

Contribution from the Departments of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and Columbia University, New York, New York 10027, and the Department of Radiology, Harvard Medical School and Peter Bent Brigham Hospital, Boston, Massachusetts 02115

Synthesis and Physical Properties of Hexakis(isothiocyanato)technetate(III) and -(IV) Complexes. Structure of the $[\text{Tc}(\text{NCS})_6]^{3-}$ Ion

H. S. TROP,^{1a} A. DAVISON,^{*1a} A. G. JONES,^{1b} M. A. DAVIS,^{1b} D. J. SZALDA,^{1c} and S. J. LIPPARD^{*1c}

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The reaction between ammonium thiocyanate and $(\text{NH}_4)_2\text{TcX}_6$, $\text{X} = \text{Cl}$ and Br , salts is shown to produce a mixture of red (λ 500 nm) $[\text{Tc}(\text{NCS})_6]^{2-}$ and air-sensitive yellow (λ 400 nm) $[\text{Tc}(\text{NCS})_6]^{3-}$ ions. These species were chromatographically separated and isolated as their ammonium, tetraphenylarsonium, or tetra-*n*-butylammonium salts. The technetium(IV) compound was also obtained through reduction of ammonium pertechnetate followed by treatment with ceric ion. Infrared, Raman, conductivity, and magnetic susceptibility data are reported for these complexes and shown to be consistent with octahedral structures. The detailed geometry of $(n\text{-Bu}_4\text{N})_3[\text{Tc}(\text{NCS})_6]$ was determined in a single-crystal X-ray diffraction study. The compound crystallizes in the cubic system, space group $P\bar{a}3$, with $a = 24.444$ (6) Å and $Z = 8$. The technetium atom is situated on a crystallographic threefold rotation axis. The Tc–N bond lengths are 2.04 (2) and 2.05 (2) Å, and the N–Tc–N angles range from 88.0 (6) to 92.1 (7)°, indicative of nearly perfect octahedral symmetry. The average Tc–N–C and N–C–S bond angles are 173 (2) and 177 (2)°, respectively. Voltammetric studies in acetonitrile show a reversible one-electron transfer between $[\text{Tc}(\text{NCS})_6]^{3-}$ and $[\text{Tc}(\text{NCS})_6]^{2-}$ with $E_{1/2}$ of 0.18 V vs. SCE. Additional chemical redox reactions of these ions are reported.

Introduction

The exact nature of the technetium complexes formed in the spectrophotometric determination of this element using thiocyanate ion^{2–5} has been of interest for many years. Solutions of pertechnetate turn red when heated with acidic thiocyanate solutions.² An intense band at 500 nm is present along with a band at 400 nm. The complex responsible for the 500-nm band could be extracted with alcohols, ketones, and ethers. The 500-nm band was assigned² to a technetium(V) complex. Further examination³ of this system revealed that addition of ascorbic acid and iron(III) promoted the formation of the 500-nm band and inhibited production of the 400-nm band. Other workers⁴ used stannous ion reduction of pertechnetate in order to ensure that only the 400-nm band, presumed to be technetium(IV), would be present.

A later, detailed study⁶ of this system led to the proposal that the 400- and 500-nm species were a redox couple, eq 1.



A purple species, formulated as $(\text{Me}_4\text{N})[\text{Tc}(\text{NCS})_6]$, with λ_{max} 500 nm, and a yellow air-sensitive species, formulated as $(\text{Me}_4\text{N})_2[\text{Tc}(\text{NCS})_6]$, λ_{max} 400 nm, were isolated. The technetium(V) species, $[\text{Tc}(\text{NCS})_6]^{-}$, was considered to be the more stable of the pair. A powder X-ray diffraction study of

the yellow salt provided little structural information, although technetium–nitrogen coordination was suggested.⁷

Recent electrochemical studies on hexahalometalate(IV) ions ($\text{M} = \text{Re}, \text{Tc}; \text{X} = \text{Cl}, \text{Br}$) demonstrated that oxidations to hexahalometalate(V) ions were very difficult and that oxidations are easier for rhenium than for technetium.⁸ Thus the reports of stable hexakis(isothiocyanato)metalate(V) complexes for technetium and the reported stability of $[\text{Tc}(\text{NCS})_6]^{-}$ over $[\text{Tc}(\text{NCS})_6]^{2-}$, which is directly opposite the expected trend based on the electrochemical results and chemical periodicity, seemed to warrant yet another examination of the complex thiocyanate chemistry of technetium. Here we report the reinvestigation of the technetium–thiocyanate system, its reformulation as a reversible one-electron redox couple (eq 2), and the single-crystal X-ray structure determination of $(n\text{-Bu}_4\text{N})_3[\text{Tc}(\text{NCS})_6]$.



Experimental Section

Prior to use, all water was passed through a Barnstead Ultrapure D8902 cartridge, followed by distillation using a Corning AG-1 water still. Ammonium, sodium, and potassium thiocyanate salts were recrystallized from methanol and stored in vacuo in a desiccator. Tetra-*n*-butylammonium perchlorate (Southwest Analytical) was dried in vacuo at 85 °C for 24 h prior to use. Other reagents were used as received. All manipulations involving various salts of $[\text{Tc}(\text{NCS})_6]^{3-}$ were carried out in N_2 or Ar atmospheres, by using standard Schlenk-line or drybox techniques.

The preparation of $(\text{NH}_4)_2[\text{TcCl}_6]$, $(\text{NH}_4)_2[\text{TcBr}_6]$, and $(n\text{-Bu}_4\text{N})_2[\text{TcCl}_6]$ has been described previously.⁸ Thiocyanogen, $(\text{SC}-$

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N_2 ,⁹ and $(\text{Me}_4\text{N})_3[\text{Fe}(\text{NCS})_6]$ ¹⁰ were prepared by published procedures.

Solutions of $(\text{NH}_4)(^{99}\text{TcO}_4)$ (0.53 mCi mL⁻¹) were obtained from New England Nuclear, Boston. The concentration was determined by a literature method.¹¹ ⁹⁹Tc is a weak β emitter (0.292 MeV, half-life 2.12×10^5 years); therefore, all manipulations were carried out in a radiation laboratory with a monitored fume hood. Personnel wore disposable lab coats and gloves at all times. Radioactive wastes, both liquid and solid, were disposed in special receptacles. Samples sent outside of the laboratories' jurisdiction were wipetested for contamination prior to shipment, and all regulations¹² regarding such transportation were followed.

