

approximately 0.6 kJ mol<sup>-1</sup> (100 cm<sup>-1</sup>) for both hydrogen-bonded and control complexes. We make the approximation  $\Delta H_m \approx D_e$ , since  $RT$  and the second term of eq 1b are small. Then, from the chemical dissociation energies for Fe compounds<sup>45</sup>

$$\begin{aligned} D_e(\text{Co}^{2+}\text{-SR}) &\approx D_e(\text{Fe}^{2+}\text{-SR}) \approx \\ &\frac{1}{2}[D_o(\text{Fe}^{2+}\text{-F}) + D_o(\text{Fe}^{2+}\text{-Cl})] = \\ &\frac{1}{2}[481 \text{ kJ mol}^{-1} + 400 \text{ kJ mol}^{-1}] = \\ &440.5 \text{ kJ mol}^{-1} \end{aligned} \quad (2)$$

The approximate stabilization energy is then determined from the frequency shift of the "A<sub>1</sub>" mode on the basis of the approximate relationship

$$\begin{aligned} \Delta D_e &= D_e(\text{Co}^{2+}\text{-SR})\{[K(A_1, \text{H-bonding})/K(A_1, \text{control})] - 1\} \\ &= D_e(\text{Co}^{2+}\text{-SR})\{[\nu(A_1, \text{H-bonding})/\nu(A_1, \text{control})]^2 - 1\} \\ &= 440.5 \text{ kJ mol}^{-1}\{[204 \text{ cm}^{-1}/201 \text{ cm}^{-1}]^2 - 1\} \\ &= 13.2 \text{ kJ mol}^{-1} \text{ (3.16 kcal mol}^{-1}\text{)} \end{aligned} \quad (3)$$

where  $K$  is the force constant for  $\nu(A_1)$ .

The stabilization effect of N-H...S hydrogen bonding on metal-sulfur bonds is expected to be similar for Co and Fe complexes and could plausibly occur in iron-sulfur centers in Fe-S proteins. Such an effect could account for the higher reduction potentials found for Fe-S proteins as compared with their non-hydrogen-bonding synthetic active-site analogues. This would require that the differential stabilization of the redox center in its reduced state be greater than that of the oxidized state,<sup>22</sup> an effect that has been substantiated in the study of metal complexes in hydrogen-bonding liquids.<sup>46</sup>

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**Conclusion.** Structural data give clear evidence for the stabilization of metal-thiolate bonds in the hydrogen-bonded complex 1. The average Co-S<sub>N</sub> and Co-S<sub>(H+N)</sub> bond lengths are shortened 0.034 and 0.026 Å, respectively, relative to those in the non-hydrogen-bonded complex [(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>P]<sub>2</sub>[Co(SC<sub>6</sub>H<sub>5</sub>)<sub>4</sub>].<sup>21</sup> This should be compared to the average bond length change of 0.089 Å in the bis(*o*-xylene- $\alpha, \alpha'$ -dithiolato)ferrate(II,III) complex anions<sup>6</sup> and 0.061 Å in R<sub>d</sub>,<sup>29</sup> which accompanies a one-electron oxidation-state change in iron. The amide C-N bond is substantially stabilized by hydrogen bonding,<sup>14</sup> as evidenced by its marked decrease in length in 1 and 2 relative to the gas phase (Table II).<sup>33,47</sup> Vibrational frequencies of normal modes related to T<sub>2</sub>(T<sub>d</sub>) and A<sub>1</sub>(T<sub>d</sub>) metal-ligand modes increase, consistent with a stabilization of certain of the metal-ligand bonds via hydrogen bonding.

The experiments described here focus on a single oxidation state of a complex where the central metal is in the 2+ state. It is expected, however, on the basis of theoretical work, that hydrogen-bond stabilization will be less for a complex with a metal in the 3+ state.<sup>22</sup> If structural studies bear this out, then an argument can be made for a substantial role for hydrogen bonding in the modulation of redox potentials in iron-sulfur proteins.

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**Supplementary Material Available:** General structure reports for compounds 1 and 2 including details of the structure determination, listings of experimental details, positional and thermal parameters, inter- and intramolecular bond distances and bond angles involving non-hydrogen atoms, and intermolecular distances involving hydrogen atoms, and PLUTO diagrams of the structures (98 pages); a listing of final observed and calculated structure factors (101 pages). Ordering information is given on any current masthead page.

