SYNTHESIS, CHARACTERIZATION, AND REACTIVITY OF TECHNETIUM AND RHENIUM COMPLEXES IN INTERMEDIATE OXIDATION STATES

by

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Thesis Supervisor

Accepted by_____
Chairman, Department Committee

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Professor Richard R. Schrock _____ Chairman

Professor Alan Davison _____ Thesis Supervisor

Professor Edward I. Solomon _____

In fond memory of a lady whose warmth, kindness, and love of life will always live in my heart.

Amy Stovell

1889 - 1977

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Submitted to the Department of Chemistry in May, 1979, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

ABSTRACT

Chapter I

Electrochemical measurements on the tetrabutylammoniumhexahalometallate(IV) salts of technetium and rhenium [$(nBu_4N)_2MX_6$: M = Tc, Re; X = Cl, Br] have been performed in acetonitrile. Oxidation of the complexes to technetium(V) and rhenium(V) is difficult; although the rhenium complexes are easier to oxidize than the technetium complexes, as expected from consideration of periodicity. The rhenium complexes exhibit reversible one-electron oxidations; whereas, the technetium complexes exhibit irreversible behavior. The rhenium complexes are difficult to reduce under the conditions used. The technetium complexes easily reduce to form kinetically labile lower valent species.

Chapter II

The synthesis and characterization of $[nBu_4N][TcOCl_4]$, a five coordinate technetium(V) complex is presented. A crystal structure on the $[(C_6H_5)_3PNP(C_6H_5)_3]^+$ salt definitively confirms the identity of this complex as an intermediate in the reduction of pertechnetate(VII) to hexachlorotechnetate(IV) by hydrochloric acid; thus, the claim that this material is the long sought after "$Tc_2Cl_8^{2-}$" anion must be dismissed. The short technetium-oxygen bond length of 1.610(4)Å is in agreement with the high ν_{TcO} observed at 1019 cm^{-1}. The oxotetrachlorotechnetate(V) anion is an extremely versatile starting material for the exploration of technetium(V) chemistry. Use of $nBu_4NTcOCl_4$ to synthesize a wide variety of technetium(V) complexes including the oxobis(dithiolato)-technetate(V) anions, trans-dioxotetrapyridinetechnetium(V) cation, μ-oxobis(oxobis(dithiocarbamato)technetate(V)), and oxodichloro-(hydrotrispyrazoylborate)technetium(V) is discussed along with some of the properties of these technetium(V) complexes. The structural features of several possible oxotechnetium(V) complexes is presented.

Chapter III

Several new technetium cyanide complexes have been prepared and characterized. The reaction of ammoniumhexaiodotechnetate(IV) with potassium cyanide in refluxing aqueous methanol under dinitrogen yields potassium heptacyanotechnetate(III) dihydrate, $K_4Tc(CN)_7 \cdot 2H_2O$, 1. Infrared and Raman measurements indicate that 1 has a pentagonal bipyramidal structure (D_{5h}) in both the solid and solution. Aqueous solutions of 1 are air sensitive, decomposing to potassiumoxopentacyanotechnetate(V) tetrahydrate, $K_2TcO(CN)_5 \cdot 4H_2O$, 2. This species can also be prepared from the reaction of $TcO_2 \cdot xH_2O$ with hot aqueous potassium cyanide solutions. Hydrolysis of 2 in water yields potassium trans-dioxotetracyanotechnetate(V), $K_3TcO_2(CN)_4$, 3. Preparation of 3 can also be achieved from the treatment of $[TcO_2(py)_4]ClO_4 \cdot 2H_2O$ with aqueous potassium cyanide. Infrared and Raman measurements on 3 are consistent with the proposed trans-dioxo (D_{4h}) structure. Reaction of the oxotetrachlorotechnetate(V) anion, $TcOCl_4^-$, with potassium cyanide in methanol produces tetrabutylammonium trans-oxomethoxytetracyanotechnetate(V), $(nBu_4N)_2TcO(OMe)(CN)_4$, 4. The full details of the synthesis and characterization of these interesting technetium(III) and (V) complexes, as well as observations on the infrared and Raman spectra of trans-dioxo metal complexes and the hydrolysis of species 2 are presented.

Chapter IV

The reduction of pertechnetate(VII) and perrhenate(VII) in the presence of thiocyanate ion has been reinvestigated. The two species observed in the rhenium system have been identified as the hexakisisothiocyanatorhenate(IV) anion and the oxopentakisisothiocyanatorhenate(V) anion. The technetium system consists of a reversible one-electron redox couple:

$$Tc(NCS)_6^{3-} \rightleftarrows Tc(NCS)_6^{2-} + e \quad E_{1/2} = 0.18 \text{ V vs. SCE}$$

where the yellow and purple colors observed are due to the technetium(III) and technetium(IV) complexes, respectively. The reaction of the oxotetrachlorotechnetate(V) anion, $TcOCl_4$, with five equivalents of thiocyanate ion in methanol produces the oxopentakisisothiocyanatotechnetate(V) anion, isolated as a tetraphenylarsonium salt, $(Ph_4As)_2TcO(NCS)_5$. This complex readily reacts with excess thiocyanate ion to form the $Tc(NCS)_6^{X-}$ species (X = 2,3). No evidence was found for the existence in solution of either $Tc(NCS)_6^{-1}$ or $Re(NCS)_6^{-1}$. The correct identification and crystal structure of $(nBu_4N)_3Re_2(NCS)_{10}$, a compound previously reported with a formula also including two CO groups, $(nBu_4N)_3Re_2(NCS)_{10}(CO)_2$, is presented. The infrared bands originally assigned as carbonyl stretches can now be correctly assigned as being due to the presence of symmetrically N-bridging thiocyanate ligands, a structural element never previously documented. The Re-Re distance of 2.613(1)Å is indicative of metal-metal bonding. The virtual

D_{2h} symmetry of the Re_2N_{10} core implies that this rhenium(III), rhenium(IV) mixed valence complex has the unpaired electron(s) delocalized equally over the two metal atoms. The synthesis, characterization, and physical studies of these complexes are presented.

Thesis Supervisor: Alan Davison
Title: Professor of Chemistry

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Abbreviations

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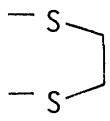

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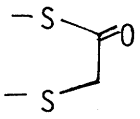

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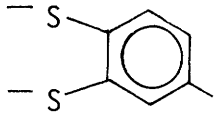

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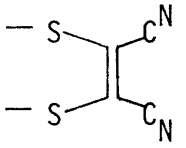

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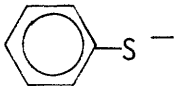

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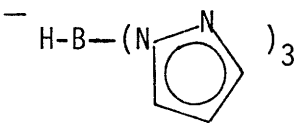

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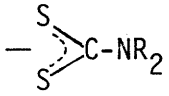

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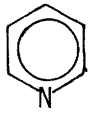

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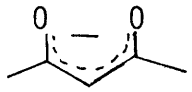
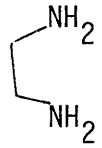
acac 

en 

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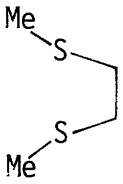
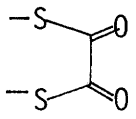
DTH 

dto 

Foreword

Although Mendeleev had predicted the existence of eka-manganese, the second row congener of manganese, in his Periodic Chart of the Elements in 1869,[1] the actual discovery of the element 43(Tc) by Perrier and Segré in 1937[2] was facilitated by the invention of the cyclotron. Since the time of those initial experiments involving irradiation of molybdenum with energetic protons and deuterons, technetium isotopes have also been found to be formed from fission of ^{235}U or ^{239}Pu; one isotope, ^{99}Tc, accounts for 6% of the fission yield from each of those two elements.[3] All of the isotopes of technetium have been shown to have half-lives much smaller than the geologic age of earth; thus the only naturally occurring terrestrial samples of technetium have been found in areas with abnormally high concentrations of uranium ore.[4,5] Technetium has been observed in M, N, and S type stars.[6,7,8] and these discoveries have had a large impact on cosmology.[9,10]

Technetium has been used in the preparation of metal alloys with superconducting properties,[11,12,13] and pertechnetate ion is an extremely effective inhibitor of corrosion in iron and steel.[14] Technetium has been used to monitor radioactive fallout in the atmosphere,[15] absorption of fallout by soil and plants,[16] and the leaching of nuclear waste.[17]

The most important use of technetium is in the field of diagnostic nuclear medicine. The use of radioactive compounds, primarily those containing a gamma emitting isotope, to

noninvasively image various organs has been shown to be of enormous clinical value.[18,19] The radioisotope which has optimum nuclear properties for such studies is ^{99m}Tc,[20] possessing a short half life (6 hr), a 140 keV gamma ray, an absence of particulate radiation in its decay, and a daughter, ^{99}Tc, which provides a negligible radiation dose.[21,22]

Technetium-containing radiopharmaceuticals are generally prepared from the reduction of tracer level amounts (10^{-11} - 10^{-9}M) of $^{99m}TcO_4^-$, eluted from a commercial generator,[23] by a reducing agent (often Sn(II)) in the presence of a complexing agent.[24] The exact nature of the radiopharmaceuticals produced remains shrouded in mystery, being complicated by the tracer level concentration and by a lack of knowledge of the basic coordination chemistry of technetium.[25,26] In order to understand how and why the radiopharmaceuticals utilized operate, and to enable one to rationally design new organ- and disease-specific ^{99m}Tc-radiopharmaceuticals, a greater understanding of the coordination chemistry of technetium is required. In addition, such a study coupled with an examination of technetium's third row cogener, rhenium, could also add new insights to the field of inorganic chemistry as a whole.

One isotope of technetium, ^{99}Tc, appears to be well suited for extensive study of its coordination chemistry. It accounts for 6.3% of the fission yield of ^{235}U and 6.1% of the fission yield of ^{239}Pu, both of which are used worldwide to power nuclear reactors. The isotope can be separated efficiently from other fission

products[27,28] and is commercially available in gram quantities as pertechnetate salts.

The isotope decays via β^- emission and the low energy (.292 MeV) of the particle is dissipated effectively by normal laboratory glassware. (Large amounts of activity, however, can result in bremstrahlung from the glass.) Another advantage is the long half-life, 2.12×10^5 yr, which allows the use of traditional methods of physical and analytical analysis. These favorable properties enable one to perform experiments that are not restricted to the tracer level and milligram quantities of ^{99}Tc-containing coordination complexes can be prepared and characterized, provided certain safety measures are followed.

The chemistry described in this thesis was performed in a laboratory designed for general synthetic manipulations. All synthetic work and sample preparation involving technetium were confined to the hood areas. Large fiberglass trays lined with commercially available industrial diapers were used to control possible spills. A Schlenk line set up inside the hood allowed for air sensitive manipulations and vacuum drying of samples using standard Schlenk line apparatus and techniques. At all times, the experimenter wore disposable gloves and lab coat to prevent accidental contamination from solids or liquids that were present. An Eberline E-120 portable beta-gamma survey meter with HP-190 probe was used to monitor the laboratory (one can detect experimentally at least 2-5 $\mu Ci/cm^2$). The laboratory was monitored

by wipe tests at least once a month by the M. I. T. Radiation Protection Office (RPO).

Radioactive waste was disposed of in two ways. Solid waste was placed in plastic bags and then stored in a special receptacle until picked up by the RPO. Liquid wastes were neutralized if they contained acid or base prior to disposal in jugs filled with a gypsum-based absorbent solid. These were replaced by the RPO when full. A record of waste activity was kept to insure a complete inventory on the amount of technetium present in the laboratory. Glassware was washed in a sink approved for radioactive waste. The maximum permissible concentration of ^{99}Tc allowed down a drain is set at 0.1 $\mu Ci/ml$[29] with a total not to exceed 10 $mCi/\frac{1}{4}$ yr.[30] A commercial radioactive decontaminant was used to clean contaminated glassware and equipment.

Solid samples were stored in glass vials or ampules kept inside metal cans within a locked cabinet.

When samples were shipped outside of M.I.T. for chemical analysis or X-ray structural analysis, they were placed in a glass vial or ampule surrounded by cotton within a sturdy mailing case. Prior to shipment, the glass would be wipetested to insure that contamination was kept to a minimum.

Federal regulations[31] allow for amounts less than 1 mCi ^{99}Tc to be considered exempt quantities and may be shipped by mail without radiation labels when packaged as described. Analytical samples generally contained 10-20 μCi ^{99}Tc. All analyses of technetium containing complexes were performed by Schwarzkopf Microanalytical Laboratory.

Technetium was purchased in 10 mCi lots as an aqueous solution of ammonium pertechnetate (New England Nuclear). The concentration was determined from the technical data (see Table I) provided and experimentally from the UV absorption spectrum of TcO_4^-.[32]

Conversion Factors and Constants for ^{99}Tc

one curie (Ci) = 3.700×10^{10} disintegrations/sec

specific activity ^{99}Tc = 0.017 Ci/gm

1.68 Ci = 1.00 mol ^{99}Tc

Determination of molarity from mCi/ml:

$$M = \frac{(mCi/ml)(1000\ ml/l)}{(99\ gm/mol)(17\ mCi/gm)}$$

Table I

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The technetium-99m is separated via elution of an alumina-chromatography column containing the $^{99}MoO_4^{2-}$ with saline.
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CHAPTER I

Electrochemical Studies on the Hexahalometallate (IV) Complexes of Technetium and Rhenium

INTRODUCTION

With the exception of ReO_4^- and TcO_4^-, the most utilized starting materials in the past for studying the chemistry of technetium and rhenium have been their hexahalometallate(IV) complexes, due to the ease of formation[1-3] and well characterized nature of these d^3 octahedral anions.[4-6]

The salts of $TcCl_6^{2-}$ and $ReCl_6^{2-}$ have been treated with pyridine in acid solution to form complexes of technetium and rhenium in the +5 oxidation state, $TcO_2(py)_4^{+}$[7] and $ReO_2(py)_4^{+}$[8], by an as yet unknown mechanism. Reaction of $ReCl_6^{2-}$ with maleonitriledithiolate ion (Na_2mnt) in aqueous methanol followed by oxidation with iodine yields another rhenium (V) species, $ReO(mnt)_2^-$.[9]

Hexachlorotechnetate ion, $TcCl_6^{2-}$, has been used to prepare $Tc_2Cl_8^{3-}$, a quadruply bonded technetium dimer containing Tc(II) and Tc(III),[11] by reduction with zinc in concentrated hydrochloric acid.[10] Reduction of $TcCl_6^{2-}$ with hydroxylamine hydrochloride[10] produced a technetium (I) species, $t\text{-}Tc(NO)(NH_3)_4(OH_2)^{2+}$ which has had its structure confirmed by X-ray crystallography.[12] Reduction of Ag_2ReBr_6 with nitric oxide at elevated temperature followed by hydrobromic acid yielded $Re(NO)Br_5^{2-}$ salts.[13]

Lower valent technetium phosphine complexes are accessible from reaction of TcX_6^{2-} and the appropriate phosphine to yield $TcX_3(PR_3)_3$[14,16] or $TcX_2(PR_3)_4$[15,16] depending upon conditions.

Interestingly, there has been no study of the electrochemistry of the hexahalometallate(IV) ions. It is of interest to assess the

relative stabilities, in a thermodynamic sense, of the neighboring oxidation states with simple ligands in which the coordination sphere remains intact. Such information could aid in planning future chemistry based on the hexahalometallates or on reduction of perrhenate or pertechnetate in the presence of potential ligands.

Unfortunately, these MX_6^{2-} salts are only stable in aqueous solutions that are strongly acidic, decomposing to give $MO_2 \cdot xH_2O$ as insoluble dark precipitates, in neutral or basic solution.[4-6] Obviously, a good non-aqueous solvent system such as acetonitrile is required, but the standard ammonium, sodium, or potassium salts are not soluble in organic solvents. For these reasons, the tetrabutylammonium salts of the hexahalometallates were prepared and studies of their electrochemistry undertaken.

EXPERIMENTAL

Constant boiling (57%) hydriodic acid was purified by addition of 50% w/w hypophosphorous acid followed by distillation under dinitrogen at 126°C prior to use. Purified hydriodic acid was stored under dinitrogen in brown bottles. All other reagents were used as received. $NaReO_4$ was obtained from Clevaland Refractory Metals, Solon, Ohio.

Purity of the hexahalometallate salts prepared was checked by optical spectroscopy, using published values.[17]

Spectro Grade acetonitrile (Eastman), run through a long activated alumina column, and nBu_4NClO_4 (Southwest Analytical), (dried at 85°C in vacuo for 24 hr.) as the supporting electrolyte, were used in the electrochemical measurements. Electrochemical measurements were obtained on a PAR Model 174 Polarograghic Analyzer equipped with either a dropping mercury electrode (DME) or a rotating platinum electrode, and a saturated calomel electrode (SCE) reference. The cyclic voltammograms were obtained at a stationary platinum electrode with scan rates of 10-200 mV sec^{-1}. Ferrocene was used as the internal calibrant.

The $(NH_4)_2TcX_6$ (X= Cl, Br, I) salts were prepared according to the literature method,[2] as were the K_2ReX_6 (X=Cl,Br,I) salts.[1] The

tetrabutylammonium salts were prepared by metathesis, ie. by adding the corresponding tetrabutylammonium halide to hot solutions of MX_6^{2-} in the respective halo acid and evaporating until crystallization occurred. In the case of $ReBr_6^{2-}$, addition of nBu_4NBr resulted in immediate precipitation of the tetrabutylammonium salt. Only nBu_4NI_3 could be recovered from solutions containing either ReI_6^{2-} or TcI_6^{2-}; in addition, these iodide salts proved to be unstable in solvents other than concentrated hydriodic acid.

The $(nBu_4N)_2MX_6$ salts (M=Tc, Re; X=Cl, Br) were recrystallized from acetone/hexane solutions three times prior to use in the electrochemical measurements.

Results and Discussion

The electrochemical studies are summarized in Table II.

The anodic scans for technetium and rhenium are similar in profile, with rhenium being easier to oxidize than technetium, as expected from considerations of periodicity. The first wave in each case is attributable to the oxidation

$$M(+4)X_6^{2-} \rightleftarrows M(+5)X_6^{1-} + e \quad .$$

The rhenium couples are reversible[18] one-electron processes (Figure I) as shown by cyclic voltammetry, whereas those for technetium are irreversible (Figure II). This is not surprising in view of the large increase in oxidizing ability (ca. 0.4 - 0.7 V) of the technetium(V) species and the scan dependence of the cyclic scans (10-200 mV $sec.^{-1}$). However, these results clearly show that MX_6^{-1} ions (M = Re, Tc) are all powerful oxidizing agents in a thermodynamic sense. Thus, it is not surprising that the only report of an MX_6^{-1} ion (M = Re, Tc; X = Cl , Br) has been the reaction of rhenium metal with PCl_5 at 500-550°C to yield $[PCl_4][ReCl_6]$.[19] These results suggest that the thermodynamically stable rhenium(V) and technetium(V) complexes may not resemble octahedral halide complexes, but rather will require different types of ligands or structural features. The isolation of $TcO_2(py)_4^+$,[7] $ReO(mnt)_2^-$,[9] and $ReOCl_3(PR_3)_2$[20] complexes supports such a viewpoint.

The cathodic behavior is not as well defined. In the rhenium complexes, the onset of reduction occurred at values more negative than approx. -0.9 V vs. SCE. Although less well defined, the technetium complexes show an irreversible reduction at a more positive potential than for the corresponding rhenium complexes by approx. 0.6 V.

Table II: Electrochemical Measurements on the Hexahalometallate (IV) Salts

Compound	Rotating Platinum $E_{1/2}$ (volts vs. SCE)	Dropping Hg $E_{1/2}$ (volts vs. SCE)
TBA_2ReCl_6	+ 1.18 (1e rev.)	-1.18
	+ 2.42	-2.23
TBA_2ReBr_6	+ 1.18 (1e rev.)	-0.90
	+ 2.30	-1.80
TBA_2TcCl_6	+ 1.88	-0.34 *
	+ 2.30	-0.68
		-1.11
		-1.83
TBA_2TcBr_6	+ 1.70	-0.27*
	+ 2.32	-0.75
		-1.00
		-1.68

TBA = tetrabutylammonium (nBu_4N^+)

All studies in CH_3CN with 0.1 M $nBu_4N^+ClO_4^-$

* Complex irreversible processes taking place

Figure I: Cyclic Voltammograms of $(nBu_4N)_2ReCl_6$ in Acetonitrile/0.1 M TBAP. a) 100 mV sec^{-1} scan rate, initially anodic, starting point 0.0V, displaying one electron reversible oxidation wave. b) 100 mV sec^{-1} scan rate, initially cathodic, starting point 0.0V, irreversible reduction wave observed.

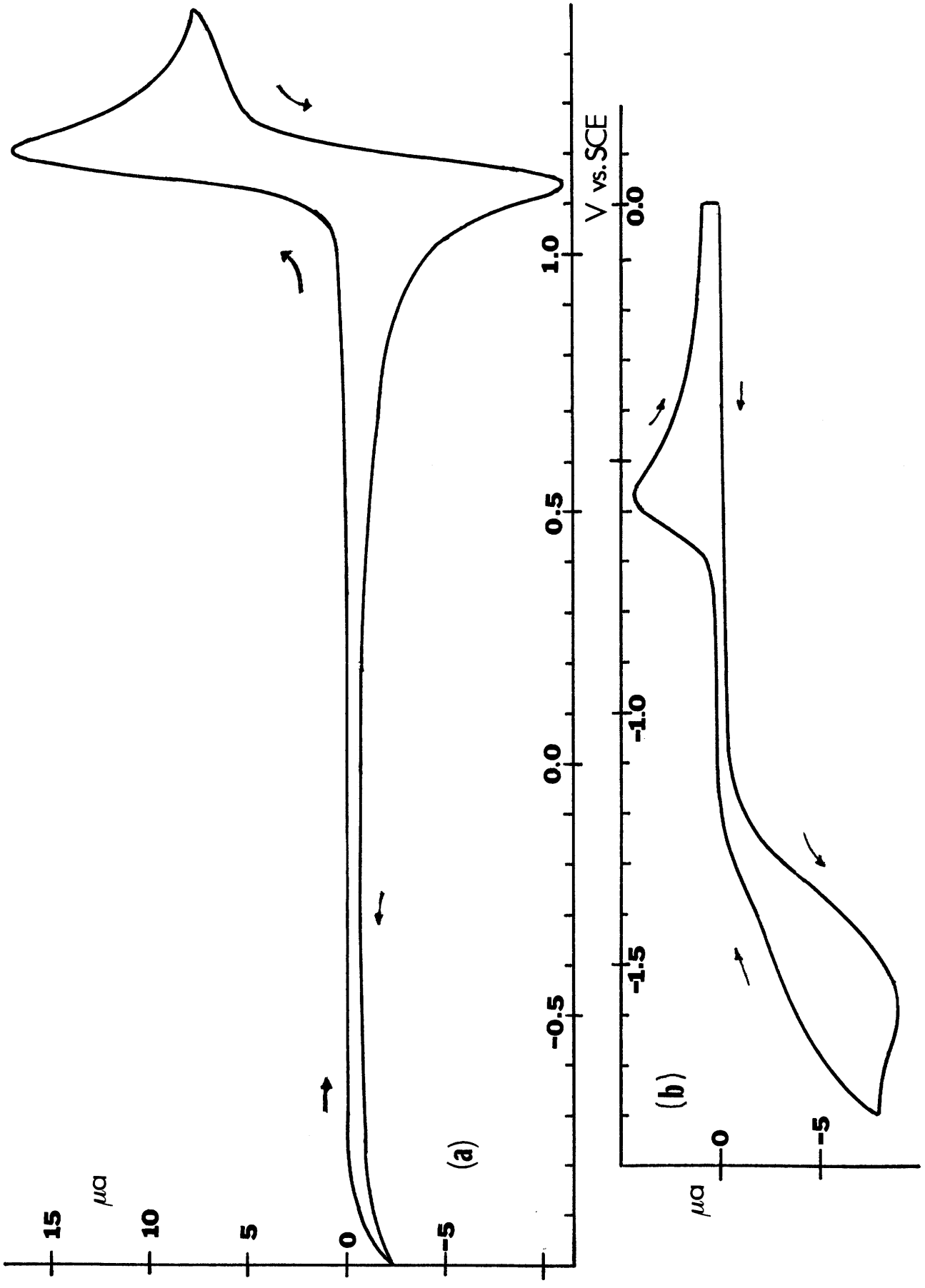
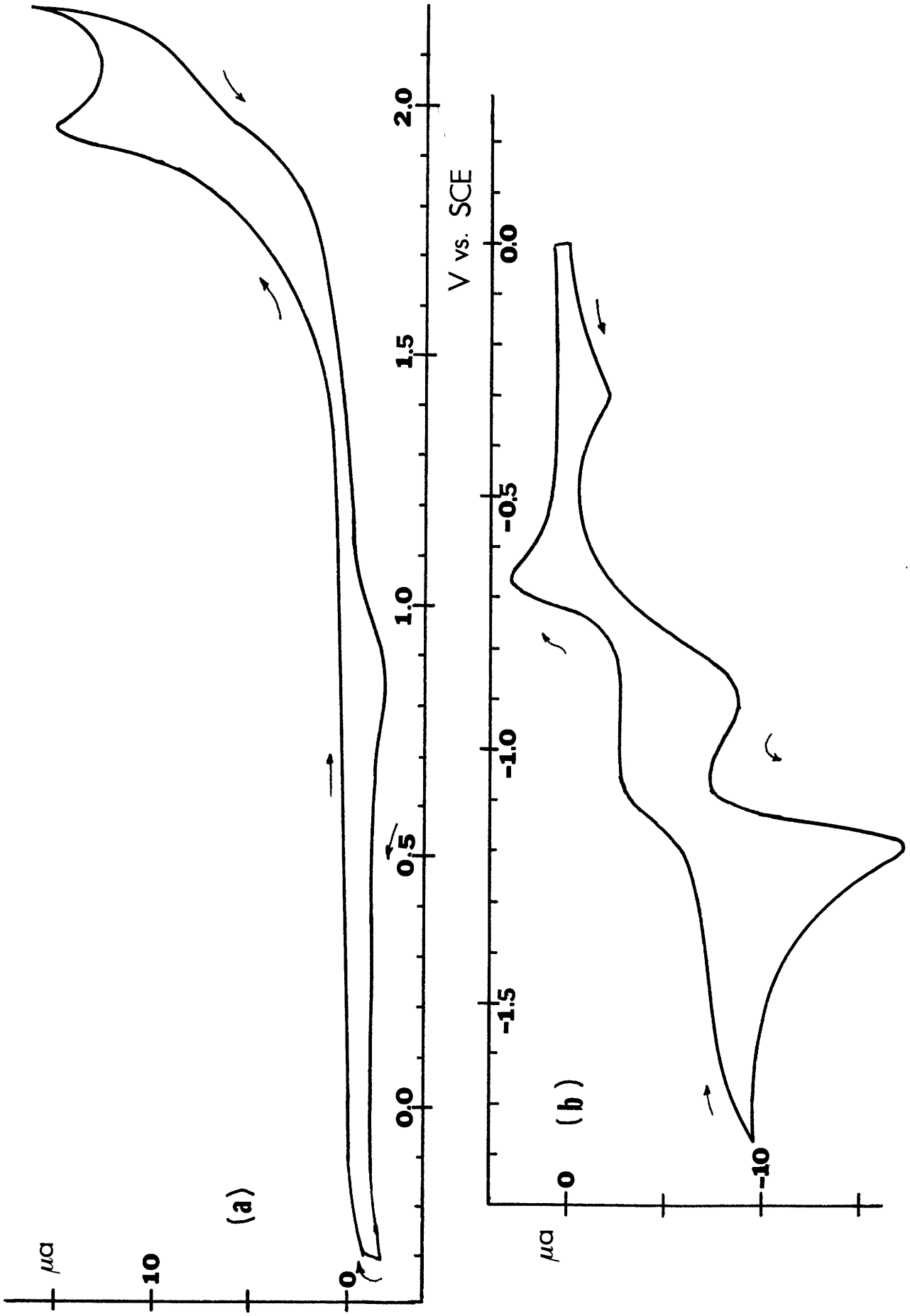

15
10
5
0
-5
μa
(a)
1.0
0.5
0.0
-0.5
V vs. SCE
0.0
-1.0
-1.5
(b)
0
-5
μa

Figure II: Cyclic Voltammograms of $(nBu_4N)_2TcCl_6$ in Acetonitrile/0.1 M TBAP. a) 100 mV sec^{-1}, initially anodic, starting pt. 0.0V, displaying irreversible one electron oxidation. b) 100 mV sec^{-1}, initially cathodic, starting point 0.0V, irreversible reductions observed.


