Technetium Complexes of 2-Aminobenzenethiole

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The simple aromatic S,N-ligand 2-aminobenzenethiole (H_2abt) may act as a dithiolene-like ligand with mono-deprotonated amino groups and forms complexes with transition metals in different oxidation states, as described for example for Mo and Re [1].

The synthesis and characterization of technetium complexes has also been reported. A neutral compound Tc(abt)$_3$ has been synthesized [2] and its trigonal-prismatic structure has been described by EPR spectroscopy [3] and by single-crystal X-ray diffraction methods [4]. Up to now, this compound is the only fully characterized tris-chelate–ligand complex of technetium in the oxidation state VI. More recently, formation of an oxotechnetium(V) compound has been described [5, 6].

There is some evidence, from the literature [6] and from our own experimental work [7, 8], that complexes with technetium in oxidation states lower than V also exist.

This work outlines the synthesis and characterization of Tc/abt complexes formed under various reaction conditions.

Experimental

Methods

Thin-layer chromatography (TLC) was carried out on Silufol plates (Kavalier/CSSR) with acetone as eluent. High voltage electrophoresis was made with phosphate buffer (pH = 6.8). The content of oxygen was determined by instrumental neutron activation analysis [9] and that of technetium by liquid-scintillation counting. IR spectra were recorded in KBr discs on a UR 20 spectrometer and UV–Vis spectra on a Specord M 40 from Carl-Zeiss Jena. Mass spectra were carried out by the electron attachment method [10]. Electrochemical measurements (d.c. polarography, cyclic voltametry on hanging mercury drop, coulometry at mercury pool) were made by an automatic d.c.–a.c. GWP-673 polarograph.

Preparations

Tc(V) gluconate was prepared as described in ref. 2 and [Tc(tu)$_6$]Cl$_3$ (tu = thiourea) by the method according to ref. 11.

Tris(2-amidobenzenethiolato(2–)-S,N)technetate(V), H[Tc^{V}(abt)$_3$] (1)

H_2abt (300 μmol) in 2 ml ethanol was added stepwise to an aqueous/ethanolic solution of 100 μmol Tc(V) gluconate. A dark brown precipitate was formed immediately, which was collected by filtration under nitrogen and washed with 0.1 N HCl. The crude product was dissolved in methylene chloride and dried with sodium sulfate. The solution was reduced in volume to about 5 ml, 1 ml ethanol was added and the volume reduced to 0.5 ml. After standing for some hours in the refrigerator, a black substance was separated, washed with a small volume of ether/hexane and dried in a vacuum; yield about 19 mg (40 μmol = 40% based on Tc). *Anal.* Calc. for $C_{18}H_{16}N_3S_3Tc$: C, 46.00; H, 3.43; N, 8.95; S, 20.49. Found: C, 46.3; H, 4.1; N, 8.6; S, 19.7%.

Tris(2-amidobenzenethiolato(2–)-S,N)technetium(VI), Tc^{VI}(abt)$_3$ (2)

The preparation was similar to that described in ref. 3 by dissolving 47 mg (100 μmol) of compound **1** in methylene chloride or ethanol and allowing it to stand overnight, reducing the volume and precipitating by hexane; yield about 19 mg (40% based on **1**).

Tetrabutylammonium bis(2-amidobenzenethiolato(2–)-S,N)oxotechnetate(V), [Bu$_4$N][Tc^{V}O(abt)$_2$] (3)

An aqueous acetonic solution (2:1 vol./vol.) of Tc gluconate (50 μmol) was adjusted to pH 11 by 1 N NaOH. H_2abt (15.6 mg, 125 μmol) in acetone was added to this mixture. The colour turned to orange–brown immediately. Addition of Bu_4NBr (32 mg, 100 μmol) gave a brown precipitate which was filtered off, washed first with water then with cold methanol, and dried. The complex was recrystallized from methanol/ethyl acetate (1:1 vol./vol.) to give dark red crystals, melting point 155 - 156 °C (149° [5]). *Anal.* Calc. for $C_{28}H_{46}N_3OS_2Tc$: C, 55.67; H, 7.68; N, 6.96; O, 2.65; S, 10.62; Tc, 16.40. Found: C, 55.3; H, 7.3; N, 6.8; O, 2.0; S, 10.5; Tc, 16.5%. IR spectrum: 920 cm^{-1}, Tc=O. The electron attachment mass spectrum has an intensive peak (*m/z* 361) corresponding to the complex anion.

Tc(III)–abt complex (4)

[Tc(tu)$_6$]Cl$_3$ (50 mg, 75 μmol) and 47 mg (375 μmol) H_2abt were dissolved in 5 ml ethanol and the mixture was refluxed for 2 h. The colour turned to brown and a blue substance precipitated. It was filtered off, washed first with ethanol, then with ether and dried; yield 23 mg. The complex is slightly soluble in the usual solvents and easily soluble in DMSO, giving a deep blue colour. A content of about 5% of chlorine was found in repeated analyses.

