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## COMPLEXES OF TECHNETIUM(V) WITH POTENTIALLY TRIDENTATE SCHIFF BASES DERIVED FROM S-METHYLDITHIOCARBAZATE

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The syntheses and characterization of several new neutral oxotechnetium(V) complexes with potentially dianionic tridentate Schiff bases, derived from S-methyldithiocarbazate, are described. For a 1:1 metal ion to ligand ratio the five-coordinate complexes TcOLCl were isolated in all cases. Only in one case could a six-coordinate TcOL<sub>2</sub>Cl, with the ligand acting as a bidentate chelate, be isolated from a 1:2 metal ion to ligand ratio. Magnetic susceptibility measurements of the complex TcO(HAF)Cl surprisingly indicate paramagnetism with a d<sup>2</sup> electronic configuration, while all the other compounds were found to be diamagnetic. The relative strength of the Tc=O bond is mainly determined by the electronic influence of the *cis*-ligands. The complexes have been characterized by elemental analyses, infrared and electronic spectra, and conductance measurements.

### INTRODUCTION

The number and diversity of sulphur-nitrogen chelating agents used to prepare new coordination and organometallic compounds have increased rapidly during the past few years.<sup>1-3</sup> The pronounced biological activity of the metal complexes of ligands derived from dithiocarbazic acids has created considerable interest in their coordination chemistry.<sup>4,5</sup> Although complexes of dithiocarbazates with many different transition metal ions have been studied extensively, no information on bonding and structural factors is available for technetium complexes.

In this account, we report the formation and characterization of oxotechnetium(V) complexes with potentially dianionic tridentate Schiff bases, derived from S-methyldithiocarbazate. Structural formulae for the Schiff base ligands used in this study are given in Figure 1. Our interest in these type of ligands is the unusual steric and electronic properties of the resulting complexes, on the basis of specific differences in polarizability, covalency and  $\pi$ -bonding ability of these ligands. Since the sulphur atoms in dithiocarbazates have the ability to participate in  $\pi$ -bonding in addition to  $\sigma$ -donation, metal ions in unusually high oxidation states can be stabilized.

The tautomeric forms of these Schiff bases, formed by the condensation of S-methyldithiocarbazate with  $\beta$ -diketones or 2-hydroxyacetophenone, can by the loss of two protons in solution, act as dianionic tridentate ligands, as is shown in Figure 2. Coordination to a metal ion can now take place *via* the anionic oxygen, mercapto sulphur and  $\beta$ -imine nitrogen of tautomeric form (b) in Figure 2

### EXPERIMENTAL

Technetium as NH<sub>4</sub>[<sup>99</sup>TcO<sub>4</sub>] was purchased from the Oak Ridge National Laboratory

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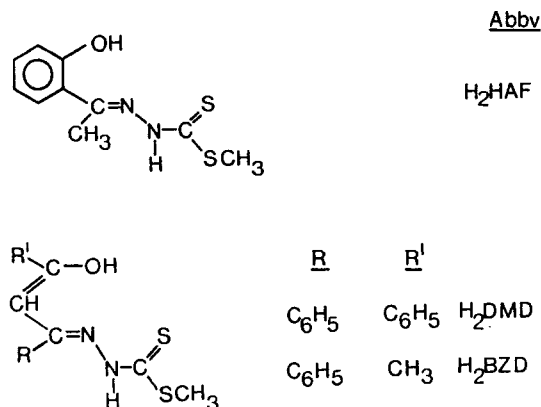


FIGURE 1 The potentially tridentate Schiff base ligands used in the study.

