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## An Isothiocyanato Complex of Technetium(II). Spectroelectrochemical and Single-Crystal X-ray Structural Studies on *trans*-[Tc(DPPE)<sub>2</sub>(NCS)<sub>2</sub>]<sup>0</sup>, Where DPPE = 1,2-Bis(diphenylphosphino)ethane

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The air-stable technetium(II) complex *trans*-[Tc(DPPE)<sub>2</sub>(NCS)<sub>2</sub>]<sup>0</sup>, where DPPE represents 1,2-bis(diphenylphosphino)ethane, has been characterized by single-crystal X-ray structural analysis refined to a conventional *R* factor of 0.069. Rose-colored crystals of this material, fw 1012.01, crystallize in the triclinic space group *P* $\bar{1}$  with *a* = 21.384 (6) Å, *b* = 12.878 (5) Å, *c* = 9.549 (4) Å,  $\alpha$  = 71.51 (3)°,  $\beta$  = 81.94 (4)°,  $\gamma$  = 83.38 (4)°, and *Z* = 2. In this complex the technetium(II) center is approximately octahedrally coordinated with four equatorial P atoms at an average distance of 2.44 (1) Å and two *trans* axial N-bonded NCS<sup>-</sup> ligands at 2.04 (2) Å. Spectroelectrochemical investigation of this complex shows that it undergoes reversible 1-equiv reduction to the Tc(I) anion and reversible 1-equiv oxidation to the Tc(III) cation, all three species being stable on the time scale of hours. The *E*<sup>o'</sup> values (0.50 M tetraethylammonium perchlorate in *N,N*-dimethylformamide) for the Tc(III)/Tc(II) and Tc(II)/Tc(I) couples are 0.392 and -0.601 V vs. Ag/AgCl, respectively. Relative to chloro or bromo ligands, in the analogous *trans*-[Tc(DPPE)<sub>2</sub>X<sub>2</sub>]<sup>+0/-</sup> (X = Cl, Br) complexes, the N-bonded NCS<sup>-</sup> ligand markedly stabilizes the lower oxidation states. This effect and the dependence of the Tc-P bond length on the technetium oxidation state are discussed in terms of  $\pi$ -back-bonding.

### Introduction

Cationic complexes of low-valent technetium stabilized by  $\pi$ -acceptor ligands have become a focus of research activity because of both their diverse chemistry and their potential use as myocardial imaging agents in diagnostic nuclear medicine.<sup>4-6</sup> A variety of bis(tertiary phosphine) (BTP) ligands have been employed to synthesize cationic and neutral complexes containing technetium in oxidation states V, III, II, and I.<sup>7,8</sup> These technetium-BTP complexes have been characterized by classical techniques, with emphasis being placed on single-crystal X-ray analyses to definitively establish connectivity and determine structural parameters. The majority of the technetium-BTP complexes prepared to date have the general formula *trans*-[Tc(BTP)<sub>2</sub>X<sub>2</sub>]<sup>n+</sup>, where X can be a variety of monodentate ligands; crystal structures have been reported for the technetium(V) complex *trans*-[Tc(DMPE)<sub>2</sub>(OH)(O)]<sup>+</sup><sup>8</sup> and the technetium(III) complexes *trans*-[Tc(DMPE)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup><sup>5</sup> and *trans*-[Tc(DPPE)<sub>2</sub>Br<sub>2</sub>]<sup>+</sup><sup>7</sup> (DMPE = 1,2-bis(dimethylphosphino)ethane; DPPE = 1,2-bis(diphenylphosphino)ethane). In previous work<sup>7</sup> a technetium(II)-BTP complex was isolated and indirectly characterized as *trans*-[Tc(DPPE)<sub>2</sub>(NCS)<sub>2</sub>]<sup>0</sup> with no information being available as to the bonding mode of the ambidentate SCN<sup>-</sup> ligands. To establish whether the SCN<sup>-</sup> ligands are N- or S-coordinated, and to assess the influence of technetium oxidation state on structural parameters, a single-crystal X-ray analysis of this technetium(II) complex has been conducted, and the results are reported herein.

