

Thiolato-Techneium Complexes. 2.¹ Synthesis, Characterization, Electrochemistry, and Spectroelectrochemistry of the Technetium(III) Complexes *trans*-[Tc(SR)₂(DMPE)₂]⁺, Where R Is an Alkyl or Benzyl Group and DMPE Is 1,2-Bis(dimethylphosphino)ethane

Takumi Konno,² Jon R. Kirchhoff, William R. Heineman, and Edward Deutsch*

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The use of a reduction-substitution route to prepare the thiolato-technetium(III) complexes *trans*-[Tc(SR)₂(DMPE)₂]⁺ from the technetium(V) starting material *trans*-[Tc(OH)(O)(DMPE)₂]²⁺ and alkane- or benzenemethanethiols has been investigated (DMPE represents 1,2-bis(dimethylphosphino)ethane). While benzenemethanethiols appear to be generally effective in this route, the efficacy of alkanethiols decreases as the size of the R group increases; reasonable yields of the desired products can be obtained with R = methyl, ethyl, *n*-propyl, but none of the desired product is obtained with R = isopropyl, *tert*-butyl. The four newly prepared *trans*-[Tc(SR)₂(DMPE)₂]⁺ complexes (R = C₂H₅, *n*-C₃H₇, CH₂C₆H₅, CH₂C₆H₄-*p*-OCH₃) are characterized by fast atom bombardment mass spectrometry, visible-UV spectrophotometry, spectroelectrochemistry, and elemental analyses of three examples. They are assigned a *trans* geometry by comparison with the known structure of *trans*-[Tc(SCH₃)₂(DMPE)₂]⁺. All five thiolato complexes exhibit a reversible Tc(III/II) couple at about -0.5 V, a reversible Tc(II/I) couple at about -1.8 V, and an irreversible redox process at about +0.9 V that is tentatively assigned as resulting from a metal-based Tc(IV/III) couple (all potentials obtained in 0.5 M TEAP/DMF vs Ag/AgCl (3 M NaCl)). The potentials of all three couples are dependent on the nature of the thiolato R group; e.g., the Tc(III/II) couple varies from -0.513 V for R = benzyl to -0.622 V for R = *n*-propyl. These dependencies are understood on the basis of competition between the σ -donating and π -accepting properties of the various thiolato ligands. The visible spectra of the five thiolato-Tc(II) complexes were obtained by spectroelectrochemical techniques. For both the Tc(III) and Tc(II) complexes the visible spectra are dominated by sulfur-to-technetium charge-transfer transitions, the energies of which depend on the technetium oxidation state but do not depend on the nature of the thiolato R group. Observations on the relative instability of *trans*-[Tc(SCH₃)₂(DMPE)₂]⁺ in 0.5 M TEAP/DMF are interpreted in terms of the possible existence of the *cis* isomer of this complex.

Introduction

During the past decade the inorganic chemistry of technetium has undergone extensive development primarily because of the importance of the isotope ^{99m}Tc to the field of diagnostic nuclear medicine.³⁻⁵ This development of technetium chemistry continues to be influenced by the aims of nuclear medicine. Thus, new classes of technetium coordination compounds are being designed and prepared with the goal of providing substitution-inert centers, the chemical and biological properties of which can be readily altered by subtle ligand variations. The recent emphasis given to the design and preparation of both neutral and cationic low-valent technetium complexes is due to the potential use of such species for, respectively, brain and heart perfusion imaging.^{6,7}

In this context, chelating diphosphine ligands are of interest because of their ability to stabilize low-oxidation-state, substitution-inert technetium complexes through π -back-bonding interactions.^{3,4} Diphosphine complexes of technetium are known to exhibit reversible redox behavior in aprotic solvents⁸⁻¹¹ and in aqueous micellar media,¹² and for the important class of Tc(III/II) couples *trans*-[TcX₂D₂]⁺⁰ (D = bidentate, neutral diphosphine ligand; X = monodentate, monoanionic ligand), these redox reactions interconvert neutral and cationic complexes. Recent studies have shown that a fundamental understanding of these redox

processes is a prerequisite to understanding and controlling the biological activity of the *trans*-[TcX₂D₂]⁺⁰ complexes.¹²⁻¹⁵ The fundamental inorganic chemistry necessary to develop this understanding and control also provides the basis for deriving correlations among the structural, spectral, and electrochemical properties of the complexes.⁹ These correlations should in turn allow inferences to be drawn about the important electronic interactions that control the bonding and reactivity of low-valent technetium complexes.

While a variety of different diphosphine (D) ligands have been incorporated into *trans*-[TcX₂D₂]⁺⁰ complexes, until recently the monodentate (X) ligands have been restricted primarily to Cl and Br, with a single example known where X = -NCS.^{8-11,16} This situation has changed with our report¹ on the preparation and characterization of a Tc(III) complex in which X = -SCH₃, the methanethiolato ligand: *trans*-[Tc(SCH₃)₂(DMPE)₂]⁺, where DMPE = 1,2-bis(dimethylphosphino)ethane. The synthetic procedure used in this initial work is in principle quite general and should allow for the preparation of a variety of thiolato (-SR) complexes of the general formula *trans*-[Tc(SR)₂(DMPE)₂]⁺. We now report on the synthesis and characterization of a series of these thiolato-technetium complexes, with emphasis on delineating how the spectral and electrochemical properties of these complexes depend on subtle variations in the nature of the thiolato R group.

Acronyms and Abbreviations

The following acronyms and abbreviations are used in this article: DEPE = 1,2-bis(diethylphosphino)ethane; diars = 1,2-bis(dimethylarsino)benzene; DMF = *N,N*-dimethylformamide; DMPE = 1,2-bis(dimethylphosphino)ethane; DPPB = 1,2-bis(diphenylphosphino)benzene; DPPE = 1,2-bis(diphenylphosphino)ethane; DPPV = *cis*-1,2-bis(diphenylphosphino)ethylene; FAB = fast atom bombardment; OT-TLE = optically transparent thin-layer electrode; PDE = platinum-disk electrode; TEAP = tetraethylammonium perchlorate.

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Experimental Section

Caution! Technetium-99 emits a low-energy (0.292-MeV) β -particle with a half-life of 2.12×10^5 years. When handled in milligram amounts, ^{99}Tc does not present a serious health hazard since common laboratory materials provide adequate shielding. Bremsstrahlung is not a significant problem due to the low energy of the β -particle emission, but normal radiation safety procedures must be used at all times to prevent contamination. In this paper the symbol Tc refers only to technetium-99; the metastable isotope ^{99m}Tc was not used in these studies.

