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# The Chemistry of Rhenium and Technetium.
# Part III. The Synthesis and Characterisation of Oxo-bis-(tetrathiomolybdenato)-Technetium(V) and its Reduction by Triphenylphosphine

J. G. H. DU PREEZ and T. I. A. GERBER*

*Uranium Research Unit, University of Port Elizabeth, P. O. Box 1600, Port Elizabeth, 6000, South Africa*

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## Abstract

The complexes $(Bu_4N)[TcO(MoS_4)_2]$ and $Tc(PPh_3)_2(MoS_4)_2$ were prepared. The former complex has a much lower Tc–O stretching frequency than is generally found for the $TcO^{3+}$ moiety. The latter technetium(IV) complex was obtained by the reduction of $Tc^{(V)}O(MoS_4)_2^-$ with triphenylphosphine and also by the substitution reaction of $TcCl_4(PPh_3)_2$ with $MoS_4^{2-}$. Previous reductions of this nature have led to the isolation of species that differ by two formal oxidation state numbers from the oxidant.

## Introduction

Whereas heteropolyanions have been known for a long time [1], novel transition-metal complexes of the type $[M(WS_4)_2]^{2-}$ (M = Ni, Zn) were first reported only recently [2, 3]. The vibrational spectra and structural analyses gave evidence that the dianionic ligands $M^1S_4^{2-}$ ($M^1$ = Mo, W) act as bidentate ligands [4]. This rather uncommon sulphur donor ligand acts as a strong $\sigma$ donor and mild $\pi$ acceptor ligand of high ligand field strength, as indicated for example by the square planar spin-paired complex formed with Ni(II) [5]. Electronic, ESR and magnetic measurements implied the existence of strong, highly covalent metal–ligand interactions [6]. This indicates an interesting type of bonding in the $S_2M^1S_2MS_2M^1S_2$ bridge with a strongly delocalised $\pi$-electron system.

Although these complexes, containing simple transition-metal complexes as ligands, have been well studied with the first row transition elements, similar complexes of the early heavy transition metals have not been reported in the literature.

Since we are interested in the influence of the extent of electron delocalisation in the planar system on the properties of the axial oxo-ligands in technetium(V) complexes [7, 8], and since the bridge system of complexes of the type $[M(MoS_4)_2]^{2-}$ provides strong electron delocalisation between metal centres of different valence states , efforts were directed towards utilising these ligands as planar coordinating groups in the synthesis of oxo-technetium(V) compounds. This approach has led to the isolation of $(Bu_4N^+)[TcO(MoS_4)_2^-]$ and $Tc(PPh_3)_2(MoS_4)_2(H_2O)$ ($Bu_4N^+$ = tetrabutylammonium). The latter technetium(IV) complex was obtained either by the reduction of $[TcO(MoS_4)_2]^-$ with triphenylphosphine, or by the reaction of $TcCl_4(PPh_3)_2$ with $(NH_4)_2MoS_4$.

The preparation of reduced monomeric complexes from Re(V) and Tc(V) in the presence of a reducing agent capable of forming an oxide is quite common [9, 10]. Neutral Tc(V) and Re(V) oxo species lead to complexes of these metals in the +3 formal oxidation state [10]. In contrast to the above, evidence is presented in this paper that reduction of an anionic Tc(V) species by triphenylphosphine leads to the formation of a Tc(IV) complex.

## Experimental

Technetium (as $NH_4\,^{99}TcO_4$) was obtained from the Oak Ridge National Laboratory, Tenn. Since $^{99}Tc$ is a weak $\beta$-emitter, all manipulations were carried out in a radiation laboratory with a monitored fume hood.

Infrared spectra were recorded on a Beckman IR 4250 grating spectrophotometer in the range 4000–200 $cm^{-1}$ as KBr pellets. Optical spectra were obtained with a Perkin–Elmer 330 UV–VIS spectrophotometer. Thermal studies were made using a Perkin–Elmer thermogravimetric balance and a System 4 microprocessor controller. Conductivity measurements were performed in N,N-dimethylformamide using a Metrohm E518 conductometer. Magnetic susceptibility measurements were made on N,N-dimethylformamide solutions using the Evans NMR method [11] on a Perkin Elmer R12A spectrometer. Elemental analyses were performed by the

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*Author to whom correspondence should be addressed.