Infrared spectra were recorded on a Perkin-Elmer 180 grating spectrophotometer as KBr pellets or solution spectra in matched AgCl cells (0.5-mm path length). Raman spectra were obtained by Dr. J. E. Smith, Union Carbide, Tarrytown, N.Y., using a yellow line of a Kr/Ar laser and a commercial instrument. Optical spectra in appropriate solvents were recorded on a Cary 17 spectrophotometer.

Voltammetric studies were carried out by using a PAR Model 174 polarographic analyzer with rotating Pt, stationary Pt, and dropping-Hg electrodes. All potentials were referenced to a saturated calomel electrode. Ferrocene was used as an internal calibrant. Tetra-*n*-butylammonium perchlorate was used as the supporting electrolyte in the solvent spectrograde acetonitrile.

Conductivity measurements were made in the concentration range 10–0.1 mM in acetonitrile with a Yellow Springs Model 3403 conductivity cell and a Serfass conductivity bridge.

Magnetic susceptibility measurements were obtained on a home-built Faraday balance equipped with a Varian V-4005 electromagnet with constant-force pole faces and a Cahn RG electrobalance. A quartz sample bucket was used. Diamagnetic corrections were taken from published tables,¹³ and the magnetic moment was derived from the expression $\mu_{\text{eff}} = 2.84(\chi_{\text{cor}}^M T)^{1/2}$. $\text{HgCo}(\text{SCN})_4$ was used as the calibrant. Electron paramagnetic resonance measurements were attempted at 77 K either on solids or on frozen-solution glasses in quartz tubes fitted in a specially designed liquid-nitrogen Dewar. Elemental microanalyses were performed by Schwarzkopf Micro-analytical Laboratory, Woodside, N.Y.

Preparation of Ammonium Hexakis(isothiocyanato)technetate(IV). In a 25-mL round-bottom flask equipped with a stir bar, 0.10 g (0.16 mmol) of $(\text{NH}_4)_2[\text{TcBr}_6]$ and 1.0 g (13 mmol) of NH_4SCN were refluxed in 15 mL of methanol for 24 h. Hexachlorotechnetate(IV) may be substituted for hexabromotechnetate(IV) by extending the reflux time to 36 h. The purple solution was reduced in volume with a rotary evaporator to ~2 mL and then chromatographed on a Sephadex LH-20 column with methanol as the eluant. The purple band was evaporated to dryness, and 0.054 g of a purple microcrystalline solid with a green reflex was collected. The yield of $(\text{NH}_4)_2[\text{Tc}(\text{NCS})_6]$ was 70% on the basis of technetium. Anal. Calcd for $\text{C}_6\text{H}_8\text{N}_8\text{S}_6\text{Tc}$: C, 14.90; H, 1.67; N, 23.17; S, 39.79. Found: C, 14.76; H, 2.15; N, 22.99; S, 39.41. Optical spectrum (CH_3CN): 575 nm (sh), 500 (ϵ 76 100), 270 (21 100). IR (KBr): 3050 (w), 2030 (s), 1395 (w), 470 (w), 320 (m) cm^{-1} . Conductivity (2:1 electrolyte in acetonitrile): $\Lambda_0 = 410 \text{ cm}^2 \Omega^{-1} \text{equiv}^{-1}$. $E_{1/2}(\text{cathodic}) = 0.18 \text{ V vs. SCE}$ (1 e reversible); $E_{1/2}(\text{anodic}) = 1.60 \text{ V vs. SCE}$ (irreversible).

Preparation of Tetraphenylarsonium Hexakis(isothiocyanato)technetate(IV). Method A. Metathesis of $(\text{NH}_4)_2[\text{Tc}(\text{NCS})_6]$ with an excess of $\text{Ph}_4\text{AsCl} \cdot \text{H}_2\text{O}$ in methanol yielded a purple precipitate. Recrystallization from acetone/isobutyl alcohol gave a large yield of purple plates with a bright green reflex.

Method B. To a solution of 0.40 g (5.3 mmol) of NH_4SCN in 5 mL of 1 N sulfuric acid in an Erlenmeyer flask was added 0.5 mL of a 0.25 M (0.13 mmol) NH_4TcO_4 solution. The solution was heated at 80 °C for 2 h. Upon cooling, the red-brown solution was filtered. The filtrate was treated with 0.10 g of $(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4$ in 4 N sulfuric acid, followed by addition of 1.0 g of Me_4NBr in 1 mL of 2 N sulfuric

acid. A purple precipitate was filtered, washed with 5 mL of 1 N sulfuric acid and 5 mL of water, and then dried in vacuo. This solid was dissolved in 1:1 acetone/water, and a solution of Ph_4As^+ in water was added, precipitating a purple salt. The solid was recrystallized from acetone/isobutyl alcohol to yield 0.27 g of $(\text{Ph}_4\text{As})_2[\text{Tc}(\text{NCS})_6]$ as purple plates with a green reflex. The yield was 42% on the basis of technetium. Freshly prepared $\text{TcO}_2 \cdot x\text{H}_2\text{O}$, obtained from hydrolysis of TcX_6^{2-} with base, can be used instead of NH_4TcO_4 in this procedure. Anal. Calcd for $\text{C}_{54}\text{H}_{40}\text{As}_2\text{N}_8\text{S}_6\text{Tc}$: C, 53.42; H, 3.32; N, 6.92; S, 15.84. Found: C, 53.95; H, 3.94; N, 7.14; S, 15.91. Optical spectrum (CH_3CN): 575 nm (sh), 500 (ϵ 76 200), 270 (sh), 262 (34 600), 257 (40 600). IR (KBr): 2020 (s), 1480 (w), 1435 (w), 1333 (w), 1306 (w), 1180 (w), 1160 (w), 1075 (w), 1015 (w), 996 (w), 734 (w), 680 (w), 480 (w), 460 (w), 325 (m) cm^{-1} . Magnetic moment: $\mu_{\text{eff}}(298 \text{ K}) = 4.1 \mu_{\text{B}}$. $E_{1/2}(\text{cathodic}) = 0.18 \text{ V vs. SCE}$ (1 e reversible); $E_{1/2}(\text{anodic}) = 1.60 \text{ V vs. SCE}$ (irreversible).

Tetraphenylarsonium hexakis(isothiocyanato)technetate(IV) is marginally soluble in dichloromethane, acetone, and acetonitrile. The purple color is so intense (λ_{max} 500 nm, ϵ 76 200) that detection of undissolved material in saturated solutions can be extremely difficult.

