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Preparation of Oxobis(dithiolato) Complexes of Technetium(V) and Rhenium(V)

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A series of oxobis(dithiolato)metalate(V) complexes of technetium and rhenium have been synthesized and studied by various physical techniques, including infrared and optical spectroscopy and cyclic voltammetry. Physical properties of the complexes are compared with respect to periodicity and the substituents on the ligand backbones. The stability of these five-coordinate complexes contradicts the current notion that Tc(V) and Re(V) complexes are inherently unstable in aqueous solution.

Introduction

Nuclear medicine[2] is relying increasingly upon radiopharmaceuticals containing the metastable isomer of technetium (^{99m}Tc) as agents of choice for imaging organ systems in the diagnosis of disease.[3] The widespread use[4] is due to the favorable nuclear properties of ^{99m}Tc (γ = 140 keV, $T_{1/2}$ = 6 h), which allow images of high resolution to be obtained with a low-radiation dose to the patient, and the ability of technetium to combine chemically with a variety of ligands to produce radiopharmaceuticals of high organ specificity.[3,4]

In spite of the great clinical strides of recent years, little is known of the identity and chemical properties[3,4] of technetium radiopharmaceuticals. The concentration of technetium in a typical preparation is ca. 10^{-8}–10^{-9} M (i.e., less than 2 ng of ^{99m}Tc per 10-mCi patient dose), which precludes characterization by most of the traditional methods of inorganic chemistry.

We are using the long-lived radionuclide ^{99}Tc, a β^- emitter ($T_{1/2}$ = 2.12 × 10^5 years), to investigate the chemistry of technetium on a scale amenable to the use of commonly available methods of study. The potential for adding to the rather small body of knowledge of the coordination chemistry of this element[5-8] adds significance to this approach. We are also preparing analogous complexes of technetium's third-row congener, rhenium, in order to compare their properties and better understand technetium in terms of chemical periodicity.

The synthesis and characterization by X-ray diffraction of n-Bu$_4$NTcO(SCH$_2$COS)$_2$, a novel oxotechnetium(V) species, have recently been reported.[9] This work outlines the synthesis, characterization, and reactivity of a broad class of five-coordinate square-pyramidal technetium and rhenium oxobis(1,2-dithiolate) complexes. The properties of these complexes are discussed in relation to both ligand type and metal atom.

Experimental Section

Technetium as NH$_4$^{99}TcO$_4$ in aqueous solution was purchased from New England Nuclear. The concentration was determined by the literature method.[10] ^{99}Tc is a weak β emitter (0.292 keV, half-life 2.12 × 10^5 years); therefore, all manipulations were carried out in a radiation laboratory with a monitored fume hood. Personnel wore disposable lab coats and gloves at all times. Radioactive wastes, both liquid and solid, were disposed in special receptacles. Samples sent outside of the laboratories' jurisdiction were wipetested for contamination prior to shipment, and all regulations[11] regarding such transportation were followed. All reagents and solvents were used without further purification except where noted. Elemental microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y., Galbraith Laboratories, Knoxville, Tenn., and Spang Microanalytical Laboratory, Eagle Harbor, Mich. (Ph$_4$As)ReOBr$_4$ and (n-Bu$_4$N)ReOBr$_4$ were prepared via literature methods.[12a]

Mercaptothioacetic acid (HSCH$_2$COSH) was obtained by a modification of the procedure of Satsumabayashi,[12b] chlorothioacetic acid was prepared as described,[12b] by the reaction of chloroacetyl chloride with H$_2$S. This was converted into mercaptothioacetic acid as follows. A solution of KOH (31.2 g) in 95 mL of EtOH/H$_2$O (95% v/v) was saturated with H$_2$S gas at 0 °C (ca. 0.75 h). This solution was cooled to −5 °C and ClCH$_2$COSH (10.4 g) was added dropwise over 2.5 h. KCl was removed by filtration, and the filtrate was concentrated to ca. 30 mL. The resulting solution was acidified (pH 3) with ice-cold 3 N HCl and extracted with Et$_2$O. This procedure was repeated; the combined ether extracts were evaporated in vacuo, and benzene (100 mL) was added. The mixture was fractionated by distillation: mercaptothioacetic acid (8.1 g, 79%), bp 40 °C (2 mmHg); ^{1}H NMR (CCl$_4$) δ 1.96 (t, J = 8.5 Hz, 1 H), 3.38 (d, J = 8.5 Hz, 2 H), 4.60 (br s, 1 H).

A 270-MHz ^{1}H NMR spectrum of commercial Eastman thioglycolic acid in CDCl$_3$ showed the methylene absorptions of mercaptothioacetic acid: ^{1}H NMR (270-MHz methylene region) δ 3.54 (d, J = 8.5 Hz, HSCH_2COSH), 3.32 (d, J = 8.5 Hz, HSCH_2CO$_2$H). The relative intensity of HSCH_2COSH:HSCH_2CO$_2$H is 0.15 ± 0.02.

n-Bu$_4$NTcOCl$_4$.[13] To a beaker equipped with a stir bar were added 16 mL of 12 N HCl and 2.0 mL of 0.32 M (0.64 mmol) aqueous NH$_4$TcO$_4$ solution. After 10 min, 4 mL of 75% w/w n-Bu$_4$NCl in water was added dropwise to the green solution. A microcrystalline powder was collected by filtration The solid was washed with 1.5 mL of 12 N HCl, followed with five 1.5-mL aliquots of isopropyl alcohol, and then dried in vacuo. The yield, of a light green microcrystalline solid, was 0.31 g (98% on the basis of Tc). Recrystallization from CH$_2$Cl$_2$/hexane produced dark green plates. Anal. Calcd for C$_{16}$H$_{36}$Cl$_4$NOTc: C, 38.49; H, 7.27; N, 2.81; Cl, 28.40. Found: C, 38.42; H, 7.22; N, 2.67; Cl, 26.34, 29.74.