Reagents. Unless otherwise noted, all chemicals were of reagent grade. Technetium-99 and the starting complex, $\text{trans}[\text{Tc}(\text{O})(\text{OH})(\text{DMPE})_2](\text{PF}_6)_2$, were prepared as described previously.¹ The magic bullet matrix (a 5:1 mixture of dithiothreitol and dithioerythritol in a small amount of methanol) was used in measurements of the FAB mass spectra. DMF from Burdick and Jackson Laboratories, Inc., and polarographic grade TEAP from G. F. Smith Chemicals were used in the electrochemical measurements. Prior to use, the TEAP was dried at 60 °C in vacuo over P_2O_5 . No significant electroactive impurities were detected in either the solvent or supporting electrolyte.

Synthesis. $\text{trans}[\text{Tc}(\text{SCH}_3)_2(\text{DMPE})_2]\text{PF}_6$ was prepared as previously described.¹

$\text{trans}[\text{Tc}(\text{SC}_2\text{H}_5)_2(\text{DMPE})_2]\text{PF}_6$. To a suspension containing 100 mg of $\text{trans}[\text{Tc}(\text{O})(\text{OH})(\text{DMPE})_2](\text{PF}_6)_2$ (1.4×10^{-4} mol) in 20 mL of degassed ethanol was added 0.08 mL of neat $\text{C}_2\text{H}_5\text{SH}$ (1.5×10^{-3} mol) followed by 0.3 mL of 1 M NaOH (3.0×10^{-4} mol). The resulting mixture was stirred at 60 °C for 30 min under an argon atmosphere, whereupon the solution became deep purple. When lesser amounts of NaOH (e.g. 0.1 mL of 1 M NaOH) were added, the reaction solution became deep blue and further additions of 1 M NaOH caused the color change to deep purple. To this purple solution was added 0.5 mL of saturated NH_4PF_6 in water, and the solution turned blue almost immediately. The blue reaction solution was cooled to room temperature, and then a small amount of water was added. After the mixture stood at room temperature for 2 h, the resultant blue precipitate of $\text{trans}[\text{Tc}(\text{SC}_2\text{H}_5)_2(\text{DMPE})_2]\text{PF}_6$ was collected by filtration; yield 30 mg (32%). Anal. Calcd for $\text{TcS}_2\text{P}_5\text{F}_6\text{C}_{16}\text{H}_{42}$: C, 28.83; H, 6.35; F, 17.10; P, 23.24; S, 9.62. Found: C, 28.87; H, 6.41; F, 15.81; P, 21.67; S, 8.66.

$\text{trans}[\text{Tc}(\text{S}-n\text{-C}_3\text{H}_7)_2(\text{DMPE})_2]\text{PF}_6$. This complex was prepared by a method similar to that described above for $\text{trans}[\text{Tc}(\text{SC}_2\text{H}_5)_2(\text{DMPE})_2]\text{PF}_6$, with $n\text{-C}_3\text{H}_7\text{SH}$ instead of $\text{C}_2\text{H}_5\text{SH}$. The reaction proceeded slowly, and the mixture was stirred at 60 °C for 1 h. Crystalline $\text{trans}[\text{Tc}(\text{S}-n\text{-C}_3\text{H}_7)_2(\text{DMPE})_2]\text{PF}_6$ was obtained by storing the blue reaction solution at -10 °C for several days; yield 15 mg (16%).

$\text{trans}[\text{Tc}(\text{SCH}_2\text{C}_6\text{H}_5)_2(\text{DMPE})_2]\text{PF}_6$. This complex was prepared by a method similar to that described above for $\text{trans}[\text{Tc}(\text{SC}_2\text{H}_5)_2(\text{DMPE})_2]\text{PF}_6$, with $\text{HSCH}_2\text{C}_6\text{H}_5$ instead of $\text{C}_2\text{H}_5\text{SH}$. When the blue reaction solution was cooled to room temperature, the blue $\text{trans}[\text{Tc}(\text{SCH}_2\text{C}_6\text{H}_5)_2(\text{DMPE})_2]\text{PF}_6$ precipitated and was collected by filtration; yield 30 mg (27%). Anal. Calcd for $\text{TcS}_2\text{P}_5\text{F}_6\text{C}_{26}\text{H}_{46}$: C, 39.55; H, 5.87; F, 14.44; P, 19.61; S, 8.12. Found: C, 39.61; H, 6.01; F, 13.14; P, 18.86; S, 8.42.

$\text{trans}[\text{Tc}(\text{SCH}_2\text{C}_6\text{H}_4\text{-}p\text{-OCH}_3)_2(\text{DMPE})_2]\text{PF}_6$. This complex was prepared by a method similar to that described above for $\text{trans}[\text{Tc}(\text{SC}_2\text{H}_5)_2(\text{DMPE})_2]\text{PF}_6$, with $\text{HSCH}_2\text{C}_6\text{H}_4\text{-}p\text{-OCH}_3$ instead of $\text{C}_2\text{H}_5\text{SH}$. Crystalline $\text{trans}[\text{Tc}(\text{SCH}_2\text{C}_6\text{H}_4\text{-}p\text{-OCH}_3)_2(\text{DMPE})_2]\text{PF}_6$ was obtained by adding diethyl ether to the blue reaction solution and then allowing the solution to stand at room temperature for 2 h; yield 30 mg (25%). Anal. Calcd for $\text{TcS}_2\text{P}_5\text{F}_6\text{O}_2\text{C}_{28}\text{H}_{50}$: C, 39.53; H, 5.92; F, 13.40; P, 18.20; S, 7.54. Found: C, 39.95; H, 6.23; F, 13.35; P, 17.37; S, 8.50.

Reaction of $\text{trans}[\text{Tc}(\text{O})(\text{OH})(\text{DMPE})_2](\text{PF}_6)_2$ with $(\text{CH}_3)_2\text{CHSH}$ and $(\text{CH}_3)_3\text{CSH}$. Attempted preparations of the complexes $[\text{Tc}(\text{SCH}(\text{CH}_3)_2)_2(\text{DMPE})_2]^+$ and $[\text{Tc}(\text{SC}(\text{CH}_3)_2)_2(\text{DMPE})_2]^+$ were unsuccessful using a method similar to that described for the preparation of $\text{trans}[\text{Tc}(\text{SC}_2\text{H}_5)_2(\text{DMPE})_2]^+$. Even when 20 mol equiv of excess thiol was added and the mixture was heated at 60 °C for 2 h, the desired purple $\text{trans}[\text{Tc}(\text{SR})_2(\text{DMPE})_2]^0$ complexes were not obtained, but rather the reaction solution turned a pale pink color. Addition of saturated NH_4PF_6 in water to the pale pink reaction solution generated a color change to pale green-brown, but no substantive formation of $[\text{Tc}(\text{SR})_2(\text{DMPE})_2]^+$ was observed.

