PREPARATION, CHARACTERIZATION, ELECTROCHEMICAL PROPERTIES AND SINGLE-CRYSTAL STRUCTURAL ANALYSIS OF [Tc(SCP)₂(DMPE)₂](PF₆)₃, WHERE SCP IS THE ZWITTER-IONIC LIGAND ⁻SCH₂P⁺(CH₃)₂(CH₂)₂P(S)(CH₃)₂ AND DMPE IS 1,2-BIS(DIMETHYLPHOSPHINO)ETHANE

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Abstract—Dithiocarbamates react with excess 1,2-bis(dimethylphosphino)ethane (DMPE) in acid conditions in the presence of $[Tc(OH)(O)(DMPE)_2]^{2+}$ to generate the novel zwitterionic ligand $-SCH_2P^+(CH_3)_2(CH_2)_2P(S)(CH_3)_2$ (abbreviated SCP). The technetium(III) complex $[Tc(SCP)_2(DMPE)_2](PF_6)_3$ has been isolated and characterized by elemental analysis, UV-vis spectroscopy and X-ray crystallography. Bond lengths around the octahedrally coordinated technetium(III) ion are Tc-S = 2.299(2) and Tc-P (average) = 2.437(8) Å. Electrochemical and spectroelectrochemical measurements are reported for the reversible technetium(III/II) couple; $E^{0'}$ has been determined to be -0.113 V vs Ag/AgCl (0.5 M TEAP/DMF). In addition, a chemically irreversible technetium(III/I) couple is observed at -1.310 V. The properties of $[Tc^{III/II}(SCP)_2(DMPE)_2]^{3+/2+}$ are compared to those observed previously for the related *cis*- and *trans*- $[Tc^{III/II}(SR)_2(DMPE)_2]^{1/0}$ complexes.

We¹⁻⁴ and others⁵ are currently engaged in the exploration of six-coordinate cationic technetiumbis(thiolato) complexes with bidentate phosphine ligands. The technetium 3 + oxidation state is most stable in this series of compounds, although solids containing technetium in the 2 + oxidation state can be isolated. Technetium(III)/(II) redox potentials

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span a range of values (~ -0.2 to -0.6 V vs Ag/AgCl) as a result of manipulation of the R group on the thiolato ligand. A study of cis vs trans isomer formation in these complexes has been evolving and a reasonable explanation for observed isomer ratios has recently been proposed.⁶ A number of crystallographic studies have shown little variability within a specific technetium oxidation state, i.e. all the technetium(III) complexes tend to have identical structural parameters and likewise for the technetium(II) complexes. The visible absorption spectra of these complexes contain sulphur-to-technetium charge-transfer bands and the energies of these bands can be related to their reduction potentials. In turn, the reduction potentials are related to the nucleophilicity of the thiolato ligand.

Most recently, the tris chelate complex [Tc(tdt)

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 $(DMPE)_2]^+$ [where tdt is 3,4-toluenedithiolate and DMPE is 1,2-bis(dimethylphosphino)ethane] has been prepared and examined.⁷ The trigonal prismatic distortion induced by the tdt ligand is accompanied by unusual properties which suggest that the technetium(III) centre in [Tc(tdt)(DMPE)_2]⁺ is displaying some "technetium(II) character". This has encouraged further studies of other complexes containing bidentate sulphur ligands.

Dithiocarbamates are an interesting group of ligands that can stabilize unusual oxidation states, have multiple bonding properties and bridging modes of coordination.⁸ The preparation and study of technetium complexes of dithiocarbamates, also known as 1,1-dithiolato ligands,[†] would allow important comparisons to [Tc(tdt)(DMPE)₂]⁺ since tdt is a member of the class of 1,2-dithiolato ligands. The following is a preliminary report of our dithiocarbamate studies, wherein under the reaction conditions utilized the intact dithiocarbamate anion does not function as a ligand to technetium. Rather, a novel zwitter-ionic thiolato ligand is formed by the reaction of dithiocarbamate with DMPE. Since the product so formed contains a new thiolato ligand, we have characterized it fully and have related it to previously studied $[Tc(SR)_2(DMPE)_2]^{+/0}$ complexes.