Preparation of Tetra-*n*-butylammonium Hexakis(isothiocyanato)technetate(III). In a round-bottom flask, 3.0 g (39.3 mmol) of NH_4SCN and 0.20 g (0.32 mmol) of $(\text{NH}_4)_2[\text{TcBr}_6]$ were refluxed in 25 mL of degassed methanol with stirring under N_2 or Ar for 24 h. After the system was cooled to room temperature, 0.35 mL of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ was added via a syringe to the purple solution, changing the color of the solution to a deep yellow. The reaction mixture was filtered under an inert atmosphere. The filtrate was then treated with 4.0 g of $n\text{-Bu}_4\text{NClO}_4$ in 12 mL of degassed methanol, added slowly via a cannula. Crystals began to form shortly after the addition of the counterion was complete. The solid was filtered under an inert atmosphere, washed with 20 mL of degassed water to remove NH_4ClO_4 , then washed with 5 mL of degassed methanol, and dried in vacuo. The isolated solid consisted of 0.35 g of air-sensitive yellow blocks of $(n\text{-Bu}_4\text{N})_3[\text{Tc}(\text{NCS})_6]$, 93% based on technetium. Anal. Calcd for $\text{C}_{54}\text{H}_{108}\text{N}_9\text{S}_6\text{Tc}$: C, 55.20; H, 9.27; N, 10.73; S, 16.37. Found: C, 54.60; H, 9.31; N, 12.17; S, 17.10. Optical spectrum (degassed methanol): 440 nm (sh), 403 (ϵ 19 400), 280 (sh). Optical spectrum (degassed CH_3CN): 412 nm (ϵ 25 800), 392 (sh), 285 (sh). IR (methanol): ν_{CN} 2050 cm^{-1} (s). IR (KBr): 2950 (m), 2920 (m), 2860 (m), 2110 (m), 2064 (s), 1483 (m), 1460 (m), 1435 (w), 1375 (w), 1360 (w), 1145 (w), 1102 (w), 1080 (w), 1062 (w), 1018 (w), 950 (w), 878 (w), 823 (w), 737 (w), 730 (w), 477 (w), 318 (m) cm^{-1} . Raman (solid): 2124 (m), 2093 (s), 2076 (s) cm^{-1} . Magnetic moment: $\mu_{\text{eff}}(298 \text{ K}) = 3.0\text{--}3.3 \mu_{\text{B}}$. Conductivity (3:1 electrolyte in acetonitrile): $\Lambda_0 = 580 \text{ cm}^2 \Omega^{-1} \text{equiv}^{-1}$. $E_{1/2}(\text{cathodic}) = -1.09 \text{ V vs. SCE}$ (irreversible); $E_{1/2}(\text{anodic}) = 0.18 \text{ V vs. SCE}$ (1 e reversible).

Preparation of Tetraphenylarsonium Hexakis(isothiocyanato)technetate(III). This salt was obtained from the yellow methanol solution prepared as mentioned above. Addition of 1.0 g of $\text{Ph}_4\text{AsCl} \cdot \text{H}_2\text{O}$ in 5 mL of degassed methanol yielded crystals that were collected under an inert atmosphere, washed with three 5-mL aliquots of degassed methanol, and then dried in vacuo. The yield of yellow-orange air-sensitive needles of $(\text{Ph}_4\text{As})_3[\text{Tc}(\text{NCS})_6]$ was 0.21 g, 91% based on technetium. Anal. Calcd for $\text{C}_{78}\text{H}_{60}\text{As}_3\text{N}_9\text{S}_6\text{Tc}$: C, 58.64; H, 3.79; N, 5.26; S, 12.04. Found: C, 57.55, 57.67; H, 4.11, 4.02; N, 5.21, 4.92; S, 14.08, 12.09. Optical spectrum (degassed CH_3CN): 411 nm (ϵ 28 300), 390 (sh), 285 (sh). IR (KBr): 3050 (w), 2070 (s), 1576 (w), 1481 (m), 1436 (m), 1390 (w), 1333 (w), 1310 (w), 1273 (w), 1180 (w), 1159 (w), 1069 (m), 1019 (w), 997 (m), 920 (w), 845 (w), 815 (w), 736 (s), 683 (s), 610 (w), 475 (m), 460 (m), 360 (w), 345 (m), 310 (m) cm^{-1} .

Reaction of $[\text{Tc}(\text{NCS})_6]^{3-}$ with $(\text{SCN})_2$. To a thoroughly purged 100-mL round-bottom flask equipped with a stir bar were added 0.10 g (0.06 mmol) of $(\text{Ph}_4\text{As})_3[\text{Tc}(\text{NCS})_6]$ and 50 mL of degassed acetone. A solution of 0.05 M $(\text{SCN})_2$ in CCl_4 , 1.0 mL, was added to the yellow solution, which then turned purple instantly. Addition of degassed isobutyl alcohol and subsequent removal of the acetone by evaporation (in vacuo) resulted quantitatively in the formation of purple crystals of $(\text{Ph}_4\text{As})_2[\text{Tc}(\text{NCS})_6]$. A similar reaction was observed when acetonitrile was used instead of acetone as the solvent.

Reaction of $[\text{Tc}(\text{NCS})_6]^{3-}$ with NO(g). To a thoroughly purged 50-mL, three-neck round-bottom flask equipped with a stir bar was added 0.050 g (0.043 mmol) of $(n\text{-Bu}_4\text{N})_3[\text{Tc}(\text{NCS})_6]$ from a Schlenk tube. The yellow solid was dissolved in 25 mL of degassed dichloromethane, added via a cannula. Nitric oxide (NO) gas was

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Table I. Experimental Details of the X-ray Diffraction Study of $(n\text{-Bu}_4\text{N})_3[\text{Tc}(\text{NCS})_6]$

