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Synthesis and Characterization of Oxopentakis(isothiocyanato)metalate(V) Complexes of Rhenium and Technetium

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The reduction of perrhenate with thiocyanate ion has been shown to produce $ReO(NCS)_5^{2-}$ and $Re(NCS)_6^{2-}$. The rhenium(V) complex, $ReO(NCS)_5^{2-}$, can be prepared from $[ReOBr_4{\cdot}CH_3CN]^-$ or $ReOCl_5^{2-}$ by ligand substitution. The analogous technetium complex, $TcO(NCS)_5^{2-}$, has been prepared by ligand substitution on $TcOCl_4^-$. Physical data for these complexes are presented, and their involvement in the reduction of MO_4^- (M = Re, Tc) with thiocyanate ion is discussed.

Introduction

The exact nature of the technetium and rhenium complexes formed in the spectrophotometric determination of these elements using thiocyanate ion[2-5] has been of interest for many years. Although the methods are quite sensitive,[2-6] small changes in procedure and concentrations can lead to large changes in band positions and intensities, suggesting that more than a single species is formed in either system.

The first treatment of the rhenium system was attempted in 1935 by Druce,[7] who observed that perrhenate reacted with thiocyanate ion in hydrochloric acid in the presence of stannous ion to produce a red species formulated as "$ReO(SCN)_4$" which was soluble in ether and other polar organic solvents. Later work by Holeman[8] concluded that the correct oxidation state was more likely to be five than six. Ryabchikov and others[9] next examined the reduction and claimed the isolation of $[Pt(NH_3)_4]_3[ReO_2(NCS)_4]_2$ although no infrared evidence was given. Bands at 350 and 420 nm were assigned to this proposed analogue of $ReO_2(CN)_4^{3-}$.[10]

Bailey and Kozak examined molten salt reactions of K_2ReCl_6[11] and $ReCl_5$[12] with KSCN, isolating species described as $Cs_2Re(SCN)_6$ and $CsRe(SCN)_6$, respectively, from the reactions. They also examined the reduction of perrhenate with thiocyanate and stannous ions in hydrochloric acid.[12] They ascribed the absorption bands observed at 365 and 420 nm to $Re(SCN)_6^-$ and $Re(SCN)_6^{2-}$, respectively.[13] Addition of excess stannous ion led to formation of $Re(NCS)_6^{2-}$, exclusively.

Recent electrochemical studies on hexahalometalate(IV) ions (M = Re, Tc; X = Cl, Br) demonstrated that oxidations to hexahalometalate(V) ions were very difficult.[14] In addition, the technetium thiocyanate system has recently been shown to consist of a redox couple between $Tc(NCS)_6^{2-}$ and $Tc(NCS)_6^{3-}$,[15] technetium(IV) and technetium(III) complexes, respectively. Thus the reports of a stable hexakis(isothiocyanato)rhenate(V) complex as well as repeated references to possible oxorhenium complexes seemed to warrant yet another examination of the complex thiocyanate chemistry of rhenium. During the course of this investigation, an examination into the chemistry of an oxotechnetium(V) complex with thiocyanate ion was also carried out.

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 (Southwestern Analytical) was dried in vacuo at 85 °C for 24 h prior to use. All manipulations with possibly air-sensitive complexes were carried out in N_2 or Ar atmospheres, with use of standard Schlenk-line or drybox techniques.

Sodium perrhenate was purchased from Cleveland Refractory Metals, Solon, OH. Rhenium pentachloride was obtained from ROC/RIC, sealed under Ar, and used in a drybox.

The preparations of K_2ReCl_6,[16] $(n\text{-}Bu)_4NReOBr_4{\cdot}CH_3CN$,[17] $Ph_4AsReOBr_4{\cdot}CH_3CN$,[17] and $[(n\text{-}Bu)_4N]_2Re_2Cl_8$[18] are described elsewhere. Both $Cs_2Re(NCS)_6$[11] and "$CsRe(NCS)_6$"[12] were prepared by the methods published by Bailey and Kozak. The literature preparation of $[(n\text{-}Bu)_4N]_2Re(NCS)_6$ from $[(n\text{-}Bu)_4N]_2Re_2Cl_8$ was followed.[19] The synthesis of $(n\text{-}Bu)_4NTcOCl_4$ was performed by the reduction of pertechnetate with concentrated hydrochloric acid;[20] the preparation of K_2ReOCl_5 was performed as described in the literature.[21]

Solutions of $(NH_4)(^{99}TcO_4)$ (0.53 mCi mL^{-1}) were obtained from New England Nuclear, Boston, MA. The concentration was determined by a literature method.[22] ^{99}Tc 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 of in special receptacles. Samples sent outside the laboratories' jurisdiction were wipetested for contamination prior to shipment, and all regulations[23] 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). Optical spectra in appropriate solvents were recorded on a Cary 17 spectrophotometer.