EXPERIMENTAL

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 ⁹⁹Tc 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, especially when dealing with solid samples, to prevent contamination and inadvertent inhalation. 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, in the form of solid ammonium pertechnetate, was obtained from Oak Ridge National Laboratory and purified.⁹ The DMPE ligand was purchased from Strem Chemical Co. and used without further purification. DMF and propylene carbonate were obtained from Burdick and Jackson Lab., Inc. Polarographic grade TEAP from G. F. Smith Chemicals was 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. Na (dedc)·3H₂O was purchased from Fisher Scientific and Na(dmdc)·2H₂O from Aldrich Chemicals.

Synthesis of [Tc(SCP)₂(DMPE)₂](PF₆)₃

The complex, trans-[Tc(OH)(O) starting $(DMPE)_2](PF_6)_2$, was prepared by a method similar to that described in a previous paper,¹ using NH_4TcO_4 (200 mg, 1.1×10^{-3} mol) and DMPE (0.8 cm³, 4.8×10^{-3} mol). To the orange-brown reaction mixture was added dropwise a solution of NH_4PF_6 (4 g) dissolved in a small amount of 1:1 methanol-water (v/v). The brown precipitate which appeared was kept at room temperature for 1 h and then refrigerated overnight. The precipitate was collected by filtration, washed with a methanolwater (1:1) solution, washed with pure water and then dried in air. Yield: 1.34 g. This material is a mixture of trans-[Tc(OH)(O)(DMPE)₂](PF₆)₂ and $H_2DMPE \cdot 2PF_6$.

To a suspension containing the above material (150 mg) in degassed ethanol (5 cm³) was added Na(dedc) · H₂O (340 mg) in degassed ethanol (10 cm³). This mixture was stirred at ca 50°C for 10 min, whereupon it became deep brown in colour. To this solution was added concentrated CF₃SO₃H (0.4 cm^3) . The solution was kept at 50°C and continuously stirred for 40 min. The colour of the solution changed gradually from deep brown to dark brown to dark yellowish green and then to deep bluish green. The solution was then cooled to ca 30° C and solid NH₄PF₆ (0.2 g) was added. After standing at room temperature for ca 30 min a blue precipitate appeared which was collected by filtration, washed with ethanol and dried in a vacuum desiccator. Yield: 15-17 mg. This blue product was recrystallized as a powder from propylene carbonate/ethanol. Found: C, 26.2; H, 5.4; N,

[†]Acronyms and abbreviations: The following acronyms and abbreviations are used in this article: tdt = 3,4-toluenedithiolate; dedc = diethyldithiocarbamate; DEPE = 1,2-bis(diethylphosphino)ethane; dmdc = dimethyldithiocarbamate; DMF = N,N-dimethylformamide; DMPE = 1,2-bis(dimethylphosphino)ethane; DMSO = dimethylsulphoxide; OTTLE = optically transparent thin-layer electrode; PDE = platinum disk electrode; Ph = phenyl; pmdc = pentamethylenedithiocarbamate; SCP = ${}^{-}SCH_{2}P^{+}(CH_{3})_{2}(CH_{2})_{2}P(S)(CH_{3})_{2};$ STTCT = sulphur-to-technetium charge transfer; TEAP = tetraethylammonium perchlorate.

< 0.1; F, 24.2; P, 24.1; S, 7.7. Calc. for $[Tc(SCH_2 P(CH_3)_2CH_2CH_2P(CH_3)_2S_{0.71})_2(DMPE)_2](PF_6)_3$ · 1.75 $(C_4H_6O_3) = C_{33}H_{78.5}O_{4.75}F_{18}P_{11}S_{3.4}Tc$: C, 26.6; H, 5.4; F, 24.4; P, 24.4; S, 7.8%. The non-stoichiometric amount of sulphur in the formulation is discussed in the crystallography sections below.