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Results and Discussion

Pertechnetate reacts with five moles of H_2abt in organic solvents or in acidic aqueous solution to give a brown substance (**1**). From aqueous solution, a brown amorphous solid precipitates. The same product is obtained with Tc(V) gluconate and three moles of H_2abt. As was found by TLC (Table 1) and high voltage electrophoresis (compound **1** migrates as an anion, whereas both a green and a blue component remain near the origin), the crude product is contaminated by further components. Besides a small amount of a blue component, formation of a green one is striking. Likewise, the colour of compound **1** changes to green on standing in ethanol or acetone and leads to the well-known neutral compound $Tc(abt)_3$ (**2**). Attempts to isolate the brown product **1** in a pure form were not successful, because the precipitates were contaminated by compound **2**. Compound **2** can be reduced to **1** by one equivalent of a suitable reducing agent, e.g. stannous chloride or H_2abt itself, as shown in Fig. 1 for the reaction of **2** with H_2abt.

Electrochemical investigations carried out on the Tc/H_2abt system [8] (Table 2) confirm that compounds **1** and **2** represent a redox couple: **2** was reduced coulometrically to **1** and the cyclic voltamogram of **2**, shown in Fig. 2, corresponds to that of **1**. The first peak ($E = -190$ mV) is caused by the reduction of Tc(VI) to Tc(V). From the difference between the reduction and oxidation peaks (70 mV) it follows that this reaction is electrochemically reversible. Compound **1** has an oxidation peak at the same potential. The other peaks could not be assigned.

In agreement with the reaction pathway (Fig. 3) as well as analytical and electrochemical data obtained in the Tc/H_2abt system, compound **1** is formulated as the anionic Tc(V) complex $[Tc(abt)_3]^-$, which easily converts to the well-characterized Tc(VI) complex $Tc(abt)_3$.

Gardner *et al.* [1] considered the brown complex resulting from the analogous reaction of perrhenate with H_2abt as being a Re(VII) species; for both Mo and Re complexes reversible electron-transfer behaviour in polar solvents was found.

Under the above conditions no oxo species could be found. However, its formation is favoured in alkaline medium. Reaction of pertechnetate with dithionite/H_2abt [6] and ligand exchange reaction of H_2abt on Tc gluconate under alkaline conditions [7] give the oxotechnetium compound **3**. Checking

TABLE 1. R_f values in TLC and UV–Vis data of Tc/abt complexes

Compound	TLC (R_f)	λ_{max} (lg ϵ)	Solvent
1	0.9	480 (4.0)	ethanol
2	1	700 (4.1) 420 (4.3)	ethanol
3	0.9	350 (3.9 310 (3.0)	chloroform
4	0.1	617 515	chloroform

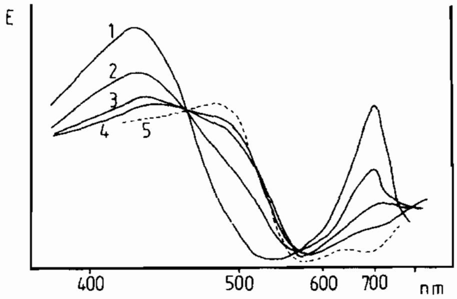

Fig. 1. Changes in the optical spectrum of **2** after stepwise addition of H_2abt in ethanol ([Tc] = 5×10^{-5} mol/l): molar ratio H_2abt/**2**: (1) 0; (2) 0.5; (3) 0.8; (4) 1.0. (5) Spectrum of **1**.

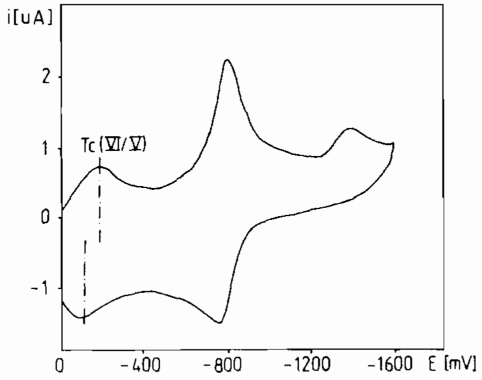

Fig. 2. Cyclic voltamogram of **2** in 0.1 M $LiClO_4$/DMSO ([Tc] = 1.3×10^{-4} mol/l).

TABLE 2. Peak potentials of cyclic voltamograms of Tc/abt complexes (E_{Red}/E_{Ox}) in mV vs. SCE.