(A) Crystal Parameters ^a at 26 °C	
$a = b = c = 24.444$ (6) Å	mol wt 1174.8
$Z = 8$	space group $Pa\bar{3}$
$V = 14\ 606$ Å ³	$\rho_{\text{calcd}} = 1.068$ g/cm ³
(B) Measurement of Intensity Data	
instrument: Enraf-Nonius CAD-4F diffractometer	
radiation: Mo K α ($\lambda_{\alpha_1} = 0.7093$ Å), graphite monochromatized	
takeoff angle: 2.5°	
detector aperture: vertical 4 mm; horizontal $A + B \tan \theta$ ($A = 3$ mm, $B = 1$ mm)	
crystal-detector dist: 173 mm	
2θ limits: 3–40°	
scan type: θ (crystal)– 2θ (counter)	
scan rate: variable, 1–20°/min in θ	
θ scan width: $A + B \tan \theta$ ($A = 0.7^\circ$, $B = 0.35^\circ$)	
bkgd measurements: moving crystal; moving detector (25% added to scan at both ends of each scan)	
stds: 3 reflections (226), (262), and (622) measured after each 3600 s of exposure time	
(C) Treatment of Intensity Data ^b	
reduction to preliminary F_o^2 and $\sigma(F_o^2)$: correction for background, attenuators, and Lorentz-polarization effects of monochromatized X radiation in the usual manner, ^c with modifications to account for the variable scan speed; a value of 0.04 was used for the "fudge factor" ^d	
absorption corr: $\mu = 3.915$ cm ⁻¹ ; transmission factors varied between 0.88 and 0.91	
obsd data: 1918 unique reflections of which 796 having $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement	

^a From a least-squares fit to the setting angles of 25 reflections. The crystals were oriented by using the automatic search and centering routines of the Enraf-Nonius CAD-4F computing package.

^b Programs for an IBM 360/91 computer used in this work are as follows: ORABS, the local version of the absorption correction program by D. J. Wehe, W. R. Busing, and H. A. Levy; FOURIER, the Dellaca and Robinson modification of the Zalkin Fourier program FORDAP; CUGLS, the local version of the Busing-Martin-Levy structure factor calculation and least-squares refinement program (ORFLS) modified by Ibers and Doedens for rigid-body refinement; ORFFE, the Busing-Martin-Levy molecular geometry and error function program; ORTEP II, the Johnson thermal ellipsoid plotting program; in addition to various local data processing programs. ^c Reference 16. ^d Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* 1967, 6, 197.

bubbled through the stirred yellow solution for 5 min; the solution quickly changed color to a bright purple. Optical spectroscopy revealed an absorption at 500 nm due to $[\text{Tc}(\text{NCS})_6]^{2-}$. No absorption at 400 nm ($[\text{Tc}(\text{NCS})_6]^{3-}$) nor any other new absorption due to a nitrosyl species could be observed.

Decomposition of $[\text{Tc}(\text{NCS})_6]^{2-}$ with Hydrogen Peroxide. (a) **Basic Media.** To a 50-mL beaker equipped with stir bar were added 0.015 g (0.03 mmol) of $(\text{NH}_4)_2[\text{Tc}(\text{NCS})_6]$, 20 mL of water, and 3.0 mL of 30% H_2O_2 . Next, 1.0 mL of 2.5% w/w NaOH solution was added, resulting in an instantaneous effervescence, $\text{O}_2(\text{g})$, and a color change from purple to yellow. Optical spectroscopy showed a band at 400 nm due to the presence of $[\text{Tc}(\text{NCS})_6]^{3-}$. The yellow color slowly bleached until only SCN^- and TeO_4^- were left.

(b) **Acidic Media.** The same conditions as above were duplicated with the exception that 1.0 mL of 18 M sulfuric acid was added instead of the base. The solution quickly turned red and then orange prior to complete bleaching of the color. Bands in the optical spectrum appeared from 430 to 490 nm as well as at 350 nm before complete oxidation to TeO_4^- was accomplished.

(c) **Neutral Media.** The reaction was run with use of conditions similar to those of the two previously described experiments, except that no acid or base was used. A slow conversion of $[\text{Tc}(\text{NCS})_6]^{2-}$ to a red-orange mixture (band maxima at 455 and 335 nm)¹⁴ followed by a slow bleaching to TeO_4^- was observed.

Collection and Reduction of X-ray Data. Several crystals of $(n\text{-Bu}_4\text{N})_3[\text{Tc}(\text{NCS})_6]$ suitable for X-ray study were mounted in Lin-

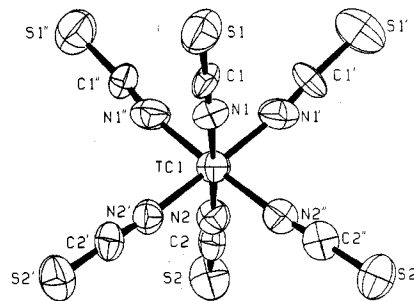


Figure 1. Geometry of the hexakis(isothiocyanato)technetate(III) anion showing the atom labeling scheme and 40% probability thermal ellipsoids. Primed and unprimed atoms are related by a crystallographic threefold rotation axis.

demann glass capillary tubes. This procedure was performed under an argon atmosphere in a glovebag with appropriate precautions taken due to the radioactivity of the technetium. The crystal density was not measured. Preliminary precession and Weissenberg photographs showed $m\bar{3}$ Laue symmetry with the systematic absences $0kl$, $k = 2n + 1$, consistent with the space group $Pa\bar{3}$ (T_h^6).¹⁵ Subsequent examination of data collected by the diffractometer confirmed the crystal class and extinctions. It was also noted that in the X-ray beam the crystal turned from yellow to orange much more rapidly than did crystals not exposed to X-rays. The intensities of the reflections were not affected, however.

The crystal used for collecting the data set was a block of dimensions $0.334 \times 0.334 \times 0.266$ mm. Crystal data and details of data collection and reduction are given in Table I. Only 1408 reflections with $3^\circ \leq 2\theta \leq 40^\circ$ had F_o^2 greater than $3\sigma(F_o^2)$, and these were further reduced to a set of 796 unique reflections. The R factor for averaging these reflections was 0.024.¹⁶ Data sets collected (one with Cu radiation) on two other crystals showed a similar ratio (796:1122; see Table I) of observed to unobserved reflections.

Determination and Refinement of the Structure. From a sharpened Patterson map, the technetium atom was found to occupy the special position on the threefold axis x, x, x , where $x = 0.193$. A structure factor calculation gave a value of 0.57 for $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. A series of difference Fourier maps revealed the positions of the two thiocyanate ligands and the one tetra- n -butylammonium ion comprising the asymmetric unit. Several cycles of least-squares refinement were then carried out, minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2 / \sigma^2(F_o^2)$.^{17a} Anisotropic temperature factors were employed for atoms in the $[\text{Tc}(\text{NCS})_6]^{3-}$ anion and isotropic temperature factors for those in the tetra- n -butylammonium cation. Corrections for anomalous dispersion effects were included for the technetium and sulfur atoms.^{17b} A difference Fourier map revealed the hydrogen atom positions. These atoms were assigned isotropic temperature factors equal to 1.5 \AA^2 plus the temperature factors of the atoms to which they were attached. Hydrogen atom contributions were included in subsequent cycles of least-squares refinement, but no attempt was made to refine their positional or thermal parameters.