Single crystals suitable for X-ray analysis were obtained by dissolving the blue product at ca 38°C in a solution of 1:7 (v/v) propylene carbonate/ ethanol. The solution was filtered to remove insoluble materials. The filtrate, which was preserved under an argon atmosphere, was held at room temperature for 4 h and then placed in a refrigerator for 4 days. The deep blue-black, diamond-plate shaped crystals which appeared were collected by filtration, washed with ethanol and dried in air.

Similar blue products were obtained by the above procedure using dmdc, pmdc and ppmdc instead of the dedc. The pmdc and ppmdc ligands were prepared by literature methods.¹⁰

Measurements

Elemental analysis was performed by Galbraith Laboratories, Knoxville, TN, U.S.A. UV-vis spectra were recorded in acetonitrile on a Cary 210 spectrophotometer (Varian) at ambient temperature. Electrochemical measurements were made with a Bioanalytical Systems, Inc. (BAS) CV-1B voltammograph. Potentials were monitored with a Keithley 178 digital multimeter and voltammograms were recorded on a Hewlett-Packard 7015B X-Y recorder. The visible spectra in the spectroelectrochemical experiment were also recorded on a 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). OTTLEs were constructed as previously described with 100 wires per inch gold minigrid.¹¹ 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.¹² In general, electrochemical experiments were performed as previously described.13-17

Crystallography. Single-crystal X-ray diffraction experiments were performed on a Nicolet R3 automated diffractometer with a graphite monochromator. Data are summarized in Table 1. All non-hydrogen atoms are refined anisotropically. Hydrogen atoms are placed in calculated positions

Table 1. Crystallographic data for $[Tc(SCP)_2(DMPE)_2]$ $(PF_6)_3 \cdot 2(C_4H_6O_3)$

$Tc_1S_{3,4}P_{1,1}F_{1,8}O_6C_{3,4}H_{80}$
13.237(3)
21.709(6)
12.409(4)
112.77(2)
3288(2)
2
0.056
0.056
1475.71
$P2_{1}/c$ (No. 14)
20
0.71073
1.490
6.84
1.000-0.692

 ${}^{a} R = (\Sigma |\Delta F|) / \Sigma |F_{o}|; wR = [(\Sigma w |\Delta F|^{2}) / \Sigma w F_{o}^{2}]^{1/2}.$

with U defined as ~ 1.5 times the equivalent isotropic U of the carbon atom to which they are bound. Absorption corrections were empirically derived from psi scans with the program SHELXTL.¹⁸ Structure solutions by Patterson methods and refinements used the programs of SHELX-76.¹⁹ Neutral atom scattering factors and corrections for anomalous dispersion were from the International Tables for X-ray Crystallography, Vol. 4.²⁰

RESULTS AND DISCUSSION

Synthesis

Excess amounts of a dithiocarbamate, such as dmdc, dedc, pmdc or ppmdc, added to a suspension of *trans*-[Tc(OH)(O)(DMPE)₂](PF₆)₂ and H₂DMPE · 2PF₆ under anaerobic conditions yield deep brown solutions. Acidification of these solutions produces gradual colour changes through dark brown to dark yellowish green and finally to a deep bluish green, ultimately yielding the title complex. These reactions do not proceed without the dithiocarbamate. Dithiocarbamates are known^{8,10,21} to undergo an acid induced C—N cleavage to produce an amine and carbon disulphide.

$H^+ + R_2 NCS_2^- \Longrightarrow HNR_2 + CS_2$

The carbon atom of CS_2 is susceptible to nucleophilic attack by the DMPE phosphorus lone pair, yielding a positively charged phosphonium ion and a negatively charged thiol:



The final step in the formation of SCP involves a two-equivalent oxidation and the transfer of a sulphido group to the terminal phosphine. This process may or may not be assisted by coordination to technetium; it is unclear at what stage in the reaction sequence the thiol ligates to technetium. Reduction of the technetium(V) ion can be accomplished by excess dithiocarbamate or excess DMPE.