Ph$_4$AsTcO(SCH$_2$CH$_2$S)$_2$ can be prepared via the reduction of TcO$_4^-$ in aqueous solution or via a nucleophilic halide displacement from TcOCl$_4^-$. Samples prepared from both routes were compared to a

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(13) [(Ph$_3$P)$_2$N][TcOCl$_4$] has recently been characterized by a single-crystal X-ray study. The original preparation utilized H$_3$PO$_2$ and HCl and the synthesis reported here is an improvement on that procedure. The full details are contained in: Cotton, F. A.; Davison, A.; Day, V. W.; Gage, L. D.; Trop, H. S. *Inorg. Chem.* **1979**, *18*, 3024–9.

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sample prepared by the method of Smith et al.[14]

(a) Reduction of TcO_4^-. To a solution of 0.08 g (0.46 mmol) of $Na_2S_2O_4$ (MCB) in 25 mL of water was added 0.07 mL (0.84 mmol) of ethanedithiol (Eastman). To the stirred suspension were added simultaneously 0.48 mL of 0.35 M (0.17 mmol) NH_4TcO_4 and 4 drops of 50% w/w NaOH. The resulting red solution was stirred for 30 min; then $Ph_4AsCl{\cdot}H_2O$ (Alfa) in water (0.15 g/15 mL) was added to precipitate an orange solid. Recrystallization from acetone/water afforded red-orange crystals, 0.12 g (99% on the basis of Tc).

(b) Reaction with $TcOCl_4^-$. n-$Bu_4NTcOCl_4$, 0.048 g (0.10 mmol), was dissolved in 5 mL of methanol. To the green, stirred solution was added a solution, adjusted to pH 7.5 with 0.1 M NaOH, consisting of 0.07 mL (0.84 mmol) of ethanedithiol and 2.0 mL of water. The resultant orange-red mixture, after addition of 1.0 g of $Ph_4AsCl{\cdot}H_2O$ in 10 mL of water, was filtered and then washed liberally with water and ether. The orange solid was recrystallized from acetone/water to yield red-orange needles: 0.051 g (77% on the basis of Tc), mp 235 °C dec.

$Ph_4AsReO(SCH_2CH_2S)_2$ can be prepared from ReO_4^- reduction or from $ReOBr_4^-$.

(a) Reduction of ReO_4^- (Performed under Ar). A 100-mL, two-necked round-bottom flask was charged with 0.29 g (1.07 mmol) of $NaReO_4$ and 40 mL of THF added via a cannula. Addition of 0.18 mL (2.1 mmol) of ethanedithiol was followed by 0.30 g (7.9 mmol) of $NaBH_4$. The stirred solution was refluxed for 18 h. Filtration yielded a red-orange solution to which was added 0.5 g of $Ph_4AsCl{\cdot}H_2O$ in 30 mL of ethanol. Cooling to −10 °C, followed by filtration and water washings (2–10-mL aliquots), afforded red-orange needles, 0.57 g (69% on the basis of Re).

(b) Reaction with $ReOBr_4^-$ (Performed under Ar). A 100-mL, two-necked round-bottom flask was charged with 25 mL of THF and 0.18 mL (2.1 mmol) of ethanedithiol and cooled to 0 °C. n-Butyllithium, 1.6 mL (4.4 mmol), was added to the stirred solution, forming a white suspension. A solution of 0.95 g (1.1 mmol) of $Ph_4AsReOBr_4$ in 50 mL of THF was added via a cannula. The mixture was warmed to room temperature and stirred for 1 h. A brown solid was collected and then recrystallized from acetone/water to yield orange crystals: 0.44 g (55% on the basis of Re), mp 238–239 °C. Anal. Calcd for $C_{28}H_{28}AsOReS_4$: C, 43.68; H, 3.67; S, 16.66. Found: C, 43.64; H, 3.81; S, 16.38.

n-$Bu_4NTcO(SCH_2COS)_2$ can be prepared from commercial thioglycolic acid ($HSCH_2CO_2H$) by using either TcO_4^- or $TcOCl_4^-$.

(a) Reaction from TcO_4^-. To a solution consisting of 6 mL (86.3 mmol) of thioglycolic acid (Eastman) and 54 mL of water, adjusted to pH 7.5 with 2.5% w/w NaOH, was added 2.1 mL of a 0.34 M (0.71 mmol) NH_4TcO_4 solution. After an 8-min stirring, a concentrated solution of Bu_4NBr in 10 mL of water was added to the dark brown solution. After 4 h, the mixture was filtered, washed with water, and then air-dried. The solid was extracted with two 4-mL aliquots of methanol and then air-dried again. The remaining solid was recrystallized from acetone/water, filtered, washed with water and methanol, and then dried in vacuo. The yield of orange brown crystals was 0.09 g (22% on the basis of Tc).