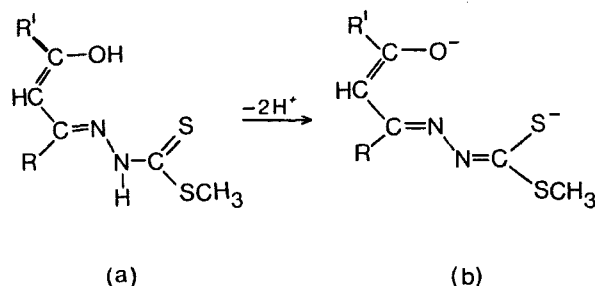


FIGURE 2 The tautomeric forms of the Schiff base ligands.

as the dry salt.  $^{99}Tc$  is a weak  $\beta$ -emitter (0.292 KeV); therefore, all manipulations were carried out in a radiation 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 IR 4250 grating spectrophotometer in the range  $4000-250\text{ cm}^{-1}$  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<sup>6</sup> on an 80 MHz Bruker spectrometer. Elemental analyses were performed by the Analytical Section of the National Chemical Research Laboratory, CSIR, Pretoria. 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.  $(n-Bu_4N)[TcOCl_4]^{7-}$  and *S*-methylthiocarbamate<sup>4</sup> were prepared by using literature methods.

#### Preparations

*S*-methyl- $\beta$ -*N*-(2-hydroxyphenylethylidene)dithiocarbamate ( $H_2HAF$ ), 1-hydroxo-1,3-

diphenyl-4,5-diaza-6-thiono-7-thiaocta-1,3-diene ( $H_2DMD$ ) and 2-hydroxo-4-phenyl-5,6-diaza-7-thiono-8-thianona-2,4-diene ( $H_2BZD$ ). S-methyldithio-carbazate (2.5 g, 20 mmol) and the corresponding ketone (20 mmol) were stirred in ethanol and hydrochloric acid ( $10 \text{ mol dm}^{-3}$ ; 2 drops) for two hours at reflux conditions. The products were precipitated by cooling in ice. These products were then filtered under vacuum, washed with cold ethanol and dried *in vacuo*. Recrystallization was from ethanol. Yield = 79–86%.

#### *TcO(HAF)Cl*

The ligand  $H_2HAF$  (23.9 mg, 0.1 mmol) in  $5 \text{ cm}^3$  ethanol was added to 50 mg of  $(n\text{-Bu}_4\text{N})[\text{TcOCl}_4]$  (0.1 mmol) in  $5 \text{ cm}^3$  ethanol, and the mixture was stirred for 30 minutes. The solution immediately became dark red, and after a few seconds a golden brown precipitate formed, which was filtered, washed with ethanol and dried under vacuum. Recrystallisation from dichloromethane/hexane gave red prisms; yield = 87%.

#### *TcO(DMD)Cl*

The mixture of 32.8 mg of the ligand  $H_2DMD$  (0.1 mmol) in  $5 \text{ cm}^3$  ethanol and 50 mg of  $(n\text{-Bu}_4\text{N})[\text{TcOCl}_4]$  in  $5 \text{ cm}^3$  ethanol was stirred for 30 minutes. The solution immediately assumed a red colour, which became darker with time. No immediate precipitate formed, as was the case in the preparation of  $\text{TcO(HAF)Cl}$ . The slow evaporation of the solvent under vacuum led to the formation of red needles, which were filtered, washed with cold ethanol and dried *in vacuo*. Yield = 62%.

#### *TcO(BZD)Cl*

The ligand  $H_2BZD$  (26.6 mg, 0.1 mmol) in  $5 \text{ cm}^3$  ethanol was added to 50 mg of  $(n\text{-Bu}_4\text{N})[\text{TcOCl}_4]$  in  $5 \text{ cm}^3$  ethanol, and the mixture was stirred for 30 minutes. A brown precipitate formed immediately, which was filtered, washed with ethanol and dried *in vacuo*. Recrystallization from dichloromethane/hexane gave red needles; yield = 71%.

#### *TcO(BZD)<sub>2</sub>Cl*

The ligand  $H_2BZD$  (79.8 mg, 0.3 mmol) in  $8 \text{ cm}^3$  ethanol was added to 50 mg of  $(n\text{-Bu}_4\text{N})[\text{TcOCl}_4]$  in ethanol, and the mixture was stirred for one hour. On addition a red solution was produced immediately, and a brown powder precipitated slowly. The product was filtered, washed with cold ethanol and dried *in vacuo*. Recrystallization from acetone/ethanol gave dark red prisms; yield = 68%, based on Tc.

