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Synthesis and Characterization of Tetrabutylammonium *trans*-Bis(2-amidobenzenethiolato(2−)-*S*,*N*)oxotechnetate(V) and its Reduction by 2-Aminobenzenethiol

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Abstract

The synthesis and characterization of the complexes $(n\text{-Bu}_4\text{N})^+[\text{Tc}^{\text{V}}\text{O(adt)}_2]^-$ (**1**) and $[\text{Tc}^{\text{III}}(\text{abt})_3]$ (**2**) (abt = 2-aminobenzenethiol(1−); adt = 2-amidobenzenethiol(2−)) are presented. A single-crystal X-ray structure determination of **1** is also reported. Crystals are orthorhombic, space group $P2_12_12_1$, with $a = 17.113(6)$, $b = 15.573(5)$, $c = 11.677(4)$ Å and $Z = 4$. The coordination geometry of technetium is distorted square pyramidal with the apical Tc=O bond of length 1.73(2) Å. The Tc–S and Tc–N bond distances average 2.30(1) and 2.08(2) Å, respectively. The dihedral angle between the two benzene rings is 34.1°.

Introduction

The importance of the metastable isomer $^{99\text{m}}$Tc ($\gamma = 140$ keV, $t_{1/2} = 6$ h) in the practice of nuclear medicine has led to intensive studies of the basic chemistry of this element using macroscopic quantities of the long-lived radionuclide ^{99}Tc, a β^- emitter ($t_{1/2} = 212000$ years). A significant portion of this work has been directed toward the synthesis of kinetically stable complexes that can be prepared easily in aqueous media by the reduction of the pertechnetate ion in the presence of a suitable ligand. Previous work has demonstrated that there is a diverse chemistry associated with oxotechnetium(V) centers [1–5].

From the literature data there appears to be two categories of Tc(V)=O bond lengths [6]. The first occurs in complexes containing the TcO_2^+ core, where the range of observed bond distances is 1.71 to 1.75 Å. The second category occurs when there is a single Tc=O linkage, and here the range of observed values is 1.61 to 1.67 Å. The difference between the two average values was explained [6] on the basis that a single oxo ligand is less effective at neutralising the charge of the Tc(V) metal center than are two oxo ligands, and will therefore be drawn more closely to the technetium. Within the series of five-coordinate TcO^{3+} complexes, the Tc=O bond length increases with increasing ability of the ancillary ligands to donate negative charge, in line with simple electrostatic considerations.

As an extension of our studies on the factors that decrease the technetium–oxo bond order in anionic monoxotechnetium(V) complexes, we prepared the complex tetrabutylammonium *trans*-bis(2-amidobenzenethiolato(2−)-*S*,*N*)oxotechnetate(V), in which a longish Tc=O bond length was found. We considered this long bond length as indicative of the partial labilization of the oxo ligand in the title complex, due to the increased covalent interaction and electron transfer to the technetium ion in the planar region. This approach led to the isolation of tris(2-aminobenzenethiolato(1−)-*S*,*N*)technetium(III), which was obtained by the reaction of the title complex with 2-aminobenzenethiol (abt) in acidic aqueous solution.

Experimental

Ammonium [^{99}Tc] pertechnetate was supplied by the Oak Ridge National Laboratory. All other chemicals were obtained from E Merck, Darmstadt, Germany.

Syntheses

$(n\text{-Bu}_4\text{N})\text{TcO(adt)}_2$

2.2 cm^3 of a 0.362 mol dm^{-3} NH_4TcO_4 solution (8.15×10^{-4} mol) were added to 3×10^{-3} mol of 2-aminobenzenethiol in 50 cm^3 of a 0.6 mol dm^{-3} sodium hydroxide solution under vigorous stirring at

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room temperature. A freshly prepared solution of 0.45 g $Na_2S_2O_4$ in 10 cm^3 of a 0.6 mol dm^{-3} NaOH solution was rapidly added to the reaction mixture, followed by the addition of 2 cm^3 of a saturated aqueous solution of n-Bu_4NCl. After 5 min of stirring the suspension was filtered, and the solids were washed with a few cm^3 of the hydroxide solution and distilled water.

The crude precipitate was extracted three times with 5 cm^3 portions of acetone. The combined filtered extracts were mixed with 5 cm^3 of water and stored for 24 h at −12 °C. The resulting dark red crystals were filtered, washed with water, and dried on a vacuum line. Yield = 77%. *Anal.* Calc. for $TcC_{28}H_{46}N_3OS_2$: C, 55.70; H, 7.68; N, 6.96. Found: C, 55.55; H, 7.61; N, 7.21%.