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## Technetium(III) Complexes with the Tetradentate "Umbrella" Ligand Tris(*o*-mercaptophenyl)phosphinate: X-ray Structural Characterization of Tc(P(*o*-C<sub>6</sub>H<sub>4</sub>S)<sub>3</sub>)(CNC<sub>3</sub>H<sub>7</sub>) and Tc(P(*o*-C<sub>6</sub>H<sub>4</sub>S)<sub>3</sub>)(CNC<sub>3</sub>H<sub>7</sub>)<sub>2</sub>

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Tris(*o*-mercaptophenyl)phosphinate (PS3) binds to Tc(III) as a tetradentate ligand to form the formally 14-electron complex Tc(PS3)(CNMe). An X-ray single-crystal structure determination of the isopropyl isocyanide derivative Tc(PS3)(CN-*i*-Pr) shows that the complex has a trigonal-bipyramidal geometry with the phosphorus and isonitrile carbon in the axial positions and the sulfurs bound in the equatorial plane (crystal data: MF = C<sub>22</sub>H<sub>19</sub>NPS<sub>3</sub>Tc, monoclinic,  $a = 10.3541$  (8) Å,  $b = 13.2274$  (6) Å,  $c = 16.437$  (1) Å,  $\beta = 90.855$  (6)°, space group  $P2_1/c$ ,  $Z = 4$ ; final  $R = 0.049$ ,  $R_w = 0.057$ ). In the presence of a large excess of isonitrile, these electron-deficient complexes bind a sixth ligand. The six-coordinate complex Tc(PS3)(CN-*i*-Pr)<sub>2</sub> was also structurally characterized (crystal data: MF = C<sub>26</sub>H<sub>26</sub>N<sub>2</sub>PS<sub>3</sub>Tc, orthorhombic,  $a = 18.896$  (1) Å,  $b = 13.2815$  (8) Å,  $c = 10.3823$  (6) Å, space group  $Pna2_1$ ,  $Z = 4$ ; final  $R = 0.044$ ,  $R_w = 0.048$ ).

### Introduction

The ligand 2,3,5,6-tetramethylbenzenethiolate (tmbt) has been shown to stabilize technetium in the +3 oxidation state.<sup>2</sup> Compounds such as Tc(tmbt)<sub>3</sub>(MeCN)<sub>2</sub> exhibit trigonal-bipyramidal geometry with three thiols in the equatorial plane and two  $\pi$ -accepting ligands in the axial positions. The acetonitrile ligands are labile and undergo substitution through a proposed six-coordinate intermediate, allowing the incorporation of any number

of  $\pi$ -accepting ligands, CN-*i*-Pr, py, CO, MeCN, or PEt<sub>3</sub>, into the axial positions.

We have now designed a chelating "umbrella" ligand, tris(*o*-mercaptophenyl)phosphinate (PS3), which provides technetium with three thiolate ligands and one of the axial  $\pi$ -accepting ligands while leaving the fifth coordination site open for ligand exchange. With this umbrella system, the six-coordinate complex can be isolated, indicating that this is the intermediate involved in the ligand-exchange reactions of the trithiolate compounds described above.

### Experimental Section

**Caution!** Technetium-99 is a weak  $\beta$ -emitter ( $E = 0.292$  MeV,  $t_{1/2} = 2.12 \times 10^5$  years). All work has been done in laboratories approved

(1) (a) Massachusetts Institute of Technology. (b) Harvard Medical School.

(2) de Vries, N.; Dewar, J. C.; Jones, A. G.; Davison, A. *Inorg. Chem.* **1988**, *27*, 1574.

