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Complexes of Technetium(V) with Bidentate Schiff Bases Derived from *S*-Methyldithiocarbazate

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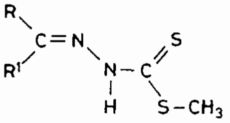
Abstract

The synthesis and characterization of several new neutral oxotechnetium(V) complexes with substituted *S*-methyldithiocarbazate Schiff bases are described. These six-coordinated complexes show a definite correlation between the strength of the Tc=O bond and the degree of double bond character of the coordinating C=N bond. The relative strength of the Tc=O bond is mainly determined by the electronic influence of the *cis*-ligands and not by the presence or influence of a ligand *trans* to the oxo groups. The complexes have been characterized on the basis of elemental analyses, infrared and electronic spectra, conductance and magnetic susceptibility measurements.

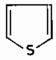
Introduction

Increasing interest is being shown in the chemistry of transition metal complexes involving dithiocarbazates as ligands [1–3]. A main stimulus for this interest is the rationalization of the increasing number of unusual steric and electronic properties of these complexes, on the basis of specific differences in polarizability, covalency, π-bonding ability, etc. of these types of ligands. Since the sulphur atoms in dithiocarbazates have the ability to participate in π-bonding in addition to σ-donation, metal ions in unusually high oxidation states can be stabilized by these ligands.

In this account, we report the formation and characterization of potentially bidentate Schiff base, derived from *S*-methyldithiocarbazate, complexes of technetium(V). Structural formulae for the Schiff base ligands used in this study (**I**) are given in Scheme 1.

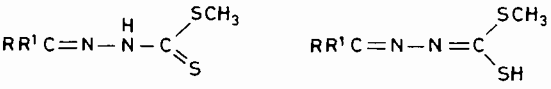


I

R	R¹	Abbreviation
H	C_6H_5	BAD
C_6H_5	C_6H_5	BFD
CH_3		AFD
CH_3		ATD
$C(CH_3)_3$	$C(CH_3)_3$	DDD
CH_3	CH_3	APD

Scheme 1.

These Schiff base ligands exist in the solid state in the form **IIa**, but in solution they exist as an equilibrium mixture of the tautomeric forms **IIa** and **IIb** [2] (Scheme 2). The form **IIb**, by loss of the proton from the thiol sulphur, act as a singly charged bidentate ligand, forming complexes with a variety of metal ions like bivalent manganese, iron, cobalt, nickel and copper [1]. Coordination to a metal ion takes place via the mercapto sulphur and imine β-nitrogen bound to the alkylidene groups [1].



IIa **IIb**

Scheme 2.

Experimental

Technetium as $NH_4[^{99}TcO_4]$ was purchased from the Oak Ridge National Laboratory, Tenn. as the dry salt. ^{99}Tc is a weak β-emitter (0.292 KeV); therefore all manipulations were carried out in a radiation

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laboratory with a monitored fume hood. Personnel wore disposable laboratory coats and gloves at all times. Radioactive wastes, both liquid and solid, were disposed in special receptacles.

Infrared spectra were recorded on a Beckman IR4250 grating spectrophotometer in the range 4000–250 cm^{-1} as KBr pellets. Optical spectra were obtained with a Perkin-Elmer 330 spectrophotometer. Conductivity measurements were performed in the appropriate solvents using a Metrohm E518 conductometer. Magnetic susceptibility measurements were made using the Evans NMR method [4] on a 500 MHz Bruker W500 spectrometer. Elemental analyses were performed using a Heraeus Rapid Analyser. Chloride was determined by potentiometric titration with standard $AgNO_3$ of solutions of the compounds decomposed by the Shoeniger method.

All solvents used were purified and dried by standard methods. All chemicals were obtained commercially and were used without any further purification. $(n\text{-}Bu_4N^+)$ $[TcOCl_4^-]$ [5] and the Schiff base ligands [6] were prepared by using literature methods.

Preparation of Complexes

Bis{S-methyl-β-N-(phenylmethylene)dithiocarbazate}oxotechnetium(V) chloride, TcO(BAD)₂Cl

$(n\text{-}Bu_4N)[TcOCl_4]$ (50 mg, 0.1 mmol) in 5 cm^3 absolute ethanol was added to 41.8 mg BAD (0.2 mmol) in 5 cm^3 ethanol, and the mixture was stirred for 4 h. A brown precipitate formed slowly, which was filtered and washed with ethanol (3 × 2 cm^3). Recrystallization from acetone/ethanol gave dark red needles. Yield, based on Tc = 71%.