Moreover, the advent of low-valent, robust technetium complexes not containing oxo groups has recently led to electrochemical investigations into the rich redox chemistry

of technetium.<sup>9-14</sup> For the technetium-BTP complexes prepared to date, the spectroelectrochemistry of *trans*-[Tc(DPPE)<sub>2</sub>X<sub>2</sub>]<sup>+</sup> (X = Cl, Br)<sup>14</sup> and the cyclic voltammetry of a series of *trans*-[Tc(BTP)<sub>2</sub>X<sub>2</sub>]<sup>+</sup> complexes<sup>7</sup> have been reported. All of these technetium complexes are stable in the III oxidation state but exhibit a reversible Tc(III)/Tc(II) couple. The title complex, *trans*-[Tc(DPPE)<sub>2</sub>(NCS)<sub>2</sub>]<sup>0</sup>, is unusual in that it is stable in the II oxidation state, and therefore a detailed spectroelectrochemical investigation of this material has been undertaken, the results of which are reported herein.

### Experimental Section

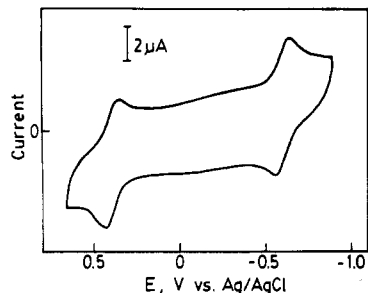
**General Information.** <sup>99</sup>Tc is a weak  $\beta$  emitter (0.292 MeV, half-life = 2.12 × 10<sup>5</sup> years); therefore, all manipulations were conducted using appropriate radiation safety procedures.

**Reagents.** Unless otherwise noted, all chemicals were of reagent grade. The *trans*-[Tc(DPPE)<sub>2</sub>(NCS)<sub>2</sub>]<sup>0</sup> compound was prepared and characterized as previously described.<sup>7</sup> *N,N*-Dimethylformamide (DMF) from Burdick & Jackson Lab., Inc., and polarographic grade tetraethylammonium perchlorate from G. F. Smith were used in the electrochemical measurements. No electroactive impurities were detected in the solvent-supporting electrolyte.

**Apparatus and Instrumentation.** The optically transparent thin-layer electrode (OTTLE) was constructed with a 500 wires/in. gold minigrad as previously described.<sup>15</sup> The cell volume and the optical thickness (calibrated by coulometry and spectrophotometry<sup>15</sup>) were 38  $\mu$ L and 0.023 cm, respectively. All potentials were measured vs. a Ag/AgCl/NaCl (3 M) electrode that was isolated from the solution by a porous Vycor plug. The auxiliary electrode consisted of a platinum wire. Electrochemical measurements were made with a Bioanalytical System Inc. CV-1A. Potentials were monitored with a Fluka 8030A multimeter. Visible spectra were recorded on a Cary 210 spectrophotometer, the cell compartment being modified to accommodate

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**Figure 1.** Cyclic voltammogram of  $trans\text{-}[\text{Tc}(\text{DPPE})_2(\text{NCS})_2]^0$  in 0.5 M TEAP-DMF (glassy carbon electrode; scan rate 25 mV/s; potential measured vs. Ag/AgCl).

electrical leads and an inert-gas inlet.

**Procedure.** Experiments were generally conducted as previously described.<sup>14,16</sup> Each spectrum in the spectropotentiostatic experiments was recorded 3 min after potential application, this time being sufficient to attain equilibrium values of  $[\text{O}]/[\text{R}]$ .

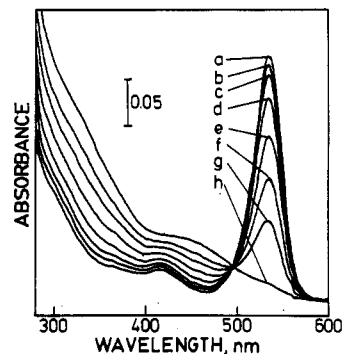
**X-ray Characterization of  $trans\text{-}[\text{Tc}(\text{DPPE})_2(\text{NCS})_2]^0$ .** The structure was solved in the space group  $P\bar{1}$ , with unit cell dimensions of  $a = 21.384$  (6) Å,  $b = 12.878$  (5) Å,  $c = 9.549$  (4) Å,  $\alpha = 71.51$  (3)°,  $\beta = 81.94$  (4)°,  $\gamma = 83.38$  (4)°,  $V = 2462.2$  Å<sup>3</sup>, and  $Z = 2$ ; density (calcd) = 1.365 g cm<sup>-3</sup>, density (obsd by flotation) = 1.35 g cm<sup>-3</sup>;  $\mu = 4.8$  cm<sup>-1</sup>. Intensity data were collected on a Philips PW1100 counter diffractometer using Mo K $\alpha$  monochromated radiation ( $\lambda = 0.7107$  Å). In the region  $2\theta \leq 44^\circ$ , 4426 reflections were collected, and 3114 reflections with  $I > 3\sigma(I)$  were used in the solution of the structure. The crystal was stable during X-ray exposure since the intensities of three standard reflections collected every 2 h showed only random fluctuations. Corrections were made for Lorentz-polarization effects but not for absorption.