## RESULTS AND DISCUSSION

It is theoretically possible that the reaction of S-methyldithiocarbazate with benzoyl-acetone in equimolar quantities can lead to a mixture of two products, depending upon whether condensation occurs at carbonyl groups (a) or (b) in Figure 3. It was possible to isolate a pure compound by fractional distillation, in which the dithiocarbazate unit condensed with carbonyl group (a). Evidence for the existence of this ligand was

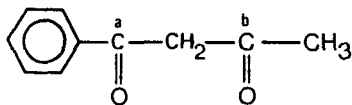


FIGURE 3 Benzoylacetone with carbonyl groups (a) and (b).

obtained by <sup>1</sup>H NMR studies. A comparison of the NMR spectra of benzoylacetone and the isolated derivative is given in Table I. No significant shift in the CH<sub>3</sub> peak of the benzoylacetone unit ( $\delta$ 2.00 versus  $\delta$ 1.97 ppm) was observed, which shows that no reaction occurred with carbonyl group (b). The phenyl peaks at  $\delta$ 7.70 and  $\delta$ 7.25 ppm in benzoylacetone are shifted to  $\delta$ 7.15 in the isolated ligand. This shift, as well as the appearance of only one phenyl peak in the NMR spectrum after reaction, shows clearly that condensation occurred with carbonyl group (a). The disappearance of the CH<sub>2</sub> peak at  $\delta$ 5.95 ppm in benzoylacetone after condensation also provides proof that the H<sub>2</sub>BZD ligand exists in the enol form.

TcOCl<sub>4</sub><sup>-</sup> reacts with potentially dianionic, tridentate dithiocarbazate Schiff base ligands (L) in ethanol under aerobic conditions to form complexes of the general formula TcOLCl. All the complexes are crystalline and indefinitely stable in the solid state. They are insoluble in water, slightly soluble in polar organic solvents and very soluble in DMF, acetone, chloroform and dichloromethane. They are also non-electrolytes in DMF solution.

TcOCl<sub>4</sub><sup>-</sup> also reacts with the potentially tridentate Schiff base H<sub>2</sub>BZD in a 1:2 molar ratio in ethanol under aerobic conditions at room temperature to form a complex of the formula TcO(BZD)<sub>2</sub>Cl. This complex is crystalline, a non-electrolyte in DMF solution and stable in the solid state. TcO(BZD)<sub>2</sub>Cl is insoluble in water and soluble in DMF, acetone, chloroform and dichloromethane. All the elemental analyses of the Schiff base ligands and complexes prepared are given in Table II.

TABLE I  
Summary of the proton NMR spectra of benzoylacetone and derivative

	Benzoylacetone <sup>a</sup>	Benzoylacetone derivative <sup>a</sup>
Phenyl	7.75; 7.25	7.15
CH <sub>2</sub>	5.95	
C-CH <sub>3</sub>	2.00	1.97
S-CH <sub>3</sub>		2.35
CH		6.30

<sup>a</sup>Chemical shift values in ppm.

TABLE II  
Elemental analyses and conductivity data

Complex/ Ligand	%C		%H		%N		%Cl		Conductivity <sup>a</sup> ( $\mu$ S cm <sup>-1</sup> )
	Calc.	Fnd.	Calc.	Fnd.	Calc.	Fnd.	Calc.	Fnd.	
H <sub>2</sub> HAF	47.60	47.62	4.79	4.87	11.10	11.34			
H <sub>2</sub> DMD	65.82	65.69	4.91	4.89	8.53	8.47			
H <sub>2</sub> BZD	54.11	54.17	5.30	5.12	10.52	10.81			
TcO(HAF)Cl	30.89	31.09	2.59	2.50	7.21	7.18	9.12	9.41	18.3
TcO(DMD)Cl	42.82	42.68	2.96	2.47	5.87	5.96	7.43	7.38	17.1
TcO(BZD)Cl	34.75	34.66	2.92	3.15	6.75	6.74	8.55	8.68	17.9
TcO(BZD) <sub>2</sub> Cl	42.32	42.35	3.85	3.34	8.23	8.29	5.20	5.22	19.2