After several cycles of refinement, the parameter shifts became less than 0.05 of their standard deviations and the refinement was terminated. The final R_1 value was 0.065, and the final values for the weighted discrepancy index, $R_2 = [\sum w(|F_o| - |F_c|)^2]^{1/2}$, and the error in an observation of unit weight, $[\sum w(|F_o| - |F_c|)^2 / (\text{NO} - \text{NV})]^{1/2}$, where $\text{NO} = 796$ independent observations and $\text{NV} = 126$ variables, were 0.072 and 2.11, respectively. Inspection of the function $\sum w\Delta^2$ for reflections ordered according to $|F_o|$ and $(\sin \theta) / \lambda$ showed satisfactory consistency.

A final difference Fourier map revealed one peak of 1 e/\AA^3 situated on the threefold axis (body diagonal) with $x \approx 0.30$. All other positive and negative peaks had magnitudes of 0.37 e/\AA^3 or less. A typical

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(17) (a) Scattering factors for the neutral, nonhydrogen atoms were taken from: "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 72 ff. Hydrogen atom scattering factors were those of: Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* 1965, 42, 3175. (b) Anomalous scattering factors were those of: Cromer, D. T.; Liberman, D. *J. Chem. Phys.* 1970, 53, 1891.

(14) This corresponds to the band maxima in $\text{TcO}(\text{NCS})_2^{2-}$: Trop, H. S.; Jones, A. G.; Davison, A., unpublished results.

Table II. Final Positional and Thermal Parameters for $[(n-C_4H_9)_4N]_3[Tc(NCS)_6]^{a-c}$

atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Tc(1)	0.193 91 (7)	0.19 391	0.193 91	2.42 (4)	2.42	2.42	-0.07 (4)	-0.07	-0.07
S(1)	0.3196 (2)	0.1438 (3)	0.3342 (2)	3.58 (19)	5.89 (22)	3.24 (16)	1.16 (15)	-0.15 (14)	-0.79 (15)
S(2)	0.0626 (2)	0.2713 (2)	0.0692 (2)	3.37 (16)	4.14 (18)	3.50 (17)	0.53 (13)	-0.08 (14)	1.03 (14)
C(1)	0.2758 (8)	0.1600 (9)	0.2848 (8)	1.9 (5)	3.5 (6)	1.0 (5)	1.1 (5)	-0.0 (4)	-0.0 (6)
N(1)	0.2484 (7)	0.1671 (7)	0.2515 (7)	2.9 (5)	3.2 (5)	2.5 (6)	-0.4 (4)	-0.2 (4)	-0.7 (4)
C(2)	0.1070 (9)	0.2446 (9)	0.1097 (9)	2.8 (7)	2.8 (6)	2.1 (7)	-0.1 (5)	0.7 (5)	0.4 (5)
N(2)	0.1380 (7)	0.2239 (7)	0.1389 (7)	2.9 (5)	2.4 (5)	2.1 (5)	0.1 (4)	0.1 (4)	0.4 (4)

atom	x	y	z	$B, \text{\AA}^2$	atom	x	y	z	$B, \text{\AA}^2$
N(4)	-0.0306 (6)	0.2388 (6)	0.2582 (6)	6.1 (4)	C(31)	-0.0550 (8)	0.2875 (7)	0.2311 (7)	6.6 (5)
C(11)	-0.0777 (7)	0.2053 (7)	0.2806 (7)	6.8 (5)	C(32)	-0.0152 (8)	0.3298 (8)	0.2089 (8)	8.6 (6)
C(12)	-0.0616 (8)	0.1521 (8)	0.3093 (8)	9.2 (6)	C(33)	-0.0468 (10)	0.3803 (11)	0.1880 (11)	12.9 (8)
C(13)	-0.1094 (10)	0.1261 (10)	0.3392 (10)	11.7 (8)	C(34)	-0.0121 (12)	0.4198 (13)	0.1653 (12)	18.0 (11)
C(14)	-0.0882 (10)	0.0745 (11)	0.3670 (10)	13.4 (8)	C(41)	0.0080 (7)	0.2525 (8)	0.3054 (8)	7.0 (5)
C(21)	0.0020 (7)	0.2024 (7)	0.2180 (7)	6.8 (5)	C(42)	-0.0167 (8)	0.2917 (8)	0.3469 (9)	8.8 (6)
C(22)	-0.0282 (7)	0.1841 (8)	0.1684 (8)	7.5 (5)	C(43)	0.0113 (11)	0.2886 (10)	0.3997 (11)	13.9 (9)
C(23)	0.0034 (9)	0.1397 (9)	0.1391 (9)	9.2 (6)	C(44)	-0.0120 (11)	0.3285 (10)	0.4411 (11)	14.4 (9)
C(24)	-0.0264 (9)	0.1214 (9)	0.0892 (9)	11.2 (7)					

^a Atoms in the anion are labeled as indicated in Figure 1. ^b Numbers in parentheses are errors in the last significant digit(s). ^c The anisotropic temperature factors are $\times 10^3$. The anisotropic temperature factors are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table III. Interatomic Distances (\AA) and Angles (Deg) for $[(n-C_4H_9)_4N]_3[Tc(NCS)_6]^{a,c}$