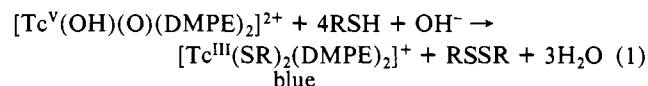
Reduction of $\text{trans}[\text{Tc}(\text{SR})_2(\text{DMPE})_2]\text{PF}_6$. To an anaerobic solution of $\text{trans}[\text{Tc}(\text{SR})_2(\text{DMPE})_2]\text{PF}_6$ in acetonitrile was added a few drops of $(\text{C}_4\text{H}_9)_4\text{NBH}_4$ in a small amount of ethanol under an argon atmosphere. The blue solution rapidly turned purple. This purple solution could also be obtained by adding NaSCH_3 in a small amount of ethanol to the blue solution. Contact with the air caused the exposed surfaces of the purple solution to turn blue, and bubbling air through the purple solution immediately caused a color change to pale yellow-brown. When several drops of NH_4PF_6 in a small amount of water or an acid such as $\text{CF}_3\text{SO}_3\text{H}$, HPF_6 , or HClO_4 was added to the purple solution under an

argon atmosphere, the color reverted back to the original blue. No color change occurred when water alone was added to the purple solution. The interconversion between blue and purple solutions is reversible through at least four cycles. This behavior is analogous to that previously reported¹ for $\text{trans}[\text{Tc}(\text{SCH}_3)_2\text{D}_2]\text{PF}_6$ (D = DMPE, DEPE).

Measurements. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Visible-UV spectra were recorded in acetonitrile on a Cary 210 spectrophotometer (Varian) at ambient temperatures. FAB mass spectra were recorded by using the magic bullet matrix on a VG 30-250 spectrometer (VG Instruments, Inc.) at the probe temperature. Xenon was used as the primary beam gas, and the ion gun was operated at 8 kV and 100 μA . Data were collected generally over the mass range 100-1000 Da at 0.7 s/scan. Electrochemical measurements were made with a Bioanalytical Systems, Inc. (BAS), CV-1B voltammograph. Potentials were monitored with a Keithly 178 digital multimeter, and voltammograms were recorded on a Hewlett-Packard 7015B X-Y recorder. Visible spectra in the spectroelectrochemical experiment were recorded on the above-noted Cary 210 spectrophotometer; the cell compartment was modified to accommodate electrical leads and an inert-gas inlet. The working electrode for conventional cyclic voltammetry was a PDE (BAS). OTTL's were constructed as previously described with 100 wires/in. gold minigrid.¹⁷ An aqueous Ag/AgCl (3 M NaCl) electrode (BAS) and a platinum wire were used as reference and auxiliary electrodes, respectively. The reference electrode was isolated from the solution by a porous Vycor plug. All potentials are reported vs the Ag/AgCl (3 M NaCl) electrode. In general, electrochemical experiments were performed as previously described.^{10,18} Each spectrum in the spectropotentiostatic experiments was recorded 5 min after potential application; this time was sufficient to attain equilibrium values of $[\text{O}]/[\text{R}]$.

Results

Synthesis. The thiolato-Tc(III) complexes $\text{trans}[\text{Tc}(\text{SR})_2(\text{DMPE})_2]^+$ (R = C_2H_5 , $n\text{-C}_3\text{H}_7$, $\text{CH}_2\text{C}_6\text{H}_5$, $\text{CH}_2\text{C}_6\text{H}_4\text{-}p\text{-OCH}_3$) can be prepared by reaction of the Tc(V) complex, $\text{trans}[\text{Tc}(\text{OH})(\text{O})(\text{DMPE})_2]^{2+}$, with excess thiol under anaerobic conditions. The reaction is initiated and enhanced by the presence of a small amount of base. Addition of a 10-fold excess of the appropriate thiol followed by a small amount of aqueous NaOH ($[\text{NaOH}]/[\text{RSH}] = 1/10$) to a suspension of $\text{trans}[\text{Tc}(\text{OH})(\text{O})(\text{DMPE})_2]^{2+}$ in ethanol at 60 °C yields a deep blue solution, the color of which is characteristic of the desired thiolato-Tc(III) product. This reaction is described by the equation below, in which RS^- acts as both a ligand and a reducing agent:



Further addition of NaOH to the blue thiolato-Tc(III) solution causes a color change to purple, indicating the presence of the reduced species, $\text{trans}[\text{Tc}^{\text{II}}(\text{SR})_2(\text{DMPE})_2]^0$. Aqueous acids such as NH_4PF_6 , $\text{CF}_3\text{SO}_3\text{H}$, and HPF_6 can be used to reoxidize the purple $\text{trans}[\text{Tc}^{\text{II}}(\text{SR})_2(\text{DMPE})_2]^0$ and restore the blue color of the Tc(III) complex. This pH-dependent Tc(III/II) redox reaction is presumably mediated by the thiol/disulfide redox couple and apparently is reversible. The preparative reactions of $\text{trans}[\text{Tc}(\text{OH})(\text{O})(\text{DMPE})_2]^{2+}$ with $\text{C}_2\text{H}_5\text{SH}$, $\text{C}_6\text{H}_5\text{CH}_2\text{SH}$, and $p\text{-CH}_3\text{O-C}_6\text{H}_4\text{CH}_2\text{SH}$ are significantly slower than the reaction with CH_3SH ,¹ while the reaction with $n\text{-C}_3\text{H}_7\text{SH}$ is slower yet. The comparable preparative reactions of $\text{trans}[\text{Tc}(\text{OH})(\text{O})(\text{DMPE})_2]^{2+}$ with the more sterically hindered thiols $(\text{CH}_3)_2\text{CHSH}$ and $(\text{CH}_3)_3\text{CSH}$ do not yield significant amounts of the analogous thiolato-technetium(III) complexes.

