# Synthesis and Characterization of Technetium(V) Complexes with Tetradentate Schiff Base Ligands Derived from *S*-Methyldithiocarbazate

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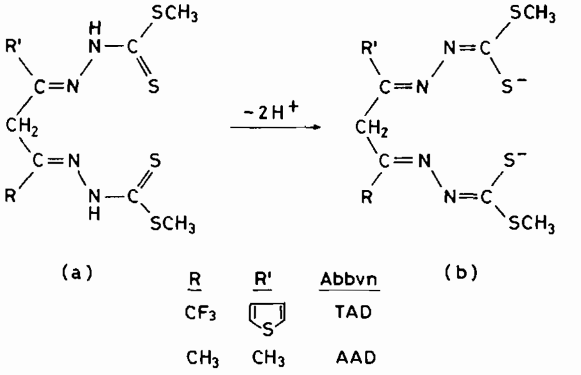
The use of sulphur–nitrogen chelating agents in the preparation of new coordination compounds has increased rapidly during the past few years [1–3]. The pronounced biological activity of the metal complexes with ligands derived from dithiocarbazic acids has created considerable interest in their coordination chemistry [4, 5]. Although complexes of dithiocarbazates with many different transition metal ions have been studied extensively, no information on the bonding and structural factors is available for technetium complexes.

In our earlier work we investigated complexes of technetium(V) with potentially bidentate [6] and tridentate [7] dithiocarbazate Schiff bases. This project has now been extended, and in this account we report the formation and characterization of oxotechnetium(V) complexes with potentially dianionic tetradentate Schiff bases, derived from *S*-methyldithiocarbazate. Structural formulae for the ligands used in this study are given, **Ia**.



I

Our interest in these ligands is the unusual steric and electronic properties of the resulting complexes, on the basis of specific differences in polarizability, covalency and π-bonding ability of these ligands.

The tautomeric forms of these tetradentate Schiff bases, formed by the condensation of *S*-methyldithiocarbazate with β-diketones, can by the loss of two protons in solution act as dianionic tetradentate ligands, **Ib**. Coordination to a metal ion can now occur via the two β-imine nitrogen and two mercapto sulphur atoms.

The two ligands TAD and AAD were prepared by heating 20 mmol of *S*-methyldithiocarbazate [4] and the corresponding β-diketone (10 mmol) in ethanol (containing 2 drops of 10 mol dm$^{-3}$ HCl) at reflux conditions for 2 h. Cooling to −15 °C precipitated the product, which was isolated by filtration, washed with cold ethanol and dried *in vacuo*. Recrystallization from ethanol gave yellow crystals, yield 81–87%. *Anal.* Calc. for TAD: C, 33.71; H, 3.06; N, 13.10. Found: C, 33.79; H, 3.11; N, 13.22%. Calc. for AAD: C, 35.04; H, 5.23; N, 18.16. Found: C, 34.98; H, 5.28; N, 18.04%. Infrared data: TAD, $\nu$(C=N) = 1600, 1548(s) cm$^{-1}$; $\nu$(CSNH) = 3150(m) cm$^{-1}$. AAD, $\nu$(C=N) = 1632(s) cm$^{-1}$; $\nu$(CSNH) = 3150(m) cm$^{-1}$.

The two complexes with the formulations TcO(TAD)Cl and TcO(AAD)Cl were prepared in identical fashion. Equimolar quantities of the specific Schiff base ligand and (n-Bu$_4$N$^+$)[TcOCl$_4^-$] [8] were stirred for 30 min in ethanol. A brown powder precipitated from the dark red solution. The precipitate was filtered, washed with cold ethanol and dried *in vacuo*. The slow evaporation of the filtrate led to the formation of dark red needles, which were filtered, washed with ethanol and dried *in vacuo*.

*Anal.* Calc. for TcO(TAD)Cl: C, 24.89; H, 1.92; N, 9.68. Found: C, 25.00; H, 1.96; N, 9.44%. Conductivity (DMF, 10$^{-3}$ mol dm$^{-3}$): $\Lambda_M$ = 26.2 ohm$^{-1}$ cm$^2$ mol$^{-1}$. Electronic spectrum ($\lambda_{max}$ (nm) ($\epsilon$)): 353(25 400), 292(24 600). Yield = 87%.

*Anal.* Calc. for TcO(AAD)Cl: C, 23.66; H, 3.09; N, 12.26. Found: C, 23.46; H, 3.01; N, 11.90%. Conductivity (DMF, 10$^{-3}$ mol dm$^{-3}$): $\Lambda_M$ = 24.2 ohm$^{-1}$ cm$^2$ mol$^{-1}$. Electronic spectrum ($\lambda_{max}$ (nm) ($\epsilon$)): 330sh, 288(20 100). Yield = 72%.

Both the complexes TcO(TAD)Cl and TcO(AAD)Cl are soluble in chloroform, dichloromethane, acetone and dimethylformamide, and insoluble in water and highly polar organic solvents. They are also non-electrolytes in DMF.