<sup>a</sup>Of 10<sup>-3</sup> mol dm<sup>-3</sup> DMF solutions of the complexes at 25°C.

*Infrared Data*

A summary of the infrared data is given in Table III. The non-coordinating C=N stretching vibrations appear in the 1515–1600  $\text{cm}^{-1}$  range, while the C=N stretching vibrations of the coordinating nitrogen are found in the 1480–1525  $\text{cm}^{-1}$  range. These low frequencies of the coordinating imine bonds (1480–1525  $\text{cm}^{-1}$ ) indicate that these only have partial double bond character, so that coordination to the technetium(V) ion takes place through the  $\beta$ -nitrogen atom.

The  $\nu(\text{CS}_2)$  vibrations appear at 995–1005  $\text{cm}^{-1}$  and are split in all the complexes, with the  $\nu(\text{Tc-S})$  signals appearing at 300–365  $\text{cm}^{-1}$ . No S-H stretching vibrations are found in the 2550–2650  $\text{cm}^{-1}$  range, indicating that coordination to the metal ion also occurs through the mercapto sulphur atom of the thioenolate form of the Schiff base ligands. The O-H vibrations at 3200–3600  $\text{cm}^{-1}$  in the spectra of the ligands disappear upon complex formation, indicating that coordination also takes place through the oxygen atom of the ligand in the  $\text{TcOLCl}$  complexes.

The Tc=O stretching vibrations appear in the range 917–985  $\text{cm}^{-1}$ . It is significant that the  $\nu(\text{Tc=O})$  bands in the  $\text{TcOLCl}$  complexes appear at the relatively high frequencies of 985  $\text{cm}^{-1}$ , 980  $\text{cm}^{-1}$  and 977  $\text{cm}^{-1}$  respectively for the complexes containing the ligands HAF, DMD and BZD. These high frequencies represent very strong Tc=O bonding. The presence of the Tc=O group also infers that the technetium ion is in the +5 oxidation state, and that only substitution of the chloride ligands in  $\text{TcOCl}_4$  takes place during reaction.

For the  $\text{TcO}(\text{HAF})\text{Cl}$  complex the non-coordinating C=N stretching vibration appears at 1600  $\text{cm}^{-1}$ , the coordinating C=N vibration at 1525  $\text{cm}^{-1}$  and the  $\nu(\text{Tc=O})$  band at 985  $\text{cm}^{-1}$ . The relatively strong Tc=O bond is ascribed to the apparent weak coordination of the *cis*-atoms in the planar region. (Coordination of the ligand to the metal ion occurs through the mercapto sulphur,  $\beta$ -nitrogen and the phenolic oxygen atoms). When coordination takes place through the phenolic oxygen atom, the induction effect of the phenyl group will tend to weaken the adjacent imine bond, so that the coordination by the imine nitrogen will be considerably weaker, as can be realized from the higher frequency of the coordinating C=N stretching vibration. The relatively weak influx of electron density to the technetium(V) ion in the basal plane is also reflected by the relatively weak Tc-S coordination, as is indicated by the comparatively low frequency of 300  $\text{cm}^{-1}$  for the Tc-S stretch.