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Analytical Chemistry Department of the University of Cape Town.

All the solvents used were purified and dried by standard methods. $(Bu_4N)[TcOCl_4]$ [12], $TcCl_4(PPh_3)_2$ [13] and $(NH_4)_2MoS_4$ [14] were prepared by literature methods. All other chemicals were used without further purification.

### *Preparation of Oxo-bis-(tetrathiomolybdenato)technetium(V) $[TcO(MoS_4)_2]^-(Bu_4N^+)$*

To a solution of 0.50 g of $(Bu_4N^+)[TcOCl_4^-]$ (1.0 mmol) in methanol (10 $cm^3$) was added 0.5204 g of $(NH_4)_2MoS_4$ (2.0 mmol) in 5 $cm^3$ methanol. The mixture was refluxed for 15 min. To this hot solution was added 0.28 g $Bu_4NCl$ in 2 $cm^3$ water, and on slow evaporation over 12 h, pale yellow crystals were obtained. This material was collected, washed with water (5 $cm^3$), ethanol (5 $cm^3$) and finally with acetone (2 $cm^3$). The product was dried in vacuum for 24 h. No further recrystallisation was necessary. Yield = 0.67 g, 83% based on Tc. *Anal.* Calcd. for $C_{16}H_{36}NOS_8Mo_2Tc$: C, 23.85; H, 4.50; N, 1.74. Found: C, 23.49; H, 4.38; N, 1.66%. Conductivity (DMF, $10^{-3}$ mol $dm^{-3}$): $\Lambda_M = 56$ $ohm^{-1}$ $cm^2$ $mol^{-1}$. Optical spectrum (DMF): 315 (sh), 308 (sh), 288 ($4.92 \times 10^3$).

### *Preparation of Bis-Triphenylphosphine-bis-(tetrathiomolybdenato)technetium(IV) $[Tc(PPh_3)_2(MoS_4)_2(H_2O)]$ by the Reduction of $TcO(MoS_4)_2^-$ with Triphenylphosphine*

To a solution of 0.20 g of $(Bu_4N^+)[TcO(MoS_4)_2^-]$ (0.25 mmol) in ethanol (15 $cm^3$) was added 0.329 g (1.25 mmol) triphenylphospine in 10 $cm^3$ ethanol. This mixture was refluxed for 3 h under nitrogen. The resulting dark orange solution was cooled to room temperature and filtered. Distilled water (5 $cm^3$) was added to the filtrate, which was then cooled at −12 °C for 24 h. The resulting dark red precipitate was washed with ethanol ($3 \times 5$ $cm^3$) and dried in vacuum for 24 h. Further recrystallisation was found to be unnecessary. Yield = 0.14 g, 51% based on Tc. *Anal.* Calcd. for $C_{36}H_{32}OP_2S_8Mo_2Tc$: C, 39.67; H, 2.96. Found: C, 39.49; H, 3.21%. Conductivity (DMF, $10^{-3}$ mol $dm^{-3}$): $\Lambda_M = 2.3$ $ohm^{-1}$ $cm^2$ $mol^{-1}$. Optical spectrum (DMF): 482, 397, 272 ($4.27 \times 10^4$).

### *Preparation of $[Tc(PPh_3)_2(MoS_4)_2(H_2O)]$ from $TcCl_4(PPh_3)_2$*

To a solution of 0.31 g of $TcCl_4(PPh_3)_2$ (0.4 mmol) in acetone (15 $cm^3$) was added 0.208 g of $(NH_4)_2MoS_4$ (0.8 mmol) in 5 $cm^3$ water under nitrogen. The resulting dark orange solution was filtered, and on slow evaporation dark crystals were obtained which were washed with acetone ($2 \times 5$ ml) and dried in vacuum for 24 h. Yield = 0.34 g, 78% based on Tc. *Anal.* Calcd. for $C_{36}H_{32}OP_2S_8Mo_2Tc$: C, 39.67; H, 2.96. Found: C, 39.37; H, 2.81; Cl, 0%. Optical spectrum (DMF): 482, 397, 272 ($4.26 \times 10^4$).