The Tc(III) complexes $\text{trans}[\text{Tc}(\text{SR})_2(\text{DMPE})_2]^+$ can be isolated by reducing the volume of and/or cooling the blue reaction solution. Addition of large amounts of water to the reaction solution is disadvantageous since this procedure yields a blue precipitate that FAB mass spectrometry shows to be contaminated with the Tc(I) complex $[\text{Tc}(\text{DMPE})_3]^+$.¹⁶ The yields of the thiolato-Tc(III) complexes are not high, especially for the bulky thiolato ligands. None of the purple Tc(II) complexes $\text{trans}[\text{Tc}(\text{SR})_2(\text{DMPE})_2]^0$ could be isolated due to oxidation and de-

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Table I. FAB Mass Spectral Data for *trans*-[Tc(SR)₂(DMPE)₂]⁺ Complexes

	complex ion, M ⁺	fragment ion			
		M - R	M - 2R	M - SR	M - R, SR
<i>trans</i> -[Tc(SC ₂ H ₅) ₂ (DMPE) ₂] ⁺	521 ^a	491	463	459 ^a	
<i>trans</i> -[Tc(S- <i>n</i> -C ₃ H ₇) ₂ (DMPE) ₂] ⁺	549	505	462	473 ^a	
<i>trans</i> -[Tc(SCH ₂ C ₆ H ₅) ₂ (DMPE) ₂] ⁺	645	554	463 ^a	522	430
<i>trans</i> -[Tc(SCH ₂ C ₆ H ₄ - <i>p</i> -OCH ₃) ₂ (DMPE) ₂] ⁺	705	584	463 ^a	551	

^a Intense peak in the spectrum.

Table II. Visible-UV Spectral Data for *trans*-[Tc(SR)₂(DMPE)₂]⁺ Complexes in Acetonitrile

	$\lambda_{\max}/10^3$, cm ⁻¹	$\epsilon/10^3$, M ⁻¹ cm ⁻¹
<i>trans</i> -[Tc(SCH ₃) ₂ (DMPE) ₂] ⁺	16.81	13.0
	28.49	2.0
	39.68	4.8
	46.08	11.6
<i>trans</i> -[Tc(SC ₂ H ₅) ₂ (DMPE) ₂] ⁺	16.72	14.4
	28.41	2.1
	39.53	7.8
	45.87	20.9
<i>trans</i> -[Tc(S- <i>n</i> -C ₃ H ₇) ₂ (DMPE) ₂] ⁺	16.67	13.1
	28.57	2.3
	40.16 sh ^a	7.6
	46.73	20.9
<i>trans</i> -[Tc(SCH ₂ C ₆ H ₅) ₂ (DMPE) ₂] ⁺	16.45	16.5
	27.93	3.1
	35.34	7.1
	43.10	36.2
	41.84	55.1
<i>trans</i> -[Tc(SCH ₂ C ₆ H ₄ - <i>p</i> -OCH ₃) ₂ (DMPE) ₂] ⁺	16.42	18.9
	27.93	3.0
	36.10	11.9
	41.84	55.1
	41.84	55.1

^a "sh" denotes a shoulder.

composition reactions that occur when they are exposed to air. Purified *trans*-[Tc(SR)₂(DMPE)₂]⁺ complexes in solution (which do not contain RS⁻) can be reduced by agents such as BH₄⁻ and reoxidized with acids, presumably in concert with the H⁺/H₂ redox couple.

Characterization. The crystal structure of the prototypical thiolato-Tc(III) complex *trans*-[Tc(SCH₃)₂(DMPE)₂]⁺ has been determined and previously reported.¹ The analogous thiolato-Tc(III) complexes newly prepared in this work are characterized by (i) elemental analyses of representative compounds, which are in acceptable agreement with the proposed formulations (vide supra), (ii) FAB mass spectrometry, and (iii) visible-UV spectrophotometry. The compositional assignments are most definitively confirmed by the positive-ion FAB mass spectra, which show parent peaks at *m/z* = 521 for *trans*-[Tc(SC₂H₅)₂(DMPE)₂]⁺, at *m/z* = 549 for *trans*-[Tc(S-*n*-C₃H₇)₂(DMPE)₂]⁺, at *m/z* = 645 for *trans*-[Tc(SCH₂C₆H₅)₂(DMPE)₂]⁺, and at *m/z* = 705 for *trans*-[Tc(SCH₂C₆H₄-*p*-OCH₃)₂(DMPE)₂]⁺. Several fragment ions corresponding to losses of R and/or SR groups from *trans*-[Tc(SR)₂(DMPE)₂]⁺ are also observed. It is noteworthy that fragment ions arising from the loss of a DMPE ligand are not observed. Tabulated FAB mass spectral data are given in Table I, and a typical example is shown in Figure 1.

All of the thiolato-Tc(III) complexes exhibit similar, characteristic, well-defined, intense absorption bands in the visible and UV regions. Spectral data are collected in Table II. The visible spectra of *trans*-[Tc(SCH₃)₂(DMPE)₂]⁺ and *trans*-[Tc(SCH₂C₆H₅)₂(DMPE)₂]⁺ are shown in Figure 2 to illustrate their similarity.

The *trans*-[Tc(SR)₂(DMPE)₂]⁺ complexes have been further characterized by cyclic voltammetry and thin-layer spectroelectrochemistry to determine the redox potentials of accessible couples and the spectral characteristics of the component complexes (vide infra).

Electrochemistry. The results of electrochemical measurements in 0.5 M TEAP/DMF are summarized in Table III. Slow

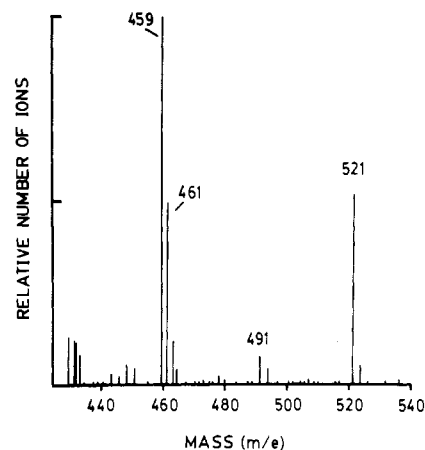


Figure 1. FAB mass spectrum of *trans*-[Tc(SC₂H₅)₂(DMPE)₂]⁺ over the *m/z* 440-540 range.