Hexakis(isothiocyanato) technetate(III) Anion			
Tc-N(1)	2.04 (2)	Tc-N(2)	2.05 (2)
N(1)-C(1)	1.07 (2)	N(2)-C(2)	1.16 (2)
C(1)-S(1)	1.67 (2)	C(2)-S(2)	1.60 (2)
N(1)-Tc-N(2)''	88.0 (6)	Tc-N(1)-C(1)	170 (2)
N(1)-Tc-N(1)'	89.0 (7)	N(1)-C(1)-S(1)	176 (3)
N(2)-Tc-N(2)'	92.1 (7)	Tc-N(2)-C(2)	175 (2)
N(1)-Tc-N(2)'	90.9 (6)	N(2)-C(2)-S(2)	178 (2)
N(1)-Tc-N(2)	177.0 (8)		
Tetra- <i>n</i> -butylammonium Cation			
N(4)-C(11)	1.51 (2)	N(4)-C(21)	1.55 (2)
C(11)-C(12)	1.53 (2)	C(21)-C(22)	1.49 (2)
C(12)-C(13)	1.52 (3)	C(22)-C(23)	1.51 (2)
C(13)-C(14)	1.52 (3)	C(23)-C(24)	1.49 (2)
N(4)-C(31)	1.49 (2)	N(4)-C(41)	1.53 (2)
C(31)-C(32)	1.52 (2)	C(41)-C(42)	1.52 (2)
C(32)-C(33)	1.54 (3)	C(42)-C(43)	1.46 (3)
C(33)-C(34)	1.40 (3)	C(43)-C(44)	1.52 (3)
C(11)-N(4)-C(21)	108 (1)	C(21)-N(4)-C(31)	112 (1)
C(11)-N(4)-C(31)	107 (1)	C(21)-N(4)-C(41)	107 (1)
C(11)-N(4)-C(41)	108 (1)	C(31)-N(4)-C(41)	114 (1)
N(4)-C(11)-C(12)	115 (2)	N(4)-C(21)-C(22)	116 (2)
C(11)-C(12)-C(13)	112 (2)	C(21)-C(22)-C(23)	110 (2)
C(12)-C(13)-C(14)	107 (2)	C(22)-C(23)-C(24)	111 (2)
N(4)-C(31)-C(32)	117 (2)	N(4)-C(41)-C(42)	113 (1)
C(31)-C(32)-C(33)	110 (2)	C(41)-C(42)-C(43)	112 (2)
C(32)-C(33)-C(34)	112 (2)	C(42)-C(43)-C(44)	112 (2)

^a See footnotes *a* and *b* of Table II and Figure 1.

carbon atom had an electron density of $2.0 e/\text{\AA}^3$.

The final nonhydrogen atomic positions and thermal parameters together with their standard deviations are reported in Table II. The interatomic distances and angles are contained with their standard deviations in Table III. A listing of the final observed and calculated structure factor amplitudes and root-mean-square amplitudes of thermal vibration are available as Tables S1 and S2, respectively.¹⁸ Hydrogen atom positions and thermal parameters are listed in Table S3.¹⁸ A view of the $[Tc(NCS)_6]^{3-}$ anion and the atom labeling scheme are given in Figure 1.

Results and Discussion

The reaction between $(NH_4)_2TcX_6$ ($X = Cl, Br$) and NH_4SCN in refluxing methanol produces a deep red-violet solution with absorption bands in the visible region of the spectrum at 400 and 500 nm. Chromatography of the reaction

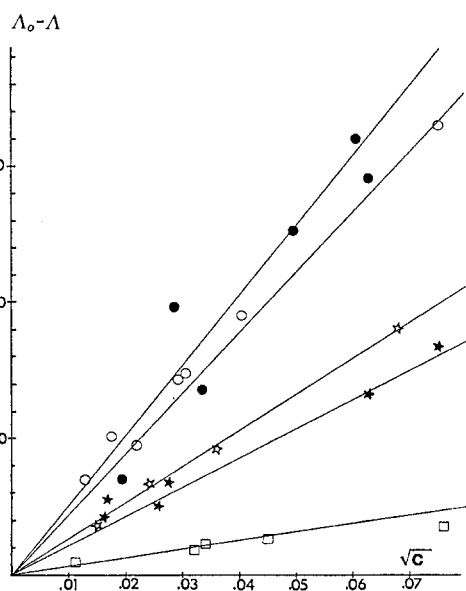


Figure 2. Equivalent conductance measurements in acetonitrile: $(n-Bu_4N)(ClO_4)$, \square ; $(n-Bu_4N)_2[TcCl_6]$, \star ; $(Me_4N)_3[Fe(NCS)_6]$, \circ ; $(NH_4)_2[Tc(NCS)_6]$, \star ; $(n-Bu_4N)_3[Tc(NCS)_6]$, \bullet . The data plotted are $\Lambda_0 - \Lambda$ ($\text{cm}^2 \Omega^{-1} \text{equiv}^{-1}$) vs. the square root of the equivalent concentration.

mixture on a column filled with Sephadex LH-20 resin (lipophilic) with methanol as the eluant results in the separation of ammonium thiocyanate, a yellow band (λ_{max} 400 nm), and a purple band (λ_{max} 500 nm), successively. Evaporation of the purple solution produces a purple microcrystalline powder with a bright green reflex. Elemental analysis of this material is in agreement with its formulation as $(NH_4)_2[Tc(NCS)_6]$, a d^3 octahedral technetium(IV) complex. Metathesis of this with tetraphenylarsonium ion results in the formation of $(Ph_4As)_2[Tc(NCS)_6]$, which can be recrystallized from acetone/isobutyl alcohol mixtures as dark purple plates with a green reflex.

The reaction of either TcO_4^- or $TcO_2 \cdot xH_2O$ (freshly prepared from the hydrolysis of $[TcX_6]^{2-}$ with base) with hot acidic solutions of thiocyanate ion produces dark brown solutions with visible absorption bands at 400 and 500 nm. Treatment of such solutions with cerium(IV) salts, followed by precipitation with univalent organic cations, leads to the isolation of $[Tc(NCS)_6]^{2-}$ salts.

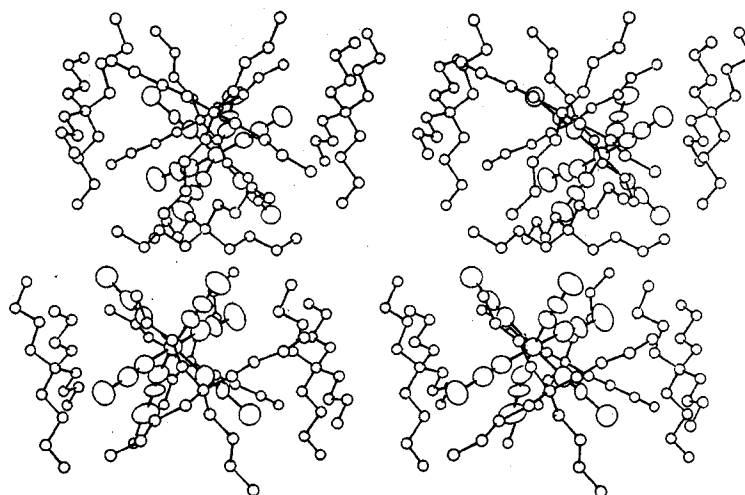


Figure 3. Stereoscopic crystal packing diagram of $(n\text{-Bu}_4\text{N})_3[\text{Tc}(\text{NCS})_6]$ viewed approximately along the $[010]$ direction with a horizontal.