(b) Reaction with $TcOCl_4^-$. To a 50-mL round-bottom flask with stir bar were added 0.045 g (0.090 mmol) of n-$Bu_4NTcOCl_4$ and 7 mL of methanol to yield a green solution. Thioglycolic acid, 1.5 mL, was dissolved in 2 mL of water and the pH adjusted to 7.5 with 10 M NaOH. The thiol solution was added to the green solution; the resultant mixture was dark brown. A saturated solution of n-Bu_4NBr in water (3 g/10 mL) was added, and the mixture chilled in an ice bath. Yellow-brown crystals were filtered, washed with 15 mL of water and 15 mL of ether, and then dried in vacuo. The yield of brown needles was 0.035 g (68% on the basis of Tc). Anal. Calcd for $C_{20}H_{40}NO_3S_4Tc$: C, 42.18; H, 7.03; N, 2.46; S, 22.50. Found: C, 41.42; H, 7.14; N, 2.80; S, 22.02.

(c) Reaction of $TcOCl_4^-$ with $HSCH_2COSH$. A solution of 12 μL (1.2×10^{-4} mol) of $HSCH_2COSH$ in 10 mL of MeOH was added dropwise to a solution of $Bu_4NTcOCl_4$ (0.027 g, 5.37×10^{-5} mol) in 10 mL of MeOH. The yellow-brown reaction mixture began to deposit a fine, dark solid within a few minutes. To this mixture was added 1 mL of NaOH solution (pH 11) followed immediately by 1.5 mL of Bu_4NCl (50% aqueous). The solvent was removed by rotary evaporation, and the resulting solid was separated and washed with water. The solid was dissolved in acetone and filtered, and water was added to the filtrate to the point of incipient crystallization. After 24 h at room temperature, two types of crystals were observed: light yellow needles and dark yellow-brown plates. These were separated by filtration; attempts to separate the mixture into two pure components by fractional crystallization were not successful. A 270-MHz ^1H NMR (in CD_2Cl_2) spectrum of the combined reaction products indicated that there are two components. The methylene protons of the (SCH_2COS) ligand appear as two AB pairs (δ 3.93, $J_{AB} = 17.3$ Hz; δ 3.87, $J_{AB} = 14.8$ Hz). The optical spectra and infrared spectra of the various fractions were similar to the *cis*-[n-Bu_4N][$TcO(SCH_2COS)_2$] obtained in reaction a.

n-$Bu_4NReO(SCH_2COS)_2$. To a 50-mL round-bottom flask with stir bar were added 0.40 g (0.52 mmol) of n-$Bu_4NReOBr_4$ and 15 mL of methanol to yield a dirty red solution. In a beaker, 6 mL of water and 6.0 mL of thioglycolic acid were combined, and the pH was adjusted to 7.5 with 10 M NaOH. Upon addition of the thiol to the rhenium solution, a color change to dark red was apparent. After a 10-min stirring, 6 g of n-Bu_4NBr in 20 mL of water was added. The reaction mixture was transferred to a 100-mL beaker and allowed to stand for 5 days. Long, orange needles were filtered, washed liberally with water and ether, and then dried in vacuo. The yield of orange needles was 0.11 g (32% on the basis of Re; mp 129–132 °C). Anal. Calcd for $C_{20}H_{40}NO_3ReS_4$: C, 36.56; H, 6.14; N, 2.13; S, 19.52. Found: C, 36.78; H, 6.37; N, 2.14; S, 19.23.

n-$Bu_4NTcO(C_2O_2S_2)_2$. To a 25-mL round-bottom flask with stir bar were added 0.10 g (0.19 mmol) of n-$Bu_4NTcOCl_4$ and 0.08 g (0.40 mmol) of dipotassium dithiooxalate (Eastman). Upon addition of 8 mL of acetone, the stirred mixture appeared orange-red. After 1 h, KCl was filtered off, and then water was added to the mother liquor to induce crystallization. The solid was filtered, washed with water and ether, and then dried in vacuo. The yield of burgundy maroon crystals was 0.08 g (72% on the basis of Tc; mp 126–127 °C). Anal. Calcd for $C_{20}H_{36}NO_5S_4Tc$: C, 40.19; H, 6.07; N, 2.34; S, 21.46. Found: C, 41.08, 39.52; H, 6.41, 6.20; N, 2.38; S, 20.97, 20.17.