Voltammetric studies were carried out by use of a PAR Model 174 polarographic analyzer with rotating Pt, stationary Pt, and dropping-Hg electrodes. All potentials were referenced to a saturated

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calomel electrode. Ferrocene was used as an internal calibrant. The electrolysis of perrhenate in acidic thiocyanate solutions was carried out in a two-compartment cell with platinum-gauze electrodes connected to a PAR Model 173 potentiostat/galvanostat.

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[24] and the magnetic moment derived from the expression

$$\mu_{\text{eff}} = 2.847(\chi^{\text{M}}_{\text{cor}}T)^{1/2}$$

$HgCo(SCN)_4$ was used as a calibrant.

Elemental analyses for the rhenium complexes prepared were performed by Galbraith Laboratories, Knoxville, TN. The technetium complexes were analyzed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Melting points are uncorrected.

Preparation of Tetraphenylarsonium Oxopentakis(isothiocyanato)rhenate(V). Method A. To a beaker containing 25 mL of 2 N hydrochloric acid, 0.20 g (0.73 mmol) of $NaReO_4$, and 0.50 g (5.14 mmol) of NH_4SCN was added dropwise a solution consisting of 0.16 g (0.71 mmol) of $SnCl_2{\cdot}2H_2O$ in 5 mL of 2 N hydrochloric acid with stirring to produce a red solution. The solution was extracted with 100 mL of ether, and the red ether layer was collected and diluted with 200 mL of ethanol. Tetraphenylarsonium chloride monohydrate, 0.35 g, was added, and upon addition of 100 mL of ether, yellow crystals formed. The solid was collected, washed with water and ether, and then dried in vacuo; yield of $(Ph_4As)_2ReO(NCS)_5$ 0.42 g, 46% based on rhenium.

Method B. A cherry red solution of $Ph_4AsReOBr_4{\cdot}CH_3CN$, 0.38 g (0.40 mmol) in 10 mL acetonitrile, was treated with 0.16 g (2.76 mmol) of NH_4NCS, resulting in an immediate color change to yellow and precipitation of a white solid (NH_4Br). The mixture was filtered, and the filtrate was treated with 0.19 g of Ph_4AsBr. A yellow precipitate formed upon addition of isobutyl alcohol or ether. Recrystallization from hot acetone/isobutyl alcohol mixtures yielded 0.42 g of golden orange crystals of $(Ph_4As)_2ReO(NCS)_5$, 80% yield based on rhenium. Recrystallizations from slow evaporation of acetone/isobutyl alcohol mixtures formed yellow-green blocks of $(Ph_4As)_2ReO(NCS)_5$.

Method C. Dipotassium oxopentachlororhenate, K_2ReOCl_5, 0.058 g (0.13 mmol), was suspended in 5 mL of acetonitrile. Upon addition of 0.048 g (0.63 mmol) of NH_4SCN, a white precipitate (NH_4Cl, KCl) and a yellow solution formed. The mixture was filtered, and the filtrate was treated with 0.106 g (0.25 mmol) of $Ph_4AsCl{\cdot}H_2O$. The solid was precipitated with isobutyl alcohol. The solid was recrystallized as in method B. Yield of $(Ph_4As)_2ReO(NCS)_5$ was 0.134 g, 84% based on rhenium.