μa
10
0
(a)
0.0
0.5
1.0
1.5
2.0
V vs. SCE
-0.5
-1.0
-1.5
0.0
(b)
0
-10
μa

These results indicate that a clean, reversible reduction to MX_6^{3-} is not possible electrochemically under these conditions; however, reduction does occur more easily for the technetium halo-species than for the rhenium analogs. This suggests that the MX_6^{3-} ions (X=Cl,Br) are extremely kinetically labile. It is known that both technetium and rhenium halo-complexes can be produced chemically through the reduction of the hexahalometallates in the presence of other ligands.[10-16] These electrochemical results suggest that such processes will be easier for technetium than for rhenium.

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18. Reversible behavior is defined by three observable properties in the cyclic voltammogram:

1) 60 mV peak to peak separation ($E_p a - E_p c = 60$ mV) independent of scan rate.

2) $E_{1/2}$ independent of scan rate (determined from either $(E_p a + E_p c)/2$ or $i_{d3/4}(E_p a)$).

3) Diffusion current proportional to the square root of the scan rate ($i_d(E_p a) \propto \sqrt{\text{scan rate}}$)

Reversibility was determined by comparison of the scans obtained with the scans of a known reversible system (ferrocene to ferricinium) under the same conditions.

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CHAPTER II

Preparation and Characterization of the Oxotetrachlorotechnetate(V) Anion and Its Use as an Intermediate in Technetium(V) Chemistry

Introduction

The chemistry of rhenium(V) and technetium(V) is dominated by the presence of oxo- or nitrido-ligands.[1,2] A wide variety of rhenium(V) complexes based on the reaction chemistry of $ReOCl_3(PPh_3)_2$[3] are known; $ReO(OEt)Cl_2(PPh_3)_2$[3], t-$ReO(OEt)(py)_2Cl_2$[4], t-$Re_2O_3(py)_4Cl_4$[4], t-$Re_2O_3(dtc)_4$,[5-7] $Re(NPh)Cl_3(PPh_3)_2$[8] are representative of some of the species obtainable. Reaction of perrhenate, triphenylphosphine, and hydrazinedihydrochloride in ethanol/benzene afforded $ReNCl_2(PR_3)_n$[8] (n = 2, PR_3 = PPh_3; n = 3, PR_3 = $P(alkyl)_2Ph$) which contains the Re≡N moiety. There have been no reports of technetium(V) analogues of any of these species.

The aqueous solution chemistry of rhenium(V) and technetium(V) is not well documented. Oxy-halo species for both elements have been claimed; the rhenium complexes K_2ReOCl_5,[9] various salts of $ReOCl_4^-\cdot$solv (solv = water or acetonitrile),[10,11] and salts of $ReOBr_4^-$ [11] have been prepared. X-ray structures have been performed on $Ph_4AsReOBr_4\cdot CH_3CN$[12] and $Et_4NReOBr_4\cdot H_2O$,[13] as well as K_2ReOCl_5.[14] These species disproportionate rapidly to ReO_4^- and $ReO_2\cdot xH_2O$ in aqueous solutions that are weakly acidic.[10,11] This fact has limited the exploration of any aqueous reaction chemistry these salts might possess.[11]

A green intermediate formed in the reduction of pertechnetate to hexachlorotechnetate(IV) by hydrochloric acid has been postulated as a technetium(V) species, $TcOCl_4^-$[15] or $TcOCl_5^{2-}$ [16]. This material has been reported to be even more susceptible to hydrolysis[16,17] than the rhenium

analogues. In concentrated hydrochloric acid solution it is reduced to hexachlorotechnetate(IV).[15,16]

Other rhenium(V) and technetium(V) complexes prepared include the well characterized rhenium cyanide complexes, $K_3ReO_2(CN)_4$,[18] $K_4Re_2O_3(CN)_8$,[19] and $K_2ReN(CN)_4(H_2O)$.[20] A class of cationic rhenium(V) and technetium(V) transdioxo complexes have been prepared with the general formula t-$MO_2(ammine)_4^+$, where the ammine can be pyridine[21,22] ethylenediamine[23] or 2,2'-dipyridyl[24] in the case of rhenium, and pyridine [25] in the case of technetium.

Recently, DePamphilis, et al., isolated a water stable technetium(V) complex, $nBu_4NTcO(SCH_2C(O)S)_2$, from the reduction of pertechnetate by thioglycolic acid.[26] The structure has been confirmed crystallographically.[26] Smith, et al., have recently isolated a similar compound, $Ph_4AsTcO(SCH_2CH_2S)_2$ via the reduction of pertechnetate by $NaBH_4$ in the presence of ethanedithiol. Both species are extremely important as dithiol-containing ligands are used in technetium 99^m-radiopharmaceuticals.[28-30] The isolation of these two water stable complexes suggests that technetium(V) solution chemistry is much more varied than initially believed.[1]

A report by Schwochau, et al.,[31] concerning the synthesis and isolation of $(nBu_4N)_2Tc_2Cl_8$, the technetium analog of the well known $(nBu_4N)_2Re_2Cl_8$,[32] from the reduction of pertechnetate by hypophosphorous acid in hydrochloric acid has resulted in the discovery of a versatile synthetic tool for examining technetium(V) chemistry.

An X-ray structure of the PPN^+[34] salt of the green solid isolated by the method of Schwochau, et al.,[31] reveals that the material is not

$Tc_2Cl_8^{2-}$, but rather a technetium(V) complex, $TcOCl_4^-$. Isolation of the green intermediate in the reduction of pertechnetate by hydrochloric acid[15,16] by addition of tetrabutylammonium ion results in the formation of $nBu_4NTcOCl_4$.

The preparation and characterization of this important compound, an investigation of its uses as an intermediate in the exploration of technetium(V) chemistry, and a survey of coordination geometries currently accessible to technetium(V) and rhenium(V) is presented.

Experimental

All water used was passed through a Barnstead Ultrapure D8902 Cartridge followed by distillation using a Corning AG-1 water still prior to use. All other reagents were used as received. $nBu_4NReOBr_4$ was prepared according to the literature procedure.[11] Gifts of $Ph_4AsReO(SCH_2CH_2S)_2$ and $Ph_4AsReO(mnt)_2$ by Chris Orvig, M.I.T., are gratefully acknowledged.

Infrared spectra were recorded on a Perkin-Elmer 180 grating spectrophotometer as KBr pellets. Raman spectra were obtained as solid samples using a Spex Ramalog with the 5145 Å line of an Ar laser. Optical spectra in appropriate solvents were recorded on a Cary 17 spectrophotometer.

Voltammetric studies were carried out using a PAR model 174 polarographic analyzer with rotating Pt, stationary Pt, dropping Hg, and stationary Hg pool electrodes. All potentials were referenced to a saturated calomel electrode (SCE). Tetrabutylammoniumperchlorate (Southwestern Analytical) was dried *in vacuo* at 85°C prior to use as supporting electrolyte. Spectro-grade acetonitrile was used as the solvent. Ferrocene was used as an internal calibrant.

Magnetic susceptibilities 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[33] and the magnetic moment derived from the expression:

$$\mu_{eff} = 2.84\sqrt{\chi_M^{corr} T}$$

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

Electron paramagnetic resonance measurements were obtained with a Varian E-Line spectrophotometer. Measurements at 77°K were made using frozen solution glasses and a specially designed liquid nitrogen dewar.

Elemental analyses for the new rhenium complexes prepared were performed by Galbraith Laboratories, Knoxville, Tenn.

Melting points are uncorrected.

Preparation of $nBu_4NTcOCl_4$

This light green solid can be prepared via the reduction of pertechnetate by hypophosphorous acid in hydrochloric acid (Method A), which parallels the conditions used in the preparation of "$Tc_2Cl_8^{2-}$",[31] or via the reduction of pertechnetate by hydrochloric acid (Method B). Method B provides the easiest and highest yield route to $nBu_4NTcOCl_4$.

Method A

To a thoroughly purged 15 mL two neck flask equipped with a magnetic stir bar were added 4.5 mL Ar purged 12N hydrochloric acid and 0.7 mL 50% w/w hypophosphorous acid (Baker) via syringes. To the stirred solution were added 3.6 mL of a 0.33 M (1.19 mmol) aqueous ammonium pertechnetate solution via a syringe. After $1\frac{1}{2}$ h stirring, the dark green solution was treated with 3.5 mL of a 75% w/w tetrabutylammonium chloride solution. The light green microcrystalline solid was filtered under N_2 and washed with 2 mL 12N hydrochloric acid, followed by six 5 mL

portions of isopropanol. The light gray-green solid was dried in vacuo, yield 0.42 gm, 70% based on technetium.

Method B

To a beaker equipped with a stir bar were added 16 mL of 12 N hydrochloric acid and 2.0 mL of 0.32 M (0.64 mmol) aqueous NH_4TcO_4 solution. After 10 min., 2 mL of 75% w/w tetrabutyl ammonium chloride were added dropwise to the green solution. A microcrystalline powder was collected by filtration. The solid was washed with 1.5 mL 12N hydrochloric acid, followed with five 1.5 mL aliquots of isopropanol, then dried in vacuo. Yield, of light green solid, 0.31 gm, 98% based on technetium.

Both methods produce material that is suitable for further experimentation. Attempted recrystallization from methanol or acetone yielded green plates; however upon filtration or drying these crystals crazed and broke apart. Recrystallization from CH_2Cl_2/hexane afforded stable dark green plates.

Analysis, $C_{16}H_{36}NOCl_4Tc$, Calc.: C, 38.49; H, 7.27; N, 2.81; Cl,28.40.
Found: C, 38.42; H, 7.22; N, 2.67; Cl, 26.34, 29.74.

Optical Spectrum (CH_2Cl_2) 840 nm(17 L mol^{-1} cm^{-1}), 585 (7), 475 (15), 370 (140), 293 (4450)

Infrared Spectrum(KBr) 2990 (sh), 2955 (s), 2935(s), 2862 (s), 1465 (s), 1402(w), 1376 (m), 1358(w), 1340 (w), 1335 (w), 1315 (w), 1303 (w), 1279 (w), 1235 (w), 1163 (m), 1160 (m), 1145 (w), 1125 (w), 1103 (w), 1060 (m), 1053 (m), 1019 (s), 990 (w), 920 (w), 890 (sh), 880 (m), 790 (w), 770 (w), 750 (w), 730 (m), 525 (w), 378 (s), 355 (w), 330 (w)

Magnetic Moment-50.7 x 10^{-6} cgs units (diamagnetic). This salt is soluble in methanol, acetone, acetonitrile, methylene-chloride, and tetrahydrofuran. It is insoluble in isopropanol and non-polar organic solvents.

Preparation of Bis(triphenylphosphine)iminiumoxotetrachlorotechnetate(V).

A round bottom flask was charged with 0.067 gm (0.13 mmol) $Bu_4NTcOCl_4$, 1.0 gm PPN^+Cl^-, enough methanol to dissolve both solids was added, and the pale green solution refrigerated at -5 °C. Slowly, dendritic green crystals formed. This solid was recrystallized from CH_2Cl_2/hexane to yield some yellow $(PPN)_2TcCl_6$ and well formed dark green blocks of $PPNTcOCl_4$, yield of green blocks 0.028 gm. These crystals were of suitable quality for use in a single crystal X-ray structure.

Infrared Spectrum (KBr) 3041 (w), 1585 (m), 1482 (m), 1435 (s), 1322 (s), 1305 (s), 1265 (s), 1180 (m), 1157 (w), 1112 (s), 1105 (sh,m), 1070 (w), 1016 (s), 997 (ms), 853 (w), 843 (w), 790 (w), 755 (sh,m), 745 (m), 723 (s), 690 (s), 615 (w), 540 (s), 530 (s), 525 (sh), 497 (s), 445 (w), 390 (m), 372 (m), 350 (w), 313(w).

Attempted isolation of $TcOCl_4^-$ with other cations.

Isolation of $TcOCl_4^-$ from the reaction solution was attempted with several cations other than tetrabutylammonium. None proved to be adequate, but several showed a remarkable tendency to produce hexachlorotechnetate(IV) rapidly. Green solutions with tetrabutylammonium ion also present in solution produced $(nBu_4N)_2TcCl_6$ upon refrigeration.

Tetraethylammonium ion

Addition of tetraethylammonium chloride to solutions of $TcOCl_4^-$ resulted in the rapid precipitation of yellow crystals.

The $(Et_4N)_2TcCl_6$ was filtered, washed with ethanol, ether, and dried in vacuo. This reaction is virtually quantitative.

Infrared Spectrum (KBr) 3010 (m), 2997 (s), 2960 (m), 2890 (w), 1460 (s), 1404 (s), 1370 (w), 1351 (w), 1340 (w), 1335 (w), 1306 (m), 1260 (w), 1182 (s), 1118 (w), 1077 (w), 1030 (s), 1003 (s), 890 (w), 796 (m), 790 (s), 580 (w), 465 (w), 312 (s).

N-methylquinolinium ion

Addition of N-methylquinolinium chloride to a dark green solution of $TcOCl_4^-$ resulted in precipitation of yellow needles, $(MeQ)_2TcCl_6$. The crystals were filtered, washed with ethanol and ether, and dried in vacuo.

Infrared Spectrum (KBr) 3076 (w), 3040 (w), 3000(w), 1622 (m), 1600 (m), 1585 (m), 1540 (w), 1525 (s), 1442 (w), 1436 (w), 1420 (w), 1395 (w), 1383 (w), 1369 (w), 1343 (m), 1287 (w), 1280 (w), 1250 (w), 1230 (w), 1216 (w), 1166 (m), 1142 (w), 1121 (w), 1088 (w), 1030 (w), 1000 (w), 970 (w), 960 (w), 872 (w), 859 (w), 815 (s), 803 (w), 778 (s), 709 (w), 610 (w), 567 (w), 504 (w), 487 (w), 463 (w), 420 (w), 402 (w), 310 (s).

Tetraphenylarsonium ion

Addition of tetraphenylarsonium chloride to green solutions of $TcOCl_4^-$ in hydrochloric acid resulted in immediate precipitation of $(Ph_4As)_2TcCl_6$ as yellow needles. No solid was obtained by the attempted metathesis of $nBu_4NTcOCl_4$ in methanol by addition of Ph_4AsCl.

Infrared Spectrum (KBr) 3050 (w), 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), 360 (w), 312 (s).

Tetrapropylammonium ion

Addition of tetrapropylammonium chloride to hydrochloric acid solutions of $TcOCl_4^-$ failed to immediately precipitate either $TcOCl_4^-$ or $TcCl_6^{2-}$. The mixture was placed in the refrigerator and after 24 h, crystals of $(NH_4)_2TcCl_6$ were isolated!* The solid isolated matches samples prepared according to the method of Nelson, et. al.[35]

Optical Spectrum (12N HCl) 385 nm (1380 L mol^{-1} cm^{-1}), 338 nm (10,600), 308 (7130), 240 (18,000)

Infrared Spectrum (KBr) 3310 (m), 3217 (s), 3145 (m), 1610 (w), 1400 (s), 330 (s)

Attempted Preparation of Oxotetrabromotechnetate (V) Anion.

A 25 mL r.b. flask with sidearm and stir bar was thoroughly purged with Ar and then charged with 1.5 mL 48% hydrobromic acid, 0.1 mL 50% w/w hypophosphorous acid, and 0.5 mL of 0.33 M aqueous NH_4TcO_4 solution (0.17 mmol), all added sequentially via syringes. The solution went orange brown instantly. Within an hour the solution was ruby red, with some red solid. One equivalent NH_4Br in 48% hydrobromic acid was added and the resulting suspension was filtered. The red solid was washed with cold 48% hydrobromic acid, ethanol, and ether, then dried in vacuo. Yield of $(NH_4)_2TcBr_6$, 0.079 gm, 78% based on technetium. This solid matches samples of $(NH_4)_2TcBr_6$ prepared according to the method of Nelson, et al.[35]

Optical Spectrum (48% HBr) 443 nm (5750 L mol^{-1} cm^{-1}), 385 (6650), 325 (10,200)

Infrared Spectrum (KBr) 3180 (m), 1390 (s), 455 (w), 249 (m)

* The source of NH_4^+ ion is NH_4TcO_4.

Reaction of $TcOCl_4^{-1}$ with Concentrated Hydrochloric Acid.

To a 50 mL beaker with stir bar were added 0.109 gm (0.22 mmol) $nBu_4NTcOCl_4$, 20 mL concentrated hydrochloric acid, and 10 mL acetone. The solution was stirred for one half hour, at which time the solution had turned yellow. Added 0.075 gm (0.22 mmol) nBu_4NClO_4 to the solution and evaporated the solution down to 5 mL over heat. Bright yellow crystals of $(nBu_4N)_2TcCl_6$ were collected by filtration, washed with 2 mL cold 12N HCl, ethanol, and ether. The solid was dried in vacuo. Yield of yellow crystals, 0.15 gm, 85% based on technetium. This material is identical to samples of $(nBu_4N)_2TcCl_6$ prepared via metathesis of $(NH_4)_2TcCl_6$ in hydrochloric acid.[36]

Optical Spectrum (CH_3CN) 383 nm (1270 L mol^{-1} cm^{-1}), 340 (11,000), 310 (7290), 242 (19,500)

Infrared Spectrum (KBr) 2990 (w), 2955 (s), 2923 (s), 2860 (s), 2720 (w), 1478 (s), 1472 (ms), 1460 (ms), 1416 (w), 1375 (m), 1353 (w), 1315 (w), 1280 (w), 1246 (w), 1236 (w), 1204 (w), 1168 (w), 1145 (w), 1103 (w), 1063 (w), 1050 (w), 1030 (w), 1020 (w), 1000 (w), 880 (m), 805 (w), 790 (w), 785 (w), 740 (m), 736 (w), 310 (s)

Reaction of $nBu_4NTcOCl_4$ with Water.

To a 30 mL beaker were added a stir bar and 0.181 gm (0.36 mmol) $nBu_4NTcOCl_4$. Upon addition of 5 mL water, a black mixture was formed. Acetone, 2 mL, and 1.0M NaOH, 2 mL, were added to insure complete hydrolysis. A Büchner funnel with a bed of fine Filter-Cel was used to filter the reaction mixture; a clear solution and a black solid

were separated. The filter bed was washed with 20 mL water followed by 20-30 mL acetone. The combined filtrates were transferred to a large beaker and 1.0 gm $Ph_4AsCl.H_2O$ in 10 mL water was added. A white precipitate formed instantly. After evaporation of the acetone, the white solid was filtered, washed with water, and recrystallized from acetone/water to yield white needles of Ph_4AsTcO_4, 0.063 gm, 32% based on technetium.

The filter bed, containing the black solid ($TcO_2.xH_2O$), was treated with two 10 mL aliquots of 15% H_2O_2, followed by 30 mL water. To the clear, colorless solution, 1.0 gm $Ph_4AsCl.H_2O$ in 10 mL water was added, producing an immediate white precipitate. The white solid was filtered, washed with 10 mL water, and then recrystallized from acetone/water to yield 0.127 gm of Ph_4AsTcO_4, 65% based on technetium. Molar ratio of TcO_4^-:$TcO_2.xH_2O$ formed in disproportionation of $TcOCl_4^-$ in H_2O was 1:2. Both sets of white needles compared favorably with samples of Ph_4AsTcO_4 prepared from a stock solution of NH_4TcO_4 and Ph_4As^+ in water. Total yield of Ph_4AsTcO_4 recovered, 0.190 gm, 98% based on technetium.

Infrared Spectrum (KBr) 3050 (w), 1477 (m), 1435 (m), 1380 (s), 1333 (w), 1305 (w), 1180 (w), 1160 (w), 1077 (m), 1020 (w), 997 (m), 925 (w), 897 (s), 846 (m), 745 (s), 685 (s), 610 (w), 475 (m), 455 (m), 350 (m)

Preparation of Tetraphenylarsoniumoxobis(ethanedithiolato)technetate(V).

$nBu_4NTcOCl_4$, 0.048 gm (0.097 mmol), was dissolved in 5 mL of methanol. To this stirred solution was added a solution consisting of 0.07 mL (0.84 mmol) ethanedithiol (Eastman) in 2.0 mL water adjusted to pH 7.5

with 0.1M NaOH. The resultant red orange solution was treated with 1.0 gm $Ph_4AsCl.H_2O$. A red-orange solid was filtered, and washed with water and ether. The solid was recrystallized from acetone/water to produce red-orange needles of $Ph_4AsTcO(SCH_2CH_2S)_2$, 0.051 gm, 77% based on technetium. This solid was identical to samples prepared from the reduction of TcO_4^- with $Na_2S_2O_4$ and ethanedithiol [37] or via the original procedure published by Smith, et.al. [27]

Optical Spectrum (CH_3CN) 485 nm (sh), 434 (sh), 398 (3400), 279 (7750)

Infrared Spectrum (KBr) 3040 (w), 3025 (w), 3000 (w), 2930 (w), 2890 (w), 2805 (w), 1895 (w), 1820 (w), 1570 (w), 1479 (m), 1437 (s), 1380 (m), 1334 (w), 1306 (w), 1266 (m), 1229 (w), 1180 (w), 1165 (w), 1140 (w), 1078 (m), 1066 (w), 1018 (w), 997 (m), 935 (s), 850 (w), 825 (w), 815 (w), 748 (s), 738 (s), 688 (s), 610 (w), 475 (m), 466 (m), 457 (m), 370 (m), 356 (m), 337 (w), 308 (w)

Magnetic Moment μeff (298K) 0.82 - 1.16 BM

$E_{1/2}$ (anodic, rot Pt) = 0.68V, 2.05V vs. SCE (irrev)

$E_{1/2}$ (cathodic, DME) =-1.86V vs. SCE (irrev)

mp. 235°C dec.

Preparation of Tetrabutylammoniumoxobis(thiomercaptoacetate)technetate(V).

To a 50 mL r.b. flask with stir bar were added 0.045 gm (0.09 mmol) $nBu_4NTcOCl_4$ and 7 mL methanol to yield a green solution. Thioglycolic acid (Eastman practical grade), 1.5 mL, was dissolved in 2 mL water and the pH adjusted to 7.5 with 10M NaOH. This pale pink solution was added to the stirred green solution which instantly turned dark brown. A saturated solution of nBu_4NBr in water (3 gm/10 mL) was added and the

mixture chilled in an ice bath. The yellow-brown crystals were filtered and washed with 15 mL water, followed by ether, and then the solid was dried *in vacuo*. Yield of $nBu_4NTcO(SCH_2C(O)S)_2$ as yellow-brown needles, 0.035 gm, 68% based on technetium. Samples prepared by this route are identical to samples prepared according to the method described by DePamphilis, *et. al.*[26] from TcO_4^- and thioglycolic acid at pH 7.4.

Optical Spectrum (CH_3CN) 415 nm (3670 L mol^{-1} cm^{-1}), 325 (3100)

Infrared Spectrum (KBr) 2950 (ms), 2918 (m), 2883 (m), 2860 (m), 1645 (vs), 1467 (m), 1445 (m), 1380 (m), 1190 (w), 1162 (w), 1120 (w), 1041 (m), 950 (s), 923 (w), 890 (w), 880 (w), 775 (w), 735 (w), 600 (m), 535 (w), 470 (w), 412 (w), 396 (w), 378 (w), 359 (m), 331 (w)

Magnetic Moment μeff (298 K) = 1.19 - 1.50 BM

$E_{1/2}$(cathodic, DME) =-1.35V vs. SCE, $1e^-$ pseudoreversible

Preparation of Tetrabutylammoniumoxobis(thiomercaptoacetate)rhenate(V).

To a 50 mL r.b. flask with stir bar were added 0.40 gm (0.52 mmol) $nBu_4NReOBr_4$ and 15 mL methanol to yield a dirty red solution. Thioglycolic acid, 6.0 mL, was dissolved in 6 mL water and the pH of the solution was adjusted to 7.5 with 10M NaOH. The slightly pink thiol solution was added to the methanol solution, producing a deep red solution. After 10 min stirring, 6 gm nBu_4NBr in 20 mL water were added. The reaction mixture was set aside for five days, at which time long orange needles were filtered, washed with water and ether, then dried *in vacuo*. Yield of $nBu_4NReO(SCH_2C(O)S)_2$, 0.11 gm, 32% based on rhenium.

Analysis, $C_{20}H_{40}NO_3ReS_4$, Calc.: C, 36.56; H, 6.14; N, 2.13; S, 19.52.

Found: C, 36.78; H, 6.37; N, 2.14; S, 19.23.

Optical Spectrum(CH_3CN) 520 nm (55 L $mol^{-1}cm^{-1}$), 425 (270), 365 (sh), 335 (3370), 280 (sh), 248 (12,300)

Infrared Spectrum (KBr) 3275 (w), 3000 (w), 2960 (s), 2922 (m), 2895 (m), 2865 (m), 2715 (w), 1650 (vs), 1468 (s), 1450 (m), 1405 (w), 1385 (m), 1377 (m), 1356 (w), 1321 (w), 1304 (w), 1280 (w), 1240 (w), 1196 (m), 1180 (w), 1165 (w), 1120 (w), 1107 (w), 1042 (s), 970 (s), 923 (w), 888 (w), 880 (m), 847 (w), 795 (w), 775 (m), 736 (m), 596 (ms), 530 (w), 470 (w), 417 (w), 397 (w), 378 (w), 349 (m), 318 (w), 292 (w), 280 (w)

Magnetic Moment μ eff (298K) = 0.31 - 0.50 BM

$E_{1/2}$(anodic, rotating Pt) 0.72V, 2.11V vs. SCE (irrev)

$E_{1/2}$(cathodic, DME) - 1.84V vs. SCE (irrev)

mp 129-132°C

Preparation of Tetrabutylammoniumoxobis(toluene-3,4-dithiolato)technetate (V).

To a 25 mL r.b. flask with stir bar were added 0.075 gm (0.15 mmol) $nBu_4NTcOCl_4$ and 5 mL methanol to produce a green solution. In a 10 mL beaker, 0.05 mL 3,4-dimercaptotoluene(Aldrich) were suspended in 2 mL water adjusted to pH 7.5 with 0.1MNaOH. This solution was added to the stirred green solution which went immediately cloudy maroon. Tetrabutylammonium bromide, 1.5 gm in 5 mL water, was added to the mixture. The reaction mixture was filtered through a bed of fine Filter-Cel and washed with water and ether; the ether wash showed a reddish tint. The complex was extracted from the bed with acetone to produce a red-brown solution. Addition of water resulted in precipitation of fine, yellow-brown crystals which were

filtered, washed with water, ether, toluene, and again ether, then dried in vacuo. Yield of $nBu_4NTcO(S_2C_6H_3CH_3)_2$ 0.049 gm, 49% based on technetium. This material had previously been prepared from the reduction of pertechnetate by $Na_2S_2O_4$ in the presence of toluenedithiol in alkaline media.[38] Samples prepared via both routes are identical.

Optical Spectrum (CH_3CN) 480 nm (sh), 400 (sh), 360 (13,000), 311 (7400)

Infrared Spectrum (KBr) 3020 (w), 2950 (ms), 2930 (m), 2860 (m). 1575 (w), 1540 (w), 1480 (w), 1470 (m), 1451 (s), 1415 (w), 1373 (m), 1280 (w), 1250 (w), 1220 (w), 1200 (w), 1178 (w), 1165 (w), 1148 (w), 1030 (w), 930 (s), 880 (m), 810 (m), 798 (m), 735 (w), 705 (w), 688 (w), 545 (w), 430 (w), 400 (w), 375 (w), 360 (m).

Magnetic Moment μ eff (298K) 0.0 - 0.42 BM

$E_{1/2}$(anodic, rotating Pt) 0.95V vs. SCE (irrev)

$E_{1/2}$(cathodic, DME) -1.52V vs. SCE (irrev)

mp 166-167°C.