For the  $\text{TcO}(\text{DMD})\text{Cl}$  and  $\text{TcO}(\text{BZD})\text{Cl}$  complexes the non-coordinating  $\nu(\text{C}\cdots\text{N})$  vibrations are found at 1540  $\text{cm}^{-1}$  and 1530  $\text{cm}^{-1}$ , the coordinating  $\nu(\text{C}\cdots\text{N})$  at 1480  $\text{cm}^{-1}$  and 1490  $\text{cm}^{-1}$ , the  $\nu(\text{Tc=O})$  vibrations at 980  $\text{cm}^{-1}$  and 977  $\text{cm}^{-1}$  and the  $\nu(\text{Tc-S})$  bands at 345  $\text{cm}^{-1}$  and 350  $\text{cm}^{-1}$ , respectively. The coordinating and non-coordinating  $\nu(\text{C}\cdots\text{N})$  bands are found at lower energy than in the complex  $\text{TcO}(\text{HAF})\text{Cl}$ . This result can be explained by viewing the DMD and BZD ligands as a conjugated system, as is shown in Figure 4. The imine bonds of the ligands in such a conjugated system will only have partial double bond character, with the result that the  $\nu(\text{C}\cdots\text{N})$  bands will shift to lower energy. The coordinating band will be at lower

TABLE III  
Selected infrared spectral data for the complexes ( $\text{cm}^{-1}$ )<sup>a</sup>.

Complex	$\nu(\text{Tc=O})$	$\nu(\text{C=N})_{\text{nc}}^b$	$\nu(\text{C=N})_{\text{c}}^c$	$\nu(\text{CS}_2)$	$\nu(\text{Tc-S})$	$\nu(\text{C=O})$
$\text{TcO}(\text{HAF})\text{Cl}$	985	1600	1525	1005	300	
$\text{TcO}(\text{DMD})\text{Cl}$	980	1540	1480	995	345	
$\text{TcO}(\text{BZD})\text{Cl}$	977	1530	1490	1000	350	
$\text{TcO}(\text{BZD})_2\text{Cl}$	917	1515	1490	998	365	1685

<sup>a</sup>In KBr discs; <sup>b</sup>nc=non-coordinating; <sup>c</sup>c=coordinating

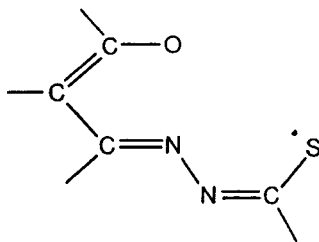


FIGURE 4 The Schiff base ligand viewed as a conjugated system.

energy than the non-coordinating band, since the  $\beta$ -nitrogen atom will also be used for coordination to the metal ion.

The influence of the *cis*-ligands in the basal plane on the strength of the Tc=O bond is also clearly illustrated by the two complexes TcO(DMD)Cl and TcO(BZD)Cl. TcO(DMD)Cl has a stronger Tc=O bond (higher Tc=O stretching frequency) than TcO(BZD)Cl, but a weaker Tc-S bond.

The TcO(BZD)<sub>2</sub>Cl complex has a non-coordinating C=N stretching vibration at 1515 cm<sup>-1</sup>, with the coordinating  $\nu(\text{C}\cdots\text{N})$  stretch appearing at 1490 cm<sup>-1</sup>. These lower C=N frequencies can again be explained in terms of a conjugated ligand system. The  $\nu(\text{Tc}=\text{O})$  band at 917 cm<sup>-1</sup> is at considerably lower energy than in the TcOLCl complexes. The strength of the Tc=O bond depends mainly on the nature of the ligands in the *cis* positions. From the lower energy values of the C=N stretching frequencies, and especially the stronger Tc-S bond (365 cm<sup>-1</sup>), it is clear that there is a greater influx of electron density in the basal plane to the technetium(V) ion, so that the Tc=O bond will weaken accordingly. In contrast to the TcOLCl complexes, the TcO(BZD)<sub>2</sub>Cl complex is six coordinated, with the ligand BZD acting as a mono-anionic bidentate chelate. From the presence of the Tc-S vibrations, as well as the presence of a C=O stretching vibration at 1685 cm<sup>-1</sup>, it is clear that coordination to the metal ion occurs through the mercapto sulphur and the  $\beta$ -nitrogen atoms. Since the complex TcO(BZD)<sub>2</sub>Cl is a non-electrolyte, the complex geometry will be distorted octahedral, with the oxo oxygen and chloride atoms presumably in the apical positions and the ligand sulphur and nitrogen atoms in the square plane.