Bis{S-methyl-β-N-(diphenylmethylene)dithiocarbazate}oxotechnetium(V) chloride, TcO(BFD)₂Cl

$(n\text{-}Bu_4N)[TcOCl_4]$ (50 mg) in 5 cm^3 absolute ethanol was added to BFD (57.3 mg, 0.2 mmol) in 5 cm^3 ethanol. The resulting red solution was stirred for 5 h at room temperature, with the concomitant slow formation of a brown precipitate. The solution was filtered, and the product was washed with ethanol (3 × 2 cm^3) and dried *in vacuo*. Recrystallization from dichloromethane/hexane gave dark red needles, yield = 63%.

Bis{S-methyl-β-N-(fur-2-ylethylidene)dithiocarbazate}oxotechnetium(V) chloride, TcO(AFD)₂Cl

A mixture of 42.8 mg of AFD (0.2 mmol) and 50 mg of $(n\text{-}Bu_4N)[TcOCl_4]$ was stirred in 15 cm^3 ethanol for 30 min. After one minute a brown product precipitated rapidly from the red solution. The product was filtered, washed with ethanol (3 × 2 cm^3) and dried *in vacuo*. Recrystallization from acetone gave red blocks, yield = 83%, based on technetium.

Bis{S-methyl-β-N-(thien-2-ylethylidene)dithiocarbazate}oxotechnetium(V) chloride, TcO(ATD)₂Cl

The addition of 46.1 mg ATD (0.2 mmol) in 5 cm^3 ethanol to $(n\text{-}Bu_4N)[TcOCl_4]$ (50 mg; 0.1 mmol) in 5 cm^3 ethanol led to the formation of a red solution, from which $TcO(ATD)_2Cl$ precipitated rapidly as a brown powder. After stirring for one hour, the product was filtered and washed with ethanol (3 × 2 cm^3). The filtrate was evaporated down slowly, with the formation of a brownish black precipitate, which was isolated and washed with ethanol (3 × 1 cm^3). This compound analysed for $Tc(ATD)_3$. Recrystallization of $TcO(ATD)_2Cl$ from acetone gave red blocks, yield = 46%. Dark red needles were obtained from the recrystallization (under nitrogen) of $Tc(ATD)_3$ from dichloromethane/hexane, yield = 22%.

Bis{S-methyl-β-N-(prop-2-ylidene)dithiocarbazate}oxotechnetium(V) chloride, TcO(APD)₂Cl

S-methyl-β-N-(2-dimethyl-4-dimethylpent-3-ylidene) dithiocarbazate (DDD) (49.1 mg, 0.2 mmol) in 10 cm^3 acetone was added to $(n\text{-}Bu_4N)[TcOCl_4]$ (50 mg, 0.1 mmol) in 5 cm^3 methanol. After stirring for 30 min the addition of water precipitated a brown compound from the dark red solution. The product was filtered and washed with ethanol (3 × 2 cm^3). Recrystallization from dichloromethane/hexane gave dark red blocks, yield = 69%.

This compound surprisingly did not analyze for $TcO(DDD)_2Cl$, but for $TcO(APD)_2Cl$, in which the isobutyl groups were displaced by acetone.

Bis{S-methyl-β-N-(2-dimethyl-4-dimethylpent-3-ylidene) dithiocarbazate}oxotechnetium(V) chloride, TcO(DDD)₂Cl

The complex $TcO(DDD)_2Cl$ was prepared in exactly the same manner as the above preparation for $TcO(APD)_2Cl$, with the only difference being that the reaction was carried out in ethanol, as for all the previous preparations. The recrystallization of $TcO(DDD)_2Cl$ from dichloromethane/hexane gave dark red blocks, yield = 77%.

Results

The physical data of the complexes are given in Table I. All the complexes were prepared in an alcoholic medium under aerobic conditions at room temperature by treating $(n\text{-}Bu_4N)[TcOCl_4]$ with the corresponding dithiocarbazate ligands. The complexes are all non-electrolytes in DMF solution, indicating that they are not dissociated in solution. $TcO(BAD)_2Cl$, $TcO(BFD)_2Cl$, $TcO(DDD)_2Cl$ and $TcO(APD)_2Cl$ are all insoluble in water and soluble in acetone, DMF, chloroform and dichloromethane. $TcO(AFD)_2Cl$ and $TcO(ATD)_2Cl$ are also insoluble

