2) exhibited a complicated pattern, which is probably attributable to an axial signal split strongly by the 9/2 spin on one Tc and less strongly by a second Tc.

Cyclic voltammetry (CV) in DMF revealed two nearly reversible (on the CV time scale) electron transfer processes (see Fig. 3); however, irreversible chemical change was immediately evident in acetonitrile. Formal reduction potentials as determined in 0.1 M $(Et_4N)ClO_4$ in DMF (corrected *vs.* NHE) at room temperature are: 0.74 and −0.74 V. Peak separations ($\Delta E_{pc,pa}$) were similar to those of the ferrocene internal standard at the same scan rate and approached 59 mV at slow scan rates. Peak heights essentially identical with equimolar solutions of ferrocene indicate the couples to involve the transfer of a single electron. The couples appeared to be both chemically and electrochemically reversible at relatively fast scan rates. However, subsequent scans revealed new current peaks to grow in around 0.4 and −0.3 V. These processes also fulfilled the criteria for an electrochemically reversible couple on the CV time scale with nearly equal anodic and cathodic current peaks.

Single crystals obtained by crystallization from acetone and then chloroform were found to be in the monoclinic space group, *P*2_1/*c*. Unit cell cons-

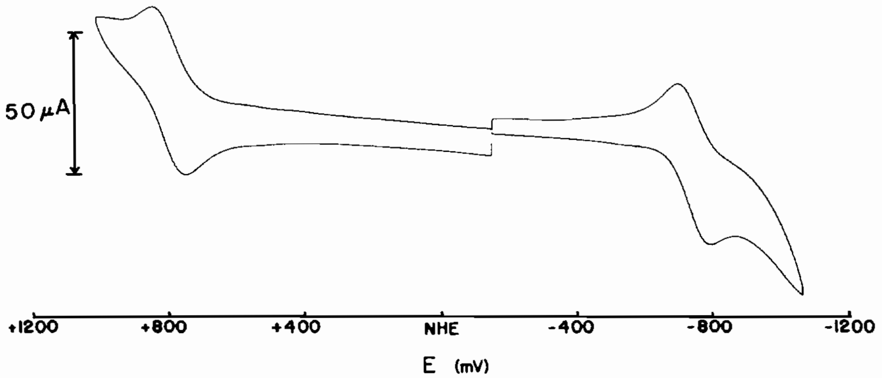

Fig. 3. Cyclic voltammetric scan of $[Co(Pyr)_4Tc{-}O{-}TcCl_4(Pyr)]$ in 0.1 M $(Et_4)ClO_4$ in DMF at room temperature.

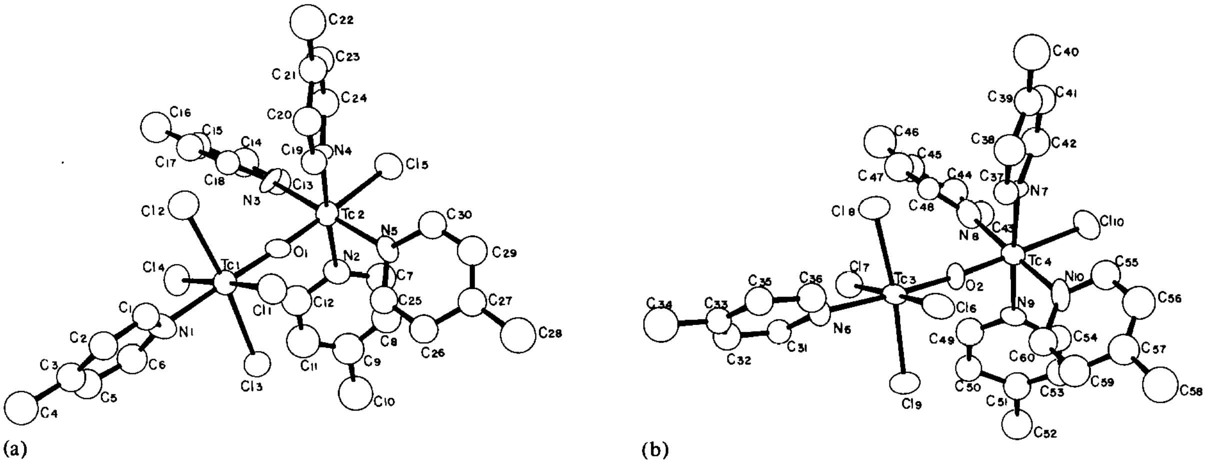

Fig. 4. ORTEP diagrams of the two independent molecules of [Cl(Pic)$_4$Tc–O–TcCl$_4$(Pic)] in the unit cell. Thermal ellipsoids are given at 50% probability for Tc, Cl, O and N atoms. Carbon atoms are isotropic at 50% probability.