## Results and Discussion

The pale yellow crystalline complex $(Bu_4N^+)[TcO(MoS_4)_2^-]$ was obtained under aerobic conditions by treating $(Bu_4N^+)[TcOCl_4^-]$ in methanol with a methanolic solution of $(NH_4)_2MoS_4$. The complex is diamagnetic, soluble in ethanol and dimethylformamide, and conductivity measurements indicate an 1:1 electrolyte in DMF. The complex also appears to be indefinitely stable in the solid state.

The complex $(Bu_4N^+)[TcO(MoS_4)_2^-]$ was also reduced under anaerobic conditions in ethanol by triphenylphosphine to produce the dark red complex $Tc(PPh_3)_2(MoS_4)_2(H_2O)$. The latter complex could also be prepared by the substitution reaction of $TcCl_4(PPh_3)_2$ with $(NH_4)_2MoS_4$. $Tc(PPh_3)_2(MoS_4)_2(H_2O)$ is indefinitely stable in DMF and in the solid state, and is non-conducting in DMF. Thermal analysis of the complex indicates a hydrate, with a water molecule (1.65% of molecular mass) being removed at 110 °C (1.72% experimentally). The presence of water was also indicated by infrared spectra and microanalysis. The magnetic moment of this complex was found to be 3.51 B.M., which is indicative of a $d^3$ ($t_{2g}^3$) configuration. From the above evidence, the technetium in this complex appears therefore to be in the +4 oxidation state.

Infrared data are given in Table I. The $\nu$(Mo–S) bands of both the complexes show the characteristic splitting pattern for bidentate thiometallate complexes of the degenerate vibrations of the free ligand. The $\nu_{as}$(Tc–S) vibration in the complex $TcO(MoS_4)_2^-$ occurs at 335 $cm^{-1}$. In the complex $Tc(PPh_3)_2(MoS_4)_2$ this vibration is shifted to a lower wavenumber at 325 $cm^{-1}$, which can possibly be ascribed to the transfer of some metal electron density to the phosphorus atom via the $\pi$-back-bonding abilities of the triphenylphosphine ligands, which will decrease the Tc–S bond order. The strong signal at 543 $cm^{-1}$ in the latter complex is ascribed to the $\nu$(Tc–P) vibrations.

The complex $TcO(MoS_4)_2^-$ exhibits an intense infrared absorption at 895 $cm^{-1}$, which differs appreciably from the Tc=O stretching frequencies observed in monoxotechnetium(V) compounds, which typically occur in the range 920–1020 $cm^{-1}$. In a previous communication [8] we reported that the replacement of an ionic oxygen donor ligand atom with a sulphur donor ligand atom in distorted square pyramidal oxotechnetium systems leads, without exception, to a reduction of the Tc=O stretching frequency in anionic as well as neutral monoxotechnetium(V) complexes. We thus ascribe the vibration at 895 $cm^{-1}$ to the $\nu$(Tc=O) stretching frequency.

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

| | $(Bu_4N)[TcO(MoS_4)_2]$ | $Tc(PPh_3)_2(MoS_4)_2(H_2O)$ |
|---|---|---|
| $\nu_{as}(Tc{=}O)$ | 895 | |
| $\nu(Tc-P)$ | | 543 |
| $\nu_s(Mo-S)_t$ | 478 | 462 |
| $\nu_{as}(Mo-S)_t$ | 459 | 447 |
| $\nu_s(Mo-S)_{br}$ | 405 | 407 |
| $\nu_{as}(Mo-S)_{br}$ | 397 | 397 |
| $\nu_{as}(Tc-S)$ | 335 | 325 |

[a] As KBR discs; t = terminal; br = bridging.

This phenomenon should in our view be interpreted in terms of the fact that the anionic sulphur donor atoms in $MoS_4^{2-}$ greatly increase the covalent interaction and electron transfer to the technetium in the planar region (the diamagnetism of this complex is ample evidence for this fact), leading to an unusually large weakening of the Tc=O bond (uncommonly low Tc=O stretching frequency). This study again emphasises the marked influence of the extent of electron delocalisation in the planar system on the properties of the axial ligands in anionic monoxotechnetium(V) complexes.