Compound	$E_1(Tc^{VI/V})$	E_2	E_3	E_4
2	−190/−120	−800/−755		−1380/
1	−210/−120	−770/−730		−1400/
5			−1075/	
4			−1100/−1060	

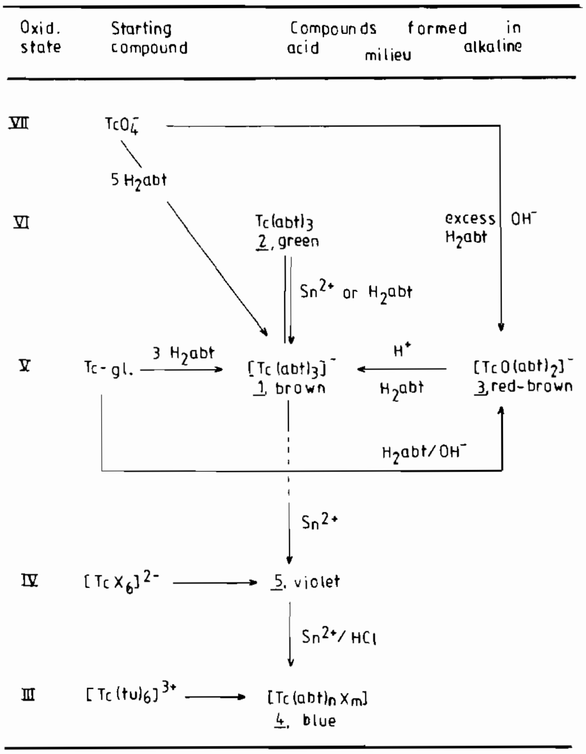

Fig. 3. Reaction scheme of formation of Tc/abt complexes.

its composition by mass spectrometry and elemental analysis, including that of oxygen [11], delivered the formula $[TcO(abt)_2]^-$ and showed that the compound is identical to a compound obtained earlier by Gerber *et al.* [5] and correctly formulated on the basis of single-crystal X-ray structure determination [6].

It is interesting to note that compound **3** is also formed when Schiff bases of H_2abt react with Tc gluconate in an alkaline medium [12].

A further point of interest is the relation of oxo- and tris-ligand complexes in acid media. We found that conversion of **3** to **1** already occurs during standing of compound **3** in acidic solution. The abstraction of oxygen by the aminothiole ligand is practically quantitatively accomplished by treatment of **3** with H_2abt in acidic media [6]. We consider compound **1** as an intermediate due to the fact that H_2abt reduces **2** to **1** and oxidation to **2** does not occur until the excess H_2abt is consumed.

Gerber and Bandoli [6] suggested that the product formed in the above reaction is a complex of Tc(III). However, the green component is identical to compound **2**, as shown by EPR spectroscopy [13].

Nevertheless, there is some evidence for the existence of complexes of technetium at lower oxidation states. Treatment of **1** with stannous chloride in acetonitrile solution turns the colour of the brown solution to red and, subsequently, to deep blue. The blue compound **4** was also obtained starting from $[Tc(tu)_6]Cl_3$ and is likely to be the same component as was found on TLC plates after reduction of pertechnetate by H_2abt (see above). A red-coloured compound **5** is formed by the action of H_2abt on $[TcBr_6]^{2-}$. Compound **5** is not stable in solution and changes to compound **4** (Fig. 3). As can be seen in Table 2, compound **5** forms a redox couple with compound **4**.

However, there is no correspondence between the Tc(V/VI) and the Tc(IV/III) pair. Obviously, and this is underlined by analytical data, the latter compounds could be coordinated by an abt/halogen arrangement in contrast to the pure abt coordination of both compounds at oxidation states V and VI.

References

1 J. K. Gardner, N. Pariyadath, J. L. Corbin and E. Stiefel, *Inorg. Chem., 17* (1978) 897.
2 B. Johannsen and H. Spies, *Chemie und Radiopharmakologie von Technetiumkomplexen,* Akademie der Wiss. d. DDR, Dresden, 1981.
3 R. Kirmse, J. Stach and H. Spies, *Inorg. Chim. Acta, 45* (1980) L251.
4 J. Baldas, J. Boas, J. Bonnyman, M. F. Mackay and G. A. Williams, *Aust. J. Chem., 35* (1982) 2413.
5 J. G. H. du Preez, T. I. A. Gerber, P. J. Fourie and A. J. van Wyk, *Inorg. Chim. Acta, 82* (1984) 201.
6 G. Bandoli and T. I. A. Gerber, *Inorg. Chim. Acta, 126* (1987) 205.
7 H.-J. Pietzsch and H. Spies, *ZfK-Report, 622* (1986) 39.
8 I. Hoffmann, H.-J. Pietzsch and H. Spies, *ZfK-Report, 640* (1987) 43.
9 H. Foerster, to be published.
10 M. v. Ardenne, K. Steinfelder and R. Tuemmler, *Elektronenalagerungs-Massenspektroskopie Organischer Substanzen,* Springer-Verlag, Berlin, 1971.
11 M. J. Abrams, A. Davison, R. Faggiani, A. G. Jones and C. J. L. Lock, *Inorg. Chem., 23* (1984) 3284.
12 H. Spies and H.-J. Pietzsch, *Inorg. Chim. Acta,* in press.
13 R. Kirmse, U. Abram and H.-J. Pietzsch, unpublished results.