$Ph_4AsTcO(C_2O_2S_2)_2$. For preparation of the Ph_4As^+ salt, 0.1 g of $Ph_4AsCl{\cdot}H_2O$ was added to the mother liquor following removal of KCl. Recrystallization from acetone/water yields red-brown crystals, 0.11 g (80% on the basis of Tc). Anal. Calcd for $C_{28}H_{20}AsO_5S_4Tc$: C, 45.53; H, 2.73; S, 17.36. Found: C, 45.29; H, 2.51; S, 17.06.

n-$Bu_4NReO(C_2O_2S_2)_2$. To a 50-mL round-bottom flask with stir bar were added 0.20 g (0.26 mmol) of n-$Bu_4NReOBr_4$ and 0.12 g (0.54 mmol) of dipotassium dithiooxalate. Upon addition of 10 mL of acetone, a dark violet solution formed. After 1 h, filtration of KBr left a dark violet solution. Water was added to induce crystallization. The solid was filtered, washed with water and ether, and then dried in vacuo. The yield of red brown crystals was 0.13 g (71% on the basis of Re; mp 137–138 °C). Anal. Calcd for $C_{20}H_{36}NO_5ReS_4$: C, 35.07; H, 5.03; N, 2.05; S, 18.72. Found: C, 34.87; H, 5.46; N, 1.99; S, 17.93.

$Ph_3MeAsReO(C_2O_2S_2)_2$. This salt can be prepared by substituting $Ph_3MeAsReOBr_4$ for n-$Bu_4NReOBr_4$ in the previous synthesis. Yield was 43% on the basis of Re. Anal. Calcd for $C_{23}H_{18}AsO_5ReS_4$: C, 36.17; H, 2.38; S, 16.79. Found: C, 36.35; H, 2.42; S, 16.56.

n-$Bu_4NTcO(S_2C_2(CN)_2)_2$. To a 25-mL round-bottom flask with stir bar were added 0.067 g (0.36 mmol) of disodium maleonitriledithiolate (Na_2mnt) and 0.087 g (0.17 mmol) of n-$Bu_4NTcOCl_4$. A brown reaction mixture resulted upon addition of 7 mL of acetone. After 1 h, NaCl was filtered off, leaving a coffee-colored mother liquor. Addition of water caused precipitation of a brown microcrystalline solid. Recrystallization of the solid from acetone/isobutyl alcohol yielded large, dark brown needles: 0.045 g (50% on the basis of Tc), mp 128–129 °C. Anal. Calcd for $C_{24}H_{36}N_5OS_4Tc$: C, 45.19; H, 5.69; N, 10.98; S, 20.11. Found: C, 45.09; H, 5.83; N, 10.50; S, 19.80.

$Ph_4AsReO(S_2C_2(CN)_2)_2$. To a 50-mL round-bottom flask were added 0.38 g (0.40 mmol) of $Ph_4AsReOBr_4{\cdot}CH_3CN$ and 0.19 g (1.03 mmol) of Na_2mnt, followed by 25 mL of acetone. The red-brown mixture was stirred for 1 h and then the NaBr removed by filtration. Addition of water to the filtrate resulted in formation of well-formed orange-brown plates which were filtered, washed with water and ether, and then dried in vacuo. The yield was 0.26 g (75% on the basis of Re; mp 167–168 °C). Anal. Calcd for $C_{32}H_{20}AsN_4OReS_4$: C, 44.39; H, 2.33; N, 6.47; S, 14.81. Found: C, 43.90; H, 2.46; N, 6.24; S, 13.33. This material is identical with the compound reported by McCleverty et al.[15] from $ReCl_6^{2-}$, Na_2mnt, and I_2.

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Table I. Metal–Oxygen Stretching Frequencies

compd	freq, cm^{-1}	compd	freq, cm^{-1}
$Ph_4AsTcO(edt)_2$	935	n-$Bu_4NReO(dto)_2$	990
$Ph_4AsReO(edt)_2$	952	$Ph_3MeAsReO(dto)_2$	991[a]
n-$Bu_4NTcO(tma)_2$	950	n-$Bu_4NTcO(tdt)_2$	930
n-$Bu_4NReO(tma)_2$	970	n-$Bu_4NReO(tdt)_2$	958
n-$Bu_4NTcO(dto)_2$	972	n-$Bu_4NTcO(mnt)_2$	947
$Ph_4AsTcO(dto)_2$	980	$Ph_4AsReO(mnt)_2$	963

[a] Partially obscured by Ph_3MeAs cation.

n-$Bu_4NTcO(S_2C_7H_6)_2$ can be prepared from either TcO_4^- or $TcOCl_4^-$ in the presence of 3,4-dimercaptotoluene (tdt).

(a) Reaction with TcO_4^-. To a solution of 0.10 g (0.59 mmol) of 3,4-dimercaptotoluene (Aldrich) in 25 mL of 2.5% w/w NaOH was added 0.88 mL of a 0.34 M (0.30 mmol) NH_4TcO_4 solution. A solution of 0.21 g (1.23 mmol) of $Na_2S_2O_4$ (MCB) in 10 mL of 2.5% w/w NaOH was added over a 2-min period, resulting in a very dark solution. A concentrated solution of n-Bu_4NBr in 10 mL of water was added, and the precipitate was filtered and washed with 5 mL of 2.5% w/w NaOH, followed by two 5-mL aliquots of water. The crude solid was dried in vacuo for several hours. The solid was dissolved with three 4-mL portions of acetonitrile and filtered. To the filtrate was added 50 mL of ether, followed by refrigeration at −25 °C. The crystalline product was filtered, washed with ether, and then dried in vacuo. The yield of yellow-brown crystals was 0.048 g (24% on the basis of Tc).