Preparation of Tetrabutylammoniumoxobis(toluene-3,4-dithiolato)rhenate(V).

To a 50 mL r.b. flask with stir bar were added 0.20 gm (2.62×10^{-4} mol) $nBu_4NReOBr_4$ and 10 mL methanol to produce a dirty red solution to which was added 0.084 gm (0.54 mmol) of 3,4-dimercaptotoluene(Aldrich), followed by 2 mL of water adjusted to pH 7.5 with 0.1MNaOH. A yellow brown mixture quickly formed. Bu_4NBr, 3.0 gm in 10 mL water, was added and the resultant solid was filtered, washed with 20 mL water and quickly dried. A green impurity was removed via repeated washings with toluene. After a quick ether wash, the solid was taken up in 25 mL acetone, then water was added to the point of incipient crystallization. The bright orange crystals

were filtered, washed with water and ether, then dried in vacuo. Yield of $nBu_4NReO(tdt)_2$, 0.12 gm, 59% based on rhenium.

Analysis, $C_{30}H_{48}NOReS_4$, Calc.: C, 47.84; H, 6.42; N, 1.86; S, 17.03.

Found: C, 47.83, H, 6.63; N, 1.84; S, 16.86.

Optical Spectrum (CH_3CN) 510 nm (sh), 440 (sh), 395 (sh), 350 (6700), 310 (22,200)

Infrared Spectrum (KBr) 3028 (w), 2957 (m), 2925 (m), 2865 (m), 2720 (w), 2007 (w), 1900 (w,brd), 1730 (w,brd), 1578 (w), 1540 (w), 1478 (m), 1473 (sh), 1453 (ms), 1435 (sh), 1430 (w), 1420 (w), 1375 (m), 1358 (w), 1281 (w), 1246 (w), 1200 (w), 1174 (w), 1165 (w), 1145 (w), 1130 (w), 1100 (w), 1060 (w), 1030 (w), 1020 (w), 1001 (w), 958 (s), 880 (m), 870 (w), 865 (w), 810 (m), 800 (m), 750 (w), 736 (w), 708 (w), 687 (w), 546 (w), 540 (w), 432 (w), 396 (w), 385 (w), 365 (m), 344 (w), 330 (w), 310 (w), 280 (w)

Magnetic Moment μ eff (298K) 0.21 - 0.37 BM

$E_{1/2}$ (anodic, rotating Pt) 1.00V vs. SCE (irrev)

$E_{1/2}$ (cathodic, DME) -2.00V vs. SCE (irrev)

mp 170.5 - 171.5°C

Preparation of Tetrabutylammoniumoxobis(maleonitriledithiolato)technetate(V).

To a 25 mL r.b. flask with stir bar were added 0.067 gm (0.36 mmol) diso-diummaleonitriledithiolate(Na_2mnt) and 0.087 gm (0.17 mmol) $nBu_4NTcOCl_4$. A brown reaction mixture resulted upon addition of 7 mL acetone. After one hour, an off white solid (NaCl, unreacted Na_2 mnt) was removed by filtration. Water was added to the coffee colored filtrate to the point of incipient crystallization. The microcrystalline brown solid was recrystallized from cold acetone isobutanol to yield large coffee colored needles of $nBu_4NTcO(mnt)_2$,

0.045 gm, 50% based on technetium.

Analysis, $C_{24}H_{36}N_5OS_4Tc$, Calc.: C, 45.19; H, 5.69; N, 10.98; S, 20.11.

Found: C, 45.09; H, 5.83; N, 10.50; S, 19.80.

Optical Spectrum (CH_3CN) 570 nm (sh), 475 (510), 380 (sh), 339 (15,500), 290 (sh), 270 (sh), 253 (23,300), 232 (sh), 210 (35,000)

Infrared Spectrum (KBr) 2950 (m), 2918 (m), 2860 (m), 2206 (m), 2200 (ms), 1510 (ms), 1480 (m), 1472 (m), 1461 (m), 1455 (m), 1437 (w), 1410 (w), 1374 (m), 1180 (w), 1170 (w), 1146 (m), 1103 (w), 1033 (w), 1019 (w), 975 (w), 947 (s), 900 (w), 878 (m), 855 (w), 800 (w), 740 (m), 495 (m), 365 (m), 345 (w), 300 (w).

Magnetic Moment $Xm^{corr} = -59.8 \times 10^{-6}$ cgs units (diamagnetic)

$E_{1/2}$ (anodic, rotating Pt) 1.73V vs. SCE (irrev)

$E_{1/2}$ (cathodic, DME) -0.64V vs. SCE (1e-reversible)

mp 128-129°C

Preparation of Tetrabutylammoniumoxobis(dithiooxalate)technetate(V).

To a 25 mL r.b. flask with stir bar were added 0.097 gm (0.19 mmol) $nBu_4NTcOCl_4$ and 0.081 gm (0.40 mmol) dipotassiumdithiooxalate (K_2dto). Approximately 8 mL acetone were added to produce an orange-red solution. After one hour, an off white solid (KCl, K_2dto) was filtered off, and water was added to the burgundy colored filtrate to the point of incipient crystallization. Burgundy-maroon crystals of $nBu_4NTcO(dto)_2$ were filtered, washed with water and ether, then dried in vacuo. Yield was 0.083 gm, 72% based on technetium.

Analysis, $C_{20}H_{36}NO_5S_4Tc$, Calc.: C, 40.19; H, 6.07; N, 2.34; S, 21.46.

Found: C, 41.08, 39.52; H, 6.41, 6.20; N, 2.38; S, 20.97.

Optical Spectrum (CH_3CN) 505 nm (sh), 480 (275), 410 (sh), 375 (3,440), 298 (14,700)

Infrared Spectrum (KBr) 3300 (w), 2958 (s), 2922 (m), 2860 (m), 2020 (w), 1760 (m), 1665 (vs), 1570 (m), 1470 (ms), 1410 (w), 1380 (m), 1358 (w), 1317 (w), 1303 (w), 1280 (w), 1240 (w), 1179 (m), 1169 (m), 1128 (w), 1110 (w), 1060 (w-m), 1030 (vs), 972 (vs), 927 (w), 896 (w), 885 (m), 800 (w), 738 (m), 530 (m), 495 (w), 405 (w), 380 (w), 342 (m), 335 (w-m), 280 (w).

Magnetic Moment μ eff (298K) 0.17 - 0.34 BM

$E_{1/2}$(anodic, rotating Pt) 1.91V, 2.28V vs. SCE (irrev)

$E_{1/2}$(cathodic, DME) -0.75V vs. SCE (1e-pseudoreversible)
-1.35V vs. SCE (irrev)

mp 126-127°C

Preparation of Tetraphenylarsoniumoxobis(dithiooxalate)technetate(V).

This salt is prepared similarly to the tetrabutylammonium salt. To the filtered acetone solution were added 0.1 gm $Ph_4AsCl.H_2O$ in 3 mL 1:1 acetone/water. Water was then added to the point of incipient crystallization. Red brown crystals of $Ph_4AsTcO(dto)_2$ were separated and washed with water and ether, then dried *in vacuo*. Yield was 0.11 gm, 80% based on technetium.

Analysis, $C_{28}H_{20}AsO_5S_4Tc$, Calc.: C, 45.53; H, 2.73; S, 17.36.

Found: C, 45.29; H, 2.51; S, 17.36.

Optical Spectrum (CH_3CN) 505 nm (sh), 480 (275), 410 (sh), 375 (3310), 297 (14,600)

Infrared Spectrum (KBr) 3307 (w), 3292 (w), 3045 (w), 1895 (w), 1814 (w), 1760 (w-m), 1670 (s), 1660 (s), 1575 (m), 1480 (m), 1435 (m), 1405 (w), 1335 (w), 1307 (w), 1275 (w), 1180 (w), 1160 (w), 1080 (m), 1068 (w), 1030 (s), 1020 (sh), 997 (m), 980 (s), 920 (w), 883 (m), 848 (w), 845 (w), 750 (ms), 743 (s), 740 (s), 705 (w), 685 (s), 610 (w), 530 (m), 475 (m), 463 (m), 450 (m), 405 (w), 380 (w), 362 (w), 350 (w), 340 (m), 275 (w).

Tetrabutylammoniumoxobis(dithiooxalate)rhenate(V).

To a 50 mL r.b. flask with stir bar were added 0.20 gm (0.26 mmol) $nBu_4NReOBr_4$ and 0.12 gm (0.53 mmol) K_2dto. Upon addition of 10 mL of acetone, a dark violet solution developed. After one hour, an off white solid (KBr, K_2dto) was filtered, and water was added to the dark violet solution to the point of incipient crystallization. Red-brown crystals were filtered, washed with water and ether, then dried in vacuo. Yield of $nBu_4NReO(dto)_2$, 0.125 gm, 71% based on rhenium.

Analysis, $C_{20}H_{36}NO_5S_4Re$, Calc.: C, 35.07; H, 5.03; N, 2.05; S, 18.72.
Found: C, 34.87; H, 5.46; N, 1.99; S, 17.93.

Optical Spectrum (CH_3CN) 520 nm (sh), 474 (340), 448 (330), 417 (480), 340 (2620), 292 (18,460)

Infrared Spectrum (KBr) 3310 (w), 2960 (m), 2920 (m), 2860 (m), 1760 (w), 1665 (vs), 1470 (m), 1380 (m), 1355 (w), 1315 (w), 1305 (w), 1280 (w), 1260 (w), 1240 (w), 1178 (w), 1169 (w), 1105 (w), 1060 (w), 1028 (s), 990 (s), 925 (w), 885 (m), 795 (w), 737 (m), 528 (m), 410 (w), 325 (m)

Magnetic Moment μ eff (298K) 0.99 - 1.46 BM

$E_{1/2}$(anodic, rotating Pt) 1.64V, 2.17V vs. SCE (irrev)

$E_{1/2}$(cathodic, DME) -0.94V vs. SCE ($1e^-$ pseudoreversible)
-1.35V vs. SCE (irrev)

mp 137-138°C

Preparation of Tetrabutylammoniumoxotetrakis(benzenethiolato)technetate(V).

To a 25 mL r.b. flask with stir bar were added 0.068 gm (0.14 mmol) $nBu_4NTcOCl_4$ and 6 mL of methanol to produce a green solution. Benzenethiol (Aldrich), 0.06 mL (0.55 mmol), was suspended in 2 mL of water adjusted to pH 7.5 with 0.1M NaOH. This mixture was added to the stirred methanol

solution, producing a dark mixture of indeterminate color. A saturated aqueous solution of nBu_4NBr (3 gm/10 mL) was added and after 1/2 hour the oily mixture was filtered through a bed of diatomaceous earth and washed with water. The filtrate appeared pale green. The bed was washed with ether; this filtrate also appeared pale green. Extraction of the bed with 25 mL of acetone yielded a dark green solution, red when viewed by transmitted light. Addition of 10 mL of water produced a dark green solid that was filtered, washed with water and ether, then dried in vacuo. This solid was recrystallized from methylenechloride/hexane as large black blocks (deep red by transmitted light) of $nBu_4NTcO(SPh)_4$, 0.064 gm, 59% based on technetium.

Analysis, $C_{40}H_{56}NOS_4Tc$, Calc.: C, 60.50; H, 7.11; S, 16.15.

Found: C, 60.61; H, 7.27; S, 16.13.

Optical Spectrum (CH_3CN) 570 nm (3300 L $mol^{-1}cm^{-1}$), 425 (5700), 259 (52,500)

Infrared Spectrum (KBr) 3045 (w-m), 2980 (w), 2950 (m), 2920 (m), 2860 (w-m), 1573 (m), 1480 (m), 1471 (m), 1467 (m), 1455 (m), 1430 (m), 1375 (m), 1350 (w), 1315 (w), 1295 (w), 1265 (w), 1167 (w), 1150 (w), 1103 (w), 1075 (w), 1060 (w), 1020 (m), 1000 (w), 933 (s), 900 (w), 890 (w), 875 (w), 840 (w), 800 (w), 752 (m), 742 (m), 695 (s), 687 (s), 496 (m), 427 (w), 370 (w), 355 (w), 345 (w)

Magnetic Moment X m^{corr} = 79.6 x 10^{-6} cgs units (diamagnetic)

mp 148-156°C dec

Attempted Preparation of $nBu_4NTcO(SPh)_4$ from Pertechnetate.

To a 30 mL beaker with stir bar were added 15 mL of water adjusted to pH=12 with 10 M NaOH, 0.30 mL of a 0.33 M aqueous NH_4TcO_4 solution (0.10 mmol), and 0.05 mL (0.45 mmol) benzenethiol. $Na_2S_2O_4$, 0.2 gm, was

added slowly and the solution went dark brown quickly. After 10 min, the reaction mixture was filtered through a bed of diatomaceous earth; the filtrate was virtually colorless and a dark solid was left on the bed ($TcO_2 \cdot xH_2O$). Treatment of the filtrate with $Ph_4AsCl.H_2O$ resulted in the precipitation of a white solid, which was washed with water and ether, then dried in vacuo. Yield of Ph_4AsTcO_4, 0.051 gm, 93% based on technetium.

Reaction of $nBu_4NTcOCl_4$ with other monodentate thiols.

The reaction between $nBu_4NTcOCl_4$ and nBuSH or t-BuSH in methanol yields dark brown solutions with some $TcO_2.xH_2O$. The brown materials do not appear to be easy to isolate; in fact, often non-radioactive brown crystals are isolated upon workup.

Preparation of Tetrabutylammoniumoxotetrakis(benzenethiolato)rhenate(V)

To a 50 mL r.b. flask with stir bar were added 0.23 gm (0.29 mmol) $nBu_4NReOBr_4$ and 10 mL of methanol to produce a dull red solution. Benzenethiol, 0.12 mL (1.18 mmol), was suspended in 1.5 mL of water adjusted to a pH of 8 with 0.1M NaOH. This homogenized mixture was added to the stirred methanol solution; a dark solution immediately formed. After 10 min, a saturated aqueous solution of nBu_4NBr (3 gm/10 mL) was added and the burgundy solid formed was filtered and washed with water. The solid was then washed with three 15 mL aliquots of ether; the first wash was green, subsequent washes quickly paled. The dried solid was recrystallized from aceton/water to yield dark burgundy needles of $nBu_4NReO(SPh)_4$, 0.20 gm, 79% based on rhenium.

Analysis, $C_{40}H_{56}NOReS_4$, Calc.: C, 54.51; H, 6.40; N, 1.59; S, 14.55.

Found: C, 54.45; H, 6.68; N, 1.31; S, 14.64.

Optical Spectrum (CH_3CN) 575 nm(sh), 483 (2200), 390 (sh), 356 (9600), 283 (sh)

Infrared Spectrum (KBr) 3040 (w-m), 3000 (w), 2983 (w), 2950 (m), 2920 (m), 2860 (m), 1935 (w), 1865 (w), 1798 (w), 1571 (s), 1480 (s), 1471 (s), 1463 (s), 1430 (m), 1383 (m), 1310 (w), 1295 (w), 1265 (w), 1162 (w), 1145 (w), 1120 (w), 1100 (w), 1072 (m), 1060 (m), 1020 (m), 1000 (w), 953 (s), 900 (w), 870 (w-m) 835 (w), 795 (w), 752 (m), 740 (s), 695 (s), 684 (s), 495 (m), 425 (w), 340 (w).

Magnetic Moment X m^{corr} = -67.6×10^{-6} cgs units (diamagnetic)

Preparation of μ-Oxobis(oxobis(diethyldithiocarbamato)technetate(V)).

To a 25 mL r.b. flask equipped with stir bar were added 0.068 gm (0.14 mmol) $nBu_4NTcOCl_4$ and 0.114 gm (0.51 mmol) $Et_2NCS_2Na.3H_2O$. Upon addition of 10 mL acetone, a red mixture quickly formed. After one hour, NaCl was filtered, and water was added to the clear red solution to the point of incipient crystallization. Burgundy red crystals were filtered and washed with water and ether, then dried in vacuo. Yield of $Tc_2O_3(Et_2NCS_2)_4$, 0.046 gm, 80% based on technetium.

Analysis, $C_{20}H_{40}N_4O_3S_8Tc_2$, Calc.: C, 28.63; H, 4.81; N, 6.68; S, 30.57.

Found: C, 28.90; H, 5.03; N, 6.13; S, 30.18.

Optical Spectrum (CH_3CN) 565 nm (sh), 485 (8400), 385 (5900), 262 (58,500)

Infrared Spectrum (KBr) 2960 (w), 2917 (w), 2860 (w), 1565 (w), 1505 (s), 1497 (s), 1455 (m), 1446 (m), 1430 (m), 1373 (w), 1352 (w), 1340 (w), 1292 (w), 1270 (m), 1204 (m), 1145 (m), 1090 (w), 1070 (w), 1065 (w), 992 (w), 922 (w), 907 (w), 845 (w), 777 (w), 630 (s), 560 (w), 390 (w), 353 (w), 315 (w)

Magnetic Moment X m^{corr}= -115 x 10^{-6} cgs units (diamagnetic)

mp 118°C black 123°C dec.

Preparation of μ-Oxobis(oxobis(diethyldithiocarbamato)rhenate(V)).

To a 50 mL r.b. flask equipped with stir bar were added 0.20 gm (0.22 mmol) $nBu_4NReOBr_4$, 0.16 gm (0.67 mmol) $Et_2NCS_2Na.3H_2O$, and 12 mL of acetone to produce a dark red-brown solution. After one hour, NaBr was filtered, and water added to the filtrate to the point of incipient crystallization. Dark brown crystals were filtered and washed with water and ether, then dried in vacuo. Yield of $Re_2O_3(Et_2NCS_2)_4$, 0.072 gm, 64% based on rhenium. Samples of $Re_2O_3(Et_2NCS_2)_4$ prepared by this method are identical to samples prepared from $ReOCl_3(PPh_3)_2$ by published methods.[6,7]

Analysis, $C_{20}H_{40}N_4O_3Re_2S_8$, Calc.: C, 23.70; H, 3.98; N, 5.53; S, 25.31.
Found: C, 24.70; H, 4.52; N, 5.48; S, 24.85.

Optical Spectrum (CH_3CN) 590 nm (325 L $mol^{-1}cm^{-1}$), 475 (sh), 435 (sh), 383 (12,700), 255 (66,100)

Infrared Spectrum (KBr) 2960 (m), 2918 (w), 2858 (w), 2060 (vw), 1890 (w), 1505 (vs), 1453 (s), 1445 (s), 1430 (s), 1373 (m), 1090 (m), 1070 (m), 995 (m), 955 (m), 907 (m), 845 (m), 780 (m), 665 (vs), 560 (m), 550 (w), 495 (w), 460 (w), 425 (w), 390 (w), 370 (w), 360 (w), 330 (s), 319 (w)

Preparation of Dioxotetrapyridinetechnetium(V)perchlorate dihydrate.

To a 25 mL r.b. flask with stir bar were added 0.310 gm (0.62 mmol) $nBu_4NTcOCl_4$ and 15 mL methanol. Upon addition of 5.0 mL of pyridine, the stirred green solution turned yellow orange. Several drops of water were added to complete the color transformation. A very concentrated $NaClO_4$ solution, 15 mL, was added and the resultant yellow solution was set aside

and the methanol evaporated at room temperature. Yellow-orange needles were filtered and washed with 7 mL of cold water. The solid bleached to a bright yellow and lost its pyridine odor. The yellow needles were dried *in vacuo* overnight. Yield of $[TcO_2(py)_4]ClO_4.2H_2O$ was 0.247 gm, 70% based on technetium. This material has the same physical properties as the $TcO_2(py)_4^+$ species prepared from hexachlorotechnetate(IV) and pyridine in aqueous hydrochloric acid.[25]

Analysis, $C_{20}H_{24}N_4ClO_8Tc$, Calc.: C, 41.21; H, 4.15; N, 9.61.

Found: C, 41.66; H, 4.20; N, 9.67.

Optical Spectrum (MeOH) 450 nm (250 L $mol^{-1}cm^{-1}$), 290 (3400)

Infrared Spectrum (KBr) 3410 (wm), 3125 (w), 3095 (w), 3060 (w), 2955 (w), 2863 (w), 1635 (w), 1600 (w), 1475 (m), 1465 (w), 1446 (s), 1340 (w), 1230 (w), 1206 (m), 1151 (w), 1090 (s), 1060 (ms), 1040 (w), 1009 (w), 990 (w), 960 (w), 875 (w), 825 (s), 767 (s), 762 (s), 702 (ms), 692 (s), 647 (w), 635 (w), 618 (m), 461 (w)

Raman (solid) 1595 (ms), 1475 (m), 1213 (m), 1205 (m), 1156 (w), 1071 (m), 1020 (s), 936 (m), 889 (m), 863 (m), 800 (m), 643 (m).

Preparation of Oxodichloro(tris(1-pyrazoyl)borato)technetate(V).

To a 100 mL beaker were added a stir bar, 15 mL of 12N hydrochloric acid, and 0.81 mL of a 0.367M NH_4TcO_4 aqueous solution (0.30 mmol). After 10 min, 40 mL water were slowly added to the $TcOCl_4^-$ solution to make it 3N in hydrochloric acid. Potassiumtris(1-pyrazoyl)borate ($KHBPz_3$), 0.078 gm (0.31 mmol), were dissolved in 20 mL of 3N hydrochloric acid and added to the $TcOCl_4^-$. Within one hour, a green solid had precipitated out of the solution. This solid was filtered and washed with 5 mL of water and dried

in vacuo. The mother liquor was still green, but no more solid precipitated. Yield of $TcOCl_2(HBPz_3)$, 0.029 gm, 25% based on technetium. This material is identical to the material prepared by Deutsch, et. al.[39] from pertechnetate, $NaBH_4$, and $KHBPz_3$ in 3N hydrochloric acid.

Infrared Spectrum (KBr) 3138 (w), 3110 (m), 2980 (w), 2947 (w), 2600 (w), 2505 (m), 1750 (w,brd), 1630 (w, brd), 1506 (w), 1498 (ms), 1434 (w), 1400 (s), 1381 (ms), 1355 (w), 1305 (s), 1207 (s), 1200 (s), 1181 (m), 1176 (ms), 1119 (s), 1112 (s), 1098 (w), 1070 (m), 1042 (s), 992 (m), 980 (ms), 972 (s), 940 (w), 924 (w), 920 (w), 900 (w), 886 (w), 872 (w), 855 (w), 813 (w), 790 (m), 768 (s), 760 (m), 719 (m), 708 (ms), 668 (w), 662 (w), 647 (m), 642 (m), 612 (m), 460 (w), 378 (m), 350 (s), 315 (w), 306 (w)

Reaction of $TcOCl_4^-$ with PPh_3

To a 25 mL r.b. flask with stir bar were added 0.193 gm (0.39 mmol) $nBu_4NTcOCl_4$ and 9 mL acetonitrile, followed by 0.31 gm (1.16 mmol) triphenylphosphine. Addition of PPh_3 caused an immediate color change from green to dark brown. Within five min, the color had changed to orange and orange crystals had precipitated. The crystals were filtered and washed with 2 mL of acetonitrile and 15 mL of ether, then dried in vacuo. The yield was 0.159 gm of orange crystals.

Analysis, Found: C, 58.68; H, 4.28; P, 7.97; Cl, 15.31. This corresponds to an empirical formula of $Tc_2Cl_5(PPh_3)_3$. The optical spectrum in CH_2Cl_2 displays bands at 327 nm, 375 nm (sh), 500 nm, 590 nm (sh), and a weak broad band between 750-800 nm. Solutions of this material appear to change slowly with time; this may be due to oxidation in air. The orange solid is insoluble in ethanol, acetone, benzene, toluene, or other non-polar solvents.

Infrared Spectrum (KBr) 3042 (w), 1583 (w), 1567 (w), 1479 (m), 1430 (ms), 1363 (w), 1330 (w), 1311 (w), 1275 (w), 1183 (w), 1156 (w), 1116 (w), 1087 (m), 1065 (w), 1024 (w),

996 (w), 923 (w), 848 (w), 750 (sh), 740 (m),
720 (w), 700 (sh), 692 (s), 616 (w), 517 (s),
509 (ms), 490 (m), 450 (w), 430 (w), 415 (w),
329 (m), 317 (w)

Magnetic Moment Xg = 4.35 x 10^{-6}cgs units (no EPR Spectrum was obtainable as low as 77K)

mp. 150°C red, 157°C black, 161°C dec.

Reaction of $nBu_4NTcOCl_4$ with Hg

Solutions of $nBu_4NTcOCl_4$ in acetonitrile react with Hg° and turn dark brown, with bands in the optical spectrum appearing at 930 nm, 600 nm, 380 nm, 345 nm, and 308 nm. In addition, room temperature EPR spectra can be obtained, although the spectra are quite complex and uninterpretable at this time.

X-Ray Crystallographic Study of $[PPN][TcOCl_4]$[40]

Air-stable olive-green single crystals of $[(C_6H_5)_3PNP(C_6H_5)_3]$ $[TcOCl_4]$ obtained as described (vide infra), were suitable for x-ray diffraction studies. Weissenberg and precession photographs, used to determine the probable space group and a preliminary set of lattice constants, indicated orthorhombic, mmm, Laue symmetry. The systematically absent reflections were those required by the centrosymmetric space group Pnam (an alternate setting of P_{nma}-D_{2h}^{16}; No. 62 [41a]) or the noncentrosymmetric space group $Pna2_1$-C_{2v}^{9} (No. 33[41b]). The choice of the noncentrosymmetric space group was fully supported by all stages of the subsequent structure determination and refinement.

Intensity measurements utilized a spherical specimen 0.61 mm. in diameter which was glued to the end of a thin glass fiber with a tip diameter

of 0.15 mm. This crystal was then carefully aligned on a computer-controlled syntex P$\bar{1}$ autodiffractometer and a total of 15 high-angle ($2\theta_{MoK\bar{\alpha}}>25°$) reflections, chosen to give a good sampling of reciprocal space and diffractometer settings, were used to align the crystal and calculate angular settings for each reflection. A least-squares refinement of the diffraction geometry for these 15 reflections, recorded at the ambient laboratory temperature of 20±1° with graphite-monochromated $MoK\bar{\alpha}$ radiation (λ = 0.71073Å) gave the lattice constants: a= 21.618(5)Å, b = 16.870(5)Å and c= 9.658(3)Å. A unit cell content of four $[(C_6H_5)_3PNP(C_6H_5)_3][TcOCl_4]$ moieties gives a calculated density of 1.500 g/cm^3 which is in excellent agreement with the observed density of 1.496 g/cm^3 measured by flotation in a 1,2-dichloroethane/carbon tetrachloride mixture.

Diffraction measurements utilized graphite-monochromated $MoK\bar{\alpha}$ radiation and the ω scanning technique with a 4° takeoff angle and a normal-focus x-ray tube. Two Friedel octants of data (+h, +k, +l and -h, -k, -l) were collected at a scanning rate of 3°/min. for 4350 reflections having $0°<2\theta_{MoK\bar{\alpha}}<43°$ and a single positive octant (+h, +k, +l) at 2°/min for reflections having $43° \leq 2\theta_{MoK\bar{\alpha}} < 55°$. The scan for each reflection was between ω settings 0.50° above and below its calculated $K\bar{\alpha}$ (λ = 0.71073Å) doublet value. Counts were accumulated for nineteen equal time intervals during each scan and those fifteen contiguous intervals which had the highest single accumulated count at their midpoint were used to calculate the net intensity from scanning. A careful and systematic preliminary

study of peak-widths (half-height to half-height) indicated little variation from a value of 0.28° in ω for various orientations of the crystal. Background counts, each lasting for one-fourth the total scan time used for the net scan, were measured at ω settings 1.00° above and below the calculated value for each reflection.

A total of 4281 independent positive-octant reflections having $2\theta_{MoK\alpha}$-<55° (the equivalent of a limiting $CuK\bar{\alpha}$ sphere) were measured in three concentric shells of increasing 2θ. The six standard reflections, measured every 250 reflections as a monitor for possible disalignment and/or deterioration of the crystal, gave no indication of either. The linear absorption coefficient of the crystal for $MoK\bar{\alpha}$ radiation[42] is 0.82 mm^{-1}, yielding a μr of 0.25 for the spherical crystal used in data collection. Since the absorption of x-rays by a spherical crystal having μr= 0.25 is virtually independent of scattering angle, [43] the intensities were reduced without absorption corrections to relative squared amplitudes, $|F_o|^2$, by means of standard Lorentz and polarization corrections.