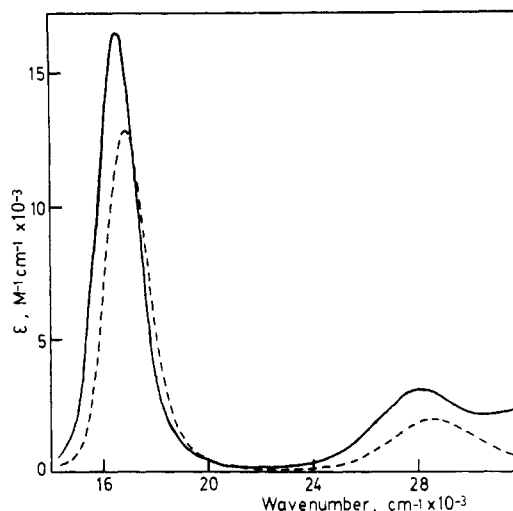


Figure 2. Visible spectra of *trans*-[Tc(SCH₃)₂(DMPE)₂]⁺ (dashed line) and *trans*-[Tc(SCH₂C₆H₅)₂(DMPE)₂]⁺ (solid line) recorded in acetonitrile.

Table III. Electrochemical Data for [Tc(X)₂(DMPE)₂]⁺ Complexes in 0.5 M TEAP/DMF^{a,b}

	<i>E</i> ^{o'}		<i>E</i> _{pa} Tc(III/IV) ^c
	Tc(III/II)	Tc(II/I)	
<i>trans</i> -[Tc(Br) ₂ (DMPE) ₂] ⁺ ^d	-0.098	-1.27	
<i>trans</i> -[Tc(Cl) ₂ (DMPE) ₂] ⁺ ^d	-0.231	-1.41	
<i>trans</i> -[Tc(SCH ₃) ₂ (DMPE) ₂] ⁺ ^e	-0.550	-1.72	+0.925
<i>trans</i> -[Tc(SC ₂ H ₅) ₂ (DMPE) ₂] ⁺	-0.566	-1.75	+0.915 ^f
<i>trans</i> -[Tc(S- <i>n</i> -C ₃ H ₇) ₂ (DMPE) ₂] ⁺	-0.622	-1.85	+0.870 ^f
<i>trans</i> -[Tc(SCH ₂ C ₆ H ₅) ₂ (DMPE) ₂] ⁺	-0.513	-1.68	+0.980
<i>trans</i> -[Tc(SCH ₂ C ₆ H ₄ - <i>p</i> -OCH ₃) ₂ (DMPE) ₂] ⁺	-0.559	-1.72	+0.920 (sh) ^g

^a 25 °C; PDE working electrode; scan rate 100 mV/s; all values in V.
^b *E*^{o'} = (*E*_{pc} + *E*_{pa})/2 vs Ag/AgCl (3 M NaCl) from cyclic voltammetry.
^c Irreversible oxidation at 25 °C. ^d Reference 10. ^e Reference 1. ^f Becomes chemically reversible at -70 °C (see text). ^g Not well defined.

decomposition of some of the Tc(III) complexes in this medium (vide infra) does not interfere with electrochemical characterization

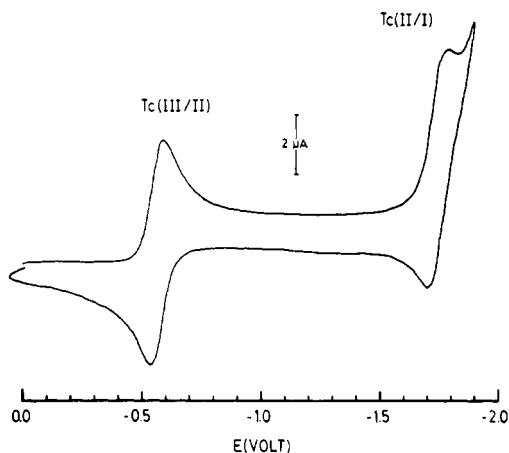


Figure 3. Cyclic voltammogram of 0.99 mM *trans*-[Tc(SC₂H₅)₂(DMPE)₂]⁺ in 0.5 M TEAP/DMF at a PDE (scan rate 100 mV/s, initial potential 0.0 V).

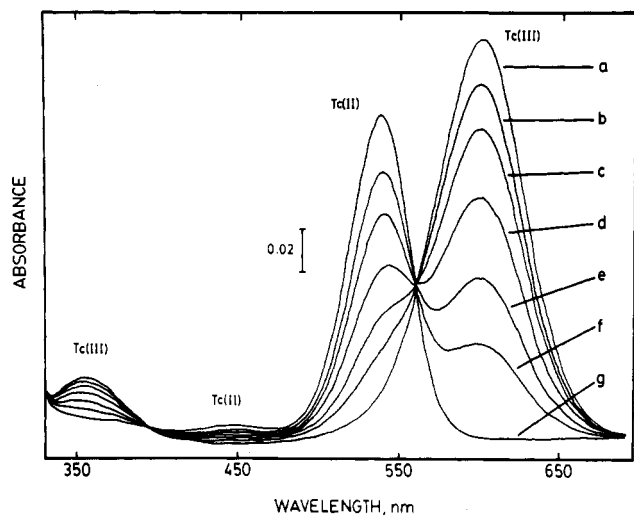


Figure 4. Sequential absorption spectra obtained during an OTTLE spectropotentiostatic experiment on 0.75 mM *trans*-[Tc(SC₂H₅)₂(DMPE)₂]⁺ in 0.5 M TEAP/DMF at the following applied potentials (V vs Ag/AgCl): (a) 0.000; (b) -0.510; (c) -0.530; (d) -0.550; (e) -0.570; (f) -0.590; (g) -0.900.

at the PDE. Figure 3 shows the cyclic voltammogram obtained for *trans*-[Tc(SC₂H₅)₂(DMPE)₂]⁺, which is characteristic of the *trans*-[Tc(SR)₂(DMPE)₂]⁺ series.

Each thiolato–Tc(III) complex is characterized by two reversible one-electron reductions that are assigned as the Tc(III/II) and Tc(II/I) redox processes.^{9,10} The reversibility of these couples is established by the following: (i) linear plots of peak currents versus the square root of the scan rate, (ii) typical peak-to-peak separations for one-electron redox processes of inorganic complexes in nonaqueous solvents, and (iii) ratios of peak currents that are approximately unity. The $E^{0'}$ values for the Tc(III/II) couples range from -0.513 to -0.622 V, while the corresponding Tc(II/I) couple occurs at a potential about 1.18 V more negative than that of the Tc(III/II) couple. At 100 mV/s, slight decomposition is observed only for the Tc(I) species [Tc(SCH₂C₆H₅)₂(DMPE)₂]⁻; this decomposition yields an additional, although minor, redox couple at approximately -0.36 V. Electrochemical oxidation of the thiolato–Tc(III) complexes can also be observed. At room temperature, positive potential scans reveal a single irreversible oxidation wave for all the complexes; concurrent decomposition of the complex is indicated by several small waves that appear on the subsequent negative scan. At -70 °C, the rate of chemical decomposition of the oxidized species is slowed to the point that the corresponding reduction wave can be observed for the complexes with R = C₂H₅, *n*-C₃H₇.