(b) Reaction with $TcOCl_4^-$. To a 25-mL round-bottom flask with stir bar were added 0.075 g (0.15 mmol) of n-$Bu_4NTcOCl_4$ and 5 mL of methanol. A suspension of 0.05 g (0.32 mmol) of 3,4-dimercaptotoluene in 2 mL of water adjusted to pH 7.5 with NaOH was added to the stirred green solution. A saturated aqueous n-Bu_4NBr solution (1.5 g/5 mL) was added to the brown mixture. The oily reaction mixture was filtered through a bed of diatomaceous earth (Filter-Cel) and washed with H_2O and then ether. The ether had a pink tint. The complex was extracted from the Filter-Cel with acetone and then crystallized with the addition of water. Yellow-brown crystals were filtered, washed with water and ether, and then dried in vacuo. The yield was 0.050 g (49% on the basis of Tc; mp 166–167 °C). Anal. Calcd for $C_{30}H_{48}NOS_4Tc$: C, 54.14; H, 7.22; N, 2.11; S, 19.25. Found: C, 54.30; H, 7.23; N, 2.11; S, 19.92.

n-$Bu_4NReO(S_2C_7H_6)_2$. To a 50-mL round-bottom flask with stir bar were added 0.20 g (0.26 mmol) of n-$Bu_4NReOBr_4$ and 10 mL of methanol. Next, 0.084 g (0.54 mmol) of 3,4-dimercaptotoluene was added, followed quickly by a solution of 2 mL of pH 7.5 water and 3 mL of methanol. To the yellow-brown mixture was added 3.0 g of n-Bu_4NBr in 10 mL of water, and the solid produced was filtered, washed with 20 mL of water, and then air-dried. A green impurity ($Re(S_2C_7H_6)_3^{x-}$?) was removed via repeated washings with toluene. The remaining solid was washed with ether and then extracted into 25 mL of acetone. Addition of water precipitated bright orange crystals which were filtered, washed with H_2O and ether, and then dried in vacuo; mp 170.5–171.5 °C. Anal. Calcd for $C_{30}H_{48}NOReS_4$: C, 47.84; H, 6.42; N, 1.86; S, 17.03. Found: C, 47.83; H, 6.63; N, 1.84; S, 16.86.

Attempted Reaction with Ph_3P. (a) $TcO(edt)_2^-$ + Ph_3P. In a 50-mL round-bottom flask, 0.013 g (0.02 mmol) of $Ph_4AsTcO(edt)_2$ and 0.09 g (0.34 mmol) of Ph_3P were dissolved in 20 mL of acetonitrile and refluxed under Ar for 24 h. Upon workup, only starting material could be recovered. (Convenient abbreviations for the ligands are found in Table I.)

(b) $Reo(edt)_2^-$ + Ph_3P. The analogous reaction, substituting $ReO(edt)_2^-$ for $TcO(edt)_2^-$, was performed; starting material was recovered unchanged.

Attempted Reaction with Me_2SO. (a) $TcO(tdt)_2^-$ + Me_2SO. A solution composed of 25 mL of ethanol, 4 mL of acetonitrile, and 1.0 mL (14.0 mmol) of dimethyl sulfoxide was refluxed with 0.016 g (0.024 mmol) of n-$Bu_4NTcO(tdt)_2$ for 24 h. Only starting material could be recovered.

(b) $ReO(edt)_2^-$ + Me_2SO. The analogous reaction, using $ReO(edt)_2^-$, yielded only starting material.

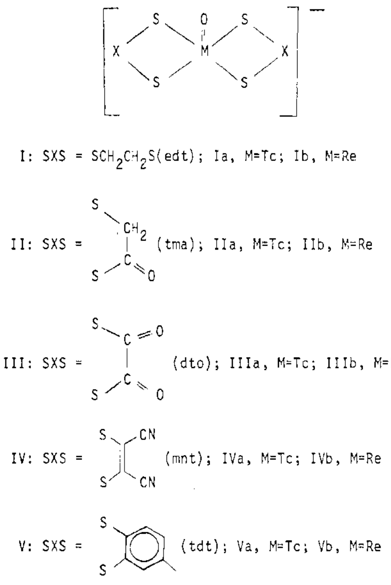

Figure 1.

Attempted Coordination of Pyridine. Samples of $TcO(tma)_2^-$ and $ReO(edt)_2^-$ were dissolved in methylene chloride and the optical spectra compared to samples prepared in methylene chloride/pyridine medium ranging from a ratio of 10:1 methylene chloride:pyridine to neat pyridine. In each case, no change in the absorption spectra of the anions could be discerned.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer 180 grating spectrophotometer in the range 4000–200 cm^{-1} as KBr pellets. Optical spectra were obtained with a Cary Model 17 spectrophotometer. Voltammetric studies were carried out by using a PAR Model 174 polarographic analyzer with rotating-Pt, stationary-Pt, dropping-Hg, and stationary-Hg pool electrodes. Tetrabutylammonium perchlorate (TBAP) (Southwestern Analytical) was dried in vacuo at 85 °C prior to use as supporting electrolyte. Spectrograde acetonitrile (Eastman), run through a long, activated alumina column, was used as solvent in the electrochemical measurements. Magnetic susceptibilities were obtained on a home-built Faraday balance with a Varian V-4005 electromagnet with constant-force pole faces and a Cahn RG electrobalance. Diamagnetic corrections were taken from published tables,[16] and the magnetic moment was derived from the expression

$$\mu_{\text{eff}} = 2.84(X_m^{\text{corr}}T)^{1/2}$$

$HgCo(SCN)_4$ was used as the calibrant. In addition to the above methods these complexes were examined by field desorption mass spectroscopy (FDMS) to determine their exact masses. The details of this study and the application and potential of FDMS to coordination chemistry will be discussed elsewhere.[17] NMR spectra were measured on either a Bruker 270-MHz spectrometer or a Perkin-Elmer Hitachi R24B 60-MHz spectrometer.