Of the 4281 positive-octant reflections examined, 1068 were eventually rejected as objectively unobserved by applying the rejection criterion, $I<3\sigma(I)$ where $\sigma(I)$ is the standard deviation in the intensity computed from C_t being the total count from scanning, k the

$$\sigma^2(I) = (C_t + k^2 B)$$

ratio of scanning time to total background time (in this case, k=2) and B the total background count. The heavy-atom technique, difference

Fourier syntheses and full-matrix least-squares refinement were used with the remaining 3213 independent positive octant reflections in the determination and refinement of the structure. A Wilson plot and set of normalized structure factors, E_{hkl}, were calculated from these reflections; the various statistical indicators using these normalized structure factors were all in agreement with the choice of a noncentrosymmetric space group.

The atomic coordinates of the technetium atom were readily derived from a Patterson synthesis calculated with the 4350 Friedel pairs having $2\theta_{MoK\bar{\alpha}}<43°$. Least-squares refinement of the structural parameters for the Tc atom resulted in a conventional weighted residual, of 0.411 for 3888 Friedel-pair reflections having $I>3\sigma(I)$. The

$$\underline{R}_1 = \Sigma||F_o| - |F_c||\Sigma|F_o|$$

inclusion of chlorine atoms whose positions were selected from the four sets of enantiomeric pairs which appeared in a difference Fourier calculated at this point, reduced $\underline{R}_1$ to 0.349 and permitted the proper choice of phosphorus atoms from the two sets of previously-equivalent enantiomeric pairs. Unit-weighted isotropic least-squares refinement of the structural parameters for the Tc, 4Cl and 2P atoms gave $\underline{R}_1$=0.273 and a conventional weighted residual of 0.353 for 3888 Friedel-pair re-

$$\underline{R}_2=\{\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$$

flections. The remaining 38 nonhydrogen atoms appeared in a difference Fourier synthesis calculated at this point and isotropic full-matrix

least-squares refinement for the 45 nonhydrogen atoms gave $\underline{R}_1$ = 0.075 and $\underline{R}_2$ = 0.078. Utilization of anisotropic thermal parameters in further cycles of unit-weighted least-squares minimization of the function $\Sigma w(|F_o|-K|F_c|)^2$ (where K is the scale factor and w is the weight assigned each reflection) gave $\underline{R}_1$=0.044 and $\underline{R}_2$=0.049 for 3888 Friedel-pair reflections having $2\theta_{MoK\alpha}$< 43° and I>3σ(I). Atomic positions were then calculated for the 30 phenyl hydrogen atoms using idealized geometry and a C-H bond length of 0.95Å. These atomic positions were varied in additional cycles of unit-weighted full-matrix least-squares refinement which converged to $\underline{R}_1$=0.027 and $\underline{R}_2$=0.027 for 3888 Friedel-pair reflections. These and all subsequent structure factor calculations employed anisotropic thermal parameters for nonhydrogen atoms and isotropic thermal parameters for hydrogen atoms, the scattering factors compiled by Cromer and Mann[44] anomalous dispersion corrections[45] to the scattering factors of Tc, Cl and P atoms and a least-squares refineable extinction correction [46] of the form $1/(1+gI_c)^{1/2}$ (where the extinction coefficient, g, refined to a final value of 4.76×10^{-7}). At this point, the enantiomeric structure (mirrored about z=0.25) was similarly least-squares refined with the Friedel-pair data to give $\underline{R}_1$=0.030 and $\underline{R}_2$=0.031 for 3888 unit-weighted reflections. Since these $\underline{R}$ value differences clearly indicated the correctness of the initial enantiomeric choice, it was used with the more complete ($2\theta_{MoK\alpha}$<55°) positive-octant data in all subsequent refinement cycles.

Unit-weighted full-matrix least-squares refinement of the model with anisotropic nonhydrogen atoms and isotropic hydrogen atoms converged to $\underline{R}_1$=0.034 and $\underline{R}_2$=0.033 for 3213 positive-octant reflections having $2\theta_{MoK\alpha}$<55° and I>3σ(I). Empirical weights ($w=1/\sigma^2$) were then calculated from the a_n being coefficient derived from the

$$\sigma=\sum_{o}^{3} a_n |F_o|^n = 1.06-5.41 \times 10^{-3}|F_o| + 8.72 \times 10^{-5}|F_o|^2$$

least-squares fitting of the curve where the F_c values were calculated

$$||F_o|-|F_c|=\sum_{o}^{3} a_n |F_o|^n$$

from the fully refined model using unit weights and an I>3σ(I) rejection criterion. The final cycles of full-matrix least-squares refinement utilized these weights with 3213 independent positive-octant reflections to vary the scale factor, extinction coefficient and the positional and thermal parameters for 45 anisotropic nonhydrogen atoms and 30 isotropic hydrogen atoms to give final values of 0.033 and 0.037 for $\underline{R}_1$ and $\underline{R}_2$, respectively.[47] During the final cycle of refinement, no parameter (including those of hydrogen atoms) shifted by more than $0.31\sigma_p$, with the average shift being $0.05\sigma_p$, where σ_p is the estimated standard deviation of the parameter.

The following computer programs were employed in this work with an IBM 360/65 or 370/158 computer: MAGTAPE, SCALEUP and SCTFT4, data reduction programs written by V.W. Day; FAME, a Wilson plot and normalized structure factor program by R. Dewar and A. Stone; FORDAP, Fourier and Patterson synthesis program, a modified version of A. Zalkin's program; ORFLSE, full-matrix least-squares refinement program, a highly

modified version of Busing, Martin and Levy's original ORFLS; ORFFE, bondlengths and angles with standard deviations by Busing, Martin and Levy; ORTEP2, thermal ellipsoid plotting program by C.K. Johnson; and MPLANE, least-squares mean plane calculation program from L. Dahl's group.

Results and Discussion

The reduction of pertechnetate by hydrochloric acid has been examined by several researchers.[15, 16, 31] As early as 1959, Busey[15] had studied the reduction of pertechnetate in hydrochloric acid solutions of varying concentration with ultraviolet spectroscopy and postulated the existence of a green technetium (V) complex formulated as a mono-oxo anion, $TcOCl_4^-$, although his only quantitative information at the time was based on titration with $SnCl_2$ and the further reduction of the green complex to hexachlorotechnetate (IV) in concentrated hydrochloric acid. It was also observed at this time that pertechnetate was also reduced by hypophosphorous acid (H_3PO_2) in 8M hydrochloric acid.

Jezowska-Trzebiatowska and Baluka [16] further explored the reduction of pertechnetate by hydrochloric acid and isolated a green diamagnetic solid with an elemental analysis consistent with the formula $(NH_4)_2TcOCl_5$. They were later able to isolate several other salts of $TcOCl_5^{2-}$, notably K^+ and Cs^+, all of which had strong infrared absorption bands, 956 cm^{-1} for the Cs^+ salt and ca.990 cm^{-1} for the others, assigned as Tc=O stretches. These salts would also be reduced in hydrochloric acid to hexachlorotechnetate(IV).

Recently, Schwochau, et. al., [31] reported the synthesis of $(nBu_4N)_2Tc_2Cl_8$ from the addition of $[nBu_4N]Cl$ to a green solution resulting from reduction of pertechnetate by H_3PO_2 in hydrochloric acid. X-ray data was cited showing it to be isomorphous with the well established $(nBu_4N)_2Re_2Cl_8$.[48]

Electrochemical oxidation of $Tc_2Cl_8^{3-}$ showed evidence for the existence of $Tc_2Cl_8^{2-}$; however, attempts to isolate the material failed.[49] In addition, the synthesis of $Tc_2Cl_8^{3-}$ involves the reduction of $TcCl_6^{2-}$ with mossy zinc in hydrochloric acid.[50] Thus, the report of $(nBu_4N)_2Tc_2Cl_8$ was extremely interesting and a single crystal X-ray structure study was undertaken.

Attempted crystallization of the reported green powder from methanol or acetone yielded green plates that crazed and broke apart upon drying, in marked contrast to the behavior of crystals of $(nBu_4N)_2Re_2Cl_8$ crystallized from these solvents.

Examination of the polarographic behavior of the green solid failed to show a well defined reduction wave at a rotating platinum electrode in acetonitrile. This was puzzling, since $Tc_2Cl_8^{3-}$ had been observed to have a well defined oxidation wave at a platinum electrode.[49] The attempted use of a dropping mercury electrode resulted in a reaction of the green solution with the elemental mercury, turning the acetonitrile solution brown. Reduction of "$Tc_2Cl_8^{2-}$" to $Tc_2Cl_8^{3-}$ by Hg° might have been expected; however $Tc_2Cl_8^{3-}$ solutions are deep blue, not brown.

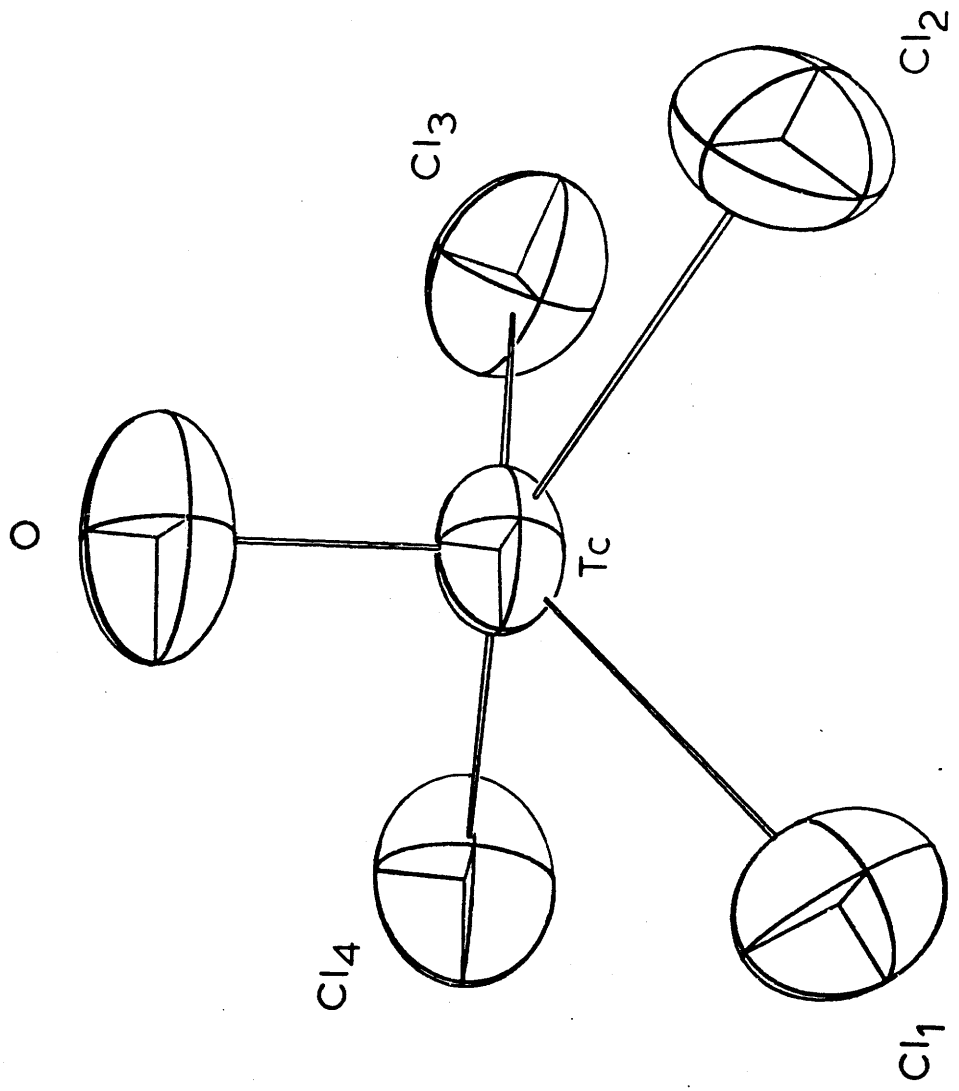
Finally, stable green plates were obtained from methylenechloride/hexane mixtures and although the crystals proved to be hopelessly disordered, preliminary information strongly suggested that a Tc-Tc quadruple bond was not present.[51]

Fortunately, metathesis of the green tetrabutylammonium salt in methanol by bis(triphenylphosphine)iminium cation (PPN^+) followed by recrystallization from methylenechloride/hexane yielded well formed olive blocks suitable for X-ray crystallography. The identity of the green salt formulated by Schwochau as "$Tc_2Cl_8^{2-}$" has been determined unequivocally to be a five-coordinate, square pyramidal technetium (V) complex, $[PPN]TcOCl_4$, consistent with its formation from the reduction of pertechnetate by H_3PO_2 in hydrochloric acid.

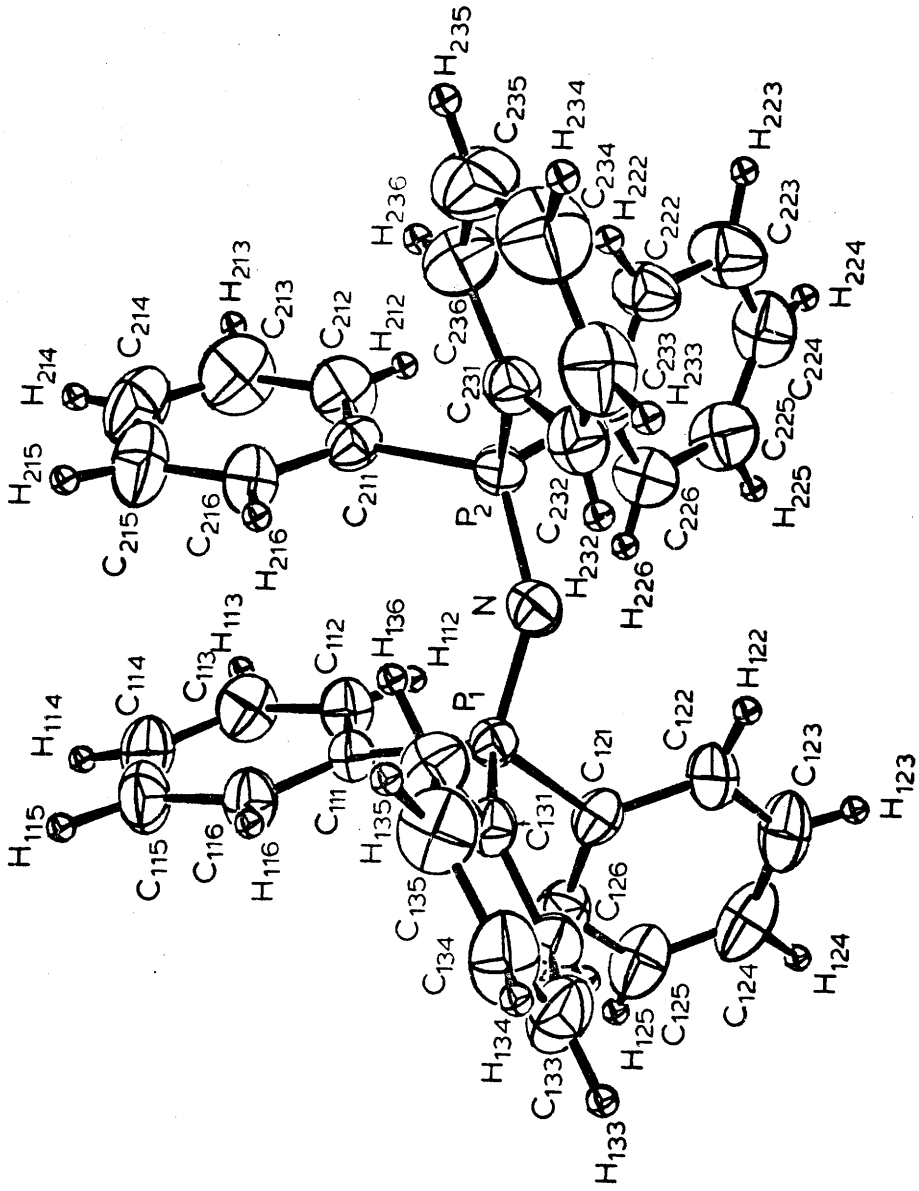
The labelling scheme used in the X-ray crystallographic analysis to designate atoms of the oxotetrachlorotechnetate anion and the bis(triphenylphosphine)iminium cation is given in the computer generated drawings of Figure III. The final coordinates for all atoms and the anisotropic thermal parameters for the nonhydrogen atoms are given in Appendix I. Covalent bond lengths are given in Table III and bond angles for nonhydrogen atoms in Table IV.

Whereas the gross structural feature of the $TcOCl_4^-$ anion is square pyramidal, with the oxygen atom at the apex and the chlorines forming the base, this anion is somewhat distorted from ideal C_{4v} symmetry and possesses only approximate C_{2v} symmetry with Cl_1-Tc-Cl_3 and Cl_2-Tc-Cl_4 angles of 139.2 (1)° and 153.7 (1)°, respectively. Although this distortion produces two distinct sets of Tc-Cl bond lengths and O-Tc-Cl bond angles, the average values for these parameters agree well with those previously observed for related $[MoOCl_4L]^-$ compounds.[52] The average Tc-Cl bond length of 2.305 Å here is in agreement with

Figure III: Perspective ORTEP drawings of the solid-state structures of (a) the oxotetrachlorotechnetate anion and (b) the bis(triphenylphosphine)iminium cation as observed in crystalline $[(C_6H_5)_3PNP(C_6H_5)_3][TcOCl_4]$. All non-hydrogen atoms are represented by (50% probability) ellipsoids having the shape, orientation, and relative size consistent with the refined anisotropic thermal parameters. Hydrogen atoms are represented by arbitrarily small spheres for purposes of clarity.



a


H235
C235
H234
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H222
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C212
H212
C231
C233
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H214
C214
C225
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H215
C215
C216
H216
C211
P2
C232
C226
H232
H226
N
H113
H136
H112
C112
C113
P1
C122
H122
H114
C114
C121
C123
H123
C111
C131
H135
H115
C115
C116
H116
C135
C126
C134
C124
H124
H134
C125
H125
C133
H133

b

Table III. Covalent Bond Lengths (Å) in Crystalline $\{TcOCl_4\}^-\{(C_6H_5)_3PNP(C_6H_5)_3\}^+$

Bond[b]	Length	Average[c]	Bond[b]	Length	Average[c]
Tc-O	1.610(4)		C_{221}-C_{226}	1.389(8)	
Tc-Cl_1	2.291(2)	2.295(2,5,5)	C_{222}-C_{223}	1.386(9)	
Tc-Cl_3	2.300(2)		C_{223}-C_{224}	1.369(10)	
Tc-Cl_2	2.317(2)	2.314(2,4,4)	C_{224}-C_{225}	1.369(10)	
Tc-Cl_4	2.310(2)		C_{225}-C_{226}	1.389(9)	
			C_{231}-C_{232}	1.369(8)	
			C_{231}-C_{236}	1.396(8)	
P_1-N	1.562(4)	1.567(4,5,5)	C_{232}-C_{233}	1.388(8)	
P_2-N	1.572(4)		C_{233}-C_{234}	1.376(10)	
			C_{234}-C_{235}	1.374(11)	
P_1-C_{111}	1.802(6)		C_{235}-C_{236}	1.375(9)	
P_1-C_{121}	1.800(5)				
P_1-C_{131}	1.808(5)	1.803(5,3,5)	C_{112}-H_{112}	0.97(5)	
P_2-C_{211}	1.801(5)		C_{113}-H_{113}	1.15(7)	
P_2-C_{221}	1.804(5)		C_{114}-H_{114}	0.92(6)	
P_2-C_{231}	1.800(6)		C_{115}-H_{115}	1.03(6)	
			C_{116}-H_{116}	0.92(5)	
C_{111}-C_{112}	1.411(7)		C_{122}-H_{122}	0.93(7)	
C_{111}-C_{116}	1.359(7)		C_{123}-H_{123}	0.87(6)	
C_{112}-C_{113}	1.376(8)		C_{124}-H_{124}	1.07(6)	
C_{113}-C_{114}	1.379(9)		C_{125}-H_{125}	0.89(7)	
C_{114}-C_{115}	1.374(9)		C_{126}-H_{126}	0.94(6)	
C_{115}-C_{116}	1.386(8)		C_{132}-H_{132}	0.91(6)	
C_{121}-C_{122}	1.392(8)		C_{133}-H_{133}	0.93(6)	
C_{121}-C_{126}	1.383(8)		C_{134}-H_{134}	0.83(6)	
C_{122}-C_{123}	1.386(8)		C_{135}-H_{135}	0.99(5)	
C_{123}-C_{124}	1.364(10)		C_{136}-H_{136}	1.01(6)	0.94(6,7,21)
C_{124}-C_{125}	1.371(10)		C_{212}-H_{212}	0.88(8)	
C_{125}-C_{126}	1.389(8)		C_{213}-H_{213}	1.10(7)	
C_{131}-C_{132}	1.384(7)		C_{214}-H_{214}	0.79(7)	
C_{131}-C_{136}	1.391(7)		C_{215}-H_{215}	0.94(5)	
C_{132}-C_{133}	1.388(8)		C_{216}-H_{216}	0.91(5)	
C_{133}-C_{134}	1.354(9)		C_{222}-H_{222}	0.97(5)	
C_{134}-C_{135}	1.368(9)		C_{223}-H_{223}	0.97(7)	
C_{135}-C_{136}	1.375(8)	1.380(9,10,31)	C_{224}-H_{224}	0.80(6)	
C_{211}-C_{212}	1.392(8)		C_{225}-H_{225}	1.04(6)	

Table III. Covalent Bond Lengths (Å) in Crystalline $\{TcOCl_4\}^-\{(C_6H_5)_3PNP(C_6H_5)_3\}^+$ Cont.

Bond[b]	Length	Average[c]	Bond[b]	Length	Average[c]
C_{211}-C_{216}	1.389(8)		C_{226}-H_{226}	0.85(6)	
C_{212}-C_{213}	1.387(11)		C_{232}-H_{232}	0.80(6)	
C_{213}-C_{214}	1.371(12)		C_{233}-H_{233}	0.96(6)	
C_{214}-C_{215}	1.396(11)		C_{234}-H_{234}	1.00(9)	
C_{215}-C_{216}	1.370(9)		C_{235}-H_{235}	0.87(5)	
C_{221}-C_{222}	1.382(8)		C_{236}-H_{236}	0.87(6)	

[a]Figures in parentheses are the estimated standard deviation in the last significant digit. [b]Atoms are labelled in agreement with Figure 1. [c]The first number in parentheses following an averaged value of a bond length is the root-mean-square estimated standard deviation of an individual datum; the second and third numbers are the average and maximum deviations from the averaged value, respectively.

Table IV. Bond Angles (deg.) for Nonhydrogen Atoms in Crystalline $\{TcOCl_4\}^-\{(C_6H_5)_3PNP(C_6H_5)_3\}^{+a}$

Type[b]	Angle	Average[c]	Type[b]	Angle	Average[c]
$OTcCl_1$	111.5(2)	110.4(2,11,11)	$C_{116}C_{111}C_{112}$	120.1(5)	
$OTcCl_3$	109.3(2)		$C_{111}C_{112}C_{113}$	119.1(5)	
$OTcCl_2$	103.0(2)	103.2(2,2,2)	$C_{112}C_{113}C_{114}$	120.1(6)	
$OTcCl_4$	103.3(2)		$C_{113}C_{114}C_{115}$	120.4(6)	
			$C_{114}C_{115}C_{116}$	119.9(6)	
Cl_1TcCl_2	85.1(1)		$C_{115}C_{116}C_{111}$	120.3(5)	
Cl_1TcCl_4	85.8(1)	85.5(1,2,4)	$C_{126}C_{121}C_{122}$	119.8(5)	
Cl_2TcCl_3	85.4(1)		$C_{121}C_{122}C_{123}$	119.4(6)	
Cl_3TcCl_4	85.6(1)		$C_{122}C_{123}C_{124}$	120.6(6)	
			$C_{123}C_{124}C_{125}$	120.3(6)	
Cl_1TcCl_3	139.2(1)		$C_{124}C_{125}C_{126}$	120.2(6)	
			$C_{125}C_{126}C_{121}$	119.7(6)	
Cl_2TcCl_4	153.7(1)		$C_{136}C_{131}C_{132}$	119.4(5)	
			$C_{131}C_{132}C_{133}$	119.2(5)	
P_1NP_2	147.4(3)		$C_{132}C_{133}C_{134}$	121.1(6)	
			$C_{133}C_{134}C_{135}$	120.0(5)	120.0(6,5,16)
NP_1C_{111}	113.3(2)		$C_{134}C_{135}C_{136}$	120.5(6)	
NP_1C_{121}	110.1(2)		$C_{135}C_{136}C_{131}$	120.0(5)	
NP_1C_{131}	109.2(2)	110.9(2,24,47)	$C_{216}C_{211}C_{212}$	119.9(6)	
NP_2C_{211}	115.6(2)		$C_{211}C_{212}C_{213}$	118.8(7)	
NP_2C_{221}	108.4(2)		$C_{212}C_{213}C_{214}$	120.9(6)	
NP_2C_{231}	108.7(2)		$C_{213}C_{214}C_{215}$	120.2(7)	
			$C_{214}C_{215}C_{216}$	119.1(7)	
$C_{111}P_1C_{121}$	106.9(2)		$C_{215}C_{216}C_{211}$	120.8(6)	
$C_{111}P_1C_{131}$	109.6(2)		$C_{226}C_{221}C_{222}$	119.7(5)	
$C_{121}P_1C_{131}$	107.6(2)	108.0(2,8,16)	$C_{221}C_{222}C_{223}$	119.6(6)	
$C_{211}P_2C_{221}$	108.6(2)		$C_{222}C_{223}C_{224}$	120.4(7)	
$C_{211}P_2C_{231}$	107.1(2)		$C_{223}C_{224}C_{225}$	120.6(6)	
$C_{221}P_2C_{231}$	108.2(2)		$C_{224}C_{225}C_{226}$	119.8(6)	
			$C_{225}C_{226}C_{221}$	119.8(6)	

Table IV. Bond Angles (deg.) for Nonhydrogen Atoms in Crystalline $\{TcOCl_4\}^-$ $\{(C_6H_5)_3PNP(C_6H_5)_3\}^{+a}$ continued

Type[b]	Angle	Average[c]	Type[b]	Angle	Average[c]
$P_1C_{111}C_{112}$	116.9(4)		$C_{236}C_{231}C_{232}$	119.3(5)	
$P_1C_{111}C_{116}$	122.6(4)		$C_{231}C_{232}C_{233}$	121.6(6)	
$P_1C_{121}C_{122}$	119.7(4)		$C_{232}C_{233}C_{234}$	118.5(6)	
$P_1C_{121}C_{126}$	120.5(4)		$C_{233}C_{234}C_{235}$	120.6(6)	
$P_1C_{131}C_{132}$	122.0(4)		$C_{234}C_{235}C_{236}$	120.9(6)	
$P_1C_{131}C_{136}$	118.5(4)	120.1(4,13,32)	$C_{235}C_{236}C_{231}$	119.2(6)	
$P_2C_{211}C_{212}$	120.8(5)				
$P_2C_{211}C_{216}$	119.3(4)				
$P_2C_{221}C_{222}$	121.8(4)				
$P_2C_{221}C_{226}$	118.4(4)				
$P_2C_{231}C_{232}$	119.8(4)				
$P_2C_{231}C_{236}$	120.8(4)				

[a]Figures in parentheses are the estimated standard deviation in the last significant digit. [b]Atoms are labelled in agreement with Figure 1. [c]The first number in parentheses following an averaged value of a bond angle is the root-mean-square estimated standard deviation of an individual datum; the second and third numbers are the average and maximum deviations from the averaged value, respectively.

other Tc-Cl bonds (Table V) when differences in metal oxidation state and coordination number are taken into account. The Tc-Cl bond length generally decreases as a function of increasing oxidation state and this has been generally attributed to substantial ionic character in the bonding.[53,54]

The Tc=O bond length of 1.610(4)Å is shorter than in any of the recently determined technetium (V) complexes (Table V). Both the nBu_4N^+ and PPN^+ salt exhibit a strong infrared absorption at ca. 1020 cm^{-1} assignable to the Tc=O stretch; this stretch is higher than other Tc=O stretches reported (Table VI) and is consistent with the short Tc=O bond length. It is important to point out that the salts of $TcOCl_5^{2-}$ prepared by Jezowska-Trzebiatowska and Baluka had Tc=O stretching frequencies at ca. 990 cm^{-1}, [17] obviously due to the presence of the trans-chloro ligand in those salts. The analogous $ReOBr_4^-$ salts, [11] have Re=O stretching frequencies that vary from 1020-990 cm^{-1} depending upon the counter ion and presence of solvent in the crystal.