Under anaerobic conditions, a small amount of 1 M NaOH aqueous solution added to an aqueous solution of trans-[Tc(SCP)₂(DMPE)₂]³⁺ yields a brown precipitate. When dissolved in acetonitrile this brown precipitate exhibits the identical absorption spectrum as that obtained at -0.500 V in the spectroelectrochemistry experiment (vide infra, spectrum B in Fig. 4). This suggests that the brown precipitate is the technetium(II) complex trans- $[Tc(SCP)_2(DMPE)_2]^{2+1}$ When a small amount of concentrated HCl is added to an acetonitrile solution of the brown precipitate under an argon atmosphere, the colour of the solution changes to greenish blue and its spectrum coincides with that of the starting technetium(III) complex. Apparently the pH controlled interconversion between the technetium(III) and (II) complexes trans-[Tc(SCP)₂ $(DMPE)_2$ ^{2+/3+} under anaerobic conditions is reversible; this pH induced redox interconversion is a general feature of trans-[Tc^{III}(SR)₂(DMPE)₂]^{+/0} ($\mathbf{R} = alkyl \text{ or benzyl}$) complexes.^{1,2}

The trans- $[Tc(SCP)_2(DMPE)_2](PF_6)_3$ salt is soluble in water, methanol, acetone, acetonitrile, propylene carbonate, DMF and DMSO, but is insoluble in 2-propanol, dichloromethane, chloroform, carbon tetrachloride and hexane. The complex is slightly soluble in ethanol and *p*-dioxane. These observations are consistent with the presence of a 3 + charged cation.

The synthesis of the novel ligand SCP has its basis in the acid induced C—N cleavage of dithiocarbamates. Consequently, reactions intending to preserve the dithiocarbamate ligand for intact coordination to technetium must be conducted in alkaline conditions. Even so, the zwitter-ionic ligand SCP is interesting in its own right. For one thing, the negatively charged ligating thiol is α to a positively charged phosphonium group and this is expected to significantly decrease the nucleophilicity of the thiol. Nucleophilicity, or σ -donating ability, of the thiol has been one of the properties we have been tracking through a series of technetium and rhenium thiolato complexes, in order to explore how changes in R are expressed in the redox potentials and spectral energies of the complexes.^{1-4,6,22,23} Further interest in SCP might come from its potential use for bidentate coordination. In addition, modification of the terminal sulphido group could make SCP a valuable starting material.

UV-vis spectrum

The absorption spectrum of trans- $[Tc(SCP)_2(DMPE)_2]^{3+}$ exhibits three bands at 15.88 ($\varepsilon = 15.8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$), 26.60 ($\varepsilon = 4.6 \times$ $10^3 \text{ M}^{-1} \text{ cm}^{-1}$) and 36.90 kK ($\varepsilon = 7.2 \times 10^3 \text{ M}^{-1}$ cm^{-1}). The spectrum of the complex in acetonitrile is shown in Fig. 1. The absorption pattern over the entire region is similar to those of the corresponding bis-thiolato-DMPE complexes, *trans*- $[Tc(SR)_2(DMPE)_2]^+$, where R = methyl, ethyl, n-propyl, benzyl and p-methoxybenzyl.² By analogy,⁴ the two lower energy bands are assigned to be sulphur $(\pi) \rightarrow Tc(\pi^*)$ transitions. The higher energy UV absorption at 36.9 kK represents a $P \rightarrow Tc$ charge transfer band arising from the DMPE ligand.

Crystallography of trans- $[Tc(SCP)_2(DMPE)_2]$ (PF₆)₃·2(C₄H₆O₃)

The independent portion of the structure consists of a half-cation, half-anion, complete PF_6 anion and a loosely held solvent molecule. The technetium atom and the phosphorus atom [P(5)] from the halfanion each occupy crystallographic inversion



Fig. 1. The absorption spectrum of trans-[Tc(SCP)₂ (DMPE)₂]³⁺ recorded in acetonitrile.

centres. The general position PF₆ anion shows obvious disorder, so the six fluorine atoms around P(6) are described by 12 partial fluorine atoms. F(4)–F(9) are at 0.65 occupancy and F(10)–F(15) are at 0.35 occupancy. The assignment of these partial fluorine atoms makes little difference in the *R* value, but does improve the final ΔF map. Bond lengths and angles for the cation are presented in Table 2. Figure 2 illustrates the geometry and assigned labelling scheme for the cation.