Results and Discussion

It has been suggested[18–22] that certain ^{99m}Tc-containing radiopharmaceuticals involve the coordination of sulfur atoms to technetium. Recent structural studies on two technetium complexes $(n\text{-}Bu_4N)TcO(tma)_2$[9] (IIa) and $Ph_4AsTcO(edt)_2$[14] (Ia) have demonstrated that kinetically stable, five-coordinate

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technetium oxobis(dithiolato) species are formed from TcO_4^- and chelating thiol ligands under reducing conditions. This study was undertaken in order to investigate general synthetic routes to this type of complex and simultaneously to study their physical properties.

The complexes prepared in this work (Figure 1) are representative of this class of coordination compounds for Tc(V) and Re(V). The chelating ligands utilized span a wide range, from a saturated dithiolate derived from ethanedithiol to "non-innocent"[23] dithiolenes (e.g., maleonitriledithiolate).

Of the complexes reported herein, the syntheses of Ia, IIa, and IVb have been reported previously.[9,14,15] Oxidation of $Re(mnt)_3^{2-}$ with I_2 gave IVb[15] instead of the desired $Re(mnt)_3^-$. Reduction of TcO_4^- with borohydride in the presence of ethanedithiol produced Ia in moderate yield.[14] Neither of these preparations appeared to be generally applicable, and thus alternative routes were investigated that would be more general and would produce the desired products in higher yield. Full details of the synthesis of IIa are reported here for the first time.

Oxobis(dithiolato)metalates can be formed via the reduction of MO_4^- and/or a substitution reaction involving the well-characterized $ReOBr_4^-$[12] or $TcOCl_4^-$.[13] The substitution reaction is the most general preparative procedure, whether the starting material is the free dithiol or an alkali metal salt of the dithiolate dianion. When the free dithiol is utilized, the reaction can be viewed as a nucleophilic substitution on the metal, resulting in the formation of a metal–sulfur bond and the expulsion of the corresponding haloacid. The reaction is enhanced by the addition of a small amount of base. The substitution of halide ions by thiols has been previously demonstrated[24] in the conversion of $Fe_2S_2X_4^{2-}$ and $Fe_4S_4X_4^{2-}$ to $Fe_2S_2(SR)_2^{2-}$ and $Fe_4S_4(SR)_4^{2-}$, respectively.

From considerations of periodicity, the reduction of technetium is expected to be more facile than the reduction of rhenium. This has been previously observed voltammetrically.[25,26] In this study, the reduction of TcO_4^- was accomplished efficiently by using $Na_2S_2O_4$ in aqueous solution;[27] however, the reduction of ReO_4^- required the use of a strong reducing agent ($NaBH_4$) in a nonaqueous medium, under anaerobic conditions. These reductions required the presence of the free dithiol, rather than the dithiolate dianion. Reduction of TcO_4^- by $Na_2S_2O_4$ in the presence of the alkali metal dithiolate salts yielded $TcO_2 \cdot xH_2O$ as the only product, indicating that the protons on the dithiol are probably mechanistically important.

The novel formation of IIa and IIb from commercially available "thioglycolic acid" ($HSCH_2CO_2H$) illustrates the avidity of both the oxotechnetium and rhenium(V) cores for dithiolato ligands. We suspected that mercaptothioacetic acid ($HSCH_2COSH$) was a significant impurity in commercial "thioglycolic acid". It was synthesized by a modification of the published procedure[12b] and shown to occur at sizeable concentrations (ca. 15%) as an impurity.

The general structural features of these complexes have been determined through crystal structures of Ia[14] and IIa.[9] The metal atom is coordinated by one oxygen and four sulfur atoms in very nearly a square pyramid, with the oxygen atom at the apex and the sulfur atoms forming a basal plane, out of which the metal atom is displaced toward the apex.