**Structure Solution and Refinement.** The structure was refined to convergence by full-matrix least-squares techniques using the SHELX system.<sup>17</sup> Anisotropic temperature factors were refined for the technetium, phosphorus, and sulfur atoms, isotropic temperature factors were refined for the nitrogen and carbon atoms, and each phenyl ring was constrained as a rigid body. In the final stages of refinement the weights were assigned as  $w = k/[\sigma^2(|F_o|) + g|F_o|^2]$ .<sup>17</sup> The final residuals were  $R_1 = 0.069$  and  $R_2 = 0.073$ . Inspection of the function  $\Sigma w\Delta^2$  for reflections ordered according to  $|R_o|$  and  $(\sin \theta)/\lambda$  showed no peaks of higher intensity than  $0.8 e \text{ \AA}^{-3}$ , and these were at expected hydrogen atom positions. Listings of calculated and observed structure factors are available as supplementary material (Table A).<sup>18</sup>

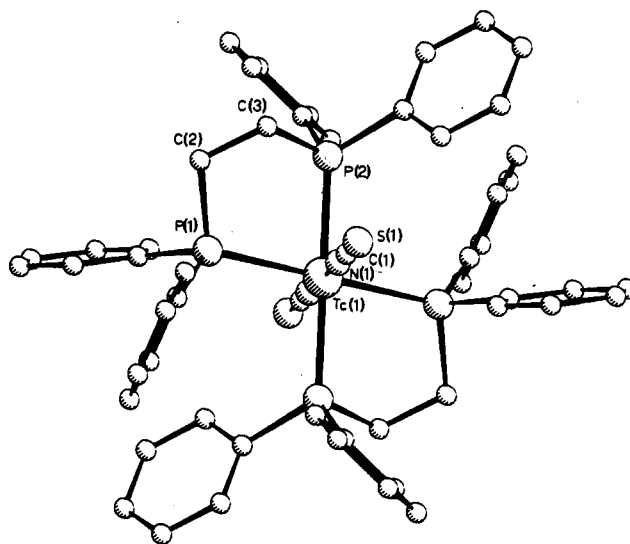
## Results

**Spectroelectrochemistry.** Figure 1 shows a typical bulk cyclic voltammogram for  $trans\text{-}[\text{Tc}(\text{DPPE})_2(\text{NCS})_2]^0$  in DMF containing 0.5 M TEAP. A negative potential scan initiated at 0.650 V gives two reduction waves with peak potentials of 0.35 and -0.63 V, respectively. Reoxidation peaks corresponding to the respective reduction peaks appear on the reverse scan. At a scan rate of 25 mV/s the ratio of anodic to cathodic peak currents is approximately unity, and the peak separations are 70 mV, for each process. From this, and other (vide infra) evidence, the two redox processes are assigned as the Tc(III)/Tc(II) and Tc(II)/Tc(I) interconversions. From the average of the anodic and cathodic peak potentials, approximate  $E^{\circ'}$  (formal reduction potential) values of 0.39 and -0.60 V vs. Ag/AgCl are obtained for the Tc(III)/Tc(II) and Tc(II)/Tc(I) couples, respectively.

A spectropotentiostatic experiment on the Tc(III)/Tc(II) couple shows that the Tc(III) and Tc(II) complexes exhibit maxima at 583 and 533 nm, respectively. The absorption maxima determined in this experiment are in good agreement



**Figure 2.** Spectra recorded during OTTLE spectropotentiostatic experiments on the Tc(II)/Tc(I) couple of  $trans\text{-}[\text{Tc}(\text{DPPE})_2(\text{NCS})_2]^0$  in 0.5 M TEAP-DMF. Applied potentials in V vs. Ag/AgCl are as follows: (a) -0.420; (b) -0.560; (c) -0.580; (d) -0.600; (e) -0.620; (f) -0.640; (g) -0.660; (j) -0.800.