Tc(abt)₃

To 70 mg of (n-Bu_4N)TcO(adt)$_2$ in 30 cm^3 of a 0.2 mol dm^{-3} HCl solution was added a threefold excess of 2-aminobenzenethiol under nitrogen. The dark red solution was kept at room temperature for 3 h, after which a green solution was formed. This solution was extracted with 20 cm^3 chloroform, and the chloroform extract was washed twice with 0.06 mol dm^{-3} HCl and dried over anhydrous sodium sulphate. The chloroform was evaporated to about 10 cm^3 under nitrogen, and was left at room temperature with the formation of lime-green crystals, which were separated and dried under vacuum. Yield = 62%. *Anal.* Calc. for $TcC_{18}H_{18}N_3S_3$: C, 45.85; H, 3.85; N, 8.91. Found: C, 45.63; H, 3.91; N, 8.73%.

Crystallography

Details of the crystal data of (Bu_4N)TcO(adt)$_2$, measurement of intensities and data processing are summarized in Table I. The structure was solved by Patterson and Fourier techniques and refined by least-squares methods. Since observed reflections were limited in number (crystal of poor quality, high thermal motion and some disorder in the tetrabutylammonium cation), anisotropic thermal parameters were assigned only to the Tc and S atoms and the two phenyl rings were treated as rigid groups. See also 'Supplementary Material'.

The *R* factor reached in this structure determination is not very low, but we think that the molecular positional parameters are well defined; we are especially interested in the 'inner coordination core' of the technetium, where the errors are surely lower.

Spectra

Infrared spectra of solid samples (as KBr discs) were recorded on a Beckman IR 4250 spectrophotometer in the range 4000–250 cm^{-1}.

TABLE I. Crystallographic Data, Data Processing and Refinement Procedure Information of (n-Bu_4N)Tc(adt)$_2$

Formula; *M*	$[TcO(NHC_6H_4S)_2]^-(C_4H_9)_4N^+$; 603.7
System; space group	Orthorhombic; $P2_12_12_1$
Cell parameters	a = 17.113(6); b = 15.573(5); c = 11.677(4) Å
V; D_x; Z; $F(000)$; μ(Mo Kα)	3111.9(1.9) $Å^3$; 1.29 g cm^{-3}; 4; 1272; 6.0 cm^{-1}
Diffracrometer; scan mode; λ	Philips PW1100; ω–2θ; 0.7107 Å
Scanning range for 2θ	$3 \leq 2\theta \leq 40°$
Scan width; scan speed; background time	1.20°; 0.03° s^{-1}; 20 s
Total no. of independent reflections	1694
No. above three e.s.d.s	1096
Weighting scheme	$w = 1$
Function minimized	$\Sigma w(\|F_o\| - \|F_c\|)^2$
No. of parameters	132 (phenyl rings as rigid groups and anisotropy only for Tc and S)
Final $R = \Sigma(\|F_o\| - \|F_c\|)/\Sigma\|F_o\|$	0.094
Peaks in the final Δ*F*	None greater than 0.8 e $Å^{-3}$
Programs package	SHELX-76 system [19]

Results

Pertechnetate reacts with 2-aminobenzenethiol in alkaline aqueous solution, using sodium dithionite as reducing agent, to yield the complex (n-Bu_4N)TcO(adt)$_2$, a red crystalline solid. Magnetic susceptibility measurements of this compound revealed it to be diamagnetic, in accordance with the d^2 spin-paired electron configuration. This compound also appears to be indefinitely stable in the solid state, and it is soluble in Me_2CO, $CHCl_3$, MeOH and $MeNO_2$.