The reduction of metal oxo complexes by phosphines is well established in the literature [15, 16]. Since we observed the unusually low vibration for the $\nu(Tc{=}O)$ stretching frequency in the infrared for the complex $TcO(MoS_4)_2^-$, which is indicative of a weak Tc(V)–oxo bond, an attempt has been made to abstract the oxo ligand in this complex with triphenylphosphine. These attempts have led to the isolation of an apparent six-coordinate technetium(IV) complex, $Tc(PPh_3)_2(MoS_4)_2$. The compound $TcO(MoS_4)_2^-$ can in a certain sense now be looked upon as a metastable intermediate in the reaction of $TcOCl_4^-$ with $MoS_4^{2-}$ in the presence of the mild reducing agent and π-acceptor ligand $PPh_3$ under nitrogen.

In previous examples the abstraction of an oxo ligand by phosphines in 4d and 5d transition metals have generally led to the reduction of the metal complex by two formal oxidation state numbers. The reduction of the Ru(IV) cation, $[RuO(py)(bipy)_2^{2+}]$, by $PPh_3$ forms a Ru(II) species [17], while the reduction of $TcOCl_2HB(pyz)_3$ by the same ligand led to the isolation of the technetium(III) complex $TcCl_2(PPh_3)HB(pyz)_3$ [16]. The reduction of even a dioxomolybdenum(VI) complex, $MoO_2$[N-(5-X-Salicylidene)-2-aminoethanethiolato], by $PPh_2Et$ leads to a monoxomolybdenum(IV) species. In the light of the above, the reduction of Tc(V) only to Tc(IV) in this case is therefore somewhat surprising. The pronounced σ-donicity of the dianionic sulphur donor ligands can, in our view, possibly account for this less common behaviour.

The reduction reaction of $TcO(MoS_4)_2^-$ with $PPh_3$ at 60 °C proceeds to near completion within a matter of hours. The reaction followed in this study was:

$$TcO(MoS_4)_2^- + 3PPh_3 \longrightarrow Tc(PPh_3)_2(MoS_4)_2 + OPPh_3 \quad (1)$$

This relatively slow reaction could therefore be followed spectrophotometrically in the electronic spectral region. The $TcO(MoS_4)_2^-$ complex exhibits a charge transfer electronic transition at 288 nm in a DMF solution, which increases in intensity as a function of time on reaction with $PPh_3$. A new absorbance band appeared at 272 nm and increased in intensity as the reaction proceeded. The absence of an isosbestic point suggests strongly that the oxo-complex is being converted to a product by going through some type of reaction intermediate, possibly $Tc(PPh_3)(MoS_4)_2$. This could possibly mean that in solution, a triphenylphosphine molecule occupies the vacant coordination site *trans* to the oxo group. This will have the effect of further removal of electron density from the Tc-oxo core by means of its π-backbonding abilities, and thus also weakening the Tc=O bond because of its strong *trans*-effect. These electronic effects will cause the oxo-oxygen to become electrophilic, and reaction (1) will then proceed by an electrophilic attack of the oxo-oxygen on the electron-rich $PPh_3$ base. This could lead to the formation of a coordinated triphenylphosphine oxide molecule *trans* to the $PPh_3$, which is then gradually replaced by the excess triphenylphosphine, leading to a stable entity. The release of a $OPPh_3$ molecule is feasible since the Tc(IV) core can be regarded as a soft centre. Such a behaviour has already been observed previously with the isolation of $TcCl_2(OPPh_3)HB(pyz)_3$, and the resulting displacement of the $OPPh_3$ molecule from this complex by $PPh_3$ to produce $TcCl_2(PPh_3)HB(pyz)_3$ [10].

In conclusion, it could be stated that under selective conditions of special co-ligands, indefinitely stable oxo-technetium(V) complexes having relatively weak Tc=O bonds can be isolated in the solid state. The complexes can be readily reduced by mild reducing agents, provided the reducing agent is at the same time a mild $\pi$-acceptor ligand capable of stabilising the lower oxidation state.

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