The infrared data of the complexes are given in Table I. The presence of both coordinating and non-coordinating C$\cdots$N vibrations could be distinguished in the infrared spectra of the complexes, as well as the disappearance of the N–H vibrations of the ligands. This seems to indicate that the β-imine nitrogen atoms of the ligands are used for coordination. The presence of Tc–S stretching vibrations at 350 cm$^{-1}$, and the absence of S–H vibrations in the range 2650–2550 cm$^{-1}$, indicate coordination by the mercapto sulphur atom of the thioenolate tautomer of the ligands.

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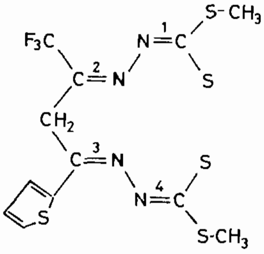
TABLE I. Selected Infrared Data of the Complexes ($cm^{-1}$)

| | $\nu(C\overset{\cdots}{-}N)_{nc}$[a] | $\nu(C\overset{\cdots}{-}N)_{c}$[a] | $\nu(CS_2)$ | $\nu(Tc=O)$ | $\nu(Tc-S)$ |
|---|---|---|---|---|---|
| TcO(TAD)Cl | 1520 | 1472<br>1480 | 1005 | 951 | 350 |
| TcO(AAD)Cl | 1512 | 1499 | 990 | 942 | 350 |

[a] nc = non-coordinating; c = coordinating.

For the complex TcO(TAD)Cl the non-coordinating $\nu(C\overset{\cdots}{-}N)$ appears at 1520 $cm^{-1}$, and the coordinating $\nu(C\overset{\cdots}{-}N)$ at 1472 and 1480 $cm^{-1}$. The Tc=O and Tc–S stretching vibrations are found at 951 and 350 $cm^{-1}$ respectively. As could be expected, the coordinating $\nu(C\overset{\cdots}{-}N)$ is split, since these $C\overset{\cdots}{-}N$ bonds lie in different electronic environments. In addition to the fact that nitrogen coordination of the imine bond 2 in **II** will decrease the double bond character of this bond, the electron-withdrawing $CF_3$-group will decrease the double bond character even further, so that the $C\overset{\cdots}{-}N$ stretching vibration will shift to even lower energy. The vibration at 1472 $cm^{-1}$ is thus ascribed to imine bond 2. The vibration at 1480 $cm^{-1}$ is assigned to imine bond 3, due to the greater induction effect of the thiophene group, which is partially weakened by the electron-withdrawing power of the trifluoromethyl group.



**II**

The partial double bond character of the non-coordinating $C\overset{\cdots}{-}N$ groups (at 1512 $cm^{-1}$) in the TcO(AAD)Cl complex is mainly the result of the strong metal–sulphur interaction ($\nu(Tc-S) = 350$ $cm^{-1}$). The possible conjugation of the imine bonds may also be a contributing factor. The appearance of the coordinating $\nu(C\overset{\cdots}{-}N)$ vibrations at higher energy in TcO(AAD)Cl (at 1499 $cm^{-1}$) than in TcO(TAD)Cl can be ascribed to the greater total induction effect of the two methyl groups relative to the trifluoromethyl and thiophene groups. This greater induction effect of the two methyl groups will lead to stronger metal–imine nitrogen coordination in TcO(AAD)Cl than in TcO(TAD)Cl, a fact which is also manifested by the weaker Tc=O bond in the former complex ($\nu(Tc=O) = 942$ $cm^{-1}$).

The UV–Vis spectra of the two complexes in chloroform exhibit two bands in the 250–500 nm region. The absorption bands at 288 and 292 nm of the respective TcO(AAD)Cl and TcO(TAD)Cl complexes are, according to their intensities, assigned to charge transfer transitions between the oxo oxygen and technetium(V) ion. The absorption bands at 330 and 353 nm are attributed to charge transfer transitions between the sulphur atoms and the technetium(V) ions.

Magnetic measurements indicate that both complexes are diamagnetic, which is reminiscent of a spin-paired $d^2$ electronic configuration in an octahedral or square pyramidal complex geometry. Conductivity measurements in DMF also indicated that both complexes are non-electrolytes, which seems to indicate that they are six coordinated in an octahedral geometry. In such an octahedral arrangement the chloro ligand will be coordinated in a position *trans* to the oxo oxygen, with the four donor atoms of the ligand in the basal plane.

Crystal structures of complexes of the type TcOLCl (L = tetradentate ligand like *N,N'*-ethylenebis(salicylideneaminato)) have shown six coordination in a distorted octahedral geometry, in which the coordinated chloride ligand is in the position *trans* to the oxo oxygen [9].

Efforts to prepare tetradentate ligands of *S*-methyldithiocarbazate with benzoylacetone or dibenzoylmethane were unsuccessful. Infrared spectra of the products of these attempted preparations showed that the β-diketone exists in the enol form after the addition of the first *S*-methyldithiocarbazate, which will prevent the addition of the second. This tendency can be explained by the fact that the phenyl groups will donate a significant electron density to the system in a slightly acidic medium, causing the stabilization of the enol tautomer.

## Acknowledgements

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