Both four-atom groupings which contain Tc, O, and a pair of trans Cl atoms are coplanar to within 0.005Å and their least squares mean planes intersect near the pseudo-C_2 axis in a dihedral angle of 89.9°.

The O...Cl and cis Cl...Cl contacts in the technetium coordination sphere average 3.168Å and 3.128Å, respectively. The technetium atom is displaced by 0.66Å toward the oxygen atom from the S_4-ruffled "square base" of the four chlorine atoms (average chlorine displacement

Table V: Comparison of Some Metal-Oxo and Technetium-Chlorine Bond Lengths (Å).

	M=O	Tc-Cl
$PPNTcOCl_4$	1.61	2.29, 2.31, 2.30, 2.32
$nBu_4NTcO(SCH_2C(O)S)_2$[26]	1.67	
$Ph_4AsTcO(SCH_2CH_2S)_2$[27]	1.64	
$TcOCl_2(HBPz_3)$[39]	1.66	
Tc_2O_7[55]	1.65, 1.67, 1.70	
$(TcOF_4)_3$[56]	1.66	
$MoO(S_2CNPr_2)_2$[57]	1.66	
$Et_4NReOBr_4 \cdot H_2O$[13]	1.71	
$Ph_4AsReOBr_4 \cdot CH_3CN$[12]	1.73	
$TcOCl_2(HBPz)_3$[39]		2.33, 2.32
$K_3Tc_2Cl_8 \cdot nH_2O$[58]		2.34, 2.35, 2.37, 2.37
$Tc_2(O_2CCMe_3)_4Cl_2$[59]		2.41
$TcCl_3(Me_2PhP)_3$[54]		2.33, 2.33, 2.46
$TcCl_3(CO)(Me_2PhP)_3 \cdot EtOH$[60]		2.47, 2.48, 2.49
$TcCl(acac)_2(Ph_3P)$[61]		2.42
$TcCl_2((EtO)_2PhP)_4$[62]		2.41, 2.42

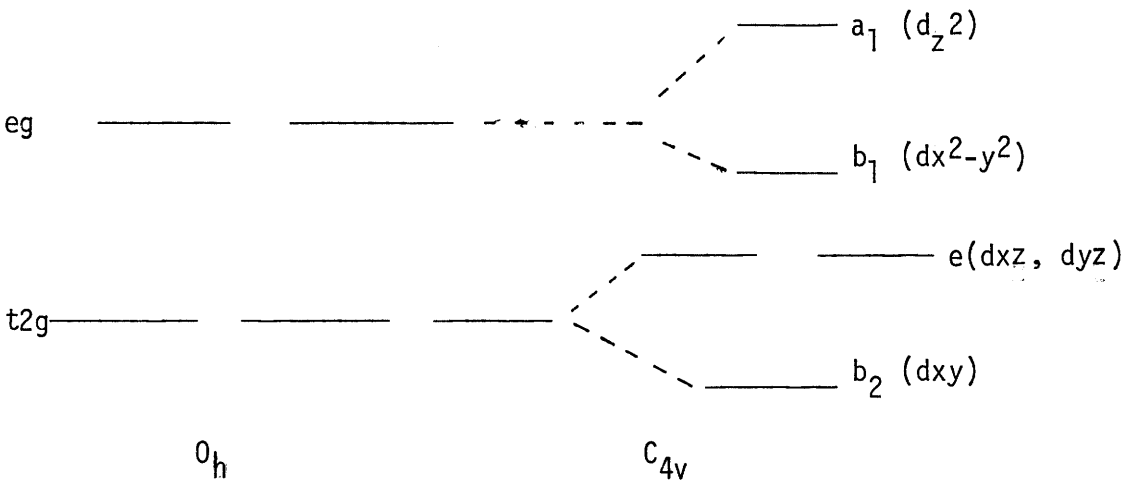
Table VI: Comparison of Some Technetium-Oxo and -Chlorine Stretching Frequencies (cm^{-1}).

	Tc=O	Tc-Cl
$PPNTcOCl_4$	1016	372
$nBu_4NTcOCl_4$	1019	378
$TcOCl_2(HBPz)_3$ [39]	972	355
$nBu_4NTcO(SCH_2C(O)S)_2$ [26]	950	
$Ph_4AsTcO(SCH_2CH_2S)_2$ [27]	940	
$(NH_4)_2TcCl_6$		330
$(nBu_4N)_2TcCl_6$		310
$(NH_4)_2TcOCl_5$ [17]	992	331
$TcCl_3(CO)(PMe_2Ph)_3$ [63]		338
t-$TcCl(CO)_3(PMe_2Ph)_2$ [63]		275
$TcCl_3(PMePh_2)_3$ [64]		334
$TcCl_4(PMePh_2)_2$ [64]		346

from the four-atom mean plane is 0.14Å). The average O-Tc-Cl and trans Cl-Tc-Cl angles of 106.8° and 146.5° are in close agreement with the corresponding parameters observed for the square pyramidal $[MoOCl_4]^-$ anion which possesses crystallographic C_{4v} site symmettry.[52a] Since no interionic contacts here are significantly less than the pertinent sum of the van der Waal's radii, [65] it is not clear that crystal packing forces may be invoked as being responsible for the distortion of $TcOCl_4^-$ from the idealized C_{4v} symmetry, but, this is possible.

Although a three atom grouping joined by adjacent double bonds would normally be expected to be linear, the observed P=N=P angle of 147.4(3)Å is only slightly outside the 137-142° range observed by other workers[66] for this angle in the bis(triphenylphosphine)iminium cation. The remainder of the structural parameters listed in Table III and IV are rather unexceptional. The bis(triphenylphosphine)iminium cation adopts a cisoidal conformation and the atoms of each phenyl group are coplanar to within 0.02Å.

Salts of $TcOCl_4^-$ are diamagnetic, as expected for d^2 ions with a $^1A_1$ ground state. Molecular orbital and ligand field calculations have been carried out on several C_{4v} symmetry mono-oxo complexes; for example, vanadyl ion, [67] molybdenyl complexes of molybdenum (V),[68,69] and even $(NH_4)_2TcOCl_5$.[70] The d-orbitals are split into four sets of orbitals; a_1 (d_{z^2}), b_1 ($d_{x^2-y^2}$), e(dxz, dyz), and b_2(dxy). These orbitals are arranged energetically as shown below.



The observed optical spectrum of $nBu_4NTcOCl_4$ in methylene chloride is tabulated in Table VII and comparisions are made with the optical spectra observed for the oxychloro-technetium (V) species prepared by Busey [15] and Baluka, et. al. .[17] The absorption spectrum of $TcOCl_4^-$ should have d-d transitions originating from the ground state, $^1A_1(b_2^2)$, to excited states $^1E(b_2e)$, $^1A_2(b_2b_1)$, and $^1B_2(b_2a_1)$. Indeed, three absorption bands with extinction coefficients <20 L mol^{-1} cm^{-1} are observed.

As was noted previously, [15,16] solutions of $TcOCl_4^-$ in concentrated hydrochloric acid are reduced to hexachlorotechnetate (IV) slowly at room temperature, but rapidly at 100°C. This is consistent with the preparation of hexachlorotechnetate(IV) from pertechnetate ion in hot hydrochloric acid.[35] Attempts to prepare $TcOBr_4^-$ by the same method as used to prepare $TcOCl_4^-$ resulted in isolation only of $(NH_4)_2TcBr_6$.

Table VII: Optical Spectra for $TcOCl_4^-$ and $TcOCl_5^{2-}$ Species.

Compound	Solvent	Band Maxima(nm)	ε_{mol}	Transition
$nBu_4NTcOCl_4$	CH_2Cl_2	840	17	$^1A_1 \rightarrow {}^1E$
		585	7	$^1A_1 \rightarrow {}^1A_2$
		475	15	$^1A_1 \rightarrow {}^1B_2$
		370	140	
		293	4450	
$TcOCl_4^-$ [15]	12N HCl	293	4700	
		2300	10400	
$(NH_4)_2TcOCl_5$ [17]	11N HCl	934	18	
		598	6	
		485	24	
		294	4400	

Bromide ion is a much better reducing agent than chloride ion and presumably the $TcOBr_4^-$ formed was not stable under the conditions of the reaction, reducing rapidly to $TcBr_6^{2-}$.

Disproportionation of oxotetrachlorotechnetate(V) occurs rapidly in aqueous solutions that are not strongly acidic. The disproportionation reaction was shown to follow the stoichiometry through isolation

$$3TcOCl_4^- + 10OH^- \longrightarrow TcO_4^- + 2TcO_2.2H_2O \downarrow + 12Cl^- + H_2O$$

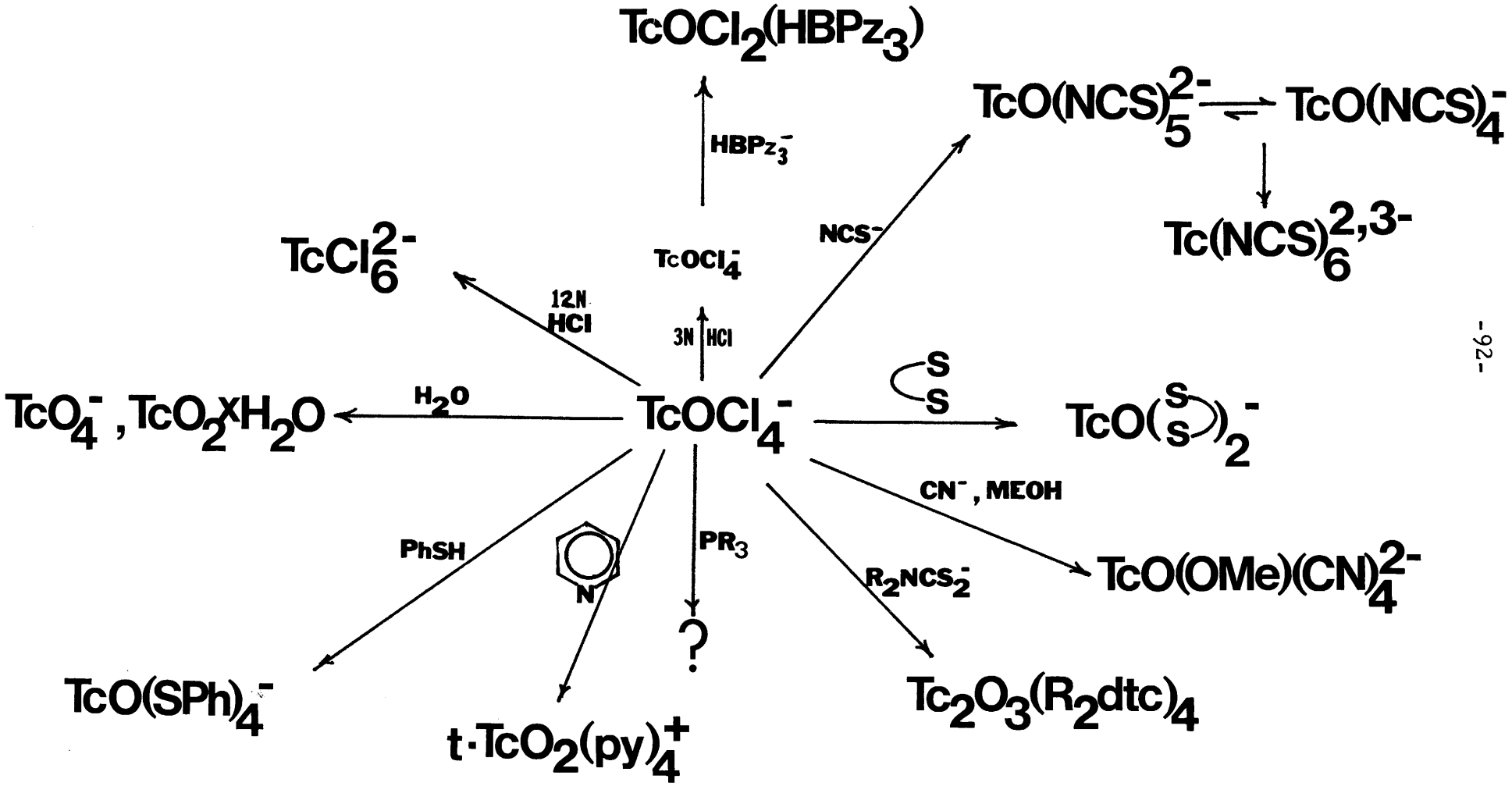
$$3Tc(V) \longrightarrow Tc(VII) + 2Tc(IV)$$

of the pertechnetate ion produced as the Ph_4As^+ salt, followed by oxidation with peroxide of the insoluble $TcO_2.xH_2O$ produced to pertechnetate ion, also isolated as the Ph_4As^+ salt. The molar ratios of TcO_4^- to $TcO_2.xH_2O$ produced were 1:2 with 98% of the technetium recovered. The oxohalo-rhenium(V) salts have also been shown to be very susceptible to hydrolysis and disproportionation with similar results.[10,11]

Fortunately, the presence of tetrabutylammonium ion rather than ammonium or cesium ion makes it possible to dissolve the oxotetrachlorotechnetate(V) ion in a wide variety of polar organic solvents such as methanol, acetone, acetonitrile, and methylenechloride. Thus, the problem of hydrolysis in aqueous solution can be circumvented, and as shown in Scheme I, $nBu_4NTcOCl_4$ can be used as a verstatile starting material for the exploration of the coordination chemistry of technetium (V).

The rest of this chapter examines the initial exploration of the coordination chemistry of technetium (V), shown in Scheme I. Where appropriate, rhenium(V) complexes are discussed and compared with the tech-

Scheme I: Some of the Reaction Chemistry of $TcOCl_4^-$.


TcOCl2(HBPz3)
HBPz3-
TcO(NCS)52- ⇌ TcO(NCS)4-
TcO(NCS)62,3-
NCS-
TcCl62-
TcOCl4-
12N HCl
3N HCl
S
S
TcO4- , TcO2XH2O
H2O
TcOCl4-
TcO(S S)2-
CN- , MEOH
PhSH
N
PR3
R2NCS2-
TcO(OMe)(CN)42-
?
TcO(SPh)4-
t-TcO2(py)4+
Tc2O3(R2dtc)4

netium(V) analogues. The species $TcO(NCS)_5^{2-}$ and $TcO(OMe)(CN)_4^{2-}$ are discussed fully in later chapters; however, they are significant in that they can currently only be prepared from $TcOCl_4^-$. They are both six-coordinate oxo-technetium(V) complexes.

The oxobis(1,2-dithiolato)metallate(V) complexes of technetium and rhenium are extremely interesting due to their stability in aqueous solutions, and in light of the current use of dithiol-containing ligands in technetium 99m-radiopharmaceuticals.[28-30] McCleverty, et. al.,[71] prepared $Ph_4AsReO(mnt)_2$ from the reaction of hexachlororhenate(IV) and maleonitriledithiolatedianion(mnt) in aqueous alcohol, followed by oxidation with iodine. No mechanism was proposed, nor was much attention paid to this species at the time. Very recently, the technetium analog, $Et_4NTcO(mnt)_2$, was reported from an aqueous reduction of pertechnetate by stannous ion with gluconate present, followed by addition of Na_2mnt and Et_4N^+ ion.[72] Very little information was provided about the species.

Recently, Smith, et. al.,[27] isolated a five-coordinate complex, $Ph_4AsTcO(SCH_2CH_2S)_2$, from reduction of pertechnetate ion in ethanol by $NaBH_4$ in the presence of ethanedithiol. The structure has been confirmed by X-ray structural analysis.[27] It has since been discovered that reduction of pertechnetate by $Na_2S_2O_4$ in alkaline solution with ethanedithiol rapidly produces this complex in high yield.[37]

DePamphilis, et. al.,[26] isolated $nBu_4NTcO(SCH_2C(O)S)_2$ from the reaction of pertechnetate ion with a large excess of thioglycolate at pH 7.5. The structure has been confirmed by X-ray structural analysis.[26]

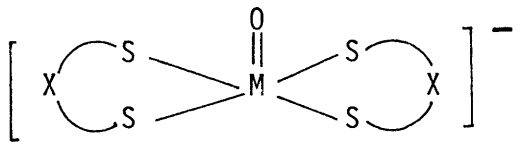
Another dithiol-derived complex, $nBu_4NTcO(tdt)_2$, has been prepared from reduction of pertechnetate by $Na_2S_2O_4$ in alkaline solution with 3,4-toluenedithiol(H_2tdt).[38]

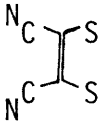
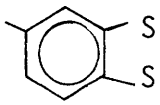
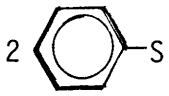
The rhenium analogues of these complexes are not easily obtainable through the reduction of perrhenate, and in addition, several interesting 1,2-dithiolate species such as dithiooxalate(dto) and maleonitriledithiolate(mnt) are available only as dianions. The reduction of pertechnetate or perrhenate in the presence of these species leads only to formation of $MO_2.xH_2O$. [38b]

Fortunately, all the complexes listed in Table VIII can be prepared from either $ReOBr_4^-$ or $TcOCl_4^-$. The chelating ligands span a wide range, from a saturated dithiolate derived from ethanedithiol to "non-innocent"[73] dithiolenes (eg. maleonitriledithiolate). In addition, the oxotetrakis(benzenethiolato)metallate(V) complexes can also be prepared.

The substitution reaction of the ligand on the MOX_4^- species can be viewed as a nucleophilic displacement on the metal, resulting in the formation of a metal-sulfur bond and the expulsion of halide either as a haloacid when the free thiol is present or as the alkali metal salt when the thiolate anion is used. The reaction with thiols is enhanced by the addition of a small amount of base. The substitution of halide ions by thiols has been previously demonstrated in the conversion of $Fe_2S_2X_4^{2-}$ and $Fe_4S_4X_4^{2-}$ to $Fe_2S_2(SR)_2^{2-}$ and $Fe_4S_4(SR)_4^{2-}$, respectively.[74]

Table VIII: Thiolate Species of Technetium and Rhenium.



SXS =	
	$MO(edt)_2^-$
	$MO(tma)_2^-$
	$MO(dto)_2^-$
	$MO(mnt)_2^-$
	$MO(tdt)_2^-$
	$MO(SPh)_4^-$

M = Tc, Re

The preparation of the $MO(tma)_2^-$ (M=Tc, Re) species from either $ReOBr_4^-$ or $TcOCl_4^-$ is performed in the presence of a large excess of commercial thioglycolic acid ($HSCH_2CO_2H$), as was the original preparation of $nBu_4NTcO(tma)_2$.[26] Mercaptothioacetic acid ($HSCH_2C(O)SH, H_2tma$)[75] has recently been shown by 270 MHz NMR measurements to be present as an impurity in commercial thioglycolic acid.[38b] The formation of the $MO(tma)_2^-$ complexes from such mixtures clearly illustrates the avidity of both the oxotechnetium and -rhenium(V) cores for dithiolate ligands.

Benzenethiol, C_6H_5SH, forms a complex with both technetium and rhenium of general formula $MO(SPh)_4^-$ from either $ReOBr_4^-$ or $TcOCl_4^-$ in methanol. Attempted reduction of pertechnetate by $Na_2S_2O_4$ in alkaline solution with benzenethiol failed to produce the technetium (V) complex. Attempts to prepare other monodentate thiolate complexes have been unsuccessful, to date.

Crystal structures on both $Ph_4AsTcO(edt)_2$[27] and $nBu_4NTcO(tma)_2$[26] indicate that these complexes are discrete five-coordinate square pyramidal molecules with the oxygen atom at the apex and the technetium atom displaced toward the apex from the square base formed by the sulfur atoms. In the case of the oxobis(thiomercaptoacetate)technetate(V) anion, high resolution NMR evidence suggests that two isomers are present with <u>cis</u> or <u>trans</u> arrangements of the carbonyl group on the ligand backbone.[38b] It is reasonable to expect that the rhenium analog, $ReO(tma)_2^-$, will show similar behavior, although it is possible that one isomer would crystallize out before the other.

It is interesting to note the similarity of the $M(V)OS_4$ core of these complexes to the isoelectronic $Mo(IV)OS_4$ core of $MoO(Pr_2dtc)_2$[57] and the recently prepared [76] $MoO(tdt)_2^{2-}$ and $MoO(edt)_2^{2-}$. Referring to Cotton and Wing's correlation,[77] the Mo-O bond order has been assigned as 3. The infrared stretching frequencies for the molybdenum oxo bond of the dithiocarbamate complexes $MoO(Et_2dtc)_2$[78] and $MoO(Me_2dtc)_2$[79] (962 and 975 cm^{-1}, respectively) as well as the $MoO(tdt)_2^{2-}$ and $MoO(edt)_2^{2-}$ species (903 and 918 cm^{-1}, respectively)[76] correspond well to a strong band in the infrared spectrum of each of the technetium and rhenium complexes (in the range 1000-900 cm^{-1}) assigned to a metal-oxygen stretch as shown in Table IX.

These frequencies are lower than the metal-oxygen stretching frequencies observed for $ReOBr_4^-$ salts[11] and the $TcOCl_4^-$ salts (vide infra). This is not unexpected, since the thiolate ligands are better electron donating groups than halogens and the greater electron density on the metal would be reflected by a decrease in π-donation from the oxygen, thereby lowering the stretching frequency.

The rhenium-oxo stretch occurs at a higher frequency (10-20 cm^{-1}) than the corresponding technetium-oxo stretch in the complexes studied. This difference can be explained by the greater orbital overlap of 5d orbitals (Re) contrasted with that of 4d orbitals (Tc). The metal-oxygen stretches of the technetium and rhenium analogues are higher in energy than the frequencies observed in $MoO(edt)_2^{2-}$ and $MoO(tdt)_2^{2-}$ (vide infra) due to the increased positive charge on the group VII metals

Table IX: Metal-Oxygen Stretching Frequencies in Oxo(tetra-thiolate)metallate(V) Complexes.

Compound	$\nu_{MO}(cm^{-1})$
$Ph_4AsTcO(edt)_2$	935
$Ph_4AsReO(edt)_2$ [38b]	952
$nBu_4NTcO(mta)_2$	950
$nBu_4NReO(mta)_2$	970
$nBu_4NTcO(dto)_2$	972
$Ph_4AsTcO(dto)_2$	980
$nBu_4NReO(dto)_2$	990
$nBu_4NTcO(tdt)_2$	930
$nBu_4NReO(tdt)_2$	958
$nBu_4NTcO(mnt)_2$	947
$Ph_4AsReO(mnt)_2$ [38b]	963
$Bu_4NTcO(SPh)_4$	933
$Bu_4NReO(SPh)_4$	953

as contrasted to the group VI metal atom. The metal-oxygen stretch varies with the dithiolate ligand and the frequency decreases in the order dto>tma>edt. The presence of electron withdrawing groups on the sulfur atom results in an increase in the metal-oxygen stretch.

Details of the optical spectra of these complexes are summarized in Table X. In general, there is at least one band in the range 330-450 nm (ε ~3500 L mol^{-1} cm^{-1}) and the complexes range in color from yellow-orange to red-brown. A bathochromic shift is observed for the technetium complexes compared to their rhenium analogues, as expected from considerations of periodicity. The complexes are generally weak paramagnets in the solid state. The effective magnetic moments, which are field dependent, generally lie in the range 0.1 - 1.5 BM (298K). Similar behavior has been observed for some oxomolybdenum and oxorhenium complexes, with a d^2 configuration having local C_{4v} symmetry, where the ground state is $^1A_1$. This has been suggested to be due to temperature-independent paramagnetism.[79-81]

The voltammetric behavior of these complexes has been examined at both mercury and platinum electrodes, as summarized in Table XI. The apparatus was calibrated by use of ferrocene ($Fc \rightleftharpoons Fc^+ + e^-$, E 1/2=0.41V vs. SCE) used as an internal standard. A dropping mercury electrode or a stationary mercury pool electrode was used in the reduction studies after it was observed that the platinum electrode and the reduced species reacted with one another.

Table X: Optical Spectra of Oxo(tetrathiolate)metallate(V) Complexes in Acetonitrile.

$Ph_4AsTcO(edt)_2$	484(sh), 433(sh), 399(3400), 279(7750)
$nBu_4NTcO(tma)_2$	415(3665), 325(3100)
$nBu_4NTcO(dto)_2$	500(sh), 480(275), 410(sh), 375(3,400), 298(14,700)
$Ph_4AsTcO(dto)_2$	510(sh), 480(275), 410(sh), 375(3310), 297(14,600)
$nBu_4NTcO(tdt)_2$	405(sh), 361(13,000), 312(7400)
$nBu_4NTcO(mnt)_2$	570(sh), 475(510), 380(sh), 339(15,500), 290(sh), 270(sh), 253(23,300)
$nBu_4NTcO(SPh)_4$	570(3300), 425(5700), 259(52,500)
$Ph_4AsReO(edt)_2$ [38b]	483(sh), 417(550), 363(sh), 328(4200)
$nBu_4NReO(tma)_2$	520(55), 425(270), 365(sh), 335(3370), 280(sh), 248(12,300)
$nBu_4NReO(dto)_2$	520(sh), 474(340), 448(330), 417(480), 340(sh), 292(18,460)
$nBu_4NReO(tdt)_2$	510(sh), 440(sh), 395(sh), 350(6,700), 310(22,200)
$Ph_4AsReO(mnt)_2$ [38b]	352(4,400), 303(21,750)
$Bu_4NReO(SPh)_4$	575(sh), 483(2200), 390(sh), 356(9600), 283(sh)

Band maximum in nanometers (ε in $Lmol^{-1}cm^{-1}$).

The tendency for technetium to reduce more easily than rhenium has been demonstrated voltammetrically for hexahalometallate(IV) complexes in acetonitrile,[82] and this trend is also observed for the oxobis(dithiolato)metallate(V) complexes. McCleverty, et.al.,[71] reported a one-electron reversible reduction for $ReO(mnt)_2^-$ at -1.24V vs. SCE. However, the only reversible one-electron reduction observed for this compound occurs at -1.05V vs SCE in this study, even with samples prepared from $ReCl_6^{2-}$ and mnt. [38b,71] Although pseudo-reversible (Figure IV) or ideally reversible (Figure V) one-electron reductions are observed for several of the complexes, none of the reductions appears to be chemically significant. In general, the ease of reduction is proportional to the electron withdrawing capabilities of the ligand backbone in the series dto>tma>edt.

Oxidatively, there appears to be no tendency to form technetium(VI) or rhenium(VI) complexes and the oxidative waves observed may be due to oxidation of the ligands. This is in marked contrast to the behavior of $MoO(tdt)_2^{2-}$ and $MoO(edt)_2^{2-}$, which readily oxidize to produce EPR detectable molybdenum(V) complexes in ethanol which are believed to be monomeric (The final products are molybdate and the dithiols.).[76] Whereas $MoO(dtc)_2$ complexes will oxidize to form cis $MoO_2(dtc)_2$ complexes, there is apparently no tendency for the rhenium or technetium complexes to produce dioxobis(dithiolato)metallate(VII) species.[38b] It seems apparent that the technetium and rhenium complexes described represent

Table XI: Voltammetric Data for Oxobis(dithiolato)metallate(V) Complexes.