Table I. X-ray Data for the Structure Determinations of 2 and 4

Compound 2	
$C_{22}H_{19}NPS_3Tc$	$T = 22\text{ }^\circ\text{C}$
fw = 521.55	$\lambda = 0.71069\text{ \AA}$ , graphite monochromated
space group = $P2_1/c$	$\rho_{\text{calcd}} = 1.54\text{ g/cm}^3$ , $\rho_{\text{exp}} = 1.48\text{ g/cm}^3$
$a = 10.3541(8)\text{ \AA}$	$\mu = 9.59\text{ cm}^{-1}$
$b = 13.2274(6)\text{ \AA}$	transm coeff = 1.17–0.81
$c = 16.437(1)\text{ \AA}$	final residuals: $R = 0.049$ , $R_w = 0.057$
$\beta = 90.855(6)^\circ$	
$V = 2251.0(4)\text{ \AA}^3$	
$Z = 4$	
Compound 4	
$C_{26}H_{26}N_2PS_3Tc$	$T = 22\text{ }^\circ\text{C}$
fw = 590.66	$\lambda = 0.71069\text{ \AA}$ , graphite monochromated
space group = $Pna2_1$	$\rho_{\text{calcd}} = 1.505\text{ g/cm}^3$ , $\rho_{\text{exp}} = 1.46\text{ g/cm}^3$
$a = 18.896(1)\text{ \AA}$	$\mu = 8.38\text{ cm}^{-1}$
$b = 13.2815(8)\text{ \AA}$	transm coeff = 1.0–0.87
$c = 10.3823(6)\text{ \AA}$	final residuals: $R = 0.044$ , $R_w = 0.048$
$V = 2605.7(6)\text{ \AA}^3$	
$Z = 4$	

for the use of low levels of radioactive materials. Precautions have been detailed elsewhere.<sup>3</sup>

Ammonium pertechnetate was supplied as a gift of Du Pont/Biomedical Products. Methyl isocyanide was prepared according to the method of Schuster, Scott, and Casanova,<sup>4</sup> and isopropyl isocyanide was used as received from Strem Chemicals. <sup>1</sup>H and <sup>31</sup>P NMR spectra were recorded on a Varian XL-300 spectrometer. Infrared spectra were obtained on a Mattson Cynus 100 FTIR and UV-visible spectra on an HP 8451A Diode Array spectrophotometer. Fast atom bombardment mass spectra (FABMS) of samples dissolved in a 3-nitrobenzyl alcohol matrix were recorded with a MAT 731 mass spectrometer equipped with an Ion Tech B11N FAB gun and operating at an accelerating voltage of 8 keV. The FAB gun produced a beam of 6–8 keV xenon neutrals. Elemental analyses were performed by Atlantic Microlabs, Norcross, GA.

**Syntheses. Tris(*o*-mercaptophenyl)phosphine ( $H_3PS_3$ ).** Tris(*o*-methylthio)phenyl)phosphine (8.5 g), prepared by the method of Dyer and Meek,<sup>5</sup> was suspended in 100 mL of  $NH_3(l)$ . Small chunks of sodium metal were added until the blue color persisted for at least 15 min, at which point the reaction mixture was quenched by careful addition of excess  $NH_4Cl$ . The  $NH_3$  was allowed to evaporate, the product was dissolved in 1 M NaOH, and the mixture was filtered. The filtrate was brought to pH 1 with HCl (concentrated), and a white precipitate formed, which was collected on a fritted disk, washed with 0.1 M HCl, and dried in vacuo. As determined by mass spectrometry, <sup>1</sup>H NMR, and IR data, this compound was found to be spectroscopically identical with that prepared by Zubieta and Block<sup>6</sup> via a different route. Yield: 96%.

**Tc( $PS_3$ )(CNMe) (1).** To a solution of  $PS_3$  (36 mg) in 1:1 MeCN/ $H_2O$  at pH 12 were added 0.1 mmol of  $(NH_4)[TcO_4]$  and sodium dithionite (10 mg, excess). A chloroform solution (2 mL) of MeNC (0.1 mL, excess)<sup>4</sup> was added, and the mixture was allowed to stir for 20 min. The bright blue organic layer was collected, evaporated to dryness, and chromatographed on a silica gel column eluted with chloroform. The orange band was collected and layered with diethyl ether, and the product was isolated as X-ray-quality crystals. Yield: 40.6 mg (82%).