Anal. Calcd for $C_{53}H_{40}As_2N_5OReS_5$: C, 50.55; H, 3.20; N, 5.56; S, 12.73. Found (yellow-orange crystals): C, 51.02; H, 3.56; N, 5.69; S, 12.94. Found (yellow-green crystals): C, 50.98; H, 3.40; N, 5.57; S, 12.55. Optical spectrum (CH_3CN): 970 nm (ϵ 110 L mol^{-1} cm^{-1}), 905 (135), 365 (24 900), 307 (13 300). Infrared spectrum (KBr): 3050 (w), 2100 (w), 2060 (s), 2031 (*m*), 1575 (w), 1483 (m), 1437 (s), 1390 (w), 1335 (w), 1310 (w), 1275 (w), 1180 (w), 1160 (w), 1079 (m), 1020 (w), 997 (m), 953 (m) (yellow-orange), 961, 954 (m) (yellow-green), 855 (w), 737 (s), 685 (s), 610 (w), 490 (w), 476 (m), 463 (m), 410 (w), 355 (w), 349 (w), 290 (w) cm^{-1} [ν_{CN} (CH_3CN) 2112 (w), 2069 (s), 2036 (m) cm^{-1}]. Magnetic moment: solid, μ_{eff} (298 K) = 2.0–2.8 μ_B (yellow-orange crystals) and 1.2–2.0 μ_B (yellow-green crystals); CH_3CN solution, diamagnetic. Conductivity (2:1 electrolyte in acetonitrile): $\Lambda_0 = 348$ cm^2 Ω^{-1} M^{-1}. Melting points: yellow-orange $\xrightarrow{266\ ^\circ\text{C}}$ red $\xrightarrow{305\ ^\circ\text{C}}$ melts; yellow-green $\xrightarrow{175\ ^\circ\text{C}}$ yellow-orange $\xrightarrow{266\ ^\circ\text{C}}$ red $\xrightarrow{305\ ^\circ\text{C}}$ melts.

The yellow-orange crystals are uniaxial. A conoscopic figure characteristic of a uniaxial crystal (a black Maltese cross which did not change shape or position when the stage was rotated) was observed when the yellow-orange crystals were viewed between crossed polarizers and a Bertrand lens.

Preparation of Tetrabutylammonium Oxopentakis(isothiocyanato)rhenate(V). Method A. Use of method B for $(Ph_4As)_2ReO(NCS)_5$ but with tetrabutylammonium salts instead yielded yellow crystals. From 0.31 g (0.41 mmol) of $(n\text{-}Bu)_4NReOBr_4$, 0.16 g (2.76 mmol) of NH_4SCN, and 0.14 g of $(n\text{-}Bu)_4NBr$, 0.21 g of yellow crystals of $[(n\text{-}Bu)_4N]_2ReO(NCS)_5$ were collected, 69% yield based on rhenium.

Method B. To the cathode compartment of an electrolysis cell were added 1.0 g (4.0 mmol) of $NaReO_4$, 2.59 g (34.8 mmol) of NaSCN, and 12 mL of 4 N hydrochloric acid. The anode compartment was filled with 12 mL of 4 N hydrochloric acid. Platinum mesh electrodes were used to pass 1000 C at 0.5 A. The cell compartments were stirred continuously. The resultant red-brown mixture in the cathode compartment was filtered, and then the filtrate was extracted with two 50-mL aliquots of ether. The combined red ether extracts were treated with a concentrated solution of $(n\text{-}Bu)_4NBr$ in ethanol. Addition of water resulted in a phase separation, and crystallization occurred at the interphase. The yellow crystals were collected, washed with water and ether, and then dried in vacuo. Yield of bright yellow crystals of $[(n\text{-}Bu)_4N]_2ReO(NCS)_5$: 0.61 g, 15% based on rhenium.

Anal. Calcd for $C_{37}H_{72}N_7OReS_5$: C, 45.46; H, 7.42; N, 10.03; S, 16.40. Found: C, 46.01; H, 7.61; N, 9.77; S, 15.54. Optical spectrum (CH_3CN): 970 nm (ϵ = 105 L mol^{-1} cm^{-1}), 905 (130), 365 (24 300), 306 (14 200). Infrared spectrum (KBr): 2958 (s), 2927 (m), 2860 (m), 2105 (ms), 2060 (s), 2010 (s), 1481 (m), 1280 (w), 1240 (w), 1175 (w), 1147 (w), 1125 (w), 1104 (w), 1080 (w), 1063 (w), 1050 (w), 1022 (w), 952 (s), 895 (w), 880 (m), 857 (w), 796 (w), 790 (w), 775 (w), 736 (m), 685 (w), 490 (w), 478 (w), 462 (w), 350 (w), 290 (m) cm^{-1}.