Compound	$E_{1/2}$[a](Hg pool, DME)[b]	$E_{1/2}$[a](Pt, RPE)[b]
$Ph_4AsTcO(edt)_2$	-1.86 V	0.68 V, 2.05 V
$Ph_4AsReO(edt)_2$	-2.50 V	0.72 V, 2.11 V
$Bu_4NTcO(tma)_2$	-1.35 V $1e^-$ rev.[c]	----
$Bu_4NReO(tma)_2$	-1.84 V	1.23 V
$Bu_4NTcO(dto)_2$	-0.75 V $1e^-$ rev.[c] -1.56 V	1.91 V, 2.28 V
$Bu_4NReO(dto)_2$	-0.94 V $1e^-$ rev.[c] -1.35 V	1.64 V, 2.17 V
$Bu_4NTcO(mnt)_2$	-0.64 V $1e^-$ rev.	1.73 V
$Ph_4AsReO(mnt)_2$	-1.05 V $1e^-$ rev.	1.76 V
$Bu_4NTcO(tdt)_2$	-1.52 V	0.95 V
$Bu_4NReO(tdt)_2$	-2.00 V	1.00 V

[a] $E_{1/2}$ in volts vs. SCE, ferrocene used as reference ($E_{1/2}$ = 0.41 V).

[b] CH_3CN, 0.1 M TBAP.

[c] Pseudoreversible behavior observed in cyclic voltammetry.

Figure IV: Cyclic voltammograms of (a) $nBu_4NTcO(dto)_2$ and (b) $nBu_4NReO(dto)_2$, both in acetonitrile, 0.1M TBAP; 100 mV sec^{-1} scan rate, initially cathodic, -0.2 V vs. SCE origin, mercury pool electrode. Pseudoreversible one-electron reductions observed.

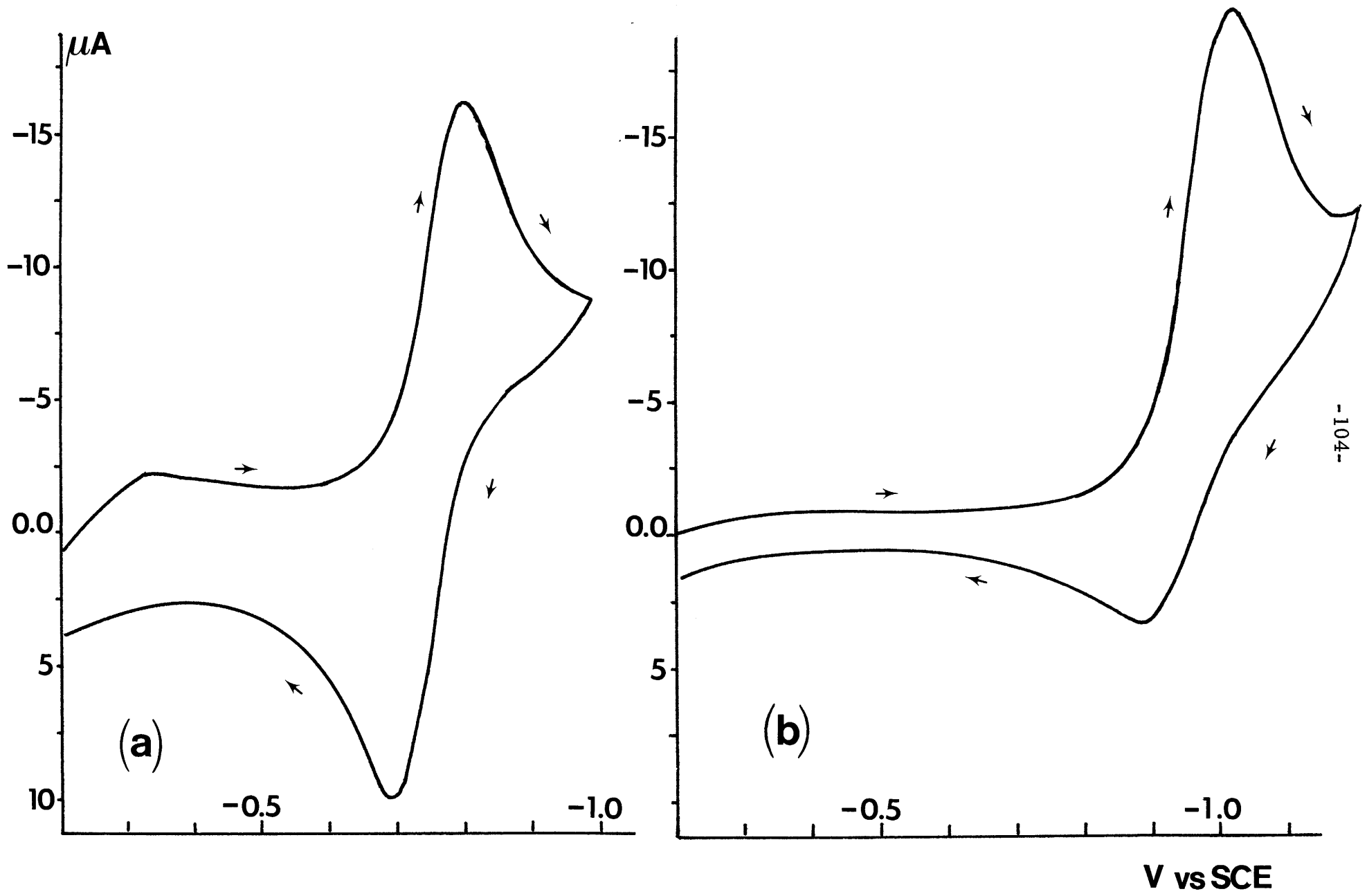
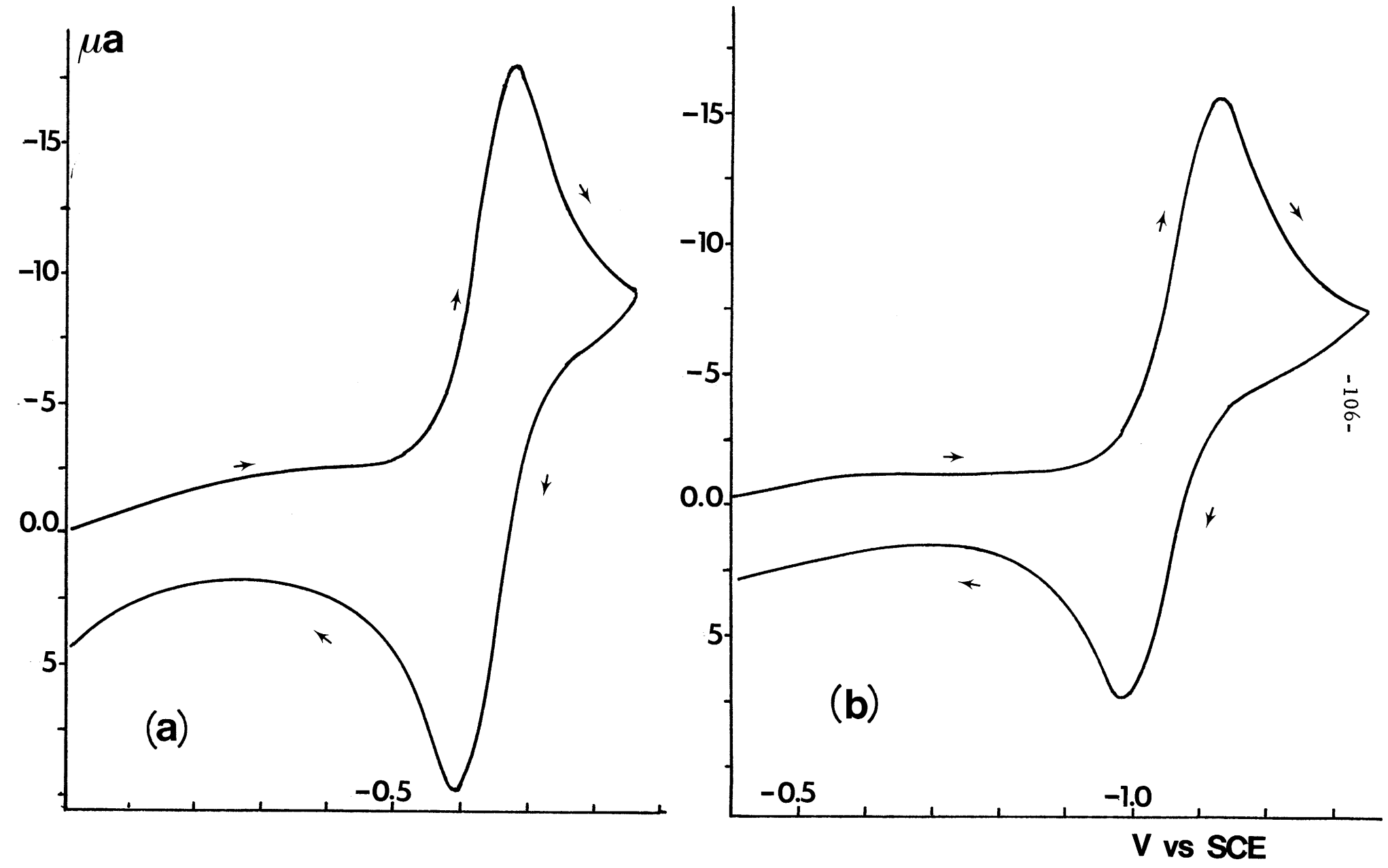

μA
-15
-10
-5
0.0
5
10
(a)
-0.5
-1.0
-15
-10
-5
0.0
5
(b)
-0.5
-1.0
V vs SCE

Figure V: Cyclic voltammograms of (a) $nBu_4NTcO(mnt)_2$ and (b) $Ph_4AsReO(mnt)_2$, both in acetonitrile/0.1 TBAP; 100 mV sec^{-1} scan rate, initially cathodic, mercury pool electrode, (a) 0.0 V vs. SCE origin; (b) -0.4 V vs. SCE origin. Reversible one-electron reductions observed.


μa
-15
-10
-5
0.0
5
(a)
-0.5
-15
-10
-5
0.0
5
(b)
-0.5
-1.0
V vs SCE

kinetically stable species.

The use of $TcOCl_4^-$ to prepare six-coordinate oxotechnetium(V) complexes such as $TcO(NCS)_5^{2-}$ and $TcO(OMe)(CN)_4^{2-}$ was briefly noted earlier. However, these two complexes are not the only six-coordinate oxotechnetium(V) complexes known. Recently, Deutsch, et. al., [39] have prepared, and crystallographically identified, another six-coordinate complex, oxodichloro(hydrotris(1-pyrazoyl)borate)-technetium(V), $TcOCl_2(HBPz_3)$ from the reduction of pertechnetate ion by $NaBH_4$ in 3N hydrochloric acid with $KHBPz_3$ present. The technetium atom is coordinated by an axial oxo group, two cis chloro ligands, and three nitrogen atoms of the $HBPz_3^-$ ligand which occupy an octahedral face. One of the nitrogens is bound trans to the oxo group, and an expected lengthening of the technetium-nitrogen bond is observed compared with the two equatorial technetium-nitrogen bonds.

The mechanism of formation of this complex probably involves the initial reduction of pertechnetate ion by $NaBH_4$ in 3N hydrochloric acid to form $TcOCl_4^-$, followed by a ligand substitution reaction to form $TcOCl_2(HBPz_3)$. In fact, reduction of pertechnetate to oxotetrachlorotechnetate(V) in 12N hydrochloric acid followed by dilution with water to 3N hydrochloric acid and addition of $KHBPz_3$ yielded $TcOCl_2(HBPz_3)$ as a green powder identical to the material prepared by Deutsch, et al. [39]

Another class of technetium(V) and rhenium(V) complexes are the transdioxotetra(ammine)metal cations. The parent, $ReO_2(py)_4^+$, can be prepared from a variety of starting materials such as: $ReOCl_3(PPh_3)_2$, [21]

K_2ReCl_6, [22] or $Ph_4AsReOBr_4.CH_3CN$.[11] Generally, chelating amines can be used, often by substitution on $ReO_2(py)_4^+$. [23,24] In the case of technetium, there have been reports of the preparation of $TcO_2(py)_4^+$ from $(pyH)_2TcCl_6$ in hydrochloric acid with excess pyridine, [25] and $TcO_2(en)_2^+$ from a reaction with $(NH_4)_2TcOCl_5$. [17]

The reaction of $nBu_4NTcOCl_4$ with pyridine in aqueous methanol produces $TcO_2(py)_4^+$ rapidly. The cation can be isolated as a perchlorate salt, which from analysis is a dihydrate salt. This material is identical to the solid prepared from hexachlorotechnetate(IV).[25] Infrared and Raman measurements reveal an assymmetric stretch at 825 cm^{-1} and a non-coincident symmetric stretch at 868 cm^{-1}. This observation is consistent with the proposed D_{4h} symmetry and in agreement with similar data obtained for transdioxo complexes of rhenium(V) and osmium(VI) (Table XII).

Solutions of the dioxotetrapyridinetechnetium(V) cation have the scent of pyridine, indicating that the pyridine is probably fairly labile; in fact, stability of the solutions is enhanced by addition of pyridine. This has been observed for the rhenium analog as well.[84]

The reaction between either $ReOBr_4^-$ or $TcOCl_4^-$ and diethyldithiocarbamate anion (Et_2dtc) in acetone produces a neutral complex of general formula $M_2O_3(Et_2dtc)_4$. The rhenium complex has been prepared previously from the reaction of $ReOCl_3(PPh_3)_2$ and $Et_2NCS_2Na.3H_2O$. [6,7] Single crystal X-ray structures revealed a linear O=Re-O-Re=O backbone

Table XII: Selected Infrared Stretching Frequencies of Some Transition Metal-Oxo Species (cm^{-1}).

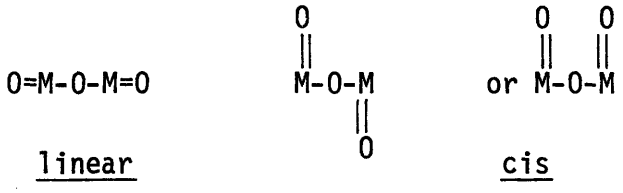
	$\nu_{M=O}$	ν_{M-O-M}	$\nu_{O=M=O}$	ν_{Other}
$nBu_4NTcOCl_4$	1019 (s)			
$nBu_4NTcO(mnt)_2$	947(s)			
$TcOCl_2(HBPz)_3$[39]	972(s)			2500 B-H
$[TcO_2(py)_4]ClO_4 \cdot 2H_2O$			825(s)	868[a]
$[ReO_2(en)_2]Cl$[83]			790(s)	890[a]
$[OsO_2(NH_3)_4]Cl_2$[83]			857(s)	865[a]
$Tc_2O_3(Et_2dtc)_4$	922(w-m)	630(vs)		
$Re_2O_3(Et_2dtc)_4$[b]	955(w-m)	665(vs)		
$Re_2O_3(Et_2dtc)_4$[6]	955(m)	670(s)		
$Mo_2O_3(EtOCS_2)_4$[88]	1047(s)	954(s) 730(m)		
$MO_2O_3(Et_2dtc)_4$[87]	930(s)	877(m) 810(m)		

[a] Raman data, MO_2 symmetric stretch.

[b] Prepared from $ReOBr_4^-$.

with the diethyldithiocarbamate ligands coordinated to the rhenium atoms at right angles to the Re_2O_3 axis.[5,7] The presence of this backbone can be detected using infrared spectroscopy; a medium intensity band corresponding to a rhenium-oxo stretch (1000-900 cm^{-1}) and a very broad and intense absorption due to Re-O-Re (700-600 cm^{-1}) are observed.[6,7,85] The important infrared absorptions of the two complexes prepared from $ReOBr_4^-$ and $TcOCl_4^-$ are tabulated in Table XII. The new technetium complex, $Tc_2O_3(Et_2dtc)_4$, has a weak-medium absorption in the infrared at 922 cm^{-1} and a very intense absorption at 630 cm^{-1} corresponding to the technetium-oxo and Tc-O-Tc stretches, respectively. All other absorptions of the technetium complex are virtually identical to that observed in the rhenium analog.

The mechanism of formation of these species has been postulated[6,19] to involve the initial coordination of water in the vacant axial position <u>trans</u> to the oxo ligand. The water molecule is deprotonated to form a <u>trans</u> oxo-metal-hydroxyl complex that subsequently dimerizes, forming the O=M-O-M=O linkage and liberating water. Interestingly the molybdenum complexes of general formula $Mo_2O_3Z_4$ ($Z=R_2NCS_2^-$ or $ROCS_2^-$)[86-88] contain not a linear <u>trans</u> M_2O_3 linkage but rather a <u>cis</u> M_2O_3 arrangement, as shown below. A linear Mo_2O_3 linkage has been observed



<u>linear</u> <u>cis</u>

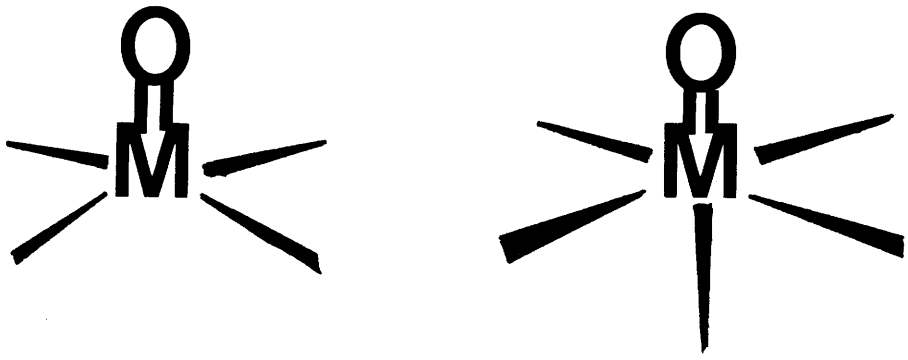
in Mo_2O_3 (porphyrin)$_2$.[89]

Although the preparation and chemistry of $ReOCl_3(PPh_3)_2$ are well known, [3-8,90] no examples of this species exist for technetium(V). When pertechnetate is reduced in the presence of ethanol, hydrochloric acid, and phosphine, production of $TcCl_4(PR_3)_2$ and $TcCl_3(PR_3)_3$ species results.[64,91] This is in contrast to the behavior of perrhenate, which produces $ReOCl_3(PR_3)_2$ in high yield under similar conditions.[3,90] Such behavior can however be explained by consideration of periodicity; technetium prefers lower oxidation states than rhenium. The reaction between $ReOBr_4^-$ and triphenylphosphine in acetonitrile produces $ReOBr_3(PPh_3)_2$.[11]

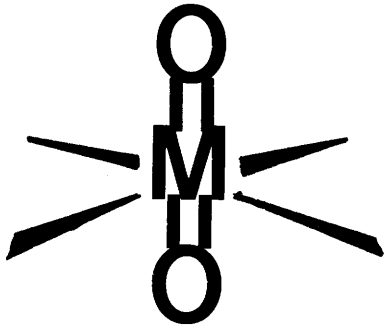
When $TcOCl_4^-$ is reacted with triphenylphosphine in acetonitrile, a rapid reaction occurs and an orange crystalline solid is precipitated. There is no evidence for a technetium-oxygen bond in the infrared spectrum. The solid is paramagnetic and is unfortunately insoluble in most solvents. Elemental analysis suggests the empirical formula "$Tc_2Cl_5P_3$"($P=Ph_3P$). This solid is not similar to other technetium-halo-phosphine complexes known.[62,64,91,92] The technetium has obviously been reduced and has lost the oxo ligand but any other conclusions are not warranted at this time.

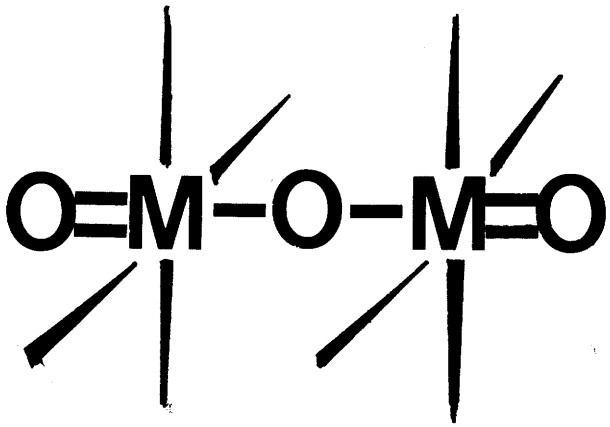
When a technetium or rhenium complex is formed in the +5 oxidation state, a number of possible coordination geometries are available, depending upon the ligands involved. As Figure VI demonstrates, four geometries, all involving oxo ligands, are currently observed. It is important to point out in the outset that just because a complex is

Figure VI: Observed Coordination Geometries for Technetium and Rhenium Complexes in the +5 Oxidation State.


O
M

O
M


O
M
O


O=M-O-M=O

formed and has a band in the infrared from 1000-900 cm^{-1}, it can not be assumed that the species produced is a five-coordinate mono-oxo complex. Other methods must be used in many cases to distinguish among the possibilities.

Infrared and Raman measurements can be helpful, nontheless, in distinguishing among the various structural types. Trans-dioxo species such as $TcO_2(py)_4^+$ and $ReO_2(py)_4^+$ have a strong absorption band in the infrared in the range 850-750 cm^{-1}, and a Raman active absorption that is non-coincident. As was shown in Table XII, $M_2O_3^{4+}$ species have absorptions in the normal metal-oxo stretching frequency range (1000-900 cm^{-1}) as well as an additional very strong absorption from 700-600 cm^{-1} generally. In cases of high symmetry and suitable ligands, infrared spectroscopy can be used to determine geometry and coordination number, eg. the $TcO(OMe)(CN)_4^{2-}$ and $TcO(NCS)_5^{2-}$ species (vide supra).

It seems apparent that both rhenium and technetium have a rather extensive and, at this time, underdeveloped chemistry in the +5 oxidation state. However, by the use of the oxotetrachlorotechnetate and oxotetrabromorhenate anions, it is possible to explore this chemistry, even when it is unaccessible from the pertechnetate or perrhenate ions.

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Chapter III

Some Aspects of Technetium Cyanide Chemistry

INTRODUCTION

Technetium cyanide chemistry has remained largely unexplored, even though there are reports in the literature[1] of a wide range of rhenium cyanide complexes with coordination numbers as high as eight[2] and oxidation states as low as zero.[3] Recently, Griffith and co-workers[4] have shown that many of those species had been misformulated; nevertheless, there still exists a wide variety of rhenium cyanide complexes.

The d^6 complexes, $K_5M(CN)_6$, are known for manganese,[5] technetium,[6] and rhenium.[5,6] The salts are isomorphous by X-ray powder patterns.[6] Raman and infrared studies[7] on the salts show higher CN stretches and lower M-C stretches as one moves down the row, as expected from considerations of d-orbital overlap.

Recently, Griffith and Kiernan[8] have isolated a seven coordinate rhenium cyanide complex, $K_4Re(CN)_7 \cdot 2H_2O$, which appears to have a pentagonal bipyramidal structure (D_5h) based on Raman and infrared as well as X-ray structural evidence.[9]

Rhenium has also been shown to form oxo-cyano complexes when in the +5 oxidation state; <u>trans</u>-$ReO_2(CN)_4^{-3}$,[10] and <u>trans</u>-$Re_2O_3(CN)_8^{4-}$[11] have had their structures confirmed through X-ray crystallographic studies. Protonation of $K_3ReO_2(CN)_4$ leads initially to the formation of $ReO(OH)(CN)_4^{2-}$.[12] In view of such findings, it is surprising that to date no technetium (V) cyano complexes have been reported.

Early polarographic studies[13] on the reduction of pertechnetate ion in the presence of cyanide ion apparently showed no tendency to

form a technetium (V) species; however, a technetium (IV) species was deemed possible, based on a three electron reduction wave ($E_{1/2}$ = 0.81 V vs. SCE). [13] Schwochau and Herr[14] had attempted to prepare $TcO_2(CN)_4^{3-}$ but instead isolated a yellow-brown species they formulated as $Tl_3Tc(CN)_4(OH)_3$, formally technetium (IV) exhibiting an infrared band at 905 cm^{-1} which they assigned as a Tc=O stretch, which is surprising in view of their formulation.

In order to compare the chemistry of technetium and rhenium, the synthesis of $Tc(CN)_7^{4-}$ was successfully achieved. During the course of this investigation it was noticed that like the rhenium analog,[4] $Tc(CN)_7^{4-}$ decomposed slowly in oxygenated water. Two different species were identified as decomposition products: $TcO(CN)_5^{2-}$ and <u>trans</u>-$TcO_2(CN)_4^{3-}$, both technetium (V) complexes. The $Tc(CN)_4(OH)_3^{3-}$ ion prepared by Schwochau and Herr[14] has to be reformulated as $TcO(CN)_5^{2-}$ by comparison of synthetic and spectroscopic information. Another technetium (V) cyano complex, <u>trans</u>-$TcO(OMe)(CN)_4^{2-}$, has been prepared from $TcOCl_4^-$ and CN^- in methanol.

The synthesis, characterization, and molecular structure of the new technetium complexes, $K_4Tc(CN)_7 \cdot 2H_2O$, $K_2TcO(CN)_5 \cdot 4H_2O$, $K_3TcO_2(CN)_4$, and $(nBu_4N)_2TcO(OMe)(CN)_4$ will be presented in this chapter.

EXPERIMENTAL

All water used was passed through a Barnstead Ultrapure D8902 Cartridge followed by distillation using a Corning AG-1 water still prior to use. All other reagents were used as received. All manipulations with $Tc(CN)_7^{4-}$ were done in N_2 purged solvents unless otherwise stated.

$(NH_4)_2TcBr_6$, $(NH_4)_2TcI_6$, $(nBu_4N)_2TcCl_6$, $nBu_4NTcOCl_4$, and $TcO_2(py)_4ClO_4.2H_2O$ were prepared as described previously in Chapter I and II.

Infrared spectra were recorded on a Perkin-Elmer 180 grating spectrophotometer either as KBr pellets or aqueous solutions in matched AgCl plates (0.5 mm path length). Raman spectra were obtained either as solid samples or aqueous solutions in a capillary using a Spex Ramalog with the 5145 Å line of an Ar laser. Optical spectra in water or acetonitrile were recorded on a Cary 17 spectrophotometer. 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 with a home built Faraday balance using a Varian V-4005 electromagnet with constant force pole faces and a Cahn RG electrobalance.

Nuclear magnetic resonance measurements on $(nBu_4N)_2TcO(OMe)(CN)_4$ were made on a Varian T-60 MHz spectrometer with CD_2Cl_2 as solvent and tetramethylsilane as the internal calibrant.

Preparation of Potassium heptacyanotechnetate(III)dihydrate.

To a 50 mL r.b. flask with sidearm and stir bar were added 0.377 gm (0.42 mmol)$(NH_4)_2TcI_6$. The flask was evacuated on a Schlenk line and backfilled with N_2, twice. Another 50 mL r.b. flask was charged with 1.20 gm (18.4 mmol) freshly ground KCN and then purged thoroughly with N_2. The TcI_6^{2-} was partially dissolved in 10 mL N_2 purged methanol added via a cannula. An aqueous cyanide solution was prepared by the addition of 10 mL of N_2 purged water to the KCN. This solution was transferred via a cannula to the TcI_6^{2-} solution. A heating mantle and a N_2 purged Hopkin's coil condensor were added as the dark mixture was refluxed under N_2 for 24 hr. The resultant orange solution was filtered under N_2, leaving behind a small amount of dark solid. N_2 purged methanol was added until the yellow solid formed appeared to contain all the color of the mixture. The yellow solid was filtered under N_2, washed with two 10 mL of N_2 purged methanol solutions, and dried in vacuo. The apparatus was backfilled with N_2 and 0.1 gm KCN was added. Both solids were dissolved with 5 mL N_2 purged water, added via a cannula. The golden solution was filtered into a N_2 purged 3-neck 50 mL r.b. flask equipped with Schlenk frit and 50 mL r.b. flask. N_2 purged methanol, 20-25 mL, was added, precipitating a yellow solid. This mixture was heated under N_2 to redissolve the solid. The golden solution was quickly filtered, then allowed to cool slowly. The solution was placed in a refrigerator at 5°C for 24 hr. Yellow-orange crystals of $K_4Tc(CN)_7.2H_2O$ were filtered and washed with methanol prior to drying in vacuo. Yield, 0.056 gm, 28% based on technetium.

Analysis, $C_7H_4K_4N_7O_2Tc$, Calc.: C, 17.75; H, 0.85; N, 20.70.

Found: C, 17.95; H, 1.30; N, 20.86.