The relative instabilities of the *trans*-[Tc(SR)₂(DMPE)₂]⁺ complexes in 0.5 M TEAP/DMF restricts the electrochemical

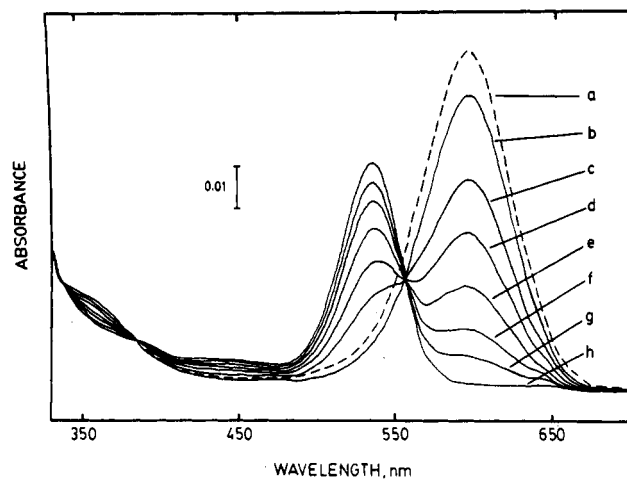


Figure 5. Sequential absorption spectra obtained during an OTTLE spectropotentiostatic experiment on 0.81 mM *trans*-[Tc(SCH₃)₂(DMPE)₂]⁺ in 0.5 M TEAP/DMF at the following applied potentials (V vs Ag/AgCl): (a) 0.000; (b) -0.460; (c) -0.520; (d) -0.540; (e) -0.560; (f) -0.580; (g) -0.600; (h) -0.750.

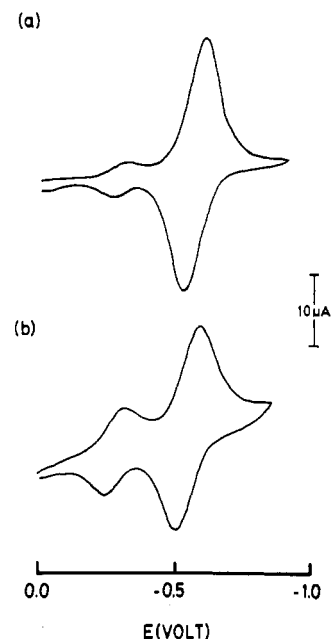


Figure 6. Thin-layer cyclic voltammograms of 0.81 mM *trans*-[Tc(SCH₃)₂(DMPE)₂]⁺ in 0.5 M TEAP/DMF (a) before and (b) after spectroelectrochemical measurements (scan rate 2 mV/s, initial potential 0.0 V).

information that can be obtained from the spectropotentiostatic technique.^{17,19,20} The stabilities of these complexes decrease in the order R = C₂H₅, *n*-C₃H₇ > CH₂C₆H₄-*p*-OCH₃ > CH₃ > CH₂C₆H₅, and thus uncomplicated spectropotentiostatic experiments were realized only for the more stable complexes with R = C₂H₅, *n*-C₃H₇. Figure 4 shows spectra recorded during a spectropotentiostatic reduction of *trans*-[Tc(SC₂H₅)₂(DMPE)₂]⁺. Absorption maxima for the Tc(III) complex occur at 601 and 355 nm, while the corresponding maxima for the Tc(II) complex occur at 538 and 444 nm. A Nernst plot^{17,19,20} of E_{app} vs log ([O]/[R]) for the 601-nm data of Figure 4 is linear and yields values of $E^{0'} = -0.561$ V and $n = 1.03$. Similar results are obtained for *trans*-[Tc(S-*n*-C₃H₇)₂(DMPE)₂]⁺, and the corresponding Nernst plot yields values of $E^{0'} = -0.606$ V and $n = 0.95$. The behavior of the less stable complex *trans*-[Tc(SCH₃)₂(DMPE)₂]⁺ during a thin-layer spectropotentiostatic experiment is shown in Figure

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Table IV. Spectrophotometric Data for *trans*-[Tc(SR)₂(DMPE)₂]⁺⁰ Complexes^a in 0.5 M TEAP/DMF

	λ_{\max} , nm		λ_{iso} , nm
	Tc(III)	Tc(II) ^b	
<i>trans</i> -[Tc(SCH ₃) ₂ (DMPE) ₂] ^{+c}	596, 358 (sh)	536, 440	
<i>trans</i> -[Tc(SC ₂ H ₅) ₂ (DMPE) ₂] ⁺	601, 355	538, 444	560, 397
<i>trans</i> -[Tc(S- <i>n</i> -C ₃ H ₇) ₂ (DMPE) ₂] ⁺	602, 355	540, 445	562, 388
<i>trans</i> -[Tc(SCH ₂ C ₆ H ₅) ₂ (DMPE) ₂] ^{+d}	610, 362	542	
<i>trans</i> -[Tc(SCH ₂ C ₆ H ₄ - <i>p</i> -OCH ₃) ₂ (DMPE) ₂] ^{+c}	611, 354	542, 450	

^a Determined by spectroelectrochemistry in an OTTE; sh denotes a shoulder. ^b The absorption at approximately 440–450 nm is very broad and weak (see Figure 4). ^c Slow reaction with pseudoisobestic points (see text). ^d Rapid decomposition.

5, while thin-layer cyclic voltammograms obtained before and after this experiment are compared in Figure 6.

All of the thiolato–Tc(III) complexes have sufficient stability in 0.5 M TEAP/DMF to allow potential step spectroelectrochemistry to be conducted in the thin-layer cell, and thus spectrophotometric data can be obtained in this medium for all five of the Tc(II) complexes *trans*-[Tc(SR)₂(DMPE)₂]⁰. These data, as well as the corresponding data for the Tc(III) analogues, are summarized in Table IV.