The technetium atom is coordinated in *trans* octahedral geometry. The DMPE ligand bite angle is the largest distortion from ideal geometry and is normal for this ligand; P(3)—Tc— $P(4) = 80.81(7)^{\circ}$. The zwitter-ionic ligand SCP is formally neutral, carrying a formal negative charge on the coordinated sulphur atom [S(1)] and a formal positive charge on the atom P(1). The terminal R₃P=S fragment is neutral since the phosphorus-sulphur bond is best described as a double bond [S(2)—P(2) = 1.920(4) Å]. For comparison, the molecule (2,4,6-Me₃C₆H₂PS₂)₂ has a terminal P=S length of 1.917(1) Å.²⁴ P-S linkages are often found in dithiophosphate molecules wherein the phosphorus atom binds to two terminal sulphur

P(3) - C(10) - C(11)

atoms, theoretically in one double bond and one single bond. In these dithiophosphate molecules there is some delocalization and the average P—S length is approximately 1.97 Å,²⁵ significantly longer than that observed in the title complex.

The terminal sulphur atom [S(2)] has been assigned an occupancy factor less than unity (0.71) based on a comparison of thermal parameters with the other terminal atoms [C(6) and C(7)] and based on the knowledge that the elemental analysis implies the presence of a sulphur atom in about 71% of these sites in a bulk sample. The remaining sites might be occupied by either the phosphorus lone pair electrons or possibly a doubly-bound oxygen atom, neither of which would disturb the overall charge of the complex or lead to serious lattice disruptions. Disorders of the sulphido/oxo type have been noted in other structures.²⁶

The solvated propylene carbonate molecule is disordered and probably exists at partial occupancy in the crystal lattice, although the solvent was assigned full occupancy in the model leading to a technetium/solvent ratio of 1/2. In fact, the elemental analysis results agree best with 1.75 solvent molecules per technetium (*vide supra*).

Tc(1)S(1)	2.299(2)	P(2)-C(6)	1.82(1)
Tc(1) - P(3)	2.442(2)	P(2)C(7)	1.80(1)
Tc(1) - P(4)	2.431(2)	P(3)-C(8)	1.79(1)
S(1)C(1)	1.842(7)	P(3)C(9)	1.805(7)
S(2)—P(2)	1.920(4)	P(3)C(10)	1.82(1)
P(1)C(1)	1.809(7)	P(4)-C(11)	1.84(1)
P(1)C(2)	1.787(7)	P(4)C(12)	1.794(9)
P(1)C(3)	1.772(6)	P(4)-C(13)	1.82(1)
P(1)C(4)	1.783(6)	C(4) - C(5)	1.55(1)
P(2)C(5)	1.802(8)	C(10)-C(11)	1.37(1)
Tc(1)S(1)C(1)	122.7(2)	P(4)-C(11)-C(1	0) 117(1)
Tc(1) - P(3) - C(8)	118.1(2)	C(1) - P(1) - C(2)	107.7(3)
Tc(1) - P(3) - C(9)	119.9(3)	C(1) - P(1) - C(3)	109.3(3)
Tc(1)-P(3)-C(10) 108.9(3)	C(1) - P(1) - C(4)	110.8(3)
Tc(1)-P(4)-C(11) 108.3(4)	C(2) - P(1) - C(3)	109.1(3)
Tc(1)-P(4)-C(12) 119.1(3)	C(2) - P(1) - C(4)	108.7(3)
Tc(1)-P(4)-C(13) 122.7(4)	C(3) - P(1) - C(4)	111.2(3)
S(1) - Tc(1) - P(3)	85.73(6)	C(5)-P(2)-C(6)	102.3(4)
S(1) - Tc(1) - P(4)	83.20(7)	C(5)-P(2)-C(7)	106.4(4)
S(1) - C(1) - P(1)	109.3(4)	C(6)-P(2)-C(7)	105.6(5)
S(2)-P(2)-C(5)	113.6(3)	C(8)-P(3)-C(9)	103.6(4)
S(2) - P(2) - C(6)	113.8(4)	C(8)-P(3)-C(10) 103.4(5)
S(2) - P(2) - C(7)	114.0(3)	C(9)-P(3)-C(10) 100.5(5)
P(1)C(4)C(5)	111.9(4)	C(11)-P(4)-C(1	2) 103.0(5)
P(2) - C(5) - C(4)	115.7(4)	C(11) - P(4) - C(1)	3) 102.6(6)
P(3) - Tc(1) - P(4)	80.81(7)	C(12)-P(4)-C(1	3) 98.6(4)