Molecular Structure of (n-Bu₄N)TcO(adt)₂

The structure contains well separated $TcO(NHC_6H_4S)_2^-$ anions and Bu_4N^+ counter cations and it confirms the square pyramidal geometry typical of transition metal complexes of the type [MO(bidentate)$_2$] [7a]. The basal plane of the pyramid is formed by N_2S_2 atoms, with the oxo ligand occupying the apical position and the technetium atom lying 0.72 Å above the basal plane towards the apex. A comparison of some structural parameters in other [MO(bidentate)$_2$] complexes allows one to note the following features [1, 2, 8–12]:

(i) the displacement of the metal atom M from the basal plane is in a narrow range between 0.64 Å in $[OsO(OCH_2CH_2O)_2$ [8] and 0.83 Å in $[MoO(S_2CNPr_2)_2]$ [9];

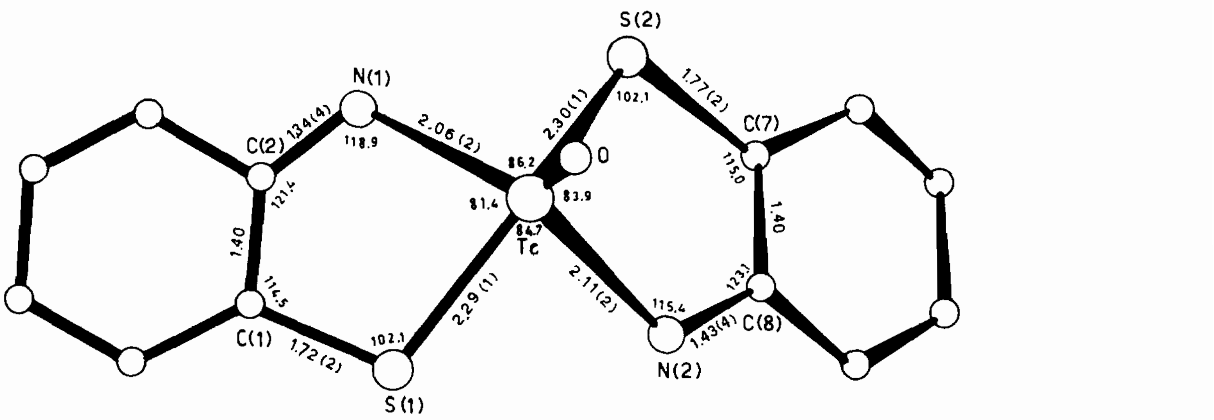

Fig. 1. Bond distances (Å) and angles (°) in the 'inner core' of the $[TcO(NHC_6H_4S)_2]^-$ anion, viewed along the *a* axis.

(ii) the four iMj bond angles, subtended by the bidentate ligands, are between 104.8 and 112.8°;

(iii) the 'normalized bite' $b = 2\sin(iMj/2)$ [7b] is comprised between 1.18 [9] and 1.38 in $[VO(MeCOCHCOMe)_2]$ [10].

In the present complex the iTcj angles are 107.4, 109.8, 107.5 and 110.6°, the large angles being in all cases a consequence of the electronic repulsion of the strongly π-donating oxo ligand upon the basal donor set atoms.

Bond lengths and angles in the $TcON_2S_2$ inner core are given in Fig. 1. An interesting phenomenon of this structure determination is the unusually long Tc–O bond length of 1.73(2) Å, which is 0.07 Å outside the previous range typically found for similar monoxotechnetium(V) compounds.

There is nothing further remarkable about the bond lengths and angles within the ligands and the tetrabutylammonium cation, although, owing to the paucity of the diffraction data and the high thermal motion, this part of the model has been poorly refined. No further attempts have been made to improve the model, since the aim of the structure analysis had been achieved.

A comparison of the Tc–S and Tc–N distances of $[Tc^{V}O(NHC_6H_4S)_2]^-$ and $[Tc^{VI}(NHC_6H_4S)_3]$ [13] indicates the following differences: (i) the Tc(V)–S mean distance (2.30 Å) is considerably less than the corresponding Tc(VI)–S distance (2.35 Å); (ii) the average Tc(V)–N distance (2.08 Å) is significantly longer than the Tc(VI)–N distance of 2.00 Å.

The dihedral angle between the two benzene rings is 34.1°; the torsion angles in the two five-membered chelate rings are Tc–S–C–C 10.1 and 6.8°; S–C–C–N −2.1 and −3.9°; the bite S---N distances are 2.84 and 2.95 Å.

Additional information on the character of the Tc=O moiety was obtained from the infrared spectrum of the title complex. It shows an intense absorption at 906 cm^{-1} which we attribute to the asymmetric stretching frequency of the Tc=O group. This frequency differs appreciably from the stretching frequencies observed for a number of dioxotechnetium(V) complexes, and is also well out of the range observed for square-pyramidal monoxotechnetium(V) complexes, which typically occur at 930–1020 cm^{-1} [2, 4]. This surprising result seems to indicate a lower technetium(V)–oxo bond order and a weaker Tc=O bond strength than in other similar complexes. The infrared spectrum of $(Bu_4N)^+[TcO(NHC_6H_4S)_2]^-$ also indicates the presence of a N–H band at 3070 cm^{-1}, a Tc–N bond at 454 cm^{-1} and a coordinated thiolic sulfur at 388 cm^{-1}.