Discussion

Synthesis and Characterization. The prototypical thiolato–Tc(III) complex *trans*-[Tc(SCH₃)₂(DMPE)₂]⁺ has recently been prepared by a reduction–substitution route³ in which NaSCH₃ both reduces and ligates to the Tc(V) starting material *trans*-[Tc(OH)(O)(DMPE)₂]²⁺.¹ This constitutes the first successful synthesis of a *trans*-[Tc(thiolato)₂(DMPE)₂]⁺ complex (where D is a tertiary bidentate phosphine ligand), although the corresponding halido complexes *trans*-[TcX₂D₂]⁺⁰ (X = Cl, Br) are well-known in both the +3 and +2 Tc oxidation states.^{8–10,21} We anticipated that this route might be utilized to generate a gamut of *trans*-[Tc(SR)₂(DMPE)₂]⁺ complexes (where SR is a thiolato ligand), the chemical and biological properties of which could be systematically altered by incorporating different series of thiolato ligands characterized by closely related R groups. Accordingly, we have investigated in this work the preparative reactions with *trans*-[Tc(OH)(O)(DMPE)₂]²⁺ of the alkane- and benzenemethanethiolates –SR, where R = CH₂CH₃, *n*-C₃H₇, CH(CH₃)₂, C(CH₃)₃, CH₂C₆H₅, CH₂C₆H₄-*p*-OCH₃. Successful preparations of the desired *trans*-[Tc(SR)₂(DMPE)₂]⁺ products were achieved with ethanethiol and *n*-propanethiol, although the efficiency of the preparative reactions (in terms of both net yield and reaction rate) decrease in the order of R groups CH₃ > CH₂CH₃ > *n*-C₃H₇. Since none of the desired *trans*-[Tc(SR)₂(DMPE)₂]⁺ product was obtained with either 2-propanethiol or 2-methyl-2-propanethiol, it appears that for simple alkanethiols the efficiency of the preparative reaction decreases with increasing bulk of the alkyl R group. However, the larger benzenemethanethiols are reasonably effective reduction–substitution agents in this preparative reaction, and they afford the desired Tc(III) complexes in yields which approach that observed for ethanethiol. Thus, the aryl moiety of the benzenemethanethiols appears to modify the purely steric effect observed for the alkanethiols, implying that the nucleophilicity of the thiol is an important factor in determining the overall efficiency of the reduction–substitution synthetic reaction.

Two geometrical isomers, *cis* and *trans*, are possible for the [Tc(SR)₂(DMPE)₂]⁺ complexes prepared herein. However, all known halido–Tc(III) and –Tc(II) complexes, [TcX₂D₂]⁺⁰, exhibit the *trans* geometry,^{8–11,16,21} and X-ray structural analysis has established that the prototypical [Tc(SR)₂(DMPE)₂]⁺ complex with R = CH₃ is also *trans*.¹ Since the visible–UV spectra of the new thiolato–Tc(III) complexes are similar to the spectrum of

the complex with R = CH₃ (Table II), it is reasonable to assign the *trans* geometry to all of the new [Tc(SR)₂(DMPE)₂]⁺ Tc(III) complexes. Moreover, since all of these Tc(III) complexes can be rapidly and reversibly converted to Tc(II) analogues, which in turn exhibit similar visible–UV spectra (Table IV), it is also reasonable to assign the *trans* geometry to all of these relatively stable Tc(II) analogues.

Electrochemistry and Spectroelectrochemistry. The electrochemistry of the *trans*-[Tc(SR)₂(DMPE)₂]⁺ complexes is qualitatively similar to that which has been described for the related series of *trans*-[MX₂(DMPE)₂]⁺ (M = Tc, Re; X = Cl, Br) complexes.^{9,10,22} This electrochemistry is dominated by a reversible M(III/II) couple, which may be accompanied by M(II/I) and M(IV/III) couples of varying degrees of chemical reversibility depending on the nature of X. For both Tc(III/II) and Tc(II/I) couples, the data of Table III show that the thiolato–Tc complexes are consistently several hundred millivolts more difficult to reduce than are the corresponding halido–Tc complexes. This gross effect results from the strong σ -donating nature of thiolato ligands, which makes the technetium center more resistant to accepting further negative charge.¹

A more subtle manifestation of the σ -donating properties of the –SR ligands can be observed in the effect of alkyl R group chain length on the $E^{0'}$ values of the Tc(III/II) and Tc(II/I) couples (Table III); i.e., the σ -donating ability of alkanethiolato ligands increases as the chain length increases, and this causes the complexes to be more difficult to reduce (more negative $E^{0'}$). This σ -donation effect is somewhat ameliorated in the benzenemethanethiol complex since the aryl substituent enhances the π -acid character of the ligand. This favors delocalization of charge density from the metal center, which preferentially stabilizes the lower oxidation state and consequently causes the benzenemethanethiolato complexes to be more easily reduced (more positive $E^{0'}$) than any of the corresponding alkanethiolato complexes. Addition of the electron-donating *p*-methoxy group to the aryl moiety counteracts this π -delocalization effect and makes the *p*-OCH₃–Tc(III) and –Tc(II) complexes more difficult to reduce than the corresponding unsubstituted (benzyl) Tc(III) and Tc(II) complexes.

The above effects on $E^{0'}$ values generated by varying the R group of the –SR ligands are paralleled by previously described effects on $E^{0'}$ values generated by varying the R' group of D ligands (D = R'₂PCH₂CH₂PR'₂) in the halido complexes *trans*-[MX₂D₂]⁺⁰ (M = Tc, Re; X = Cl, Br).^{9,22} Changing R' from methyl to ethyl (DMPE to DEPE) causes $E^{0'}$ values to shift to more negative values (average shift 28 mV),²² while changing R' from methyl to phenyl (DMPE to DPPE) causes $E^{0'}$ values to shift to more positive values (average shift 220 mV).²² The combined effects of varying the two R groups and eight R' groups of *trans*-[Tc(SR)₂(D)₂]⁺ offer the promise of being able to finely tune and control the redox potentials of these complexes.

The irreversible electrochemical oxidation of *trans*-[Tc(SR)₂(DMPE)₂]⁺ complexes could in principle involve either oxidation of the Tc(III) center or oxidation of the thiolato ligand. However, the data of Table III provide indirect evidence that strongly supports assignment of this process as primarily a metal-based Tc(III/IV) oxidation. (i) The difference in potential between the Tc(III/II) $E^{0'}$ values and the peak oxidation potentials, E_{pa} , is independent of the nature of the thiolato ligand and is consistently 1.48 V. This paralleling of E_{pa} and Tc(III/II) $E^{0'}$ values is consistent with E_{pa} being governed by a Tc(IV/III) process but is not consistent with E_{pa} being governed by oxidation of the thiolato ligand. The potential governing oxidation of the thiolato ligand would be expected to be much more strongly dependent on the nature of the thiolato ligand and less dependent on the Tc(III/II) $E^{0'}$ value. (ii) The paralleling of E_{pa} and Tc(III/II) $E^{0'}$ values is also consistent with the expected effects of the thiolato ligand donor–acceptor properties on Tc(IV/III) and Tc(III/II) couples. Thus, the complex that is most easily