Table II. Optical Spectra in CH_3CN

$Ph_4AsTcO(edt)_2$	484 sh,[a] 433 sh, 399 (3400), 279 (7750)
n-$Bu_4NTcO(tma)_2$	415 (3665), 325 (3100)
n-$Bu_4NTcO(dto)_2$	500 sh, 480 (275), 410 sh, 375 (3400), 298 (14 700)
$Ph_4AsTcO(dto)_2$	510 sh, 480 (275), 410 sh, 375 (3310), 297 (14 600)
n-$Bu_4NTcO(tdt)_2$	405 sh, 361 (13 000), 312 (7400)
n-$Bu_4NTcO(mnt)_2$	570 sh, 475 (510), 380 sh, 339 (15 500), 290 sh, 270 sh, 253 (23 300)
$Ph_4AsReO(edt)_2$	483 sh, 417 (550), 363 sh, 328 (4200)
n-$Bu_4NReO(tma)_2$	520 (55), 425 (270), 365 sh, 335 (3370), 280 sh, 248 (12 300)
n-$Bu_4NReO(dto)_2$	520 sh, 474 (340), 448 (330), 417 (480), 340 sh, 292 (18 460)
$Ph_3MeAsReO(dto)_2$	520 sh, 476 (300), 418 (430), 294 (18 300)
n-$Bu_4NReO(tdt)_2$	510 sh, 440 sh, 395 sh, 350 (6700), 310 (22 200)
$Ph_4AsReO(mnt)_2$	352 (4400), 303 (21 750)

[a] Band maximum in nanometers (ϵ in L mol^{-1} cm^{-1}).

Table III. Magnetic Data for $MO(SS)_2^-$ Complexes

	μ_{eff}, μ_B	
compd	7250 G	14 000 G
$Ph_4AsTcO(edt)_2$	1.16	0.82
$Ph_4AsReO(edt)_2$	0.10	dia
n-$Bu_4NTcO(tma)_2$	1.50	1.19
n-$Bu_4NReO(tma)_2$	0.50	0.31
n-$Bu_4NTcO(dto)_2$	0.34	0.17
n-$Bu_4NReO(dto)_2$	1.46	0.99
n-$Bu_4NTcO(mnt)_2$	dia	dia
$Ph_4AsReO(mnt)_2$	0.81	0.59
n-$Bu_4NTcO(tdt)_2$	0.42	dia
n-$Bu_4NReO(tdt)_2$	0.37	0.21

In these systems, for unsymmetrical bidentate ligands, it is reasonable to expect the occurrence of cis and trans isomers. We have demonstrated that mercaptothioacetic acid gives a mixture of both cis and trans complexes in the preparation of the complexes from $TcOCl_4^-$ and pure $HSCH_2COSH$. However, although we can obtain the pure cis material by repeated fractional crystallization, we have been unable to obtain the pure trans complex. However, it is clear that we are producing two isomers from an examination of the 270-MHz ^1H NMR spectrum of the various fractions obtained from the mercaptothioacetic acid reaction. The methylene absorptions of the ligand in the ^1H spectrum of the mixture show the presence of two AB pairs. Fractions containing the more soluble trans isomer are contaminated with the less soluble cis isomer.

It is interesting to note the similarity of the M^VOS_4 core of these complexes to the isoelectronic $Mo^{IV}OS_4$ core[28] of $MoO(n\text{-}Pr_2dtc)_2$. The Mo atom in the latter compound is coordinated in the same square-pyramidal fashion as in Ia and IIa, and corresponding bond lengths are similar. In reference to Cotton and Wing's correlation,[28,29] the Mo–O bond order has been assigned as 3, and the IR stretching frequencies for the Mo–O bond of the dithiocarbamato complexes $MoO(Et_2dtc)_2$[30] and $MoO(Me_2dtc)_2$[31] (962 and 975 cm^{-1}, respectively) correspond well to a strong band in the IR spectrum of each complex (in the range 1000–900 cm^{-1}) assigned to an M–O stretch as shown in Table I. This stretch occurs at higher energy in $Ph_4AsReOBr_4 \cdot CH_3CN$[12] (1000 cm^{-1}) and n-$Bu_4NTcOCl_4$[13] (1019 cm^{-1}) than in the oxobis(dithiolato)metalate complexes.

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Table IV. Voltammetric Data for $MO(SS)_2^-$ Complexes

	$E_{1/2}$[a]	
compd	Hg pool, DME[b]	Pt, RPE[b]
$Ph_4AsTcO(edt)_2$	−1.86	0.68, 2.05
$Ph_4AsReO(edt)_2$	−2.50	0.72, 2.11
$Bu_4NTcO(tma)_2$	−1.35 (1e⁻ rev)[c]	
$Bu_4NReO(tma)_2$	−1.84	1.23
$Bu_4NTcO(dto)_2$	−0.75 (1e⁻ rev),[c] −1.56	1.91, 2.28
$Bu_4NReO(dto)_2$	−0.94 (1e⁻ rev),[c] −1.35	1.64, 2.17
$Bu_4NTcO(mnt)_2$	−0.64 (1e⁻ rev)	1.73
$Ph_4AsReO(mnt)_2$	−1.05 (1e⁻ rev)	1.76
$Bu_4NTcO(tdt)_2$	−1.52	0.95
$Bu_4NReO(tdt)_2$	−2.00	1.00

[a] $E_{1/2}$ in volts vs. SCE; ferrocene used as reference ($E_{1/2} = 0.41$ V). [b] CH_3CN, 0.1 M TBAP. [c] Pseudoreversible behavior observed in cyclic voltammetry.

The ReO stretch occurs at higher frequency (~20 cm^{-1}) than the TcO stretch in the analogous complexes. This difference can be explained by the greater orbital overlap of 5d orbitals (Re) contrasted with that of 4d orbitals (Tc). The metal–oxygen stretch varies with the dithiolate ligand and the frequency decreases in the order dto > tma > edt. The presence of electron-withdrawing groups on the sulfur atom results in an increase in the metal–oxygen stretch.

