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The Isolation and Characterization of the Paramagnetic Oxotechnetium(V) Complex Chloro-[*S*-methyl-*β*-*N*-(2-hydroxyphenylethylidene)-dithiocarbazate] Oxotechnetium

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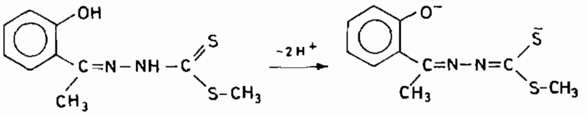
Due to the dominating role that the TcO^{3+} core plays in the chemistry of technetium(V) compounds, all previously synthesized five-coordinate oxotechnetium(V) complexes are diamagnetic in a square pyramidal geometry [1]. The TcO^{3+} core dictates the chemical behaviour of these complexes in such a way that the bond *trans* to the 'yl' oxygen is weakened, which eventually will lead to a square pyramidal configuration.

With the aim of finding other possible stable configurations around technetium(V) containing the TcO^{3+} core, the reaction of the potentially dianionic tridentate Schiff base ligand *S*-methyl-*β*-*N*-(2-hydroxyphenylethylidene)dithiocarbazate (H_2-HAF) (**I**) with $TcOCl_4^-$ in a 1:1 mole ratio in ethanol was studied. The dianionic ligand HAF can act as a tridentate chelate by coordination via the *β*-imine nitrogen, the phenolic oxygen and the thiolic sulphur atom of tautomeric form (**Ib**) [2].



Ia **Ib**

Previously synthesized oxotechnetium(V) complexes containing the tridentate ligands 2-[[(2-mercaptophenyl)imino]methyl]phenol and 2-[[(2-hydroxyphenyl)imino]methyl]phenol (H_2Ophsal) were found to be diamagnetic square pyramidal complexes, with the ligands occupying three of the four coordination sites of the basal plane of the pyramid [3]. No group was coordinated in the position *trans* to the 'yl' oxygen.

The complex with the formulation TcO(HAF)Cl was prepared in a 87% yield by the stirring of a mixture of 23.9 mg of the ligand H_2HAF (0.1 mmol) in 5 cm^3 ethanol and 50 mg of $(n\text{-}Bu_4N)[TcOCl_4]$ in 5 cm^3 ethanol at room temperature for 30 min. After a few seconds a golden-brown precipitate formed from the red solution. The product was filtered, washed with ethanol and dried *in vacuo* over P_2O_5. Recrystallization from CH_2Cl_2/EtOH gave dark red crystals. *Anal.* Calc. for TcO(HAF)Cl: C, 30.89; H, 2.60; N, 7.20; Cl, 9.12. Found: C, 31.09; H, 2.50; N, 7.18; Cl, 9.17%. Conductivity (DMF, 10^{-3} mol dm^{-3}): $\Lambda_M = 18.3$ ohm^{-1} cm^2 mol^{-1}. Optical spectrum ($CHCl_3$): 457 nm (3100), 352 nm (8900), 285 nm (18 500 dm^3 mol^{-1} cm^{-1}).

The complex TcO(HAF)Cl is clearly a non-electrolyte and is insoluble in water and alcohols, and very soluble in DMF, acetone, chloroform and dichloromethane.

The infrared spectrum of the ligand H_2HAF (KBr disc) shows the ν(C=N) stretching at 1622 cm^{-1}, and a band at 2970 cm^{-1} is attributed to the ν(O–H) vibration. The band appearing at 2868 cm^{-1} is ascribed to the ν(N–H) vibration, while there is no peak in the 2500 cm^{-1} region which can be contributed to the presence of a ν(S–H) vibration.

The complex exhibits a coordinating ν(C=N) stretching vibration at 1525 cm^{-1} in the infrared spectrum, with the non-coordinating ν(C=N) stretch appearing at 1600 cm^{-1}. The band due to the Tc=O bond stretching was found at 985 cm^{-1}, indicating a considerable strong bond. This strong Tc=O bond can be ascribed to the relative weak coordination of the atoms in the *cis* plane (relative to Tc=O), which is supported by the relatively low value of 300 cm^{-1} observed for the ν(Tc–S) vibration. The ν(O–H) vibration in the ligand at 2970 cm^{-1} also disappears upon coordination, indicating coordination of the phenolic oxygen atom to the metal ion. Coordination of the phenolic oxygen atom will decrease the induction effect of the phenyl group to the adjacent imine bond, so that coordination by the *β*-imine nitrogen atom will be weakened considerably, resulting in the relatively higher coordinating ν(C=N) stretch of 1525 cm^{-1}.