**Figure 3.** PLUTO drawing of the  $trans\text{-}[\text{Tc}(\text{DPPE})_2(\text{NCS})_2]^0$  complex in site I, with the atom-numbering scheme used.

with those previously obtained for the Tc(III) and Tc(II) complexes by using chemically generated materials.<sup>7</sup> Nernst plots at 585, 533, and 470 nm yield  $E^{\circ'} = 0.372$  V vs. Ag/AgCl and  $n = 0.99$  for the Tc(III)/Tc(II) couple. Spectra recorded during a spectropotentiostatic experiment on the Tc(II)/Tc(I) couple are shown in Figure 2, the absorption maxima for the Tc(II) and Tc(I) complexes being 533 nm and ca. 420 nm (shoulder), respectively; an isosbestic point is observed at 495 nm. A Nernst plot at 533 nm yields  $E^{\circ'} = -0.636$  V vs. Ag/AgCl and  $n = 0.99$  for the Tc(II)/Tc(I) couple.

**Crystal Structure.** Final fractional atomic positional parameters and their estimated standard deviations are given in Table I. The corresponding anisotropic and isotropic thermal parameters are given in Table B.<sup>18</sup> Bond lengths and bond angles are found in Table II. The phenyl rings have been treated as rigid bodies with the C-C bond length restricted to 1.395 Å and the C-C-C bond angle restricted to 120°.

There are two crystallographically independent molecules of  $trans\text{-}[\text{Tc}(\text{DPPE})_2(\text{NCS})_2]^0$ , I and II, in the unit cell. The technetium atoms are located at centers of symmetry at (0, 0, 0) and ( $1/2, 1/2, 1/2$ ). Figure 3 shows the molecular shape of I, while the cell contents as viewed down  $c$  are presented in Figure 4.<sup>18</sup> None of the chemically equivalent bond lengths of the two independent molecules are significantly different (Table II). In each independent molecule the technetium(II) center is six-coordinate with an approximately octahedral coordination environment. The donor phosphorus atoms of

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(18) All tables designated by alphabetic characters and Figure 4 have been deposited as supplementary material.

Table I. Atomic Positional Parameters ( $\times 10^4$ ) with Esd's in Parentheses

molecule I				molecule II			
atom	x	y	z	atom	x	y	z
Tc(1)	5000	5000	5000	Tc(2)	0	0	0
S(1)	6040 (2)	2468 (3)	9069 (5)	S(2)	999 (3)	-2382 (4)	4164 (6)
P(1)	4040 (1)	4335 (3)	6576 (4)	P(3)	-786 (1)	319 (3)	1964 (4)
P(2)	4881 (2)	6151 (2)	6606 (4)	P(4)	472 (2)	1458 (3)	538 (4)
N(1)	5440 (4)	3928 (7)	6723 (11)	N(2)	425 (5)	-1012 (8)	1770 (12)
C(1)	5683 (5)	3336 (9)	7673 (14)	C(28)	654 (5)	-1558 (8)	2724 (13)
C(2)	3934 (6)	4814 (9)	8257 (14)	C(29)	-342 (5)	718 (9)	3188 (14)
C(3)	4516 (6)	5318 (10)	8453 (14)	C(30)	77 (6)	1648 (11)	2324 (15)
C(4) <sup>a</sup>	3235 (3)	4695 (7)	6023 (10)	C(31) <sup>a</sup>	-1221 (4)	-790 (6)	3352 (9)
C(5)	2752 (3)	4002 (7)	6717 (10)	C(32)	-868 (4)	-1721 (6)	4134 (9)
C(6)	2136 (3)	4304 (7)	6332 (10)	C(33)	-1175 (4)	-2587 (6)	5176 (9)
C(7)	2003 (3)	5299 (7)	5253 (10)	C(34)	-1835 (4)	-2522 (6)	5436 (9)
C(8)	2486 (3)	5992 (7)	4558 (10)	C(35)	-2187 (4)	-1591 (6)	4653 (9)
C(9)	3102 (3)	5690 (7)	4943 (10)	C(36)	-1880 (4)	-725 (6)	3611 (9)
C(10)	4068 (4)	2824 (5)	7323 (10)	C(37)	-1416 (4)	1436 (6)	1408 (11)
C(11)	4321 (4)	2266 (5)	8653 (10)	C(38)	-1557 (4)	2233 (6)	2133 (11)
C(12)	4378 (4)	1121 (5)	9142 (10)	C(39)	-2027 (4)	3075 (6)	1675 (11)
C(13)	4182 (4)	533 (5)	8302 (10)	C(40)	-2355 (4)	3118 (6)	491 (11)
C(14)	3929 (4)	1090 (5)	6973 (10)	C(41)	-2213 (4)	2321 (6)	-234 (11)
C(15)	3872 (4)	2236 (5)	6483 (10)	C(42)	-1744 (4)	1480 (6)	225 (11)
C(16)	4346 (3)	7397 (6)	6063 (9)	C(43)	481 (5)	2910 (7)	-638 (13)
C(17)	4434 (3)	8065 (6)	4591 (9)	C(44)	122 (5)	3309 (7)	-1837 (13)
C(18)	4006 (3)	8965 (6)	4071 (9)	C(45)	101 (5)	4422 (7)	-2648 (13)
C(19)	3491 (3)	9198 (6)	5023 (9)	C(46)	439 (5)	5135 (7)	-2262 (13)
C(20)	3403 (3)	8531 (6)	6495 (9)	C(47)	798 (5)	4736 (7)	-1063 (13)
C(21)	3831 (3)	7630 (6)	7015 (9)	C(48)	819 (5)	3624 (7)	-251 (13)
C(22)	5576 (3)	6598 (6)	7161 (10)	C(49)	1314 (3)	1116 (7)	884 (11)
C(23)	5584 (3)	7652 (6)	7269 (10)	C(50)	1785 (3)	1394 (7)	-311 (11)
C(24)	6128 (3)	7963 (6)	7617 (10)	C(51)	2416 (3)	1035 (7)	-104 (11)
C(25)	6665 (3)	7241 (6)	7858 (10)	C(52)	2576 (3)	397 (7)	1296 (11)
C(26)	6657 (3)	6187 (6)	7750 (10)	C(53)	2105 (3)	119 (7)	2490 (11)
C(27)	6112 (3)	5866 (6)	7401 (10)	C(54)	1474 (3)	478 (7)	2284 (11)