Anal. Calcd for  $C_{20}H_{15}NPS_3Tc$ : C, 48.49; H, 3.05; N, 2.83; S, 19.41. Found: C, 48.17; H, 3.22; N, 2.81; S, 19.32. IR (KBr):  $\nu(CN)$  2163  $cm^{-1}$ . <sup>1</sup>H NMR ( $CDCl_3$ ):  $\delta$  3.97 (s, 3 H,  $CNCH_3$ ), 7.28 (t, 3 H, Ar), 7.37 (t, 3 H, Ar), 7.56 (d, 3 H, Ar), 8.39 (t, 3 H, Ar). UV-visible ( $CH_2Cl_2$ ):  $\lambda_{\text{max}}$  284 nm ( $\epsilon = 26000\text{ cm}^{-1}\text{ M}^{-1}$ ), 356 (8500), 454 (12000), 528 (4300). FABMS(+):  $m/z$  495 (100%) [M], 454 (52) [M - CNMe].

**Tc( $PS_3$ )(CN-*i*-Pr) (2).** This compound prepared analogously to compound 1, substituting *i*-PrNC for MeNC. Yield: 41.5 mg (83%).

Anal. Calcd for  $C_{22}H_{19}NPS_3Tc$ : C, 50.48; H, 3.66; N, 2.68; S, 18.37. Found: C, 50.22; H, 3.66; N, 2.68; S, 18.41. IR (KBr):  $\nu(CN)$  2144  $cm^{-1}$ . <sup>1</sup>H NMR ( $CDCl_3$ ):  $\delta$  1.70 (d, 6 H), 4.54 (m, 1 H), 7.28 (m, 3 H), 7.37 (m, 3 H), 7.55 (dd, 3 H), 8.38 (t, 3 H). UV-visible ( $CH_2Cl_2$ ):  $\lambda_{\text{max}}$  284 nm ( $\epsilon = 24000\text{ cm}^{-1}\text{ M}^{-1}$ ), 356 (7500), 452 (11000), 532 (3400). FABMS(+):  $m/z$  523 (100%) [M], 454 (58) [M - CN-*i*-Pr].

Table II. Non-Hydrogen Positional Parameters for 2

atom	x	y	z
Tc	0.22740 (7)	0.02473 (6)	0.21049 (5)
S1	0.0881 (2)	0.1434 (2)	0.1687 (2)
S2	0.2364 (2)	-0.0158 (2)	0.3431 (1)
S3	0.3855 (2)	-0.0225 (2)	0.1280 (1)
P	0.3597 (2)	0.1557 (2)	0.2447 (1)
N	0.0562 (8)	-0.1618 (6)	0.1466 (5)
C1	0.114 (1)	-0.0951 (7)	0.1723 (6)
C2	-0.019 (1)	-0.242 (1)	0.1076 (7)
C3	0.066 (2)	-0.304 (1)	0.0557 (9)
C4	-0.130 (1)	-0.193 (1)	0.0634 (8)
C11	0.2820 (7)	0.2758 (6)	0.2195 (5)
C12	0.1590 (8)	0.2650 (6)	0.1857 (5)
C13	0.0898 (8)	0.3518 (7)	0.1637 (5)
C14	0.143 (1)	0.4450 (7)	0.1768 (6)
C15	0.263 (1)	0.4560 (6)	0.2108 (6)
C16	0.3324 (8)	0.3722 (7)	0.2321 (5)
C21	0.3967 (8)	0.1528 (6)	0.3529 (5)
C22	0.3372 (8)	0.0755 (6)	0.3948 (5)
C23	0.352 (1)	0.0684 (7)	0.4794 (6)
C24	0.431 (1)	0.1363 (8)	0.5203 (6)
C25	0.490 (1)	0.2123 (8)	0.4784 (6)
C26	0.474 (1)	0.2203 (7)	0.3955 (5)
C31	0.5114 (7)	0.1463 (6)	0.1905 (5)
C32	0.5169 (8)	0.0636 (6)	0.1386 (5)
C33	0.628 (1)	0.462 (8)	0.0952 (5)
C34	0.732 (1)	0.1106 (9)	0.1037 (7)
C35	0.6156 (8)	0.2122 (7)	0.1973 (6)