Details of the optical spectra of these complexes are summarized in Table II. In general, there is at least one band in the range 330–450 nm (ϵ ~3500 L mol^{-1} cm^{-1}), and the complexes range in color from yellow-orange to red-brown. A bathochromic shift is observed for the technetium complexes compared to their rhenium analogues, as expected from considerations of periodicity. The complexes are generally weak paramagnets in the solid state (Table III). The effective magnetic moments, which are field strength dependent, lie in the range 0.1–1.5 μ_B (295 K). Similar behavior is found for some oxomolybdenum and oxorhenium complexes, with a d^2 configuration having local C_{4v} symmetry, where the ground state is expected to be $^1A_1$. This has been suggested[31–33] to be due to temperature-independent paramagnetism.

The voltammetric behavior of these complexes has been examined at mercury and platinum electrodes, as summarized in Table IV. The tendency for technetium to reduce more easily than rhenium has been demonstrated voltammetrically for hexahalometalate(IV) complexes in acetonitrile,[34] and this trend is observed for the oxobis(dithiolato)metalate(V) complexes. McCleverty et al.[15] reported a one-electron reversible reduction for $ReO(mnt)_2^-$ (IVb) at −1.24 V vs. SCE. However, even with samples derived from their preparation, the only reversible one-electron reduction observed for IVb occurs at −1.05 V vs. SCE. Although pseudoreversible or ideally reversible reductions are observed for several of the complexes, none of the reduction potentials indicate species which are easily accessible by conventional chemical techniques. In general, the ease of reduction is proportional to the electron withdrawing capabilities of the ligand backbone in the series dto > tma > edt. Oxidatively, there appears to be no tendency to form technetium(VI) or rhenium(VI) complexes, and the oxidative waves observed may be due to oxidation of the ligands.

Unlike $ReOBr_4 \cdot CH_3CN^-$ and $TcOCl_4^-$, which disproportionate rapidly in aqueous solution to MO_4^- and $MO_2 \cdot xH_2O$, the oxobis(dithiolato)metalate(V) complexes are exceedingly stable in aqueous solution, including highly basic media. In addition, there appears to be no tendency for the coordination of a sixth ligand, such as pyridine or triphenylphosphine, in the vacant site of these five-coordinate complexes. Oxidation of the isoelectronic $Mo^{IV}O(R_2dtc)_2$ complexes to $Mo^{VI}O_2(R_2dtc)_2$ complexes is possible,[31] and with the proper reagents, the reversal of this oxidation may be accomplished. In the rhenium and technetium complexes described, there appears to be no tendency for the formation of dioxobis(dithiolato)metalates(VII).

The ease of synthesis and the stability of the complexes described in this study are in marked contrast to the mistaken belief that rhenium(V) and technetium(V) coordination complexes are unstable in aqueous solution.[26] This belief had been based on the chemistry of the oxotetrahalometalate(V) and hexahalometalate(IV) anions. The aqueous chemistry of technetium and rhenium is probably much more varied than initially believed, and by careful selection of ligand and oxidation state, the rational design of radiopharmaceuticals containing technetium should be possible.

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Registry No. $Ph_4AsTcO(SCH_2CH_2S)_2$, 70177-06-9; $Ph_4AsReO(SCH_2CH_2S)_2$, 73396-14-2; *cis*-[*n*-Bu_4N][$TcO(SCH_2COS)_2$], 72043-36-8; *trans*-[*n*-Bu_4N][$TcO(SCH_2COS)_2$], 73465-10-8; *cis*-[*n*-Bu_4N][$ReO(SCH_2COS)_2$], 73465-08-4; *trans*-[*n*-Bu_4N][$ReO(SCH_2COS)_2$], 73396-12-0; *n*-$Bu_4NTcO(C_2O_2S_2)_2$, 73396-10-8; $Ph_4AsTcO(C_2O_2S_2)_2$, 73396-09-5; *n*-$Bu_4NReO(C_2O_2S_2)_2$, 73396-07-3; $Ph_3MeAsReO(C_2O_2S_2)_2$, 73396-06-2; *n*-$Bu_4NTcO(S_2C_2(CN)_2)_2$, 73465-06-2; $Ph_4AsReO(S_2C_2(CN)_2)_2$, 73495-01-9; *n*-$Bu_4NTcO(S_2C_7H_6)_2$, 70177-10-5; *n*-$Bu_4NReO(S_2C_7H_6)_2$, 73396-04-0; NH_4TcO_4, 13598-66-8; $NaReO_4$, 13472-33-8; $Ph_4AsReOBr_4$, 14853-12-4; *n*-$Bu_4NReOBr_4$, 15363-68-5; $Ph_3MeAsReOBr_4$, 73465-05-1; $Ph_4AsReOBr_4 \cdot CH_3CN$, 35788-73-9; *n*-$Bu_4NTcOCl_4$, 71341-65-6; $HSCH_2COSH$, 30298-36-3; $ClCH_2COSH$, 867-49-2; $HSCH_2CO_2H$, 68-11-1.

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