<sup>a</sup> Phenyl carbons: C(4)-C(27) and C(31)-C(54).Table II. Bond Distances (Å) and Angles (deg)<sup>a</sup>

Molecule I			
Tc(1)-P(1)	2.436 (5)	P(1)-Tc(1)-P(2)	79.9 (1)
Tc(1)-P(2)	2.421 (5)	P(1)-Tc(1)-P(2) <sup>c</sup>	100.1 (1)
Tc(1)-N(1)	2.047 (8)	N(1)-Tc(1)-P(1)	83.3 (2)
N(1)-C(1)	1.13 (1)	N(1)-Tc(1)-P(2)	82.1 (2)
C(1)-S(1)	1.66 (1)	Tc(1)-P(1)-C(2)	110.2 (3)
P(1)-C(2)	1.87 (1)	P(1)-C(2)-C(3)	112.7 (7)
C(2)-C(3)	1.52 (1)	C(2)-C(3)-P(2)	110.8 (6)
C(3)-P(2)	1.85 (1)	C(3)-P(2)-Tc(1)	106.2 (3)
P(1)-C <sub>Ph</sub> av	1.84 (1)	C <sub>Ph</sub> -P(1)-C <sub>Ph</sub>	102.6 (4)
P(2)-C <sub>Ph</sub> av	1.84 (1)	C <sub>Ph</sub> -P(2)-C <sub>Ph</sub>	104.8 (4)
Molecule II			
Tc(2)-P(3)	2.441 (5)	P(3)-Tc(2)-P(4)	79.9 (1)
Tc(2)-P(4)	2.450 (5)	P(3)-Tc(2)-P(4) <sup>b</sup>	100.1 (1)
Tc(2)-N(2)	2.035 (9)	N(2)-Tc(2)-P(3)	82.0 (2)
N(2)-C(28) <sup>b</sup>	1.10 (2)	N(2)-Tc(2)-P(4)	84.4 (2)
C(28)-S(2)	1.65 (1)	Tc(2)-P(3)-C(29)	105.4 (4)
P(3)-C(29)	1.83 (1)	P(3)-C(29)-C(30)	111.7 (7)
C(29)-C(30)	1.53 (1)	C(29)-C(30)-P(4)	111.9 (8)
C(30)-P(4)	1.87 (1)	C(30)-P(4)-Tc(2)	110.0 (4)
P(3)-C <sub>Ph</sub> av	1.85 (1)	C <sub>Ph</sub> -P(3)-C <sub>Ph</sub>	103.0 (4)
P(4)-C <sub>Ph</sub> av	1.85 (1)	C <sub>Ph</sub> -P(4)-C <sub>Ph</sub>	101.8 (5)