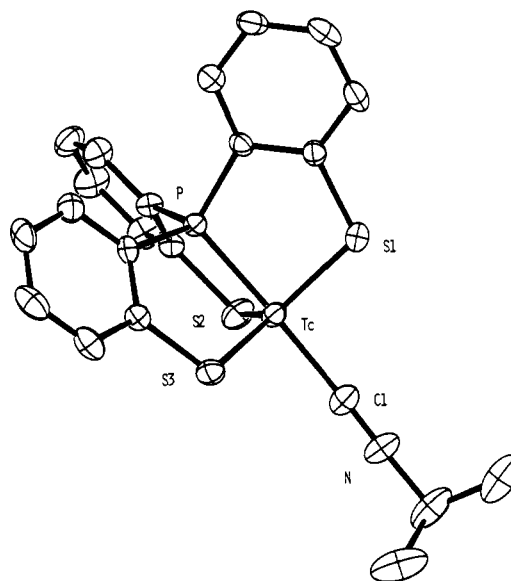


Figure 1. ORTEP-drawn diagram of 2 showing the partial atom-labeling scheme and 30% probability ellipsoids.

**Tc( $PS_3$ )(CNMe)<sub>2</sub>(3).** Compound 1 (35.0 mg) was dissolved in 1:1  $CHCl_3/MeOH$  (10 mL, containing 1% MeNC), and the  $CHCl_3$  was evaporated with stream of nitrogen. The blue microcrystalline material that formed was collected on a fritted disk, washed with methanol, and dried in vacuo. Yield: 21.9 mg (62%). This complex was submitted for elemental analysis on several occasions, but we were unable to obtain acceptable results. The volatility of MeNC made it difficult to maintain the appropriate excess of isocyanide in solution to form the six-coordinate species. Each analysis performed indicated a mixture of the mono- and bis(isocyanide) complexes.

IR (KBr):  $\nu(CN)$  2173  $cm^{-1}$ . UV-visible ( $CH_2Cl_2$ ):  $\lambda_{\text{max}}$  279 nm ( $\epsilon = 31000\text{ cm}^{-1}\text{ M}^{-1}$ ), 300 (20000), 620 (10000). FABMS(+):  $m/z$  495 (100%) [M], 454 (71) [M - 2CNMe].

**Tc( $PS_3$ )(CN-*i*-Pr)<sub>2</sub>(4).** This compound prepared analogously to compound 3, substituting *i*-PrNC (Strem) for MeNC. Yield: 24.2 mg (69%).

Anal. Calcd for  $C_{26}H_{26}N_2PS_3Tc$ : C, 52.68; H, 4.43; N, 4.73; S, 16.23. Found: C, 52.29; H, 4.43; N, 4.74; S, 16.28. IR (KBr):  $\nu(CN)$  2155, 2127, 2115  $cm^{-1}$ . UV-visible ( $CH_2Cl_2$ ):  $\lambda_{\text{max}}$  270 nm ( $\epsilon = 32000\text{ cm}^{-1}\text{ M}^{-1}$ ), 300 (16000), 618 (6500). FABMS(+):  $m/z$  523 (100%) [M - CN-*i*-Pr], 454 (75) [M - 2CN-*i*-Pr].

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**Table III.** Non-Hydrogen Positional Parameters for **4**

