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Lipophilic Technetium Complexes.
V. Synthesis and Characterization of (3-Thiapentane-1,5-dithiolato)(thiophenolato)oxotechnetium(V)

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Oxotechnetium(V) complexes with ligands containing sulfur donors have been studied intensively. Almost all attention with regard to ligands has focused on bidentate ligands [1,2], which form anionic compounds $[TcOL_2]^-$. Tridentate ligands containing an ether or thioether group are of intrinsic interest because their complexes with the TcO^{3+} core should be of the form $TcOL^+$, leaving one open coordination site to bind a second, unidentate ligand. Preliminary studies on complex formation of technetium with the tridentate ligands

$$HS{-}CH_2{-}CH_2{-}X{-}CH_2{-}CH_2{-}SH \qquad (HSXSH, X = O, S)$$

led to undefined deep-coloured compounds [3]. In the present paper we report the preparation and characterization of an oxotechnetium complex in which the $[TcO(SXS)]^+$ core is stabilized by thiophenol as co-ligand.

Experimental

Tc(V) gluconate was prepared according to ref. 4 by stepwise addition of a solution of 48 μmol stannous chloride in 0.5 ml of 0.1 N HCl to a solution of 48 μmol NH_4TcO_4 and 80 mg sodium gluconate in 1 ml of water. After dilution of Tc gluconate with 1.5 ml of acetone, a solution of 48 μmol 3-thiapentane-1,5-dithiol and 48 μmol thiophenol in 0.5 ml of acetone was added dropwise to the stirred mixture. The solution became orange–brown and a brown solid precipitated. The solid was dissolved in 5 ml of acetone, filtered and reduced in volume to 2 ml. After addition of 1 ml of methanol, the volume was reduced to 0.5 ml, giving brown crystals; yield 9.0 mg (50%). *Anal.* Calc. for $C_{10}H_{13}OS_4Tc$: C, 31.9; H, 3.5; S, 34.1; Tc, 26.3; molecular weight 376.5. Found: C, 30.8; H, 3.1; S, 32.9; Tc, 23.9%; molecular weight 374 (isothermic distillation in acetone). Optical spectrum (chloroform) (in nm (log ε)): 474 (3.9). ^1H NMR spectrum (DMSO-d_6): 7.2 ppm, 5 protons (aromatic), 4.2 ppm, 8 protons (aliphatic). IR spectrum (KBr): 935 cm^{-1}, Tc=O. Mass spectra were recorded on a UG ZAB-MSQ spectrometer (E_I^+, 70 eV). For the CAD (collision activated dissociation) spectra, argon was used as the collision gas.

Results and Discussion

Tridentate thiole ligands of the type HSXSH undergo ligand exchange reactions with Tc gluconate. However, they are not sufficient to stabilize the TcO^{3+} core to definite mononuclear units, and subsequent reactions yield products which seem to be di- or polynuclear species. Stabilization of the intermediate should be possible by appropriate monodentate ligands, which deliver the fourth donor atom necessary for the formation of a stable square-pyramidal oxotechnetium(V) coordination sphere. The first representative of a new type of Tc complex, with a stable S_4 coordination of Tc(V), is accomplished by reaction of both a tridentate dithiole ligand containing a thioether group (HSSSH, H_2L^1) and thiophenol (HL^2) with Tc gluconate. When a mixture of ligands in a 1:1 molar ratio is added to Tc gluconate in aqueous/acetonic solution, the formation of a mononuclear compound is the preferred reaction and the resulting complex can be isolated in crystalline form.

According to elemental analysis and a band at 935 cm^{-1} (Tc=O) in the IR spectrum, the compound has the formula $TcOL^1L^2$ (Fig. 1). This is confirmed by the mass spectrum, which is characterized by typical metal-containing fragment ions (Fig. 2). Some important fragmentation pathways derived from the CAD spectrum of mass selected molecular ions are shown in Fig. 3.

The principle of combined action of both a tridentate and a monodentate ligand on Tc(V) precursors to yield mononuclear neutral compounds is not limited to thiophenol as co-ligand. Results obtained with a variety of aromatic and aliphatic thioles will be dealt with [5].

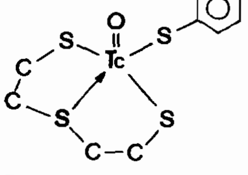

Fig. 1. Proposed structure of (3-thiapentane-1,5-dithiolato)(thiophenolato)oxotechnetium(V), $TcOL^1L^2$.

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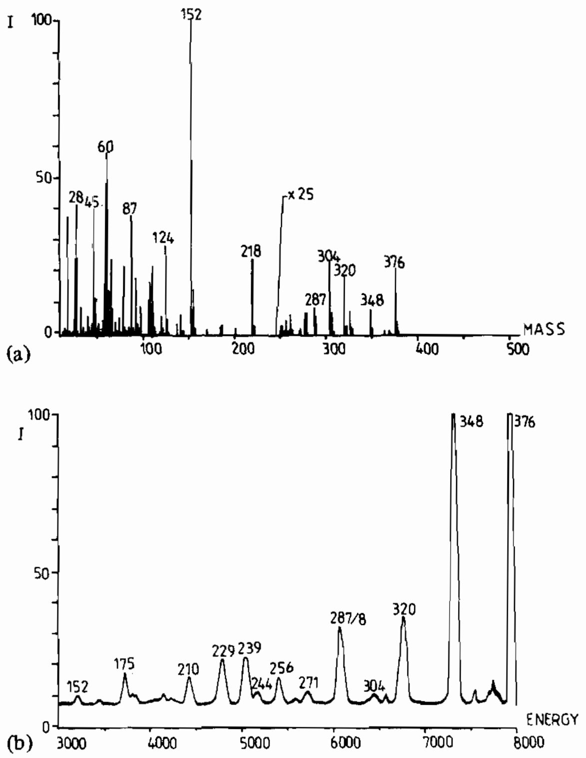

Fig. 2. (a) Mass spectrum of $TcOL^1L^2$. (b) CAD spectrum of $TcOL^1L^2$.

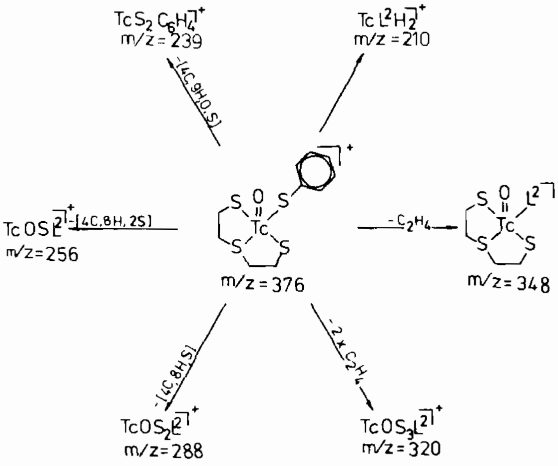

Fig. 3. Some important fragmentation pathways derived from the CAD spectrum of the molecular ion ($L^2 = S{-}C_6H_5$).

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