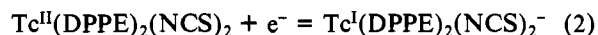
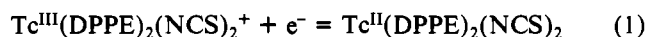
<sup>a</sup> Figures in parentheses are esd's in the last significant digit.<sup>b</sup> C(28) corresponds to C(1), C(29) to C(2), and so on. <sup>c</sup> Prime denotes the atom at -x, -y, -z position.

the two bidentate DPPE ligands occupy the four equatorial coordination sites, while two isothiocyanato moieties occupy the trans axial positions. The bidentate coordination of the DPPE ligands to the Tc(II) center results in two five-membered chelate rings. The ambidentate NCS<sup>-</sup> ligands are N-bonded to the technetium at an angle of 81° to the TcP<sub>4</sub> equatorial plane. The structure contains no intermolecular contacts that are less than the sum of the appropriate van der Waals radii, and there appear to be no unusual structural features differentiating I from II. The two SCN-Tc-NCS

lines of I and II cross with an angle of 2.8°. The dihedral angles between the phenyl rings are 60.4 and 85.2° in I and 71.3 and 86.4° in II. The value of the P-C-C-P torsion angle is 38.9° in I and 40.9° in II.

## Discussion

**Electrochemistry.** The first reduction wave in Figure 1 corresponds to the 1-equiv conversion of Tc(III) to Tc(II) (eq 1), while the second reduction wave corresponds to the subsequent 1-equiv conversion of Tc(II) to Tc(I) (eq 2). These



oxidation state assignments are defined by the spectropotentiostatic data, which (a) establish that  $n = 1.0$  for each process and (b) confirm that the complex of intermediate oxidation state (i.e. technetium(II)) has the same visible spectrum as does the chemically generated material, which has been characterized by single-crystal X-ray structure analysis (vide infra). Repetitive cycles between the Tc(III) and Tc(II) oxidation states reveal no change in the respective spectrophotometric properties, indicating that these complexes are stable on the time scale of hours. This is also true with respect to the Tc(II) and Tc(I) oxidation states. This is very unusual for the Tc(I) oxidation state of this class of mixed BTP ligand and halogen and/or pseudohalogen complexes, *trans*-[Tc<sup>I</sup>(DPPE)<sub>2</sub>(NCS)<sub>2</sub>]<sup>-</sup> being the only known *trans*-[Tc<sup>I</sup>(BTP)<sub>2</sub>X<sub>2</sub>]<sup>-</sup> complex that is stable for this long at room temperature.<sup>7,14,19</sup> This stability arises from the relatively positive  $E^{\circ'}$  value governing reduction of Tc(II) to Tc(I) (eq 2), which makes the Tc(I) state relatively accessible. It has

been well established<sup>7</sup> that the  $E^{\circ}$  values governing the Tc(III)/Tc(II) and Tc(II)/Tc(I) couples of *trans*-[Tc(BTP)<sub>2</sub>X<sub>2</sub>]<sup>+0/-</sup> complexes depend markedly on the nature of BTP and X. For example, for the three DPPE complexes *trans*-[Tc(DPPE)<sub>2</sub>X<sub>2</sub>]<sup>+0</sup> (X = Cl, Br, -NCS),  $E^{\circ}$  values governing the Tc(III)/Tc(II) reduction are -0.001, 0.103, and 0.372 V vs. Ag/AgCl, respectively.<sup>7</sup> From these data it is clear that, relative to X = Cl or Br, N-bonded NCS<sup>-</sup> dramatically stabilizes the lower oxidation state, presumably by more effectively accepting  $\pi$ -electron density from the lower valent technetium center. This observation nicely explains (a) why the Tc(II) complex *trans*-[Tc(DPPE)<sub>2</sub>(NCS)<sub>2</sub>]<sup>0</sup> is stable to air oxidation whereas the Tc(II) chloro and bromo analogues are readily oxidized by air and (b) why the Tc(I) complex *trans*-[Tc(DPPE)<sub>2</sub>(NCS)<sub>2</sub>]<sup>-</sup> is relatively accessible and stable whereas the Tc(I) chloro and bromo analogues are not even sufficiently stable to provide reversible cyclic voltammograms.<sup>7</sup>