116.0(9)

Table 2. Bond lengths (Å) and angles (°) in the cation [Tc(SCP)₂(DMPE)₂]³⁺



Fig. 2. A perspective view of trans-[Tc(SCP)₂(DMPE)₂]³⁺ showing the assigned atom labels. The technetium atom occupies a crystallographic inversion centre. Ellipsoids represent 50% probability.

Structural analyses have been published previously for *trans*- $[Tc^{III}(SCH_3)_2(D)_2]^+$, where D = DMPE and DEPE,¹ and correspond closely with the structural parameters measured herein, cf. Tc---P = 2.428(6), Tc-S = 2.300(3) Å, Tc-S-C = $122.3(8)^{\circ}$ and S--C = 1.842(7) Å for *trans*-[Tc^{III} $(SCH_3)_2(DMPE)_2]^+$; Tc---P = 2.45(1), Tc---S = 2.3025(5) Å, Tc—S—C = $121.2(1)^{\circ}$ and S—C = 1.821(4) Å for trans- $[Tc^{III}(SCH_3)_2(DEPE)_2]^+$; and Tc-P = 2.437(8), Tc-S = 2.299(2) Å, Tc-S-C $= 122.7(2)^{\circ}$ and S-C = 1.842(7) Å for trans-[Tc^{III}(SCP)₂(DMPE)₂]³⁺. Both Tc—S and Tc—P lengths in these complexes are sensitive to the technetium oxidation state and support the assignment of technetium(III) in the title complex. It should be noted that there is a substantial formal charge difference between the +1complex $[Tc(SCH_3)_2(DMPE)_2]^+$ and the +3 complex $[Tc(SCP)_2(DMPE)_2]^{3+}$, but the coordination distances around technetium remain constant. A summary table presented previously⁴ shows that Tc^{III} -SR distances are relatively insensitive to the nature of the R group.

Cyclic voltammetry

Figure 3 shows the cyclic voltammogram at a PDE for a 0.6 mM solution of *trans*-[Tc(SCP)₂ (DMPE)₂]³⁺, wherein two major redox couples are observed. A negative potential scan initiated at +0.400 V gives a reduction wave with a peak potential (E_{pc}) at -0.150 V, and upon switching the potential at -0.500 V the coupled oxidation wave (E_{pa}) is observed at -0.076 V on the positive scan. The separation between the cathodic and anodic peaks is 74 mV, which is typical for the one-electron reduction of *trans*-[Tc(SR)₂ (DMPE)₂]^{+/0} complexes¹ in TEAP/DMF. The ratio of the anodic/cathodic peak current is nearly

unity. These facts indicate that the redox couple can be identified with the following one-electron reversible reaction:

trans-
$$[Tc^{III}(SCP)_2(DMPE)_2]^{3+} + e^- \Longrightarrow$$

trans- $[Tc^{II}(SCP)_2(DMPE)_2]^{2+}$.