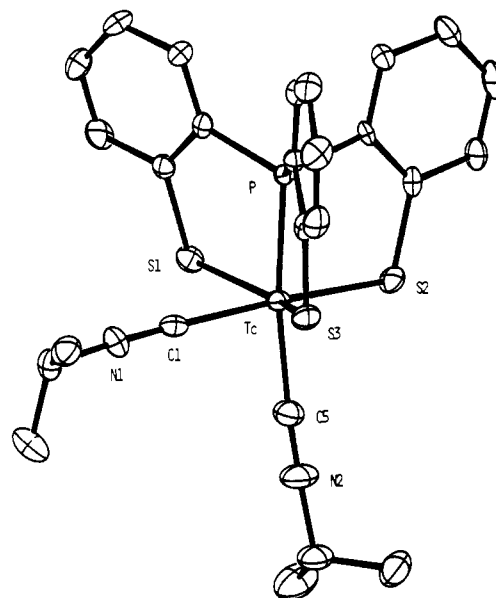
atom	x	y	z
Tc	0.84473 (3)	0.87853 (3)	1.0008
S1	0.7295 (1)	0.8247 (1)	0.9354 (2)
S2	0.8586 (1)	1.0238 (1)	0.8811 (2)
S3	0.93076 (9)	0.8832 (1)	1.1612 (2)
P	0.78141 (8)	0.9791 (1)	1.1379 (2)
N1	0.8264 (3)	0.6641 (4)	1.1444 (6)
N2	0.9473 (4)	0.7688 (5)	0.7989 (7)
C1	0.8322 (3)	0.7412 (5)	1.0946 (7)
C2	0.8292 (4)	0.5710 (5)	1.2179 (7)
C3	0.8624 (5)	0.4903 (6)	1.1387 (9)
C4	0.8690 (4)	0.5913 (6)	1.3414 (8)
C5	0.9084 (4)	0.8051 (5)	0.8703 (8)
C6	1.0021 (5)	0.7242 (6)	0.7162 (9)
C7	0.9695 (5)	0.6925 (9)	0.592 (1)
C8	1.0591 (5)	0.7997 (7)	0.703 (1)
C11	0.6908 (3)	0.9344 (4)	1.1545 (6)
C12	0.6419 (4)	0.9647 (5)	1.2462 (7)
C13	0.5744 (4)	0.9247 (6)	1.2478 (8)
C14	0.5557 (4)	0.8545 (6)	1.155 (1)
C15	0.6025 (4)	0.8246 (5)	1.0636 (8)
C16	0.6711 (3)	0.8653 (4)	1.0590 (7)
C21	0.7750 (3)	1.1055 (4)	1.0726 (6)
C22	0.7363 (4)	1.1831 (5)	1.1311 (7)
C23	0.7338 (4)	1.2773 (5)	1.070 (1)
C24	0.7684 (5)	1.2925 (6)	0.9550 (9)
C25	0.8063 (4)	1.2162 (5)	0.8995 (7)
C26	0.8092 (3)	1.1221 (5)	0.9564 (6)
C31	0.8262 (3)	0.9914 (4)	1.2915 (6)
C32	0.8029 (3)	1.0454 (5)	1.3986 (7)
C33	0.8425 (4)	1.0524 (5)	1.509 (1)
C34	0.9080 (4)	1.0065 (6)	1.5120 (9)
C35	0.9341 (3)	0.9559 (6)	1.4068 (8)
C36	0.8938 (3)	0.9483 (5)	1.2951 (6)

**Structure Determination.** **Tc(PS<sub>3</sub>)(CN-*i*-Pr) (2).** Crystal data are presented in Table I, atomic positional parameters in Table II, and selected bond distances and angles in Table IV. An ORTEP-drawn diagram is shown in Figure 1. Orange X-ray-quality prismatic crystals were grown by diffusion of diethyl ether into a chloroform solution of **2**. A monoclinic crystal having the approximate dimensions of 0.2 × 0.2 × 0.3 mm was chosen, and the space group was determined unambiguously to be *P*2<sub>1</sub>/*c*. A total of 5662 reflections (of which 5419 were unique,  $R_{int} = 0.049$ ) were collected on an Enraf-Nonius CAD4 diffractometer ( $2\theta_{max} = 54.9^\circ$ ; octants collected  $+h, +k, \pm l$ ; scan mode  $\omega-2\theta$ ). Neutral-atom scattering factors were used throughout,<sup>7</sup> and no extinction effects were observed. The structure was solved by using Patterson methods, an absorption correction was applied by using DIFABS of the Molecular Structure Corp., and all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined from their calculated positions. Final residuals are  $R = 0.049$  and  $R_w = 0.057$ .

**Tc(PS<sub>3</sub>)(CN-*i*-Pr)<sub>2</sub> (4).** Crystal data are presented in Table I, atomic positional parameters in Table III, and selected bond lengths and angles in Table IV. An ORTEP-drawn diagram is shown in Figure 2. Blue prisms were grown from a solution of **4** in methanol/H<sub>2</sub>O. An orthorhombic crystal of approximate dimensions 0.3 × 0.3 × 0.4 mm was chosen, and the space group was determined unambiguously to be *Pna*2<sub>1</sub>. The handedness was determined by examining the data including the Friedel pairs. A total of 6796 reflections were collected on an Enraf-Nonius CAD4 diffractometer ( $2\theta_{max} = 54.9^\circ$ ; octants collected  $\pm h, \pm k, \pm l$ ; scan mode  $\omega-2\theta$ ). Solution and refinement of the structure were carried out as described above. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined from their calculated positions. Final residuals are  $R = 0.044$  and  $R_w = 0.048$ .