**Electronic Spectra.** Spectropotentiostatic experiments (e.g., Figure 2) show that the Tc(III) and Tc(II) complexes exhibit intense absorption bands at 583 and 533 nm, respectively, while the Tc(I) complex exhibits a less intense, broad shoulder at ca. 420 nm. Since the extinction coefficients of all these bands are greater than 10<sup>3</sup> M<sup>-1</sup> cm<sup>-1</sup>, they are assigned as arising from charge-transfer transitions. The observation that the energies of these three transitions increase with decreasing technetium oxidation state is consistent with an earlier assignment of this type of transition being a ligand-to-metal charge transfer.<sup>7</sup>

**Crystal Structure.** The overall structure of the neutral *trans*-[Tc<sup>II</sup>(DPPE)<sub>2</sub>(NCS)<sub>2</sub>]<sup>0</sup> complex closely resembles the recently reported structures of analogous technetium(III) *trans*-[TcD<sub>2</sub>X<sub>2</sub>]<sup>+</sup> cations (D = chelating bis(tertiary phosphine or arsine)).<sup>5,7,20</sup> All of these species exhibit *trans*-substituted, approximately octahedral geometries. Indeed, this geometry appears to be universally observed for [MD<sub>2</sub>X<sub>2</sub>]<sup>n+</sup> complexes<sup>21</sup> regardless of the identity or oxidation state of the central metal. This situation presumably arises from steric interactions among the bulky D ligands causing the *trans* configuration to be favored over the *cis* configuration.

The average Tc<sup>II</sup>-P bond distance in *trans*-[Tc(DPPE)<sub>2</sub>(NCS)<sub>2</sub>]<sup>0</sup> is 2.44 (1) Å. This is significantly shorter than the

average Tc<sup>III</sup>-P bond distance (2.50 (1) Å)<sup>7</sup> observed in the analogous technetium(III) cation *trans*-[Tc(DPPE)<sub>2</sub>Br<sub>2</sub>]<sup>+</sup>, the difference being reasonably ascribed to greater  $\pi$ -back-bonding from Tc(II) to P than from Tc(III) to P. The Tc-N bond distance (2.04 (2) Å) in the title complex is equivalent to the Tc-N bond distances observed in hexakis(isothiocyanato)-technetate(III) (2.04 (2) and 2.05 (2) Å).<sup>22</sup>

The fact that the NCS<sup>-</sup> ligands of the title complex are bonded to technetium by means of the N rather than the S atom appears to be in contradiction to the principle of symbiosis proposed by Jørgensen;<sup>23</sup> this principle states that in the case of octahedral complexes, the presence of soft ligands tends to promote the addition of other soft ligands rather than hard,  $\sigma$ -bonding, species. On this basis the soft *trans*-Tc<sup>II</sup>(DPPE)<sub>2</sub> core should be expected to favor ligation by the S atom of SCN<sup>-</sup>. However, Pearson<sup>24</sup> has noted that many soft metal ions behave in an antisymbiotic manner; i.e., for certain soft centers, two soft ligands in mutually *trans* positions have a destabilizing effect on each other, which in turn promotes bonding to hard ligands in these positions. On this basis the soft *trans*-Tc<sup>II</sup>(DPPE)<sub>2</sub> core would be expected to favor ligation by the N atom of SCN<sup>-</sup>, and this is what is observed. Clearly, even though the factors that determine N vs. S bonding modes for the SCN<sup>-</sup> ligand have been studied for many years,<sup>25</sup> more data are needed in order to explain or predict the nature of SCN<sup>-</sup> bonding to second-row transition-metal ions.

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**Registry No.** *trans*-[Tc(DPPE)<sub>2</sub>(NCS)<sub>2</sub>], 91230-84-1; *trans*-[Tc(DPPE)<sub>2</sub>(NCS)<sub>2</sub>]<sup>+</sup>, 91230-85-2; *trans*-[Tc(DPPE)<sub>2</sub>(NCS)<sub>2</sub>]<sup>-</sup>, 91230-86-3.

**Supplementary Material Available:** Table A, showing  $F_c$  and  $F_o$  values, Table B, showing thermal parameters, and Figure 4, showing cell contents viewed down  $c$  (21 pages). Ordering information is given on any current masthead page.

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