The formal reduction potential, $E^{0'}$, is determined to be -0.113 V and is recorded in Table 3. If the voltammogram is continued for a second cycle with an extension of the negative potential window to -1.55 V, a second reduction wave is observed with $E_{\rm pc} = -1.345$ V. On the subsequent positive scan the corresponding oxidation is observed at $E_{\rm pa} = -1.275$ V ($E^{0} = -1.310$ V). The second process is attributed to the technetium(II/I) redox couple. A close examination of the second cyclic voltammogram indicates that i_{pa} for the oxidation of technetium(II) to technetium(III) is reduced relative to i_{pc} for the reduction of technetium(III) to technetium(II) $(i_{pc}/i_{pa} \text{ is approximately 1.85})$ and i_{pa} for the oxidation peak at +0.28 V is increased. This behaviour in the cyclic voltammogram can



Fig. 3. Cyclic voltammograms of 0.6 mM trans-[Tc(SCP)₂(DMPE)₂]³⁺ in 0.5 M TEAP/DMF at a PDE and room temperature; scan rate = 100 mV s^{-1} .

	Technetium(III/II), $E^{0'}$	Technetium(II/I), E^c	
Trans-[Tc(SCP) ₂ (DMPE) ₂] ³⁺	-0.113	-1.31 ^d	
Trans-[Tc(SCH ₃) ₂ (DMPE) ₂] ⁺¹	-0.550	-1.72	
$Cis-[Tc(SPh)_2(DMPE)_2]^{+4}$	-0.299	-1.11^{d}	
Trans-[Tc(Cl) ₂ (DMPE) ₂] ⁺¹³	-0.231	-1.41	
Trans- $[Tc(Br)_2(DMPE)_2]^{+13}$	-0.098	-1.27	

Table 3. Comparison redox potentials^{a,b}

^a25°C; PDE working electrode; scan rate 100 mV s⁻¹; 0.5 M TEAP/DMF; all values in V.

 $^{b}E^{0'} = (E_{pc} + E_{pa})/2$ vs Ag/AgCl (3 M NaCl) from cyclic voltammetry.

^c Either E_{p} or $E^{0\prime}$, as specified.

^d Irreversible at 25°C.

be ascribed to the instability of the technetium(I) species on the cyclic voltammetry time-scale, which results in a chemically irreversible technetium(II/I) redox couple.

Spectroelectrochemistry

In the thin-layer cyclic voltammogram in propylene carbonate *trans*-[Tc^{III}(SCP)₂(DMPE)₂]³⁺ exhibits a reduction wave at -0.250 V and a coupled oxidation wave at -0.106 V $(E^{0'} = -0.178$ V). The large peak separation, $E_{pc} - E_{pa} = 0.144$ V, is typical for OTTLEs used with non-aqueous solvents, because of the large solution resistance inherent to the cell arrangement.^{14,15} A similar thin-layer cyclic voltammogram was observed in DMF ($E^{0'} = -0.138$ V), but spectra could not be recorded because the complex decomposes in DMF on the time-scale of the OTTLE spectroelectrochemical experiment.

The spectra recorded for the technetium(III)/(II) couple during a potential step experiment are shown in Fig. 4. The initial spectrum recorded in the OTTLE after a potential application of +0.400 or +0.075 V is identical with that of the conventional trans-[Tc^{III}(SCP)₂ UV-vis measurement for $(DMPE)_2$ ³⁺ (vide supra). The potential was subsequently moved in the negative direction from +0.075 to -0.500 V. In the spectrum recorded at -0.500 V a new absorption band appears at 513 nm and the band at 630 nm disappears, i.e. the reduction of technetium(III) to technetium(II) causes a large blue shift, consistent with its assignment as an $S \rightarrow Tc$ CT band. The spectrum at -0.500 V does not change for 2 h in propylene carbonate under these conditions. This supports the synthetic observation that the brown technetium(II) complex obtained from alkaline solution is stable over several hours in polar or non-polar solvents

under argon. Apparently the technetium(II) complex is stable under anaerobic conditions. The potential was then moved in the positive direction from -0.500 to +0.075 V and the spectrum was scanned again. In this spectrum, a new absorption band appears at 497 nm along with the original band of the technetium(III) complex at 630 nm, although the band at 630 nm has only 30% of the initial absorbance. The spectrum at +0.400 V shows an increase in intensity of the band at 630 nm and a decrease in intensity of the band at 497 nm.