TABLE I. Physico-chemical Properties and Elemental Analyses

Complex	C (%)		H (%)		N (%)		Cl (%)		Conductivity[a] (μS cm^{-1})
	calc.	found	calc.	found	calc.	found	calc.	found	
$TcO(BAD)_2Cl$	37.99	37.81	3.19	3.17	9.85	9.54	6.24	6.15	20.3
$TcO(BFD)_2Cl$	49.96	50.37	3.63	3.85	7.77	7.49	4.92	5.16	17.2
$TcO(AFD)_2Cl$	33.30	33.27	3.14	3.16	9.71	9.69	6.14	6.32	19.3
$TcO(ATD)_2Cl$	31.55	31.90	2.98	3.27	9.20	9.08	5.82	5.97	19.6
$TcO(ATD)_3$	36.62	36.53	3.46	3.58	10.68	10.14	–	–	20.8
$TcO(APD)_2Cl$	25.39	25.57	3.84	3.82	11.85	12.28	7.50	7.19	21.2
$TcO(DDD)_2Cl$	41.20	41.38	6.60	6.58	8.74	8.93	5.53	5.40	18.9

[a] Of 10^{-3} mol dm^{-3} DMF solutions of the complexes at 25 °C.

TABLE II. Selected Infrared Spectral Data of the Complexes (cm^{-1})[a]

Complex	ν(Tc=O)	$\nu(C\underline{\cdots}N)_{nc}$[b]	$\nu(C\underline{\cdots}N)_{c}$[b]	ν(Tc–S)	$\nu(CS_2)$
$TcO(BAD)_2Cl$	960	1570	1470	322	1002
$TcO(BFD)_2Cl$	977	1555	1510	318	990
$TcO(AFD)_2Cl$	905	1535	1465		995
$TcO(ATD)_2Cl$	935	1505	1475		992
$TcO(ATD)_3$	–	1575	1530	325	995
$TcO(APD)_2Cl$	969	1589	1511	333	995
$TcO(DDD)_2Cl$	960	1576	1492	331	998

[a] As KBr discs. [b] nc = non-coordinating; c = coordinating.

in water, and only slightly soluble in acetone, DMF, chloroform and dichloromethane. All the complexes are indefinitely stable in the solid state.

$Tc(ATD)_3$ was isolated as a brown powder by concentrating the filtrate after the isolation of TcO$(ATD)_2Cl$. $Tc(ATD)_3$ is insoluble in water and soluble in acetone, DMF, chloroform and dichloromethane. It is also a non-electrolyte in DMF solution.

Infrared Data

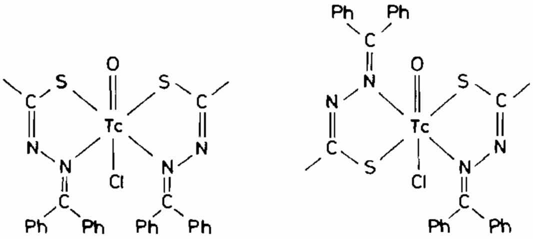
The infrared data are given in Table II. All the complexes, except $Tc(ATD)_3$, exhibit a strong Tc=O vibration in the 905 to 977 cm^{-1} range. $Tc(ATD)_3$ has no absorption band in this range which can be ascribed to a Tc=O vibration. The oxo-group is thus absent in the $Tc(ATD)_3$ complex, which contains technetium in the lower +3 oxidation state, since a multiply bonded oxygen atom is unknown in the lower oxidation states of technetium.

The strong absorption bands of the CS_2 vibration that appear at about 1000 cm^{-1} are all split or shouldered. The two sulphur atoms are thus not equivalent, indicating coordination only through the thiolic sulphur atom. This fact is also supported by the presence of Tc–S vibrations in the 320 to 335 cm^{-1} range in all the complexes.

The assignment of Tc–N vibrations is complicated by the presence of a number of peaks in the expected range, and they were therefore not assigned. Two sets of imine (>C=N–) vibrations are observed in each complex, that is, in the 1505 to 1590 cm^{-1} range and in the 1465 to 1530 cm^{-1} range. Both the ν(C=N) absorptions show partial double bonding character. This double bonding character of the imine bonds in the 1465 to 1530 cm^{-1} range is indicative of the fact that coordination also occurs through the β-nitrogen atoms.

In the $TcO(BAD)_2Cl$ complex the ν(Tc=O) was observed at 960 cm^{-1}, the coordinating ν(C=N) at 1470 cm^{-1}, the non-coordinating ν(C=N) at 1570 cm^{-1} and the ν(Tc–S) vibration at 322 cm^{-1}. For the $TcO(BFD)_2Cl$ complex the ν(Tc=O) was found at 977 cm^{-1}, the coordinating ν(C=N) at 1510 cm^{-1}, the non-coordinating ν(C=N) at 1555 cm^{-1} and the ν(Tc–S) vibration at 318 cm^{-1}. The ν(Tc=O) and coordinating ν(C=N) absorption bands are surprisingly at a higher energy in $TcO(BFD)_2Cl$ than in the $TcO(BAD)_2Cl$ complex. The expectation was that the two phenyl groups of the BFD ligand would show a greater induction effect relative to the one phenyl group of the BAD ligand. This greater induction effect would lead to stronger coordination by the imine nitrogen atom, that will consequently weaken the Tc=O bond. This is in contrast to the observations.