Preparation of Tetraphenylarsonium Oxopentakis(isothiocyanato)technetate(V). To a 25 mL round-bottom flask with a stir bar were added 0.084 g (0.17 mmol) of $(n\text{-}Bu)_4NTcOCl_4$ and 5 mL of methanol. An ice bath was placed under the green solution to cool it to 0 °C. Upon addition of 0.063 g (0.84 mmol) of NH_4SCN, a bright red solution rapidly developed. After 1 min, 0.2 g of $Ph_4AsCl{\cdot}H_2O$ was added to the solution which deposited a fine red microcrystalline solid. The solid was collected, washed with 10 mL of methanol, and dried in vacuo; yield of $(Ph_4As)_2TcO(NCS)_5$ 0.173 g, 93% based on technetium.

Anal. Calcd for $C_{53}H_{40}As_2N_5OS_5Tc$: C, 54.31; H, 3.44; N, 5.97; S, 13.68. Found: C, 53.79; H, 3.61; N, 5.94; S, 13.98. Optical spectrum: (CH_3CN, excess SCN^-) 450 nm (ϵ 23 400 L mol^{-1} cm^{-1}), 375 (9920); (CH_2Cl_2, excess SCN^-) 462, 387; (CH_3CN) 450, 380 (sh), 320 (sh); (CH_2Cl_2) 455, 390 (sh); (CH_3CN, Ag^+ added) 385, 320. Infrared spectrum (KBr): 3045 (w), 2102 (w), 2057 (s), 2022 (s), 1575 (w), 1482 (m), 1435 (m), 1380 (w), 1335 (w), 1307 (w), 1260 (w), 1181 (w), 1160 (w), 1079 (m), 1020 (w), 997 (m), 955 (vw), 945 (m), 925 (sh, w), 870 (w), 840 (w), 740 (s), 685 (m), 610 (w), 485 (w), 473 (m), 462 (m), 360 (w), 345 (sh, w), 328 (w) cm^{-1}. Magnetic moment: μ_{eff} (298 K) = 1.04 μ_B.

Reaction of $TcO(NCS)_5^{2-}$ with Thiocyanate Ion. An acetonitrile solution of $(Ph_4As)_2TcO(NCS)_5$ was treated with an approximately tenfold excess of NH_4SCN and stirred. Within 1 h, the solution had visibly darkened, and, 24 h later, spectrophotometric examination demonstrated the presence of both $Tc(NCS)_6^{2-}$ and $Tc(NCS)_6^{3-}$. No $TcO(NCS)_5^{2-}$ could be detected. Upon standing, solutions of $TcO(NCS)_5^{2-}$ without added thiocyanate ion darkened, and the appearance of $Tc(NCS)_6^{x-}$ (x = 2, 3) was detected spectrophotometrically.

Reaction of $ReO(NCS)_5^{2-}$ with $SnCl_2{\cdot}2H_2O$ and Thiocyanate Ion. A solution of $ReO(NCS)_5^{2-}$ in a mixture of 2 N hydrochloric acid/ethanol was treated with 20 equiv of $SnCl_2{\cdot}2H_2O$ and 10 equiv of NH_4SCN. The yellow-orange solution changed to a rich red-brown and a band at 420 nm ($Re(NCS)_6^{2-}$)[12,18] was observed. Attempts to isolate pure samples of $Re(NCS)_6^{2-}$ with large univalent cations by this method invariably also brought out tin salts (presumably $Sn(NCS)_6^{2-}$) that could not be separated from the rhenium complex.

Results and Discussion

The reduction of perrhenate with stannous ion in acidic thiocyanate solutions[2,7-10,12] results in the formation of rich red to red-brown solutions containing optical absorptions at 365 and 420 nm.

When Bailey and Kozak studied the reduction of perrhenate in the presence of thiocyanate ion, they concluded that two species were present, both six-coordinate thiocyanate com-

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Table I. Infrared Data for $ReO(NCS)_5^{2-}$ Salts (cm^{-1})

compd	ν_{CN}	ν_{ReO}
$[(n\text{-}Bu)_4N]_2ReO(NCS)_5$	2105 (ms) 2060 (s) 2010 (s)	952 (s)
$(Ph_4As)_2ReO(NCS)_5$ (yellow-orange)[a]	2100 (w) 2060 (s) 2031 (m)	953 (m)
$(Ph_4As)_2ReO(NCS)_5$ (yellow-green)[a]	2100 (w) 2060 (s) 2031 (m)	961 (m) 954 (m)
soln spectra (CH_3CN)	2112 (w) 2069 (s) 2036 (m)	

[a] Different crystal modifications.

plexes, $Re(NCS)_6^-$ and $Re(NCS)_6^{2-}$.[12] An electrochemical study on the hexahalometalate(IV) complexes of technetium and rhenium[14] revealed that oxidation of these salts to the hexahalometalate(V) species was extremely difficult, and the technetium thiocyanate system has recently been shown[15] to consist of two species, $Tc(NCS)_6^{3-}$ and $Tc(NCS)_6^{2-}$. The existence of $Re(NCS)_6^-$ would therefore be very interesting.