Optical Spectrum (degassed water, CN^- added) 455 nm (90 L $mol^{-1}cm^{-1}$), 280 (790), 243 (15,000)

Infrared Spectrum (KBr) 3610 (m), 3470 (m), 3410 (m), 2117 (w), 2090 (s), 2045 (s), 1625 (m), 535 (w), 375 (w), 325 (w) (water) 2089 (s), 2046 (s)

Raman (solid) 2123 (s), 2114 (s), 2109 (m), 2079 (s), 2057 (w), 1758 (w), 1550 (w), 1330 (w), 1000 (w), 860 (w), 753 (w), 464 (m), 365 (m), 240 (m) (water) 2123 (s,p), 2072 (s), 1775 (w), 1745 (w), 1700 (w), 1423 (w), 1342 (w), 1089 (w), 992 (w), 948 (w), 870 (w), 820 (w), 753 (w), 468 (s,p), 367 (m,p), 243 (s,p)

Magnetic Moment diamagnetic

Potassium heptacyanotechnetate(III) dihydrate is soluble in water. In the presence of oxygen, solutions slowly decompose to mixtures of oxopentacyanotechnetate(V) and dioxotetracyanotechnetate(V).

Preparation of Potassium oxopentacyanotechnetate(V) tetrahydrate.

A suspension of $TcO_2.xH_2O$ in water was prepared by the hydrolysis of 0.062 gm (0.10 mmol)$(NH_4)_2TcBr_6$ in 6 mL water and 1 mL of conc. NH_4OH. The black solid was centrifuged, the aqueous filtrate removed, and the solid was washed with 6 mL water. After centrifugation, the solid was suspended in 6 mL water and transferred to a 25 mL r.b. flask equipped with a stir bar. To this suspension 0.50 gm (7.68 mmol)KCN were added and the mixture refluxed for 1.5 hr., yielding a clear honey colored solution. The reaction mixture was transferred to a 100 mL r.b. flask when cool, then methanol was added (30 mL) until the yellow solid appeared to contain all the color of the solution. The solid was redissolved by heating, then allowed to cool slowly,

stoppered and placed in a 5°C refrigerator for 24 hr. Pale greenish yellow crystals of $K_2TcO(CN)_5.4H_2O$ were filtered onto a medium porosity fritted filter, washed with methanol, then dried in vacuo. Yield of green-yellow flakes, 0.012 gm, 31% based on technetium.

Analysis, $C_5H_8K_2N_5O_5Tc$, Calc: C, 15.19; H, 2.04; N, 17.71.
Found: C, 14.90; H, 1.00; N, 17.80.

Optical Spectra (water, CN^- added) 680 nm (60 L $mol^{-1}cm^{-1}$), 466 (680), 387 (46,900)

Infrared Spectra (KBr) 3440 (m), 2095 (m), 2080 (s), 2035 (w-m), 1625 (w), 910 (m), 460 (w), 449 (w), 435 (w), 420 (w), 375 (w), 350 (w).

Potassium oxopentacyanotechnetate(V) tetrahydrate can also be isolated from aerobic recrystallizations of $K_4Tc(CN)_7.2H_2O$. It is soluble in water, but in the absence of excess cyanide ion it converts to the dioxotetracyanotechnetate(V) ion.

Preparation of Potassium trans-dioxotetracyanotechnetate(V)

To a 25 mL r.b. flask with stir bar were added 0.247 gm (0.42 mmol) $TcO_2(py)_4ClO_4.2H_2O$ and 2.0 gm (30.7 mmol) KCN. Next, 12 mL water were added and the mixture was stirred overnight. The resultant yellow solution was filtered to remove some white solid and methanol was added slowly to the filtrate until crystals began to appear. Additional methanol was added until the total volume was approx. 90 mL. The solid was filtered out on a medium porosity fritted filter and recrystallized from methanol/water to yield 0.14 gm $K_3TcO_2(CN)_4$ as lemon yellow needles, 90% based on technetium.

Analysis, $C_4K_3N_4O_2Tc$, Calc.: C, 13.63; N, 15.90.
Found: C, 13.56; N, 15.42.

Optical Spectra (water) 460 nm (25 L $mol^{-1}cm^{-1}$), 325 (875), 248 (8220)

Infrared Spectra (KBr) 2120 (s), 2070 (w), 2040 (w), 785 (s), 430 (w), 334 (ms) (water) 2120 (s)

Raman (solid) 2140 (w), 2120 (w), 2110 (s), 2095 (s), 2100 (w), 2080 (s), 2050 (w), 2035 (s), 1971 (s), 1785 (w), 1545 (w), 910 (ms), 885 (m), 827 (m), 485 (m), 460 (m), 364 (m), 350 (w), 326 (m), 272 (w), 252 (w), 243 (m) (water) 2133 (p), 2127, 838 (p).

Potassium dioxotetracyanotechnetate(V) is soluble in water. It can also be prepared by repeated hydrolysis of either heptacyanotechnetate(III) or oxopentacyanotechnetate(V). Acidified solutions of $TcO_2(CN)_4^{3-}$ turn deep blue with bands appearing at 605, 315, 228 nm in aqueous solution.

Preparation of Tetrabutylammonium trans-oxomethoxytetracyanotechnetate(V).

A 25 mL r.b. flask with stir bar was charged with 0.073 gm (0.15 mmol) $nBu_4NTcOCl_4$ and 0.06 gm (0.92 mmol)KCN. Addition of 10 mL methanol resulted in a plum colored solution and some white solid. The solution was stirred for one hour, and then 0.18 mL 75% w/w nBu_4NCl was added followed by 1 mL water. The solution turned clear, plum colored. It was filtered and the filtrate was left to stand in a beaker to slowly evaporate. Large lilac needles were separated and washed with 3 mL water, followed by 20 mL ether. The solid was dried in vacuo. Yield of $(nBu_4N)_2TcO(OMe)(CN)_4$, 0.50 gm, 46% based on technetium.

Analysis, $C_{37}H_{45}N_6O_2Tc$, Calc.: C, 60.46; H, 10.29; N, 11.43.
Found: C, 60.47; H, 10.38; N, 11.00.

Optical Spectra (CH_3CN) 547 nm (45 L mol^{-1} cm^{-1}), 370 (sh), 297 (5,680)

Infrared Spectra (KBr) 2955 (s), 2930 (s), 2895 (m), 2862 (s), 2788 (m), 2730 (w), 2139 (v.w.), 2116 (ms), 1850 (w), 1485 (s), 1470 (s), 1463 (s), 1459 (s), 1419 (m), 1378 (ms), 1340 (w), 1273 (w), 1265 (w), 1240 (w), 1230 (v.w.), 1147 (m), 1100 (s), 1060 (w), 1022 (w), 1009 (w), 932 (vs), 888 (m), 880 (m), 840 (v.w.), 790 (w), 751 (m), 733 (m), 500 (s), 448 (w), 415 (w), 395 (w), 367 (w), 340 (s), 274 (w)

Conductance 2:1 electrolyte in CH_3CN, Λ_o = 367 cm^2 ohm^{-1} eq^{-1}

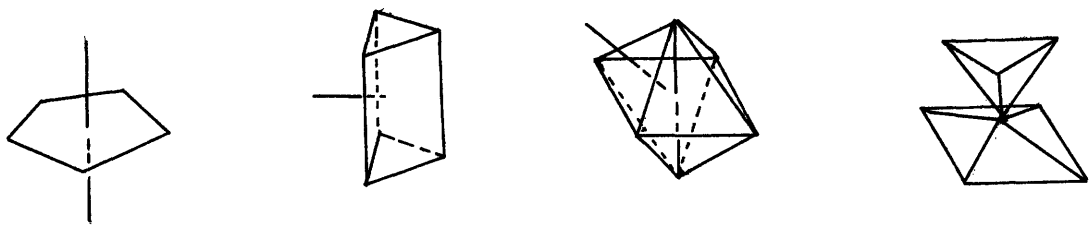
NMR δ 3.25 (broad, 19 H, OCH_3, $N\text{-}CH_2\text{-}CH_2CH_2CH_3$), δ 1.60 (broad, 32 H, $NCH_2\text{-}CH_2CH_2\text{-}CH_3$).

δ1 00 (broad, 24 H, $NCH_2CH_2CH_2\underline{CH}_3$) Tetrabutylammonium oxomethoxytetracyanotechnetate(V) is soluble in acetone, methanol, ethanol, methylene chloride, and acetonitrile and sparingly in water.

Results and Discussion

The synthesis of the yellow-orange potassium heptacyanotechnetate (III) dihydrate from hexaiodotechnetate(IV) in refluxing aqueous methanol is similar to a preparation of the rhenium analog described by Griffith and Kiernan[8] using hexaiodorhenate(IV). Technetium (IV) halide salts have been shown to undergo reduction easily; [15] in this case, iodide ion is sufficient to reduce technetium(IV) to technetium(III) and cyanide ion is able to stabilize this oxidation state.

mer-Trichlorotris(dimethylphenyphosphine)technetium[16] has been shown to react with one mole of carbon monoxide in refluxing ethanol to form the first example of a seven coordinate technetium complex.[17] Seven coordinates complexes can exist in several different geometries: (I), pentagonal bipyramidal; (II), monocapped trigonal prism; (III), monocapped octahedron; (IV), tetragonal base-trigonal base. X-Ray crystallography[18] has shown that $TcCl_3(PMe_2Ph)_3CO$ is a monocapped



(I) (II) (III) (IV)

octahedron, having C_{3V} symmetry, i.e., structure type (III). Potassium

heptacyanotechnetate(III) dihydrate, $K_4Tc(CN)_7.2H_2O$, is only the second seven coordinate technetium complex to be discovered.

It was possible to determine the coordination geometry of $K_4Tc(CN)_7.2H_2O$ through the use of Raman and infrared spectroscopy and observations of similar data obtained on heptacyanometallates whose structures are known. The infrared and Raman data for $K_4Tc(CN)_7.2H_2O$ and several other heptacyanometallate species are tabulated in Table XII. Both $K_4V(CN)_7.2H_2O$ [19] and $K_4Re(CN)_7.2H_2O$ [9] have been shown to have type (I) structures, pentagonal bipyramidal, by X-ray crystallography. For such molecules, use of group theory predicts two infrared active ($E_1' + A''_2$) and three Raman active ($2A_1' + E_2'$) cyanide stretching modes with no coincidences. In solution, there should be two polarized Raman shifts ($2A_1'$ modes). In the case of $K_4Re(CN)_7.2H_2O$, such behavior is observed. [8] For $K_4V(CN)_7.2H_2O$, only one broad unresolved polarized band could be observed.[20] The pentagonal bipyramid offers the least complex spectra in the cyanide stretching region and is the only structure that is not allowed coincidences between the infrared and Raman allowed coincidences between the infrared and Raman allowed modes.

The molybdenum(II) complexes, $Na_5Mo(CN)_7.10H_2O$ and $K_5Mo(CN)_7.H_2O$ [21] have been studied recently via X-ray crystallography.[22] One of them, $Na_5Mo(CN)_7.10H_2O$, appears to be a well behaved pentagonal bipyramid. However, crystal packing in $K_5Mo(CN)_7.H_2O$ causes a mild distortion from ideal type (I) symmetry that displaces an equitorial cyanide up out of the equitorial plane slightly. As a result, the solid infrared shows many more bands than the sodium salt. The completely anhydrous salt, $K_5Mo(CN)_7$,

Table XII: Structural Information on $M(CN)_7^{x-}$ Species.

	IR		RAMAN			
	solid	solution	solid	solution	Structure	X-Ray
$K_4Tc(CN)_7 \cdot 2H_2O$	2117(w,sh) 2090(s) 2045(s)	2089(s) 2046(s)	2123(s) 2114(s) 2109(m) 2079(s) 2057(w)	2123(s,p) 2110(s,p) 2072(s)	D_{5h}	no
$K_4Re(CN)_7 \cdot 2H_2O$[a]	2125(m) 2112(m) 2101(m) 2092(vs) 2069(m) 2062(w) 2040(vs)	2080(s) 2019(vs)	2125(s) 2115(w) 2103(w) 2068(m) 2063(s)	2123(s,p) 2106(m) 2061(m,p)	D_{5h}	yes[b]
$K_4V(CN)_7 \cdot 2H_2O$[c]	2100(s) 2070(m)	2104(s) 2072(m)	2110(m) 2104(s) 2100(s) 2094(vs)	2103(br,p)	D_{5h}	yes[d]
$K_5Mo(CN)_7$[e]	7 bands		8 bands		C_{2v}	no
$K_5Mo(CN)_7 \cdot 2H_2O$[f]	2074(s) 2058(s) 2042(s) 2030(s) 2014(s) 1989(s) 1958(s,br)				distorted D_{5h}	yes[g]
$Na_5Mo(CN)_7 \cdot 10H_2O$[g]	2142(w) 2113(sh,w) 2098(s) 2078(w) 2030(s) 1968(s)				D_{5h}	yes[g]
$K_4Mo(CN)_7 \cdot 2H_2O$[h]	2119 2115 2074 2059	2080 2040	2096 2078	2106 2063	D_{5h}(soln) C_{2v}(solid)	no

[a]Ref. 4; [b]Ref. 9; [c]Ref. 19; [d]Ref. 20; [e]Ref. 8; [f]Ref. 21; [g]Ref. 22; [h]Ref. 28.

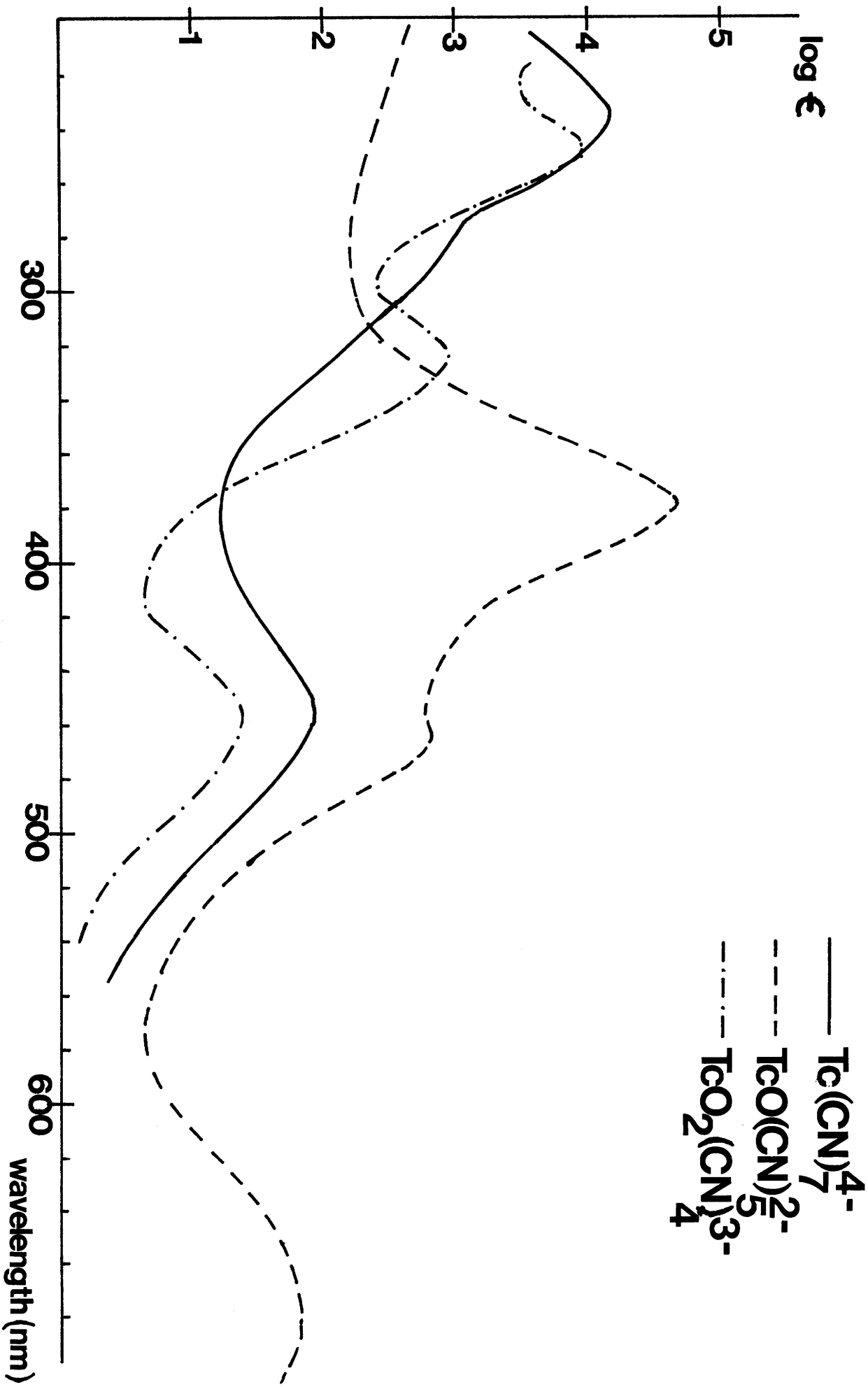
has been assigned geometry type (II) based on the infrared[8] and the crystal structure of $K_5Mo(CN)_7.H_2O$[22] although geometry (IV) can not be ruled out based on the available data.

Infrared and Raman data [23] for $K_4Mo(CN)_7 \cdot 2H_2O$ [24] seem to indicate a pentagonal bipyramidal structure in solution and a monocapped trigonal prism, (II), in the solid state.

Based on these observations and the results of the Raman and infrared studies on $K_4Tc(CN)_7 \cdot 2H_2O$, a pentagonal bipyramidal structure is indicated both in solid and solution. There are two bands in the infrared (A_2'', E_1'; 2090, 2045 cm^{-1}) and the three Raman shifts are noncoincident with the infrared absorptions; in solution, two are polarized ($2A_1'$; 2123, 2110 cm^{-1}) while the remaining one is depolarized (E_2', 2072 cm^{-1}). Magnetic susceptibility measurements on $K_4Tc(CN)_7 \cdot 2H_2O$, a d^4 ion, indicate that the solid is diamagnetic, as expected from the strong field ground state, $^1A_1'$. The yellow-orange solid dissolves in deoxygenated water (excess cyanide ion present) to yield bright golden solutions with optical absorption bands at 243, 280, 455 nm (Figure VII). In the presence of oxygen, solutions of $Tc(CN)_7^{4-}$ slowly decompose, as observed by optical spectroscopy. Optical absorption bands at 325 nm and 378 nm can be observed. Treatment of such solutions with methanol precipitates yellow solids which by infrared spectroscopy revealed several bands in the cyanide stretching region as well as the appearance of bands at 910 and 785 cm^{-1} in the metal-oxygen stretching region.

Other heptacyanometallates undergo decomposition in solution; for example, $Mo(CN)_7^{4-}$ decomposes in air to $Mo(CN)_8^{4-}$ and MoO_4^{2-}, [23] and

Figure VII: Optical spectra of $K_4Tc(CN)_7 \cdot 2H_2O$ in degassed water, cyanide ion added; $K_2TcO(CN)_5 \cdot 4H_2O$ in water, cyanide ion added; and $K_3TcO_2(CN)_4$ in water.


log ε
1
2
3
4
5
300
400
500
600
wavelength (nm)
Tc(CN)7 4-
TcO(CN)5 2-
TcO2(CN)4 3-

$V(CN)_7^{4-}$ decomposes to $VO(CN)_5^{3-}$ and $V(CN)_6^{4-}$ in the absence of excess cyanide in anaerobic solutions.[28]

Two species can be obtained from the decomposition of $Tc(CN)_7^{4-}$ in aqueous solution: $K_2TcO(CN)_5 \cdot 4H_2O$ and $K_3TcO_2(CN)_4$, both technetium (V) complexes. The preparation and characterization of these two species will be discussed below.

When $K_4Tc(CN)_7 \cdot 2H_2O$ was recrystallized from aerobic water/methanol mixtures, yellow-green flakes of $K_2TcO(CN)_5 \cdot 4H_2O$ were obtained as well as yellow-orange crystals of $K_4Tc(CN)_7 \cdot 2H_2O$. These were easily separated by the Pasteur method. The infrared spectrum of the former revealed three bands in the cyanide stretch region and one band in the Tc=O stretching region at 910 cm^{-1} (Table XIV). For a $MX(CN)_5$ system (C_{4V}) use of group theory predicts three ($2A_1 + E$) infrared allowed cyanide stretching modes; this is what is observed.

It was found that reaction of $TcO_2 \cdot xH_2O$, an insoluble black precipitate, with hot aqueous cyanide also formed $K_2TcO(CN)_5 \cdot 4H_2O$ upon crystallization with methanol. This method, interestingly, is identical to the preparation of "$Tc(CN)_4(OH)_3^{3-}$" reported by Schwochau and Herr [14] and isolated as the thallous salt. The "$Tc(CN)(OH)_3^{3-}$" species was observed to have the identical optical spectrum as the yellow $TcO(CN)_5^{2-}$ in aqueous solution with a very strong band at 378 nm and a weaker band around 460 nm. No mention of a weak band at 680 nm (ε = 25 L $mol^{-1}cm^{-1}$) as observed in $TcO(CN)_5^{2-}$ was made in the case of "$Tc(CN)_4(OH)_3^{3-}$". Only one broad band was noticed in the cyanide stretching region at 2050 cm^{-1} and a band at 905 cm^{-1} was

Table XIV: Selected Infrared Data for $(nBu_4N)_2TcO(OMe)(CN)_4$ and $K_2TcO(CN)_5 \cdot 4H_2O$.

	ν_{CN}	$\nu_{Tc=O}$	ν_{OMe}
$K_2TcO(CN)_5 \cdot 4H_2O$	2095(ms)	910(m)	----
	2080(s)		
	2035(w-m)		
$(nBu_4N)_2TcO(OMe)(CN)_4$	2139(vw)	932(vs)	2790(m) C-H str.
	2116(ms)		1460(s) C-H bend
			1097(s) C-O bend/str.

t-$MXY(CN)_4$ C_{4v} symmetry $A_1 + E$ infrared allowed ν_{CN}.

$MX(CN)_5$ C_{4v} symmetry $2A_1 + E$ infrared allowed ν_{CN}.

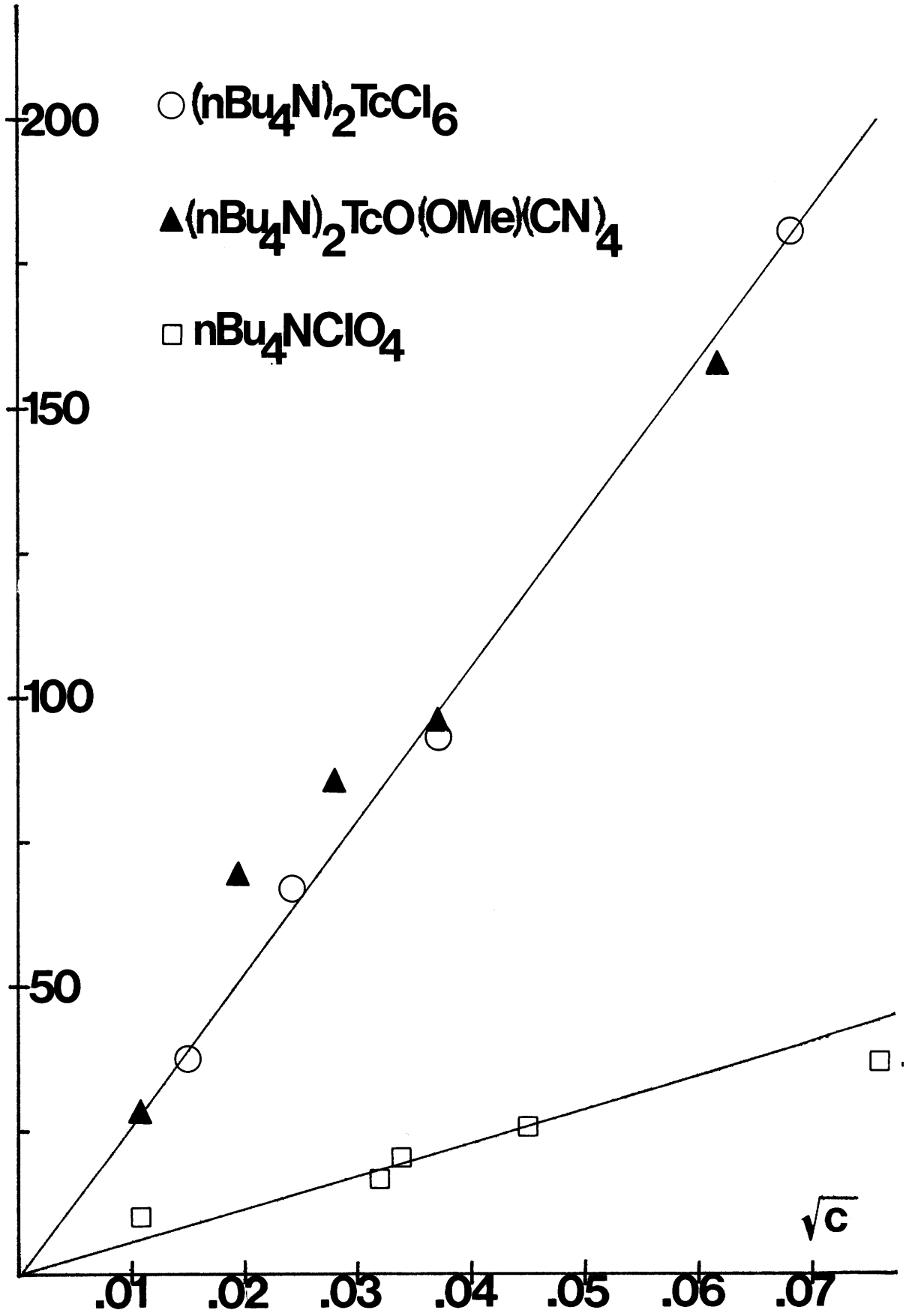
assigned to a Tc=O stretch for $Tl_3Tc(CN)_4(OH)_3$. Thus, it seems that $Tc(CN)_4(OH)_3^{3-}$ should be reformulated as $TcO(CN)_5^{2-}$.

The reaction of $ReO_2 \cdot xH_2O$ with hot aqueous cyanide led to the isolation of $Tl_3ReO_2(CN)_4$.[14] At this time, there is no report of a species formulated as $Re(CN)_4(OH)_3^{3-}$ or $ReO(CN)_5^{2-}$, although such a species might be implicated in the production of the transdioxo complex, vide infra. The yellow salt, $K_2TcO(CN)_5 \cdot 4H_2O$, will hydrolyze in aqueous solution slowly in the absence of cyanide ion to form $K_3TcO_2(CN)_4$.

The use of $nBu_4NTcOCl_4$ as a reagent for exploring oxotechnetium(V) chemistry has been demonstrated (vide infra, Chapter II). In an attempt to prepare $TcO(CN)_5^{2-}$ directly from a technetium (V) precursor, $nBu_4NTcOCl_4$ was reacted with five equivalents of potassium cyanide in methanol. Instead of the expected yellow solution, a plum colored solution resulted and well formed lilac needles were obtained upon addition of tetrabutylammomium ion and crystallization from methanol/water. Based on elemental analysis, this salt is formulated as $(nBu_4N)_2$-$TcO(OMe)(CN)_4$, an oxotechnetium (V) species. As shown in Figure VIII, equivalent conductance measurements in acetonitrile demonstrated that $TcO(OMe)(CN)_4^{2-}$ was a 2:1 electrolyte similar to $(nBu_4N)_2TcCl_6$ in acetonitrile.

Infrared measurements (Table XIV) and NMR data [25] confirmed the presence of the methoxide ligand and the two bands in the cyanide stretching region (2139 (vw), 2116 (ms) cm^{-1}) are indicative of a trans arrangement

Figure VIII: Equivalent conductance measurements of nBu_4NClO_4, $(nBu_4N)_2TcCl_6$, and $(nBu_4N)_2TcO(OMe)(CN)_4$ in acetonitrile. $\Lambda_o - \Lambda$ ($cm^2 ohm^{-1} eq^{-1}$) vs. (eq. conc)$^{1/2}$.


$\Lambda_o - \Lambda$
200
150
100
50
○ $(nBu_4N)_2TcCl_6$
▲ $(nBu_4N)_2TcO(OMe)(CN)_4$
□ nBu_4NClO_4
$\sqrt{c}$
.01
.02
.03
.04
.05
.06
.07

for the oxo-technetium-methoxide linkage.