Similar spectral changes were observed during aerobic oxidation of bulk amounts of the brown technetium(II) complex obtained from the alkaline solution. That is, when the acetonitrile solution of



Fig. 4. The absorption spectra obtained during an OTTLE potential step experiment of 0.6 mM *trans*-[Tc(SCP)₂(DMPE)₂]³⁺ in 0.5 M TEAP/propylene carbonate. Applied potentials vs Ag/AgCl are: original, -0.400 and +0.075 V (----); -0.500 V (····); +0.075 V (----); and final scan +0.400 V (-····).

the technetium(II) complex stands in air, it changes to the technetium(III) complex plus some other species; the spectrum of this solution is similar to that of the final scan in Fig. 4 in that it contains the additional peak at 497 nm which is not present in the original technetium(III) solution. Taking the stability of the technetium(III) species into consideration, these facts suggest that part of the *trans*-[Tc^{II}(SCP)₂(DMPE)₂]²⁺ complex reverts to the original technetium(III) complex, but another fraction converts to a different species during oxidation.

The technetium(III/II) $E^{0'}$ values are solvent dependent, *viz*. the value obtained in propylene carbonate is more negative than that obtained in DMF. A similar trend was also observed for the technetium(II/I) couple of $[Tc(DMPE)_3]^{2+/+}$.¹³ These data suggest that the variation of $E^{0'}$ in DMF and propylene carbonate follows the basicity of these solvents.

Electronic properties

bis(thiolato)-bis(DMPE)-technetium(III) The complexes hitherto examined have naturally separated into two classes. When the carbon atom bound to sulphur is saturated, [Tc^{III}(SR)₂ $(DMPE)_2$ ⁺ (R = alkyl or benzyl) complexes have the following characteristics: (1) their geometry tends to be trans, (2) reversible couples are observed at ca = -0.5 to |-0.6 V for technetium (III/II) in TEAP/DMF vs Ag/AgCl, and (3) there are two visible STTCT bands ca 17 and 28 kK in acetonitrile. When the R group in [Tc^{III} $(SR)_2(DMPE)_2$ ⁺ is phenyl or a phenyl derivative the following characteristics are observed: (1) the geometry tends to be |cis, (2)| reversible technetium(III/II) couples are in the range -0.19 to -0.38 V, and (3) there are three visible STTCT bands at ca 17, 22 and 29 kK. The complex $[Tc(SCP)_2(DMPE)_2]^{3+}$ newly presented here has properties that transcend those of the two classes outlined above. As with an alkylthiolato complex it has trans geometry and this is expected since it is thought that the driving force which determines cis/trans isomerism in these complexes is primarily steric. However, unlike the other alkylthiolato complexes [Tc(SCP)₂(DMPE)₂]³⁺ exhibits an uncommon ease of reduction. The technetium(III/II) reduction potential of this complex is -0.113 V, which is 437 mV more positive than that of *trans*- $[Tc(SCH_3)_2(DMPE)_2]^+$ and even 186 mV more positive than that of $cis-[Tc(SPh)_2(DMPE)_2]^+$ (see Table 3). The technetium(III/II) redox potential is strongly linked to the nature of the thiolato R group and as such is inversely related to the σ -donor ability at the thiol.⁴ This suggests that the nucleophilicity of the SCP ligand is weaker than those of the other thiolato ligands examined since this complex is the easiest to reduce. Apparently this arises from the positively charged phosphonium group α to the sulphur donor atom in SCP. Orbital mixing between the sulphur donor and the P⁺ atoms is also implied by the energies of the two STTCT bands, which are substantially lower than those found in *trans*-[Tc(SCH₃)₂(DMPE)₂]⁺.>

Speculation as to the identity of the intermediate species in the spectroelectrochemical reoxidation experiment leads to the possibility that the electron may be lost first from the terminal sulphido atom, temporarily forming an S' radical or a disulphide linked dinuclear technetium(II) species. Internal reorganization could then restore the SCP ligand and yield the original technetium(III) species.

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