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reduced from Tc(III) to Tc(II) ($R = \text{CH}_2\text{C}_6\text{H}_5$) is also the most difficult to oxidize from Tc(III) to Tc(IV). Likewise, increasing the σ -donating character of the alkanethiolato ligand (by increasing the length of the alkyl group) makes it more difficult to reduce Tc(III) to Tc(II) but easier to oxidize Tc(III) to Tc(IV). (iii) When R is CH_2CH_3 or $n\text{-C}_3\text{H}_7$, decomposition of the oxidized species is sufficiently retarded at -70°C so that a reversible redox couple is observed. Such reversibility is unlikely for a sulfur-based redox process but is consistent with a Tc(IV/III) redox process. A reversible Re(IV/III) couple has been reported for the related complex $\text{trans}[\text{ReCl}_2(\text{DPPV})_2]^+$,²³ and irreversible Re(IV/III) couples have been reported for $\text{trans}[\text{ReCl}_2(\text{DMPE})_2]^+$ ²² and $\text{trans}[\text{ReCl}_2(\text{diars})_2]^+$.²⁴

Forms of $[\text{Tc}(\text{SCH}_3)_2(\text{DMPE})_2]^{+/0}$. The instability of $\text{trans}[\text{Tc}(\text{SCH}_3)_2(\text{DMPE})_2]^+$ in 0.5 M TEAP/DMF can be qualitatively understood as the transformation of this complex from one form to another. The thin-layer cyclic voltammogram in Figure 6a shows the presence of two couples (a minor component at -0.37 V and a major component at -0.55 V) even before the spectropotentiostatic experiment is conducted. The same two couples are present after the spectropotentiostatic experiment (Figure 6b), but the minor component has increased in concentration at the expense of the major component. The fact that the overall current due to the two redox processes (defined as the area under both waves) appears to be the same in parts a and b of Figure 6 implies that the major component converts to the minor component during the spectropotentiostatic experiment.

The presence of the above two components in 0.5 M TEAP/DMF solutions of $\text{trans}[\text{Tc}(\text{SCH}_3)_2(\text{DMPE})_2]^+$ nicely accounts for the detailed results of the spectropotentiostatic experiment shown in Figure 5. At 0.0 V both components are in their oxidized forms. At the next applied potential, -0.460 V, the minor component is completely reduced while only a small portion of the major component is reduced. As subsequently applied potentials become more negative, there is no change in the oxidation state of the minor component (which is already completely reduced), but more and more of the major component is converted to the reduced form. Thus, all spectra except the initial one define an isosbestic point that corresponds to reduction of the major component. In Table IV this behavior is referred to as "pseudoisobestic".

The spectrum of the totally reduced form of the major component (Figure 5) is similar to the spectra of the stable $\text{trans}[\text{Tc}^{\text{II}}(\text{SR})_2(\text{DMPE})_2]^0$ complexes generated when $R = \text{C}_2\text{H}_5$, $n\text{-C}_3\text{H}_7$ (Table IV). Also, the E^0 value derived from the major component in the thin-layer voltammogram is -0.55 V, the same value observed for the Tc(III/II) couple of $\text{trans}[\text{Tc}(\text{SCH}_3)_2(\text{DMPE})_2]^{+/0}$ in bulk solution cyclic voltammetry at the PDE (Table III). Thus, it is reasonable to assign the major component of parts a and b of Figure 6 as resulting from the trans isomer,

$\text{trans}[\text{Tc}(\text{SCH}_3)_2(\text{DMPE})_2]^{+/0}$. A reasonable working hypothesis for the identity of the minor component is the corresponding cis isomer, $\text{cis}[\text{Tc}(\text{SCH}_3)_2(\text{DMPE})_2]^{+/0}$. This hypothesis is consistent with all observations currently in hand and in the context of Figure 6 implies that the cis form is more stable in the Tc(II) oxidation state than in the Tc(III) state. Experiments are currently in progress to test this hypothesis and implication.

Visible-UV Spectra. The absorption spectra of the thiolato $\text{trans}[\text{Tc}(\text{SR})_2(\text{DMPE})_2]^{+/0}$ complexes are similar to those of the corresponding halido $\text{trans}[\text{TcX}_2(\text{DMPE})_2]^{+/0}$ complexes ($X = \text{Cl}, \text{Br}$)⁹ in that they are dominated by intense ligand-to-metal charge-transfer (LTMCT) transitions. The UV region is populated by phosphorus-to-Tc CT bands arising from the DMPE ligands, while the visible region exhibits characteristic halogen-to-Tc (HTTCT) or sulfur-to-Tc (STTCT) bands. The STTCT bands are split into two components, which have been tentatively assigned¹ as a $S(\pi)$ -to-Tc transition at lower energy (ca. $16\,000\text{ cm}^{-1}$) and a less intense $S(\sigma)$ -to-Tc transition at higher energy (ca. $28\,000\text{ cm}^{-1}$). For both Tc(III) and Tc(II) complexes, the $S(\pi)$ -to-Tc transition is at markedly lower energy than the corresponding HTTCT bands of $\text{trans}[\text{TcX}_2(\text{DMPE})_2]^{+/0}$ complexes ($X = \text{Cl}, \text{Br}$) due to the greater reducing power of thiolates over that of halides. This STTCT band occurs at higher energy in the Tc(II) complexes than in the Tc(III) analogues (from Table IV, average shift $1980 \pm 90\text{ cm}^{-1}$; $n = 5$) since Tc(III) is a better oxidant than is Tc(II).

Even though the redox potentials of the $\text{trans}[\text{Tc}(\text{SR})_2(\text{DMPE})_2]^{+/0}$ couples are strongly dependent on the nature of the thiolato R group, the absorption spectra of these complexes are only slightly sensitive to the identity of R. This is similar to what was observed by Perkins and Schultz²⁵ for a series of eight-coordinate molybdenum dithiolato complexes; in these complexes the nature of the thiolato R group strongly affects electrochemical potentials but has little effect on absorption spectra. These authors proposed, on the basis of molecular orbital calculations, that the orbitals involved in the redox and spectroscopic processes exist in a manifold of orbitals that move up or down in absolute energy depending on the electron-donating or -withdrawing properties of the thiolato ligand. While it is the absolute energy of this manifold that determines the metal-based redox potential for each complex, it is the energy spacing of the orbitals within the manifold that determines the energies of the LTMCT bands. Since this spacing remains relatively constant from ligand to ligand, the energies of the LTMCT bands do not vary significantly as the R group of the thiolato ligand is varied.

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