### Results and Discussion

Compounds of technetium containing the "umbrella" ligand tris(*o*-mercaptophenyl)phosphinate (PS<sub>3</sub>) can be prepared under ambient conditions directly from ammonium pertechnetate, despite the 4-electron reduction involved in bringing the metal from Tc(VII) to Tc(III). An alkaline solution of pertechnetate and the PS<sub>3</sub> ligand is reduced by dithionite to give a green intermediate that readily reacts with alkyl isocyanides. The addition of acetonitrile to the initial reaction mixture improves the yield, pre-

**Figure 2.** ORTEP-drawn diagram of **4** showing the partial atom-labeling scheme and 30% probability ellipsoids.**Table IV.** Selected Bond Distances and Angles for **2** and **4**

	<b>2</b>		<b>4</b>	
	Bond Lengths (Å)			
Tc-P	2.273 (2)	Tc-P	2.290 (2)	
Tc-S1	2.233 (3)	Tc-S1	2.390 (2)	
Tc-S2	2.245 (3)	Tc-S2	2.310 (2)	
Tc-S3	2.231 (2)	Tc-S3	2.328 (2)	
Tc-C1	2.06 (8)	Tc-C1	2.081 (7)	
C1-N	1.14 (1)	Tc-C5	2.058 (8)	
		C1-N1	1.152 (8)	
		C5-N2	1.150 (9)	
	Bond Angles (deg)			
P-Tc-C1	176.1 (3)	P-Tc-C5	172.5 (2)	
P-Tc-S1	85.66 (8)	P-Tc-S1	82.81 (6)	
P-Tc-S2	85.75 (8)	P-Tc-S2	84.65 (6)	
P-Tc-S3	85.35 (8)	P-Tc-S3	84.52 (6)	
C1-Tc-S1	94.9 (3)	C5-Tc-S1	101.8 (2)	
C1-Tc-S2	97.3 (3)	C5-Tc-S2	88.6 (2)	
C1-Tc-S3	91.0 (3)	C5-Tc-S3	94.3 (2)	
S1-Tc-S2	118.9 (1)	S1-Tc-S2	106.46 (7)	
S1-Tc-S3	119.1 (1)	S1-Tc-S3	147.91 (7)	
S2-Tc-S3	120.2 (1)	S2-Tc-S3	106.46 (7)	
		C1-Tc-P	99.2 (2)	
		C1-Tc-S1	76.5 (2)	
		C1-Tc-S2	175.3 (2)	
		C1-Tc-S3	76.6 (2)	
		C1-Tc-C5	87.7 (3)	

sumably by coordinating to, and stabilizing, the intermediate complex. The chromatographed material can then either be crystallized to yield the orange diamagnetic compound Tc(PS<sub>3</sub>)(CNR) or allowed to react with excess isocyanide to give the bis(isonitrile) compound Tc(PS<sub>3</sub>)(CNR)<sub>2</sub>.

The second isonitrile ligand is labile, and in the FABMS(+) of the six-coordinate compounds the molecular ion is not observed. Instead, the peak at the highest mass is that corresponding to the five-coordinate mono(isonitrile) species. Loss of the second isocyanide ligand is also observed when the six-coordinate compounds **3** and **4** are dissolved in the absence of a large excess of the ligand. Upon dissolving, they lose their blue color and become orange, indicating that in the absence of excess isonitrile the five-coordinate species dominates. The dependence of this equilibrium on isonitrile concentration was followed by UV-visible spectral studies, and it was found that only in a large excess of isocyanide are significant quantities of the bis(isonitrile) complexes formed. At millimolar concentrations of complex, approximately 150 equiv of MeNC is necessary to convert 50% of Tc(PS<sub>3</sub>)(CNMe) to Tc(PS<sub>3</sub>)-

(7) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

(CNMe)<sub>2</sub>. Thus, even at high concentration of isocyanide, traces of the mono(isocyanide) compound remain.