tants are $a = 11.709(4)$, $b = 20.243(8)$, $c = 33.41(2)$ Å, $\beta = 91.00(5)°$, $V = 7918(7)$ Å^3 and $Z = 8$. Overall unweighted and weighted R factors for the structure are 0.096 and 0.103, respectively. A Table containing the atomic coordinates of the atoms in the asymmetric unit is available, see 'Supplementary Material'. While the precision of the structure does not allow subtle effects to be seen, the essential features are well delineated. Figures 4a and 4b are computer drawn models of the two independent molecules of [Cl(Pic)$_4$Tc–O–TcCl$_4$(Pic)]. Although crystallographically unique, the two molecules are essentially equivalent with each molecule having two technetium atoms bridged by an oxygen atom. The bond distances and angles surrounding the essentially octahedral technetium atoms are listed in Tables I and II, respectively. The Tc–O bond distances are nearly the same (average 1.82(3) Å) with the Tc–O–Tc substructure being almost linear (average bond angle 176(2)°). The average axial and equatorial Tc–N distances are 2.20(3) Å and 2.15(2) Å, respectively. Average axial and equatorial Tc–Cl distances are 2.39(1) Å and 2.37(1) Å, respectively.

The two metal atoms are in pseudo-octahedral environments, which are nearly inverse with respect to one another. One technetium is in the plane of four equatorial γ-picoline ligands, and has an axial chlorine atom opposite the bridging oxygen. The second technetium has an axial picoline ligand and four equatorial chlorine atoms, which are bent slightly back from the Tc due to steric crowding by the opposite picoline ligands. These technetium atoms are displaced 0.10 Å from the mean plane of the chlorines toward the bridging oxygen.

The closest contact between the ligand plane on one molecule with that on a second molecule is between the ring associated with N5 and that of a symmetry related ring associated with N9. These planes are nearly parallel (within 1.9°) and have closest contacts of 3.5 Å; however, the overlap

TABLE I. Bond Distances[a] in the Technetium Coordination Spheres of [Cl(Pic)$_4$Tc–O–TcCl$_4$(Pic)]

Bond type	Distance (Å)	Bond type	Distance (Å)	Bond type	Distance (Å)
Tc1–O1	1.84(1)	Tc2–N5	2.13(2)	Tc1–Cl3	2.36(1)
Tc2–O1	1.79(1)	Tc3–N6	2.22(2)	Tc1–Cl4	2.36(1)
Tc3–O2	1.83(1)	Tc4–N7	2.15(2)	Tc2–Cl5	2.39(1)
Tc4–O2	1.80(1)	Tc4–N8	2.15(2)	Tc3–Cl6	2.38(1)
Tc1–N1	2.18(2)	Tc4–N9	2.14(2)	Tc3–Cl7	2.37(1)
Tc2–N2	2.17(2)	Tc4–N10	2.10(2)	Tc3–Cl8	2.37(1)
Tc2–N3	2.15(2)	Tc1–Cl1	2.37(1)	Tc3–Cl9	2.36(1)
Tc2–N4	2.18(2)	Tc1–Cl2	2.38(1)	Tc4–Cl10	2.39(1)

[a] The numbers in parentheses are the estimated standard deviations.

TABLE II. Bond Angles[a] in the Technetium Coordination Spheres of [Cl(Pic)$_4$Tc–O–TcCl$_4$(Pic)]

Bond type	Angle (°)	Bond type	Angle (°)	Bond type	Angle (°)
O1–Tc1–N1	178.1(7)	N2–Tc2–N4	177.2(7)	Cl7–Tc3–Cl8	89.9(4)
O1–Tc1–Cl1	92.9(5)	N2–Tc2–N5	87.0(8)	Cl7–Tc3–Cl9	89.1(4)
O1–Tc1–Cl2	94.3(6)	N2–Tc2–Cl5	88.2(6)	Cl8–Tc3–Cl9	173.0(2)
O1–Tc1–Cl3	92.7(5)	N3–Tc2–N4	92.4(7)	O2–Tc4–N7	91.1(7)
O1–Tc1–Cl4	90.2(5)	N3–Tc2–N5	176.1(7)	O2–Tc4–N8	90.6(7)
N1–Tc1–Cl1	87.6(5)	N3–Tc2–Cl5	88.4(5)	O2–Tc4–N9	91.8(7)
N1–Tc1–Cl2	87.5(6)	N4–Tc2–N5	90.9(7)	O2–Tc4–N10	91.2(8)
N1–Tc1–Cl3	85.5(6)	N4–Tc2–Cl5	89.8(6)	O2–Tc4–Cl10	178.6(5)
N1–Tc1–Cl4	89.1(5)	N5–Tc2–Cl5	89.5(6)	N7–Tc4–N8	92.3(7)
Cl1–Tc1–Cl2	90.2(4)	O2–Tc3–N6	176.6(7)	N7–Tc4–N9	177.1(8)
Cl1–Tc1–Cl3	89.4(4)	O2–Tc3–Cl6	90.6(6)	N7–Tc4–N10	88.5(7)
Cl1–Tc1–Cl4	176.7(3)	O2–Tc3–Cl7	92.4(5)	N7–Tc4–Cl10	89.0(5)
Cl2–Tc1–Cl3	173.0(3)	O2–Tc3–Cl8	93.4(5)	N8–Tc4–N9	88.5(8)
Cl2–Tc1–Cl4	90.5(4)	O2–Tc3–Cl9	93.6(5)	N8–Tc4–N10	178.0(7)
Cl3–Tc1–Cl4	89.5(4)	N6–Tc3–Cl6	88.2(6)	N8–Tc4–Cl10	88.0(6)
O1–Tc2–N2	91.9(7)	N6–Tc3–Cl7	88.8(6)	N9–Tc4–N10	90.7(7)
O1–Tc2–N3	89.5(7)	N6–Tc3–Cl8	83.5(5)	N9–Tc4–Cl10	88.1(6)
O1–Tc2–N4	90.1(7)	N6–Tc3–Cl9	89.6(5)	N10–Tc4–Cl10	90.1(6)
O1–Tc2–N5	92.6(7)	Cl6–Tc3–Cl7	177.0(3)	Tc2–O1–Tc1	177.1(9)
O1–Tc2–Cl5	177.9(5)	Cl6–Tc3–Cl8	90.0(4)	Tc4–O2–Tc3	175.7(9)
N2–Tc2–N3	89.6(8)	Cl6–Tc3–Cl9	90.6(4)		