The UV–Vis spectrum of the complex TcO(HAF)-Cl in chloroform exhibits three bands at 457, 352 and 285 nm. According to the intensities of the two higher energy bands, they can only be ascribed to charge transfer transitions. The band at 352 nm is mainly associated with the sulphur to technetium charge transfer, and the 285 nm band with the charge transfer between the 'yl' oxygen and the technetium ion. The band of weaker intensity at 457 nm is attributed to the charge transfer transition between the phenolic oxygen atom and the metal ion.

The most surprising result of this study is the paramagnetism of the TcO(HAF)Cl complex. Magnetic susceptibility measurements were made on 80 and 300 MHz spectrometers, using the Evans method [4], and a magnetic moment of 2.45 BM was found for the complex. The value corresponds to the

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presence of two unpaired electrons in the 4d energy level of the technetium(V) ion. Paramagnetism has never been previously found for oxotechnetium(V) complexes, since the strong ligand field of the oxo ligand destabilizes the d_{xz} and d_{yz} sufficiently so that the two d electrons are paired in the d_{xy} orbital.

This anomalous magnetic behaviour of the TcO(HAF)Cl complex is difficult to account for, and the only possible way to explain it is to consider a trigonal bipyramidal geometry of the complex. In such a trigonal bipyramidal geometry the p-orbitals of the oxo oxygen can only interact with the d_{xy} orbital of the technetium ion, since a trigonal split of the d orbitals will place the d_{xz} and d_{yz} orbitals in energy levels close to each other in a distorted D_{3h} arrangement. The energy of electron pairing will thus be greater than the energy difference between the d_{xz} and d_{yz} orbitals, so that electron pairing does not occur.

If a tbp geometry is assumed for the complex, the oxo and phenolic oxygen atoms are presumably in the apical positions *trans* to one another, since a phenolic oxygen has always been found *trans* to the oxo oxygen in rhenium(V) and technetium(V) complexes with bidentate Schiff bases [5–7]. Coordination of the chloride ion *trans* to the oxo oxygen can be excluded due to the large *trans* effect of this oxo group. Coordination of the chloride, β-imine nitrogen and thiolic sulphur atoms will therefore occur in the trigonal plane.

The complex TcO(HAF)Cl was reacted with *S*-methyl-β-*N*-(prop-2-yline)dithiocarbazate [$(CH_3)_2$-C=N–NH–CS_2CH_3, HPAC] [8] in the following manner. TcO(HAF)Cl (38.88 mg, 0.1 mmol) in 5 cm^3 acetone was added to 32.25 mg of HPAC (0.2 mmol) in 5 cm^3 methanol, and the mixture was stirred for 30 min. The solution was filtered, and evaporation at room temperature led to the formation of dark red crystals. The product was filtered, washed with methanol and dried *in vacuo*. *Anal.* Calc. for TcO(HAF)(PAC): C, 35.01; H, 3.72; N, 10.89. Found: C, 35.67; H, 3.70; N, 10.69%. Conductivity (DMF, 10^{-3} mol dm^{-3}): $\Lambda_M = 17.9$ ohm^{-1} cm^2 mol^{-1}.

The formulation of TcO(HAF)(PAC) is supported by elemental analysis, and the observed diamagnetic character of this compound is in accordance with the behaviour of all TcO^{3+} complexes in a distorted octahedral environment. The ν(Tc=O) stretching vibration appears at 961 cm^{-1} in the infrared spectrum, and the coordinating ν(C=N) stretching bands at 1479 and 1506 cm^{-1}.

The complex TcO(HAF)(PAC) thus consists of the tridentate deprotonated Schiff base ligand HAF^{2-} and the bidentate deprotonated PAC^- ligand. This complex appears to be only the second technetium(V) complex containing both tri- and bidentate Schiff base ligands, the first being TcO[*N*-(2-oxidophenyl)salicylideneiminate](8-quinolinolate), TcO(Ophsal)(quin) [9]. An X-ray analysis of the TcO(Ophsal)(quin) structure revealed an approximate octahedral coordination around technetium, with the tridentate ligand occupying three equatorial sites and the bidentate ligand one equatorial and one apical site, *trans* to 'yl' oxygen.

A preliminary crystal structure analysis of the complex TcO(HAF)(PAC) also indicates a distorted octahedral environment around the technetium(V) centre, but with the bidentate ligand PAC occupying two equatorial sites, and the tridentate ligand HAF occupying the remaining two equatorial sites and one apical site, with the phenolic oxygen occupying the sixth position *trans* to the oxo oxygen [10]. A full crystal structure analysis of the complex TcO(HAF)(PAC) will be presented in the near future in a comprehensive report.

Acknowledgements

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