Since the addition of a second isocyanide ligand is reversible and rapid, one isonitrile can easily be exchanged for another by shifting the equilibrium in favor of the new isonitrile. By the addition of a 100-fold molar excess of CN-*i*-Pr to a solution of Tc(PS3)(CNMe), the mixed isonitrile species Tc(PS3)(CN-*i*-Pr)(MeNC) will be formed. As the excess CN-*i*-Pr and the more volatile MeNC are evaporated from the solution, the five-coordinate species Tc(PS3)(CN-*i*-Pr) can be formed quantitatively.

The structure of compound **2**, as determined by X-ray crystallography, is quite similar to the structures of a number of compounds in the series Tc(tmbt)<sub>3</sub>(L)<sub>2</sub>, which consistently show trigonal-bipyramidal geometry. Five-membered rings containing large metals (second and third row) are expected to be strained, but the umbrella ligand fits snugly around the technetium atom and is undoubtedly tetradentate (Tc-P = 2.273 Å). The technetium lies only 0.172 Å out of the plane defined by the sulfur atoms and P-Tc-S1, P-Tc-S2, and P-Tc-S3 are all close to being right angles (85.66 (8), 85.75 (8), 85.35 (8)°, respectively). The compound has virtually C<sub>3v</sub> symmetry with the phenyl rings at right angles to the equatorial plane. The <sup>1</sup>H NMR data indicate that this is also the case in solution, as the ligand shows perfect 3-fold symmetry and each of the four unique protons on the aryl rings of the umbrella ligand gives rise to a distinct multiplet. The entire hemisphere opposite the phosphorus atom is occupied solely by the isonitrile ligand, which is bound linearly.

The structure of the blue hexacoordinate compound exemplifies the flexibility of the PS3 chelate similar to that observed for RuBr<sub>2</sub>(As(*o*-As(Ph)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>).<sup>8</sup> The angle between two of the

sulfur atoms opens from 120 to 147.91 (7)° to allow the coordination of a second isonitrile. The resulting complex is a very distorted octahedron, which is consistent with a paramagnetic, d<sup>4</sup> system. The bond lengths of this compound do not vary significantly from those of compound **2** and despite the fact that the second isonitrile on **4** is labile and lost easily in the FAB(+) mass spectrum, there is very little difference between the Tc-C1 and Tc-C5 bond lengths, 2.081 (7) and 2.058 (8) Å, respectively. The same is true for the C≡N distances and linear CNC groups, both of which suggest that the two isonitriles are receiving roughly the same amount of electron density via back-bonding from the metal.

The C≡N stretching frequencies observed for the complexes described in this paper are all in the vicinity of that found for Tc(tmbt)<sub>3</sub>(CN-*i*-Pr)<sub>2</sub> (2155 cm<sup>-1</sup>). For Tc(PS3)(CN-*i*-Pr)<sub>2</sub> three C≡N stretching frequencies are observed at 2155, 2127, and 2115 cm<sup>-1</sup>. When methyl isocyanide is used, the C≡N stretching frequency appears as one broad peak at 2173 cm<sup>-1</sup>. Since the differences in the C≡N bond lengths for **2** and **4** are not statistically significant, a correlation to the crystal data cannot be made.

The isolation of the unstable 16-electron Tc(PS3)(L)<sub>2</sub> complexes suggests that the ligand-exchange patterns found for the "two up-one down" tris(thiolate) complexes proceed via an associative pathway having a six-coordinate intermediate.<sup>2</sup>

**Supplementary Material Available:** Tables S.A.I-S.A.VI, listing complete X-ray data, hydrogen positional parameters, intramolecular atomic distances, intramolecular bond angles, data for the least-squares-plane determination, and anisotropic thermal parameters for Tc(PS3)(CN-*i*-Pr), and Tables S.B.I-S.B.V, listing complete X-ray data, hydrogen positional parameters, intramolecular atomic distances, intramolecular bond angles, and anisotropic thermal parameters for Tc(PS3)(CN-*i*-Pr)<sub>2</sub> (8 pages); Tables S.A.VII and S.B.VI, listing calculated and observed structure factors for both compounds (45 pages). Ordering information is given on any current masthead page.

(8) Mais, R. H. B.; Powell, H. M.; Venanzi, L. M. *Chem. Ind. (London)* 1963, 1204.