#### Magnetic Data

The magnetic moment of TcO(HAF)Cl was surprisingly found to be 2.45 BM, corresponding to the presence of two unpaired electrons in the 4d energy level of the technetium(V) nucleus. The paramagnetism of this complex is in contrast with all previously synthesized oxotechnetium(V) complexes, found to be diamagnetic with a square pyramidal geometry.<sup>8</sup> The diamagnetism of oxotechnetium(V) complexes has been ascribed to the strong ligand field of the oxo ligand that destabilizes the  $d_{xz}$  and  $d_{yz}$  orbitals 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 explanation is to consider a trigonal bipyramidal geometry of the complex. A highly distorted square pyramidal geometry leads to a trigonal bipyramid, as recently found for the complex ReO(Et<sub>2</sub>NCS<sub>2</sub>)(NHNCSSMe).<sup>9</sup>

The complexes TcO(DMD)Cl, TcO(BZD)Cl and TcO(BZD)<sub>2</sub>Cl, in which the Schiff base ligands are derived from  $\beta$ -diketones, were all found to be diamagnetic. It therefore appears that the five-coordinated TcO(DMD)Cl and TcO(BZD)Cl complexes are square pyramidal.

*Electronic Spectra*

A summary of the electronic spectra of all the prepared complexes is given in Table IV.

TABLE IV  
Electronic spectral data for the complexes in chloroform at 20°C

Complex	$\lambda/\text{nm}(\epsilon/\text{M}^{-1} \text{cm}^{-1})$		
TcO(HAF)Cl	457(3100),	352(8900),	285(18500).
TcO(DMD)Cl	495(6000),	356(13100),	279(14800).
TcO(BZD)Cl	476(5400),	345(10700),	268(14200).
TcO(BZD) <sub>2</sub> Cl	373(11600),	291sh,	258sh.

The spectra are generally of a very complex nature, and quite a number of absorption bands appear in the 250–500 nm range. At least one strong absorption band appears in each of the ranges 345–373 nm and 268–291 nm. The interpretation of these spectra is difficult, but according to their intensities the bands in the 345–373 nm and 268–291 nm range can be considered as due to charge transfer transitions. It has previously been shown<sup>10</sup> that the transition in the 345–373 nm range can be ascribed to charge transfer between the sulphur and technetium ions, with the higher energy absorption bands at 268–291 nm mainly the result of charge transfer between the oxo oxygen and the technetium(V) ion.

For the complexes with the general formula TcOLCl an additional absorption band is found in the 457–495 nm range. This band is of lower intensity than the others in the 345–373 nm and 268–291 nm ranges, and is attributed to charge transfer transitions between the ligand oxygen atom and the technetium(V) ion. The absence of this absorption band in the spectrum of TcO(BZD)<sub>2</sub>Cl is further proof that no coordination occurs through the oxygen atom of the ligand HBZD<sup>-</sup>.

Efforts to prepare complexes with the general formula TcOL<sub>2</sub>Cl with the ligands H<sub>2</sub>HAF and H<sub>2</sub>DMD failed. These attempts led to the isolation of TcOLCl. It is thus clear that the complexes with the dianionic tridentate ligands are more stable than complexes with the mono-anionic bidentate ligands. These unsuccessful efforts can partially be ascribed to steric and electrostatic effects. Where the steric requirements of the ligands, or the electrostatic repulsion between the ligands in a *bis* complex are large, the rate of complex formation will be retarded. This delay in the binding of the second ligand will give the third donor atom of the first ligand the opportunity to coordinate thus preventing the second Schiff base ligand to bind to the metal ion.

## ACKNOWLEDGEMENTS

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