Table IV. Infrared Spectral Data of $[\text{Tc}(\text{NCS})_6]^{2-}$ Salts (cm^{-1})

compd	ν_{CN}^a	$\nu_{\text{Tc-N}}^a$	ν_{NCS^-} (bend) ^a
$(\text{NH}_4)_2[\text{Tc}(\text{NCS})_6]$	2030 (s)	320 (m)	470 (w)
$(\text{Ph}_4\text{As})_2[\text{Tc}(\text{NCS})_6]$	2020 (s)	325 (m)	460 (w)
$(n\text{-Bu}_4\text{N})_3[\text{Tc}(\text{NCS})_6]^c$	2110 (m)	318 (m)	477 (w)
	2064 (s)		
	2050 (s) ^b		
$(\text{Ph}_4\text{As})_3[\text{Tc}(\text{NCS})_6]$	2070 (s)	310 (m)	475 (m)

^a KBr pellet. ^b Solution spectra in methanol. ^c Raman (solid) spectral data: ν_{CN} 2124 (m), 2093 (s), 2076 (s) cm^{-1} .

As shown in Table IV, in the infrared spectrum of both the NH_4^+ and Ph_4As^+ salts, one strong band in the cyanide stretching region is observed, consistent with the proposed octahedral geometry. A band at $320 \pm 5 \text{ cm}^{-1}$ can be assigned as the Tc-N stretching frequency. There is no evidence for a Tc=O, Tc₂O₃, or TcO₂ linkage in the infrared spectrum. Equivalent conductance measurements¹⁹ show the ammonium salt to be a 1:2 electrolyte in acetonitrile, similar to $(n\text{-Bu}_4\text{N})_2[\text{TcCl}_6]$ (Figure 2). The visible spectrum is dominated by an intense charge-transfer absorption (λ_{max} 500 nm, ϵ 76 200) in acetonitrile.

Magnetic susceptibility measurements on the Ph_4As^+ salt, $\mu_{\text{eff}}(298 \text{ K}) = 4.1 \mu_{\text{B}}$, are consistent with a $^4\text{A}_{2g}$ ground state for an octahedral d^3 ion and in the range observed for the hexahalometalate(IV) salts.²⁰ Like salts of $[\text{TcCl}_6]^{2-}$, the complex does not show an EPR signal at room temperature or 77 K,²¹ despite the $^4\text{A}_{2g}$ ground state.

Voltammetric studies in acetonitrile (Table V) on either the NH_4^+ or the Ph_4As^+ salt reveal an irreversible oxidation at 1.60 V vs. SCE. The analogous rhenium complex $[\text{Re}(\text{NCS})_6]^{2-}$ displays an irreversible oxidation at 1.23 V vs. SCE. As was the case with the hexahalometalate(IV) species,⁸ oxidation is very difficult, and the expected periodic trend is observed; rhenium(IV) is oxidized to rhenium(V) with greater ease than technetium(IV) is oxidized to technetium(V). Salts of $[\text{Tc}(\text{NCS})_6]^{2-}$ also show a reversible one-electron reduction at +0.18 V vs. SCE. The corresponding rhenium reduction is more difficult,⁸ occurring at -0.11 V vs. SCE.

Treatment of solutions of $[\text{Tc}(\text{NCS})_6]^{2-}$ with large excesses of thiocyanate ion (10^3 :1 SCN^- :Tc) results in formation of

Table V. Electrochemical Measurements of $[\text{M}(\text{NCS})_6]^{2-}$ Species

compd	$E_{1/2}$ (cathodic), V^a	$E_{1/2}$ (anodic), V^a
$(\text{NH}_4)_2[\text{Tc}(\text{NCS})_6]$	0.18 (1 e rev)	1.60 (irrev)
$(\text{Ph}_4\text{As})_2[\text{Tc}(\text{NCS})_6]$	0.18 (1 e rev)	1.60 (irrev)
$(n\text{-Bu}_4\text{N})_3[\text{Tc}(\text{NCS})_6]$	-1.10 (irrev)	0.18 (1 e rev) ^b
$(n\text{-Bu}_4\text{N})_2[\text{Re}(\text{NCS})_6]$	-0.11 (1 e rev)	1.23 (irrev)

^a Measurements taken in acetonitrile/0.1 M TBAP; all potentials vs. SCE. ^b A plot of the diffusion current at the anodic peak potential vs. the square root of the scan rate (20–200 mV s^{-1}) in the cyclic voltammogram showed a linear dependence.

orange solutions and the appearance of a band at 400 nm in the optical spectrum. Reduction of pertechnetate with $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in the presence of thiocyanate ion produces a deep yellow solution with an absorption band at 400 nm. These solutions are air sensitive, slowly turning purple with time.

The red-violet solution resulting from the reaction between $(\text{NH}_4)_2[\text{TcX}_6]$ and NH_4SCN in refluxing methanol can be converted to a brilliant yellow solution via the addition of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$. Solutions of $(\text{NH}_4)_2[\text{Tc}(\text{NCS})_6]$, without free SCN^- , also react similarly. When degassed solutions are used and care is taken to avoid contamination with oxygen, addition of large univalent cations to the yellow methanol solutions leads to formation of air-sensitive yellow to yellow-orange crystals of $\text{M}_3[\text{Tc}(\text{NCS})_6]$ ($\text{M} = n\text{-Bu}_4\text{N}^+$, Ph_4As^+).

The structure of $[(n\text{-Bu})_4\text{N}]_3[\text{Tc}(\text{NCS})_6]$, determined by X-ray crystallography, consists of tetra-*n*-butylammonium cations packed in an approximately body-centered arrangement (Figure 3). Distances between the central and corner cations range from 7.92 to 9.67 Å. Each hexakis(isothiocyanato)technetate anion is surrounded by two sets of cations, related by a threefold axis at distances of 5.81 and 6.92 Å. The technetium atom of the $[\text{Tc}(\text{NCS})_6]^{2-}$ anion lies on the crystallographic threefold axis and has approximately octahedral symmetry (Table III). Crystal structure determinations for several other mononuclear²² and binuclear²³ compounds show that technetium(III) can have octahedral six-coordinate, distorted capped octahedral seven-coordinate, and quadruply bonded geometries. The Tc-N bond lengths of 2.04 (2) and 2.05 (2) Å found in the present study may be compared with the average Tc-O distances of 2.01 (1) Å, observed for *trans*-chlorobis(pentane-2,4-dionato)(triphenylphosphine)technetium(III),²² and 2.032 (4) Å, reported for tetrakis(pi-

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valato)dichloroditechnetate(III).²³ The slightly larger Tc-N bond lengths are consistent with the 0.04 Å larger covalent radius of nitrogen compared with oxygen.²⁴ It is interesting that the Tc-N distances are the same as those reported for (Me₄N)₃[Fe(NCS)₆], 2.03 (2)-2.06 (2) Å.²⁵ Since technetium(III) has the same octahedral covalent radius as iron(III), it might substitute for iron(III) in biological systems.