The rhenium(IV) complex, $Re(NCS)_6^{2-}$, has been prepared from the disproportionation of $Re_2Cl_8^{2-}$ with thiocyanate ion[18] and from a molten salt reaction involving K_2ReCl_6 and KSCN.[11] This material is well characterized, with an intense charge-transfer absorption in the visible region at 420 nm and a strong band at 2040 ± 10 cm^{-1} in the cyanide stretching region of the infrared found for samples from either preparation. An electrochemical study of $Re(NCS)_6^{2-}$ [14] reveals the presence of an irreversible oxidation at 1.23 V vs. SCE in acetonitrile.[25] Preparation of "$CsRe(NCS)_6$" from $ReCl_5$ and KSCN in a molten salt reaction[11] produces a dark brown solid that upon dissolution in 1 M sulfuric acid (in which it was reported to be stable)[12] showed a visible absorption band at 420 nm ($Re(NCS)_6^{2-}$), not at 365 nm as had been reported.[12] Although it is possible that "$Re(NCS)_6^-$" could be formed in the solid state,[26] it is apparent from the voltammetric and solution studies that such a species is not stable in solution, especially in the 2 N acid used in the reduction. Thus, the claim that $Re(NCS)_6^-$ was responsible for the optical absorption band at 365 nm observed in the reduction of perrhenate in the presence of thiocyanate ion in 2 N hydrochloric acid must be discounted.

The careful reduction of perrhenate with 1 equiv of $SnCl_2\cdot 2H_2O$ and 6–7 equiv of thiocyanate ion in 2 N hydrochloric acid creates a red solution whose color can be extracted with ether. Addition of Ph_4As^+ ion in ethanol results in precipitation of a yellow salt which analyzes as $(Ph_4As)_2ReO(NCS)_5$. This complex can also be prepared from the electrochemical reduction of perrhenate in acidic thiocyanate solutions and from ligand substitution on either salts of $ReOBr_4^-$ or K_2ReOCl_5 in nonaqueous solvents.

As shown in Table I these salts all exhibit three bands in the cyanide stretching region of the infrared spectrum; group theory predicts that a species such as $MX(NCS)_5$ (C_{4v}) should have three infrared-active vibrations ($2 A_1 + E$) for the cyanide stretches. In addition, a band at ~955 cm^{-1} is attributable to the rhenium–oxo stretch. The complex is a 1:2 electrolyte in acetonitrile from conductance measurements.[28]

The optical spectrum reveals two bands in the ultraviolet region at 306 and 365 nm (ϵ = 14200 and 24300 L mol^{-1} cm^{-1}, respectively). The band at 365 nm is due to the presence of $ReO(NCS)_5^{2-}$. Addition of $SnCl_2\cdot 2H_2O$ and thiocyanate ion to acidic ethanol solutions of $ReO(NCS)_5^{2-}$ results in the formation of rich red-brown solutions containing $Re(NCS)_6^{2-}$, as expected.

Chakravorti and Das[29] have reported the synthesis of $M_2ReO(NCS)_5$ (M = Cs^+, Tl^+, Me_4N^+) from the reaction of Cs_2ReOCl_5 and KSCN in hot water. They report that the three salts range from brown to black in color, with optical spectra revealing bands at 320 nm (ϵ = 9800 L mol^{-1} cm^{-1}) and 435 nm (ϵ = 13000 L mol^{-1} cm^{-1}). The existence of a strong infrared band at 2050 cm^{-1} and a rhenium–oxo stretch at ~960 cm^{-1} were also observed. On the basis of their findings, the material they have prepared is obviously contaminated with $Re(NCS)_6^{2-}$ and possibly other complexes as well. By comparison, the reaction of K_2ReOCl_5 with NH_4SCN in acetonitrile yields bright yellow solutions from which $(n\text{-}Bu)_4N^+$ or Ph_4As^+ salts of $ReO(SCN)_5^{2-}$ can be easily obtained.