Reduction of $TcO(adt)_2^-$ to $Tc(H_2NC_6H_4S)_3$ was achieved by the reaction of the monoxo complex with excess 2-aminobenzenethiol in acidic aqueous solution at room temperature. The infrared spectrum of $Tc(abt)_3$ shows no Tc=O absorption in the 790–1020 cm^{-1} region, which is a definite illustration of the absence of the TcO^{3+} moiety. Bands at 3382 and 3300 cm^{-1} are ascribed to the $-NH_2$ asymmetric stretching frequencies. A technetium–sulfur stretching frequency is observed at 372 cm^{-1} and the ν(Tc–N) occurs at 458 cm^{-1}.

Discussion

The Tc(V)=O bond distance of 1.73(2) Å in the complex $TcO(adt)_2^-$ is substantially longer than the corresponding bond lengths of 1.61–1.66 Å typically found in a number of square-pyramidal monoxotechnetium(V) complexes [6]. Bond lengths greater than 1.66 Å are usually associated with (i) the presence of a sixth ligand *trans* to the technetyl oxygen [5], (ii) trigonal-bipyramidal coordination geometry [14], or (iii) the presence of M=O···M=O linear polymers' [15, 16]. It is thus tempting to rationalize the Tc=O bond in $TcO(adt)_2^-$ as being due to (i) the greater polarizability of the amido and thiolic sulfur groups, leading to greater covalency in their technetium bonds and consequently greater net

σ and π electron density donation to the technetium and/or (ii) the dianionic nature of the ligands resulting in charge build-up at the technetium(V) ion.

Since there are four metal orbitals available for σ and π-bonding along the Tc=O (z) axis (if $d_{x^2-y^2}sp^3$ hybridization of the technetium ion is assumed), the oxo ligand may bind to the Tc ion by donating only one pair of π electrons in either the d_{xz} or d_{yz} orbitals to form a Tc=O double bond. The strong π-donor ability of the amido group may prevent the formation of a second Tc–oxygen π bond, by donating π electron density into the $d\pi$ orbitals of the technetium, thus preventing them from receiving electron density from the oxygen atom. Viewed in another way, the strong electron donating power of the deprotonated amine and thiol groups stabilize the high +5 oxidation state of the metal ion by virtue of their ability to act as π- as well as σ-donor groups, and in fact neutralize much of the formal charge on the Tc(V) center. This larger π-interaction localization in the equatorial bonds causes the weakening of the Tc=O bond.

It is thus reasonable to consider the oxo moiety to be doubly, rather than triply, bonded in this complex, by using a modification of Pauling's bond order relation [17] with standard average Tc–O bond lengths taken to be Tc–O = 1.98 Å, Tc=O = 1.74 Å and Tc≡O = 1.65 Å. This result is also supported by the Tc=O infrared stretching band (at 906 cm^{-1}) in the complex $TcO(adt)_2^-$, which occurs at the low end of the range seen for monoxo square-pyramidal oxotechnetium(V) conplexes.

The average Tc–N bond distance of 2.08 Å in $TcO(adt)_2^-$ may also be compared with the average single-bond Tc–N distance of 2.125(11) Å in $TcO_2(cyclam)^+$ [18], which seems to imply considerable multiple-bond character in the Tc–N bonds in the title compound.

Due to the apparent weakness of the technetium–oxo bond, an attempt has been made to substitute the oxo ligand from the coordination sphere. Cleavage of the technetium–oxo bond has been achieved by reacting the complex $TcO(adt)_2^-$ with 2-aminobenzenethiol in acidic aqueous solution. The reaction mechanism of this reaction presumably entails the protonation of the oxo ligand as a first step, followed by coordination of a third 2-aminobenzenethiol ligand and subsequent substitution of the oxo ligand. In the process the technetium(V) ion will be reduced to the +3 oxidation state, which implies that protonation of the amido-nitrogens occurred to form coordinated amines.

Supplementary Material

A list of final fractional atomic coordinates and thermal parameters, and a table of structure amplitudes (7 pages) are available.

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