The complex $TcO(BFD)_2Cl$ can have basically only two point symmetries, *i.e.* C_s (**IIIa**) and C_2 (**IIIb**) (Scheme 3).



IIIa **IIIb**

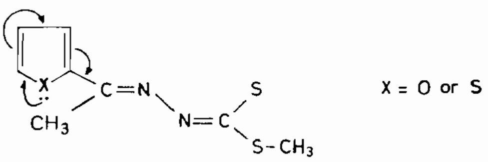
Scheme 3.

On the basis of steric considerations one would expect the TcO(BFD)$_2$Cl complex to be of C_2 symmetry; however, this arrangement would be unable to provide a sensible explanation for the above contrasts in the infrared data. The consideration of the C_s symmetry arrangement can, however, lead to an acceptable account of the observed contrasts.

The repulsion effect as a result of the large steric requirements of the benzophenone groups in the C_s symmetry arrangement will lead to considerable distortion of the ligands, and thus leading to an elongated Tc–N bond. This weakened coordination of the imine nitrogen thus leads to a stronger Tc=O bond. The explanation for the above exceptions thus indicate the point symmetry of all these oxotechnetium(V) complexes must be C_s, in which the coordinating sulphur atom of one BFD ligand is *trans* to the coordinating nitrogen atom of the second BFD ligand, and vice versa, in the TcO(BFD)$_2$Cl complex.

In the TcO(AFD)$_2$Cl complex the ν(Tc=O) is observed at 905 cm^{-1}, the non-coordinating ν(C=N) at 1535 cm^{-1} and the coordinating ν(C=N) vibration at 1465 cm^{-1}. An assignment of a ν(Tc–S) vibration could not be made with reasonable certainty. For the TcO(ATD)$_2$Cl complex the ν(Tc=O) vibration is observed at 935 cm^{-1}, with the non-coordinating ν(C=N) at 1505 cm^{-1} and the coordinating ν(C=N) at 1475 cm^{-1}. The Tc=O stretching vibrations in these two complexes are at lower energy than what were found for the TcO(BAD)$_2$Cl and TcO(BFD)$_2$Cl complexes.

These large differences in energy between the vibrations in the two classes of compounds are mainly attributed to the influence of the oxygen and sulphur atoms of the furan and thiophene groups respectively. The oxygen and sulphur atoms increase the electron density on the coordinating C=N double bonds in such a way that stronger coordination by the nitrogen atoms is possible. The stronger nitrogen coordination will shift the ν(C$\underline{\cdots\cdots}$N) vibration to lower energy. The greater influx of electron density in the planar region will weaken the Tc=O bond accordingly. This behaviour is illustrated in Scheme 4.



Scheme 4.

The induction effect of the thiophene and furan groups is thus considerably bigger than that of phenyl or methyl groups. The difference in energy between the ν(Tc=O) vibrations of TcO(AFD)$_2$Cl (905 cm^{-1}) and TcO(ATD)$_2$Cl (935 cm^{-1}) is the result of the greater ease in which an oxygen atom can participate in such a conjugated system.

There is no ν(Tc=O) vibration present in the infrared spectrum of Tc(ATD)$_3$, while the coordinating ν(C=N) absorption appears at 1530 cm^{-1} and the non-coordinating ν(C=N) vibration at 1575 cm^{-1}. The coordinating ν(C=N) absorption appears at a much higher energy as was found for the previous oxotechnetium(V) complexes, since the technetium ion is in the lower +3 oxidation state, and will require less electron density to stabilize it. Coordination by the nitrogen atoms will thus be weaker, and the coordinating C=N bond will have more double bond character and will appear accordingly at a higher energy.

In the TcO(APD)$_2$Cl complex the ν(Tc=O) was observed at 969 cm^{-1}, the coordinating ν(C=N) at 1511 cm^{-1} and the ν(Tc–S) vibration at 333 cm^{-1}. For the TcO(DDD)$_2$Cl complex the ν(Tc=O) was found at 960 cm^{-1}, the coordinating ν(C=N) at 1492 cm^{-1} and the ν(Tc–S) vibration at 331 cm^{-1}. The weaker Tc=O and coordinating C=N bonds in the TcO(DDD)$_2$Cl complex can be satisfactorily explained by the greater positive inductive effect of the tertiary butyl groups in the DDD ligand relative to the methyl groups in the APD ligand. This greater positive inductive effect will lead to stronger Tc–N coordination in the TcO(DDD)$_2$Cl complex, with the resultant weaker Tc=O and coordinating C=N bonds.