Other features of the geometry (Table III) are normal. The relatively low accuracy of the structure determination results from the small amount of high-angle data. The Tc-N-C and N-C-S angles are all within 10° of linearity. The average N-C (1.12 (5) Å) and C-S (1.64 (4) Å) distances agree with those found for the iron(III) analogue, 1.14 (4) and 1.62 (4) Å, respectively, as do the various bond angles (cf. ref 25). There was no evidence for disorder of the tetra-*n*-butylammonium carbon atoms.

The tetraphenylarsonium salt in a KBr pellet and solutions of [Tc(NCS)₆]³⁻ exhibit a single, strong band in the cyanide stretching region of the infrared spectra (Table IV), consistent with octahedral symmetry. In the case of (*n*-Bu₄N)₃[Tc(NCS)₆], two bands are observed in the infrared and three in the Raman spectra, rather than the one infrared-active and two Raman-active bands predicted for an octahedral anion. Unfortunately, satisfactory Raman spectra in solution have not been obtainable for [Tc(NCS)₆]³⁻, to date. The observed behavior of the *n*-Bu₄N⁺ salt must be due to solid-state effects; the X-ray structure determination reveals there to be two crystallographically independent thiocyanate ligands. The octahedral iron(III) thiocyanate complex (Me₄N)₃[Fe(NCS)₆] displays three bands in the cyanide stretching region of the infrared spectrum in the solid,¹⁰ and, yet, an X-ray structure has confirmed it as a generally octahedral six-coordinate complex,²⁵ although there are two crystallographically distinct octahedra, one of which has a markedly nonlinear Fe-N-C-S moiety (Fe-N-C = 146 (2)°).

The observed magnetic moment of the technetium(III) complex, 3.0-3.3 μ_B at 298 K, is in the range expected for a d⁴ ion with two unpaired electrons.¹³ No EPR spectrum was obtainable at room temperature or 77 K. Equivalent conductance measurements (Figure 2) on (*n*-Bu₄N)₃[Tc(NCS)₆] in acetonitrile are consistent with a 1:3 electrolyte; cf. (Me₄N)₃[Fe(NCS)₆]. The optical spectrum has an intense band at approximately 400 nm (ε ~ 22 000), which is solvent dependent in shape and intensity.

The voltammetric behavior of the hexakis(isothiocyanato)technetate(III) ion is summarized in Table V. The complex exhibits an irreversible one-electron reduction at -1.10 V vs. SCE. More importantly, a reversible one-electron oxidation at 0.18 V vs. SCE is observed. As mentioned earlier, solutions of [Tc(NCS)₆]³⁻ are air sensitive and convert to [Tc(NCS)₆]²⁻ upon exposure to oxygen. This reaction can be monitored spectrophotometrically. An isosbestic point occurs at ~435 nm; as the band at 400 nm decreases, the band at 500 nm increases. Addition of cerium(IV) or thiocyanogen, (SCN)₂, oxidizes solutions of [Tc(NCS)₆]³⁻ rapidly to [Tc(NCS)₆]²⁻. In addition, bubbling NO through a purged dichloromethane solution of [Tc(NCS)₆]³⁻ rapidly produces [Tc(NCS)₆]²⁻. The behavior described is consistent with both species, comprising a one-electron reversible redox couple, eq 2, with E_{1/2} = 0.18 V vs. SCE.

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Registry No. (NH₄)₂[Tc(NCS)₆], 72622-85-6; (Ph₄As)₂[Tc(NCS)₆], 71128-60-4; (*n*-Bu₄N)₃[Tc(NCS)₆], 72622-87-8; (Ph₄As)₃[Tc(NCS)₆], 72622-88-9; (*n*-Bu₄N)₂[Re(NCS)₆], 16985-65-2; NH₄SCN, 1762-95-4; (NH₄)₂[TcBr₆], 29462-54-2; (NH₄)₂[TcCl₆], 18717-26-5; NH₄TcO₄, 13598-66-8; TcO₂, 12036-16-7.

Supplementary Material Available: Tables S1-S3 listing respectively observed and calculated structure factor amplitudes, the root-mean-square amplitudes of thermal vibration along principal axes, and the hydrogen atom positional and thermal parameters (8 pages). Ordering information is given on any current masthead page.

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Contribution No. 3378 from the Department of Chemistry, Indiana University, Bloomington, Indiana 47405

Complexes of (Arylimido)molybdenum(V)

A. WINSTON EDELBLUT and R. A. D. WENTWORTH*

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The preparations of the paramagnetic Mo(V) complexes Mo(NR)(S₂P(OEt)₂)₃ and Mo(NR)Cl(S₂P(OEt)₂)₂ (R = Ph and tol) from Mo(CO)₄Cl₂, NH₄S₂P(OEt)₂, and the aryl azides are described. The stability of the imido ligand in each complex to protonation is demonstrated. The isotropic ESR spectra of these complexes are notable. Every ligand in these complexes contains a magnetic nucleus (¹⁴N, ³¹P, and ^{35,37}Cl), and coupling to each of these nuclei is manifested in the ESR spectra. Superhyperfine coupling constants are obtained unambiguously, however, only after ¹⁵N labeling. Stereochemistries cannot be deduced with certainty either from ESR or infrared spectra or from chemical evidence. The reaction of Mo(Ntol)(S₂P(OEt)₂)₃ with H₂S produces the unusual tetranuclear compound [Mo(Ntol)S(S₂P(OEt)₂)₄]. The equilibrium constant relating this complex to the dinuclear compound has been determined. A rationalization of the tetranuclear nature of the compound is discussed, and a structure is suggested.

Introduction

The affinity of the oxo ligand for molybdenum in its higher oxidation states is well-known.^{1,2} Simple arguments concerning the participation of the metal's d orbitals in π bonding with this ligand provide an adequate explanation for stereo-

chemistry as well as bond distances, stretching force constants, and ¹⁷O chemical shifts.^{3,4} Recently, we recognized that one or more NR (R = H, alkyl, or aryl) ligands should bind to molybdenum in a manner which is fundamentally equivalent to the binding of an identical number of oxo ligands since each

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