During the course of the investigation of $(Ph_4As)_2ReO(NCS)_5$, it was observed that the solid could crystallize in two different forms: one, yellow-orange uniaxial plates; the other, yellow-green crystalline blocks. Apparently, when the complex is recrystallized rapidly, for example, from a refluxing acetone/isobutyl alcohol solution, the yellow-orange form predominates. When crystals are allowed to grow slowly from solvent mixtures, for example, slow evaporation of acetone/isobutyl alcohol solutions, the yellow-green form predominates. The materials have essentially identical elemental analyses and dissolve to yield identical solutions. Although the two solids have different magnetic susceptibilities, their solutions are diamagnetic. In the infrared spectrum, no differences are observed in the cyanide stretching region; however, the yellow-orange form has a rhenium–oxo stretch at 953 cm^{-1} and the yellow-green form has two bands, one at 961 cm^{-1} and the other at 954 cm^{-1} (probably present from formation of the yellow-orange form under the conditions of preparing the KBr pellet). The change in the infrared spectrum is not great, and the existence of the two forms probably involves crystal-packing forces. The $(n\text{-}Bu)_4N^+$ salt appears to crystallize in one form only.

The use of $TcOCl_4^-$ as a synthetic intermediate in the exploration of technetium(V) chemistry has been demonstrated.[20] The reaction of a methanol solution of $(n\text{-}Bu)_4NTcOCl_4$ with 5 equiv of thiocyanate ion, followed by precipitation with Ph_4As^+, yields a bright red microcrystalline solid. Elemental analysis is consistent with its formulation as $(Ph_4As)_2TcO(NCS)_5$.

The infrared spectrum exhibits three bands in the cyanide stretching region at 2102 (w), 2057 (s), and 2022 (s) cm^{-1}, indicative of C_{4v} symmetry (vide infra). There is also a band at 945 cm^{-1} attributable to a technetium–oxo stretch. The analogous rhenium compound has a rhenium–oxo stretch at ~955 cm^{-1}; the trend observed for ν_{ReO} vs. ν_{TcO} in the oxobis(dithiolato)metalate(V) complexes[20] is also observed here. The magnetic moment of 1.04 μ_B at 298 K is in the range of other technetium(V),[20] rhenium(V),[20,30] and molybdenum(IV)[30] complexes.

The optical spectrum of $(Ph_4As)_2TcO(NCS)_5$ in acetonitrile has a broad band at 450 nm with shoulders at 380 and 320

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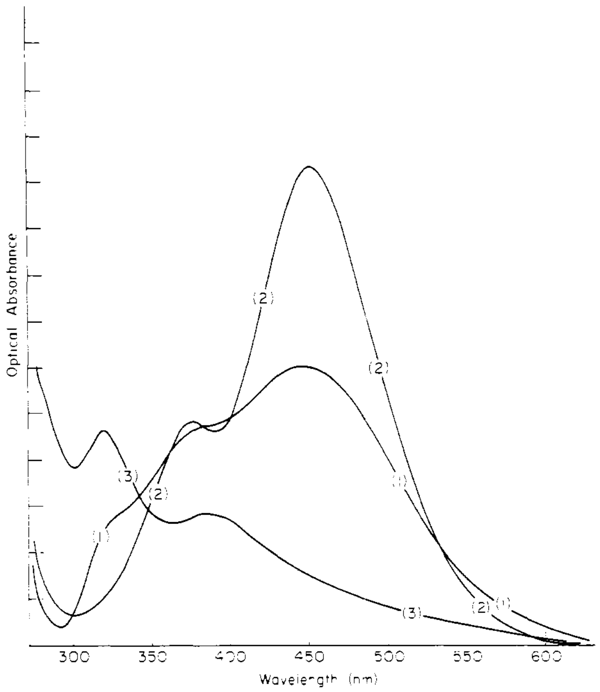

Figure 1. Optical spectra of (Ph$_4$As)$_2$TcO(NCS)$_5$: (1) acetonitrile solution; (2) same concentration as in (1), but ammonium thiocyanate added; (3) same concentration as in (1), but silver nitrate added.

nm (Figure 1). This spectrum is not similar in shape to the spectrum of (Ph$_4$As)$_2$ReO(NCS)$_5$, which has well-defined bands at 365 and 306 nm. However, when thiocyanate ion is added to the TcO(NCS)$_5^{2-}$ solution, the band at 450 nm increases in intensity, the shoulder at 380 nm becomes a well-defined band at 375 nm, and the shoulder at 320 nm disappears entirely. Now the spectrum is similar to a bathochromically shifted spectrum of (Ph$_4$As)$_2$ReO(NCS)$_5$. Similar behavior is observed in dichloromethane solutions.