Optical Data

Details from the electronic spectra of all the complexes prepared in this study are given in Table III. There is generally one strong absorption band in the 315–336 nm range and at least one band in the 275–295 nm range. The intensities of the absorption bands are such that they can be ascribed to charge transfer transitions. The bands in the 315–336 nm range are mainly associated with the charge transfer from the sulphur to the technetium(V) ion, and those in the 275–295 nm region with the charge transfer between the oxo oxygen and technetium [7].

TABLE III. Electronic Absorption Spectral Data of the Complexes in Chloroform at 20 °C

Complex	λ (nm) (ε (dm^3 cm^{-1} mol^{-1}))			
$TcO(BAD)_2Cl$	518sh,	357sh,	315(28200)	
$TcO(BFD)_2Cl$	411sh,	326(33600),	284(24300)	
$TcO(AFD)_2Cl$	474(3800),	322(29700),	273(26600)	
$TcO(ATD)_2Cl$	474(3100),	394sh,	323(26400),	292(25800)
$TcO(ATD)_3$	524(2700),	413sh,	336(39600),	273(33900)
$TcO(APD)_2Cl$	378sh,	309sh,	278(24100)	
$TcO(DDD)_2Cl$	372sh,	301sh,	280sh,	273(22800)

The sulphur to technetium charge transfer absorption band for $Tc(ATD)_3$ appears at 336 nm. The lower oxidation state of technetium in this compound reduces the charge transfer from the sulphur atom considerably, with the result that the absorption band shifts to lower energy.

Discussion

A reduced complex $Tc(ATD)_3$ was obtained from the filtrate after the isolation of $TcO(ATD)_2Cl$. The isolation of the technetium(III) compound shows that the formation of reduced species is possible by the reduction of the technetium(V) nucleus, possibly by hydrogen chloride that is formed during complex formation. Reduction by the ligand ATD is of course also possible. The isolation of $Tc(ATD)_3$ therefore leads to the following proposed reaction Scheme 5.

$$TcOCl_4^- \xrightarrow{+L} TcOLCl_2 \xrightarrow{+L} TcOL_2Cl \xrightarrow[\text{reduction}]{+L} TcL_3$$

Scheme 5.

Efforts to isolate complexes with the general formula $TcOLCl_2$ failed. It thus appears that the sulphur atom and the weak imine nitrogen coordination, together with two chloride ions, are not sufficient to stabilize the technetium(V) nucleus. The $TcOLCl_2$ species is therefore only an intermediate in the synthetic route of the $TcOL_2Cl$ complexes.

All the complexes studied are non-electrolytes in DMF solution. They are therefore all six-coordinated and the coordination geometry will thus be octahedral. In the $TcOL_2Cl$ complexes the oxo oxygen and the chloride ions will be in the apical positions *trans* to one another. It further appears that the two substituted dithiocarbazate ligands in the oxo-complexes will assume a syn arrangement of the ligand tails, rather than anti, in the planar region of the octahedral system.

Conductivity measurements of the complexes indicate that the chloride ions are coordinated, and do not exist as simple counterions. This phenomenon is not generally found, since the strong *trans* effect of the oxo oxygen will labilize the sixth coordinatin position *trans* to itself, and leads to the production of five-coordinate square pyramidal geometries. It appears therefore that the dithiocarbazate ligands weaken the *trans* influence of the oxo-group considerably, so that coordination of the chloride ion can occur. The fact that each chelate only provides one negative charge may lead to the situation that insufficient negative charge is available to neutralize the high positive charge on the technetium(V) ion. Coordination of a chloride ion will therefore contribute to the effective neutralization of the metal ion.

Although the prepared oxotechnetium(V) complexes have a d^2 electron configuration, they are all diamagnetic. This is in accordance with all the technetium(V) complexes isolated to date.

The characterized complexes in this study show a definite correlation between the strength of the Tc=O bond and the degree of double bond character of the coordinating C=N bond. The relative strength of the Tc=O bond is mainly determined by the electronic influence of the *cis*-ligands and not by the presence or influence of a ligand *trans* to the oxo group. The stronger the Tc=O bond, the weaker is the nitrogen coordination and the more double bond character will the coordinating C=N bond have.

Acknowledgements

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