[a] The numbers in parentheses are the estimated standard deviations in the least significant figure.

between the rings extends only to a single *meta*-carbon on each ring.

Discussion

The elemental analysis, ion-exchange behavior, rapid solubility and nonconductivity in low-dielectric, aprotic solvents are consistent with this compound's being formulated as a neutral species. Excluding the unlikely possibility that the water of hydration in the crystal structure is actually a hydroxide or hydronium ion, the lack of a counterion in the crystal structure verifies this to be a neutral molecule. Early Russian workers [8] had alluded to the appearance of similar dark crystalline materials on allowing *trans*-[O$_2$(Pyr)$_4$Tc]$^+$ to stand in neat pyridine for extended periods and it is likely that these are similar, if not identical, to those reported here.

The electrochemical measurements indicate that this complex can be oxidized or reduced by a single electron. While these couples appear to be nearly chemically reversible on the relatively rapid cyclic voltammetric time scale in nonaqueous media, subsequent chemical changes take place fairly quickly to produce species that are more easily oxidized and reduced.

It is remarkable that this μ-oxo complex forms by spontaneous 'self-assembly' and exhibits two such dissimilar metal centers with no mirror plane between them. Otherwise, the structure of [Cl(Pic)$_4$Tc–O–TcCl$_4$(Pic)] is similar to that commonly observed for μ-oxo complexes in that the average Tc–O bond distance of 1.82 Å is significantly shorter than that observed for a Tc–O single bond (2.02 Å [5, 9]) and the metal–oxygen–metal moiety is essentially linear [10]. This linearity and the relatively short Tc–O bonds suggest partial π-bonding with the μ-oxo bridge and make it improbable that the bridge involves hydroxide. Hydroxo-bridged species are usually strongly bent and exhibit M–O bond distances similar to those of single bonds [9–11]. The Tc–N and Tc–Cl bond distances are well within the range observed in a variety of other technetium complexes [2, 5] with the μ-oxo exhibiting a small *trans*-influence on the axial ligands. The staggered arrangement of the chloride and picoline ligands together with the substantial distance (3.64 Å) between the two technetiums precludes significant metal–metal bonding.

If standard conventions are followed, a 7+ charge must be distributed between the two technetiums. Given their coordination spheres, it seems likely that both are in mid but unequal oxidation states, *i.e.* between Tc(II) and Tc(V). This leads to probable formulations of the binuclear species as either [Tc(II)–Tc(V)] or [Tc(III)–Tc(IV)], with the ion in the lower oxidation state probably coordinating the greater number of pyridine ligands. ESCA studies are now underway to aid in oxidation state assignments.

Distribution of this 7+ charge over two Tc atoms requires that there also be seven d-electrons in the molecule. In a magnetically dilute solid these odd-electron compounds should yield a significant magnetic moment; however, the small value of μ_{eff} observed indicates the presence of only one unpaired electron strongly affected by spin–orbit coupling. The solid state EPR spectra further verify that these compounds are paramagnetic.

The frozen solution EPR spectra is complicated and interpretation not yet complete; however, it is clear that there is unequal coupling from two technetium ($I = 9/2$) nuclei. Interaction with both metal atoms verifies the compound to be dinuclear in solution and the large difference in the degree of coupling indicates the odd electron to be more localized at one center as would be expected in a dissymetric compound.

Supplementary Material

A Table of atomic coordinates is available from the authors on request.

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