Apparently, a dissociation of thiocyanate ion is taking place in the concentration range used for optical spectroscopy (10^{-5}–10^{-6} M). The thiocyanate ion most likely to dissociate would be the axial thiocyanate, trans to the oxo ligand. The rhenium complex, (Ph$_4$As)$_2$ReO(NCS)$_5$, is a well-behaved 1:2 electrolyte. This difference can be accounted for by consideration of the increased orbital overlap of 5d (Re) orbitals compared with 4d (Tc) orbitals. The rhenium atom is able to interact more strongly with the axial thiocyanate ligand than the technetium atom can. Further observations also indicate that the process is not completely reversible. Addition of silver nitrate to the optical solution results in precipitation of AgSCN and the total disappearance of the band at 450 nm. Unfortunately, subsequent addition of thiocyanate ion fails to regenerate the band at 450 nm. Other processes must be taking place in addition to the dissociation of thiocyanate ion. When concentrated solutions of TcO(NCS)$_5^{2-}$ are treated with silver nitrate, precipitation of Ag$_2$TcO(NCS)$_5$ and reduction to form Tc(NCS)$_6^{2-}$ occur as well as precipitation of AgSCN.

In the presence of thiocyanate ion, TcO(NCS)$_5^{2-}$ is easily reduced to mixtures of both Tc(NCS)$_6^{2-}$ and Tc(NCS)$_6^{3-}$. Due to the slow dissociation of thiocyanate ion from TcO(NCS)$_5^{2-}$, solutions of TcO(NCS)$_5^{2-}$ without added thiocyanate are slowly reduced to Tc(NCS)$_6^{2-}$ and Tc(NCS)$_6^{3-}$. Loss of an oxo ligand can be viewed as a two-electron reduction; it might be expected that degassed solutions of TcO(NCS)$_5^{2-}$ would yield Tc(NCS)$_6^{3-}$. Unfortunately, the oxidation product, (SCN)$_2$, thiocyanogen, has been shown to oxidize Tc(NCS)$_6^{3-}$ to Tc(NCS)$_6^{2-}$.[15]

The colorimetric determinations of rhenium and technetium with thiocyanate ion involve two different pairs of complexes. In the case of technetium, the observed pair is the redox couple Tc(NCS)$_6^{2-}$ and Tc(NCS)$_6^{3-}$, technetium(IV) and technetium(III), respectively,[15] whereas the observed pair in the case of rhenium are complexes of rhenium(V) and rhenium(IV), ReO(NCS)$_5^{2-}$ and Re(NCS)$_6^{2-}$, respectively. This difference is merely a reflection of chemical periodicity; the higher oxidation states become more stable for a third-row transition metal compared to a second-row transition metal. The rhenium(III) complex, Re(NCS)$_6^{3-}$,[14,25] may be involved in the reaction but not observed because it is quickly oxidized to Re(NCS)$_6^{2-}$ under the conditions of the reaction. In the case of the Tc determinations, TcO(NCS)$_5^{2-}$ is formed initially, but it is rapidly reduced to form the six-coordinate thiocyanate complexes Tc(NCS)$_6^{3-}$ and Tc(NCS)$_6^{2-}$.

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Note Added in Proof. The air-sensitive [(*n*-Bu)$_4$N]$_3$Re(NCS)$_6$ has been isolated as a pale yellow solid: Trop, H. S.; Davison, A., to be submitted for publication.

Registry No. [(*n*-Bu)$_4$N]$_2$ReO(NCS)$_5$, 74176-28-6; (Ph$_4$As)$_2$ReO(NCS)$_5$, 74176-29-7; (Ph$_4$As)$_2$TcO(NCS)$_5$, 74185-18-5; NaReO$_4$, 13472-33-8; Ph$_4$AsReOBr$_4$·CH$_3$CN, 35788-73-9; K$_2$ReOCl$_5$, 17443-52-6; (*n*-Bu)$_4$NReOBr$_4$·CH$_3$CN, 74185-26-5; (*n*-Bu)$_4$NTcOCl$_4$, 71341-65-6; Re(NCS)$_6^{2-}$, 48072-47-5; Tc(NCS)$_6^{2-}$, 45230-36-2; Tc(NCS)$_6^{3-}$, 72622-86-7.