The species $TcO(CN)_5^{2-}$ and t-$TcO(OMe)(CN)_4^{2-}$ are quite similar, differing only in the ligand trans to the oxo ligand. The Tc=O stretch of the methoxide complex appears at 932 cm^{-1} whereas that of the cyano complex occurs at 910 cm^{-1}.

As was noted earlier, in aqueous solution $K_2TcO(CN)_5 \cdot 4H_2O$ hydrolyzes to t-$TcO_2(CN)_4^{3-}$. Upon repeated recrystallizations from aerobic methanol/water solutions, $K_4Tc(CN)_7 \cdot 2H_2O$ yields $K_3TcO_2(CN)_4$ as a yellow crystalline salt. A more direct synthesis involved treatment of an aqueous suspension of [t-$TcO_2(py)_4$]$ClO_4 \cdot 2H_2O$ with a large excess of potassium cyanide. Addition of methanol to the resultant lemon yellow solution resulted in the formation of $K_3TcO_2(CN)_4$ in high yield.

The molecular structure has been assigned as being trans-dioxo by infrared and Raman data. A trans-dioxotetracyanometallate ion (D_{4h}) should have one infrared active mode (E_u) and two Raman active modes ($A_{1g}(p)$, B_{1g}) in the cyanide stretching region, the metal oxygen stretching region should possess one infrared active mode (A_{2u}) and one Raman active mode ($A_{1g}(p)$). The inversion center allows no coincidences. As can be seen in Table XV, $K_3TcO_2(CN)_4$ shows such behavior and is similar to other t-$MO_2(CN)_4^{x-}$ species whose structures have been confirmed by X-ray crystallography.[10,26,27] Of special interest is the relative position of the symmetric metal oxygen stretch (Raman active) with respect to the asymmetric metal oxygen stretch (infrared active). Most linear triatomic systems (or systems that can be viewed as linear triatomics) have $\nu_{asym} > \nu_{sym}$, t-UO_2^{2+} systems as

well as other inorganics such as CO_2 also demonstrate this property.[31] However, experimentally, trans-dioxo species of technetium, rhenium,[28,29] and osmium[29,30] are found to have $\nu_{sym} > \nu_{asym}$. Molybdenum and tungsten trans-dioxo species show the normal trend.[26,29] The trans-dioxoruthenium(VI) species, $M_2RuO_2Cl_4$ (M = H_3O, Cs, Rb) are unstable[32] and this has probably precluded Raman studies on these salts. Cotton and Wing[33] had observed differences between UO_2^{2+} species and $ReO_2(py)_4^+$ and $OsO_2Cl_4^{2-}$ salts where calculations of the interaction constants, k_i, derived from F matrices[34] for the trans-dioxo complexes yielded negative interaction constants for the actinides and positive interaction constants for rhenium and osmium.[33] This observation does not account for the behavior of molybdenum and tungsten; the interaction force constants, k_i, have been determined and are positive.[28] Although the change in sign of k_i for the actinide complexes relative to the d-block complexes is fundamentally quite interesting, the behavior of osmium, technetium, and rhenium cannot be explained from such analysis.

Of possible importance may be the electron attracting ability of the metal for the oxygen $2p\pi$ orbitals. Since $MoO_2(CN)_4^{4-}$, $WO_2(CN)_4^{4-}$, $TcO_2(CN)_4^{3-}$, $ReO_2(CN)_4^{3-}$, and $OsO_2(CN)_4^{2-}$ are all isostructural and isoelectronic, the only apparent difference is oxidation state of the transition metal. In fact, within the same row of the periodic table the frequency decreases as the oxidation state is lowered. The symmetric stretch would be expected to be more sensitive to changes in π-bonding than the asymmetric stretch because of the different nature of the interactions between metal and oxygen in each case.

Table XV: Comparison of Stretching Frequencies for t-$MO_2(CN)_4^{x-}$ Complexes (cm^{-1}).

	IR		Raman	
	ν_{CN}	ν_{MO_2}(asym)	ν_{CN}	ν_{MO_2}(sym)
$K_3TcO_2(CN)_4$	2120(s)	785(s)	2110(s),2080(s)	827(m)
			2141(p),2130[+]	838(p)[+]
$K_3ReO_2(CN)_4$[a,b]	2125(s)	768(s)	2141(s),2130(s)	871(m)
			2141(p),2130[+]	881(p)[+]
$K_4[MoO_2(CN)_4]\cdot 6H_2O$[b,d]	2060(s)	800(s)		779
$K_4[WO_2(CN)_4]\cdot 6H_2O$[b,d]	2060(s)	720(s)		
$K_2OsO_2(CN)_4$[b,c]	2152(s)	830(s)		886(p)[+]

[a]Ref. 28; [b]Ref. 29; [c] Ref. 30; [d]Ref. 26.

[+]Solution spectra in water.

ν_{sym} ν_{asym}

In the case of the symmetric stretch, the π-interactions between the metal and both oxygen atoms will be weakened or strengthened as the molecule vibrates in that mode. In the asymmetric stretch, the change in π-interaction that results as one oxygen moves away will be moderated by the increased π-interaction of the other oxygen atom as it moves closer to the metal atom. Since π-overlap increases down a periodic column, one would expect to see the symmetric stretching frequency also increase. This behavior is indeed observed for technetium and rhenium, with Raman shifts at 838 and 881 cm^{-1} for $K_3TcO_2(CN)_4$ and $K_3ReO_2(CN)_4$ respectively.

The optical spectrum of aqueous $TcO_2(CN)_4^{3-}$ is quite similar to the reported spectrum of aqueous $ReO_2(CN)_4^{3-}$ [14] with absorptions at 325 and 248 nm showing the expected bathochromic shift from the 270 and 215 nm absorptions reported for $ReO_2(CN)_4^{3-}$.

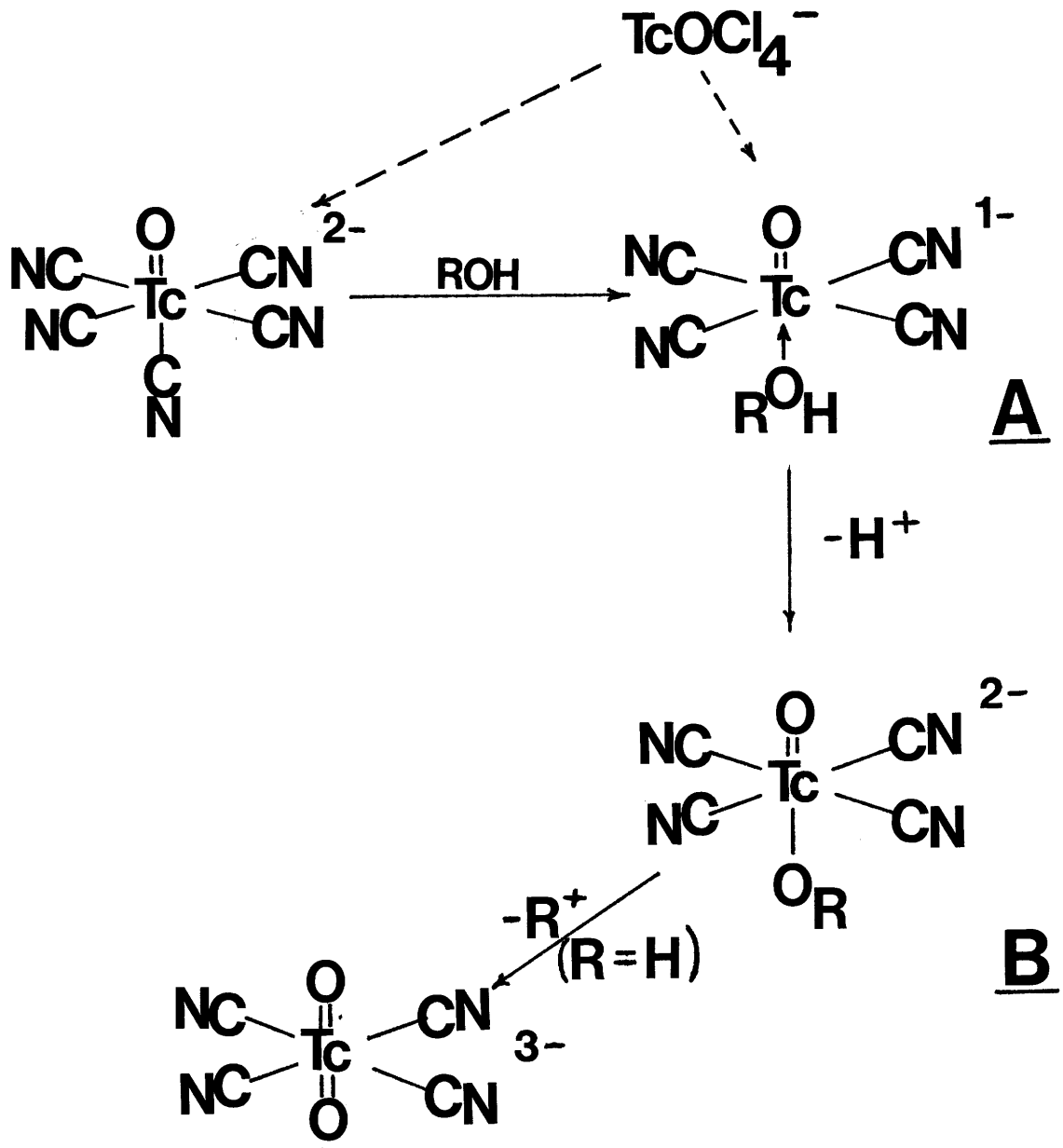
The failure of the reaction between $TcOCl_4^-$ and cyanide ion in methanol to form $TcO(CN)_5^{2-}$ was extremely fortunate. As Scheme II

demonstrates, $TcO(OMe)(CN)_4^{2-}$ can be viewed as a trapped intermediate in the hydrolysis of $TcO(CN)_5^{2-}$ to $TcO_2(CN)_4^{3-}$. The oxo ligand is apparently a strong trans labilizer; it is not surprising then that $TcO(CN)_5^{2-}$ is stable in aqueous solution only when excess cyanide ion is present. Substitution of the cyanide ion trans to the oxo by solvent[35] leads to the intermediate species A which can also be formed directly from $TcOCl_4$- and cyanide in methanol if methanol is coordinated to the technetium atom prior to reaction.[36]

Once the solvent is coordinated, the solvent oxygen is rapidly deprotonated. When methanol is the solvent, this reaction terminates at intermediate B because demethylation is energetically unfeasible. When the solvent is water, however, further deprotonation from a $TcO(OH)(CN)_4^{2-}$ intermediate to $TcO_2(CN)_4^{3-}$ is rapid. Protonation of $ReO_2(CN)_4^{3-}$ to $ReO(OH)(CN)_4^{2-}$ requires solutions of approx. 1 molar H^+.[12] In the case of $TcO_2(CN)_4^{3-}$, a color change from yellow to deep blue is observed when concentrated perchloric or hydrochloric acid is added. Although the nature of this blue material is unknown, the protonation of an oxygen atom in $ReO_2(CN)_4^{3-}$ clearly requires strongly acidic conditions; thus, deprotonation of the $MO(OH)(CN)_4^{2-}$ species would be expected to be rapid in neutral solution.

Reaction of $ReOCl_3(PPh_3)_2$ with $NaEt_2NCS_23H_2O$ in acetone solution[38,39] forms the well-characterized $Re_2O_3(Et_2NCS_2)_4$[39,40] which contains a linear O=Re-O-Re=O backbone. When the reaction is run in methanol rather than acetone, the product isolated is t-$ReO(OMe)(dtc)_2$.[39] This material is easily converted to $Re_2O_3(dtc)_4$ in methylene chloride. The reaction of $ReOCl_3(PPh_3)_2$ with pyridine in wet benzene leads to

Scheme II: Stepwise hydrolysis of $TcO(CN)_5^{2-}$ by solvent (water, methanol) to $TcO_2(CN)_4^{3-}$.


TcOCl4 −
NC
O
Tc
CN
2-
ROH
1-
A
-H+
B
-R+
(R=H)
3-

isolation of $Re_2O_3(py)_4Cl_4$,[41] another linear backbone, whereas reaction in ethanol[30] leads to the formation of $ReO_2(py)_4^+$. Addition of ethanol to $Re_2O_3(py)_4Cl_4$ results in formation of t-$ReO(OEt)(py)_2Cl_2$ which is further converted to $ReO_2(py)_4^+$ upon addition of wet pyridine.[41]

The formation of the $M_2O_3^{4+}$ unit in $Re_2O_3(dtc)_4$,[38] $Re_2O_3(py)_4Cl_4$,[40] and $K_4Re_2O_3(CN)_8$[12] has been postulated to involve an intermediate t-$MO(OH)L_4$ species, which dimerizes and dehydrates to form the t-$M_2O_3^{4+}$ core.

Of special interest is the observation that the alkoxide species $ReO(OMe)(dtc)_2$ and $ReO(OEt)(py)_2Cl_2$ are easily converted to $Re_2O_3(dtc)_4$ and t-$ReO_2(py)_4^+$, respectively.[39,41] In the case of $TcO(OMe)(CN)_4^{2-}$, there is no evidence for such a transformation under the mild conditions utilized in the rhenium complexes. Whether this behavior is due to the presence of cyanide ion, or represents a fundamental difference between technetium and rhenium cannot be clearly ascertained as this time.

The isolation of $K_4Tc(CN)_7 \cdot 2H_2O$, $K_2TcO(CN)_5 \cdot 4H_2O$, $K_3TcO_2(CN)_4$, and $(nBu_4N)_2TcO(OMe)(CN)_4$ clearly demonstrates that technetium does indeed form a wide variety of cyanide complexes which parallel the known cyanide chemistry of its third row congener, rhenium.

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CHAPTER IV

Technetium and Rhenium Thiocyanate Complexes

Introduction

The exact nature of the technetium and rhenium complexes formed in the spectrophotometric determination of these elements using thiocyanate ion[1-4] has been of interest for many years. Although the methods are quite sensitive,[1-5] 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,[6] who observed that perrhenate reacted with thiocyanate ion in hydrochloric acid with 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[7] concluded that the correct oxidation state was more likely to be five than six. Ryabchikov and others[8] 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 nm and 420 nm were assigned to this proposed analog of $ReO_2(CN)_4^{3-}$.[9]

Bailey and Kozak examined molten salt reactions of K_2ReCl_6[10] and $ReCl_5$[11] 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 once again.[11] They ascribed the absorption bands observed at 365 nm and 420 nm to $Re(SCN)_6^-$ and $Re(NCS)_6^{2-}$, respectively. Addition

of excess stannous ion led to formation of $Re(SCN)_6^{2-}$ exclusively. The mode of thiocyanate bonding was changed to N-coordination based on spectral observations on both species several years later.[12]

Cotton, et al.,[13] had examined the reaction of $(nBu_4N)_2Re_2Cl_8$ with thiocyanate ion. When methanol was used as the solvent, $(nBu_4N)_2Re_2(NCS)_8$ was isolated. Addition of tertiary phosphines to the reaction mixture resulted in formation of $(nBu_4N)_2Re_2(NCS)_8(PR_3)_2$, a binuclear complex without a Re-Re bond and two unsymmetrically bridging thiocyanate ligands.[13,14] If acetone rather than methanol was used as a solvent, the reaction took a different course; $(nBu_4N)_2Re(NCS)_6$ and a material formulated as $(nBu_4N)_3Re(NCS)_{10}(CO)_2$, based on analytical and infrared data, were isolated.[13] The hexakisisothiocyanatorhenate(IV) ion prepared via this route appeared to be identical to the sample prepared by Bailey and Kozak.[10]

Crouthamel [2] found that solutions of pertechnetate would turn red when heated with acidic thiocyanate solutions. An intense band at 500 nm was present along with a band at 400 nm. The complex responsible for the 500 nm band could be extracted with alcohols, ketones, and ethers. Crouthamel [2] proposed that the 500 nm band was due to a technetium(V) complex. Howard and Weber [3] examined this system and found that addition of ascorbic acid and iron (III) allowed for the formation of the 500 nm band and inhibited production of the 400 nm band. Other workers [4] used stannous ion reduction of pertechnetate in order to ensure that only the 400 nm band, presumed to be technetium(IV), would be present.

Schwochau, et al., [15] examined this system in detail and proposed that the 400 nm and 500 nm species were a redox couple and isolated

$$Tc(NCS)_6^{-2} \rightleftharpoons Tc(NCS)_6^{-} + e^-$$

a purple species, formulated as $(Me_4N)Tc(NCS)_6$, with λ_{max} = 500 nm, and a yellow air sensitive species, formulated as $(Me_4N)_2Tc(NCS)_6$, λ max= 400 nm. The technetium(V) species, $Tc(NCS)_6^-$, was considered to be the more stable of the pair. A single crystal X-ray structure on the yellow salt proved to be hopelessly disordered; the only information obtainable indicated probable technetium-nitrogen coordination.[16]

Recent electrochemical studies on hexahalometallate(IV) ions (M=Re, Tc; X=Cl, Br) demonstrated that oxidations to hexahalometallate (V) ions were very difficult, and that such oxidations are easier for rhenium than technetium.[17] Thus the reports of stable hexakis(isothiocyanato)metallate(V) complexes for rhenium and technetium, and the reported stability of $Tc(NCS)_6^-$ over $Tc(NCS)_6^{2-}$ (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 and rhenium.

During the course of this investigation, a single crystal X-ray structure of "$(nBu_4N)_3Re_2(NCS)_{10}(CO)_2$" [13] was undertaken in order to re-evaluate its formulation and structure. The results of this study indicate that it should be reformulated as $(nBu_4N)_3Re_2(NCS)_{10}$, a mixed valence, binuclear rhenium (III, IV) complex with two N-bonded, symmetrically bridging thiocyanate ligands.

The full details of the preparation, characterization, and properties of the technetium and rhenium thiocyanate complexes examined are presented.

EXPERIMENTAL

All water used was passed through a Barnstead Ultrapure D8902 Cartridge followed by distillation using a Corning AG-1 water still prior to use. Ammonium, sodium, and potassium thiocyanate salts were recrystallized from methanol and stored in vacuo in a dessicator. Tetrabutylammonium perchlorate (Southwest Analytical) was dried in vacuo at 85°C for 24 h prior to use. All other reagents were used as received. All manipulations involving various salts of $Tc(NCS)_6^{3-}$ were carried out in N_2 or Ar atmospheres, using standard Schlenk line or dry box techniques.

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

The preparation of K_2ReCl_6, $(NH_4)_2TcCl_6$, $(NH_4)_2TcBr_6$, and $(nBu_4N)_2TcCl_6$ has been described previously.[17] The preparation of $(nBu_4N)_2Re_2Cl_8$ from $NaReO_4$ in hydrochloric acid with hypophosphorous acid[18] was followed. Both $Cs_2Re(NCS)_6$[10] and "$CsRe(NCS)_6$"[11] were prepared by the methods published by Bailey and Kozak. The literature preparations of $(nBu_4N)_2Re(NCS)_6$ and $(nBu_4N)_3Re_2(NCS)_{10}$ (formerly $Re_2(NCS)_{10}(CO)_2^{3-}$) from $(nBu_4N)_2Re_2Cl_8$ were followed.[13] Thiocyanogen, $(SCN)_2$, was prepared by the method of Vanderzee and Quest.[19] Preparation of $(Me_4N)_3Fe(NCS)_6$ was accomplished by the method published by Forster and Goodgame.[20] The syntheses of $nBu_4NTcOCl_4$[21] and $Ph_4AsReOBr_4.CH_3CN$[22] were performed by the appropriate methods.[21,22]

Infrared spectra were recorded on a Perkin-Elmer 180 grating spectrophotometer as KBr pellets or solution spectra in matched AgCl cells (0.5 mm pathlength). 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 Raman instrument. Optical spectra in appropriate solvents were recorded on a Cary 17 spectrophotometer.

Voltammetric studies were carried out 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. Tetrabutylammonium perchlorate was used as the supporting electrolyte in the spectrograde acetonitrile used as the solvent. 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[22] and the magnetic moment derived from the

expression:

$$\mu_{eff} = 2.84\sqrt{X^{M}_{corr} \cdot T}$$

$HgCo(SCN)_4$ was used as the calibrant. Electron paramagnetic resonance measurements were attempted at 77K either as solids or frozen solution glasses in quartz tubes fitted in a specially designed liquid nitrogen dewar.

Elemental analyses for the rhenium complexes prepared were performed by Galbraith Laboratories, Knoxville, Tennessee. Melting points are uncorrected.

Preparation of Ammonium hexakisisothiocyanatotechnetate(IV).

In a 25 mL r.b. flask equipped with stir bar, 0.10 gm (0.16 mmol) $(NH_4)_2TcBr_6$ and 1.0 gm (13 mmol) NH_4SCN were refluxed in 15 mL methanol for 24 h. The purple solution was reduced in volume with a rotary evaporator to approx. 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 gm of a purple microcrystalline solid with a green reflex were collected, yield of $(NH_4)_2Tc(NCS)_6$, 70% based on technetium.

Analysis, $C_6H_8N_8S_6Tc$, Calc.: 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 (76,100), 270 (21,100)

Infrared Spectrum (KBr) 3050 (w), 2030 (s), 1395 (w), 470 (w), 320 (m)

Conductivity 2:1 electrolyte in acetonitrile, Λ_o= 410 $cm^2 ohm^{-1} eq^{-1}$

$E_{1/2}$(cathodic) 0.18V vs. SCE ($1e^-$ reversible)

$E_{1/2}$(anodic) 1.60V vs. SCE (irreversible)

Hexachlorotechnetate(IV) may be substituted for hexabromotechnetate(IV) by extending the reflux time to 36 h.

Preparation of Tetraphenylarsonium hexakisisothiocyanatotechnetate(IV)

METHOD A

Metathesis of $(NH_4)_2Tc(NCS)_6$ with an excess of $Ph_4AsCl.H_2O$ in methanol yielded a purple precipitate. Recrystallization from acetone/isobutanol gave a large yield of purple plates with a bright green reflex.

METHOD B

To a solution of 0.40 gm (5.3 mmol) NH_4SCN in 5 mL of 1 N sulfuric acid in an erlenmeyer 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 gm $(NH_4)_4Ce(SO_4)_4$ in 4N sulfuric acid, followed by addition of 1.0 gm $Me_4N^+Br^-$ in 1 mL of 2N sulfuric acid. A purple precipitate was filtered, washed with 5 mL of 1N sulfuric acid, 5 mL of water, 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/isobutanol to yield 0.27 gm of $(Ph_4As)_2Tc(NCS)_6$ as purple plates with a green reflex, 42% based on technetium. Freshly prepared $TcO_2.xH_2O$, obtained from hydrolysis of TcX_6^{2-} with base (c.f. Chapter III) can be used instead of NH_4TcO_4 in this procedure.

Analysis, $C_{54}H_{40}As_2N_6S_6Tc$, Calc.: 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 (76,200), 270 (sh), 262 (34,600), 257 (40,600)

Infrared Spectrum (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)

Magnetic Moment μ eff (298K)= 4.1 BM

$E_{1/2}$ (cathodic) 0.18V vs. SCE (1e-reversible)

$E_{1/2}$ (anodic) 1.60V vs. SCE (irreversible)

Tetraphenylarsonium hexakisisothiocyanatotechnetate(IV) is marginally soluble in dichloromethane, acetone, and acetonitrile. The purple color is so intense (λ max = 500 nm, ε = 76,200 L mol^{-1} cm^{-1}) that detection of undissolved material in saturated solutions can be extremely difficult.

Preparation of Tetrabutylammonium hexakisisothiocyanatotechnetate (III)

In a round bottom flask, 3.0 gm (39.3 mmol) NH_4SCN and 0.20 gm (0.32 mmol)$(NH_4)_2TcBr_6$ were refluxed in 25 mL degassed methanol with stirring under N_2 or Ar for 24 h. After cooling to room temperature, 0.35 mL $N_2H_4.H_2O$ were added via a syringe to the purple solution, this changed 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 gm of nBu_4NClO_4 in 12 mL degassed methanol, added slowly via a cannula. Crystals began to form shortly after the add-

ition of the counter ion was complete; the solid was filtered under an inert atmosphere, washed with 20 mL degassed water to remove NH_4ClO_4, then washed with 5 mL degassed methanol and dried <u>in vacuo</u>. The isolated solid consisted of 0.35 gm of air sensitive yellow blocks of $(nBu_4N)_3Tc(NCS)_6$, 93% based on technetium.

Analysis, $C_{54}H_{108}N_9S_6Tc$, Calc.: 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 (19,400), 280, (sh)

(degassed CH_3CN) 412 nm (25,800 L $mol^{-1}cm^{-1}$), 392 (sh), 285 (sh)

Infrared Spectrum (methanol) νCN 2050 cm^{-1} (s)

(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)

Raman (solid) 2124 (m), 2093 (s), 2076 (s)

Magnetic Moment μ eff (298K) = 3.0 - 3.3 BM

Conductivity 3:1 electrolyte in acetonitrile, Λ_o= 580 cm^2 ohm^{-1} eq^{-1}

$E_{1/2}$(cathodic) -1.09V vs. SCE (irreversible)

$E_{1/2}$ (anodic) 0.18V vs. SCE (le-reversible)

<u>Preparation of Tetraphenylarsonium hexakisisothiocyanatotechnetate(III)</u>.

This salt was prepared from the yellow methanol solution prepared as mentioned above. Addition of 1.0 gm $Ph_4AsCl.H_2O$ in 5 mL of degassed methanol yields crystals that were collected under an inert atmosphere,

washed with three 5 mL aliquots of degassed methanol and then dried *in vacuo*. Yield of yellow-orange air sensitive needles of $(Ph_4As)_3Tc(NCS)_6$ was 0.21 gm, 91% based on technetium.

Analysis, $C_{78}H_{60}As_3N_6S_6Tc$, Calc.: 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 (28,300 L mol^{-1} cm^{-1}), 390 (sh), 285 (sh)

Infrared Spectrum (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).

Reaction of $Tc(NCS)_6^{3-}$ with $(SCN)_2$

To a thoroughly purged 100 mL r.b. flask with stir bar, were added 0.10 gm (0.06 mmol) $(Ph_4As)_3Tc(NCS)_6$ and 50 mL degassed acetone. A solution of 0.05M $(SCN)_2$ in CCl_4, [19] 1.0 mL, was added to the yellow solution which then turned purple instantly. Addition of degassed isobutanol, and subsequent removal of the acetone by evaporation (*in vacuo*) resulted in the formation of purple crystals of $(Ph_4As)_2Tc(NCS)_6$, quantitatively. A similar reaction was observed when acetonitrile was used instead of acetone as the solvent.

Reaction of $Tc(NCS)_6^{3-}$ with NO(g)

To a thoroughly purged 50 mL, 3 neck r.b. flask equipped with stir bar, 0.050 gm (0.043 mmol) $(nBu_4N)_3Tc(NCS)_6$ were added from a Schlenk tube. The yellow solid was dissolved in 25 mL of degassed

Figure XI: Cyclic Voltammogram of $(nBu_4N)_3Tc(NCS)_6$ in Acetonitrile/0.1M TBAP, 100 mV sec^{-1} scan rate, initially anodic.

dichloromethane, added via a cannula. Nitric oxide gas (NO) was 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 $Tc(NCS)_6^{2-}$, no absorption at 400 nm ($Tc(NCS)_6^{3-}$) or any other new absorption due to a nitrosyl species could be observed.

Decomposition of $Tc(NCS)_6^{2-}$ with Hydrogen Peroxide

(a) Basic media. To a 50 mL beaker with stir bar were added .015 gm (0.03 mmol) $(NH_4)_2Tc(NCS)_6$, 20 mL water, and 3.0 mL 30% H_2O_2. Next, 1.0 mL 2.5% w/w NaOH solution was added, resulting in an instantaneous effervesence, $O_2(g)$, and a color change from purple to yellow. Optical spectroscopy showed a band at 400 nm due to the presence of $Tc(NCS)_6^{3-}$. The yellow color slowly bleached until only SCN^- and TcO_4^- were left.

(b) Acidic media. The same conditions as above were duplicated with the exception that 1.0 mL 18M sulfuric acid was added instead of base. The solution quickly turned red, then orange, prior to complete bleaching of the color. Bands in the optical spectrum appeared from 430-490 nm as well as 350 nm before complete oxidation to TcO_4^- was accomplished.

(c) Neutral media. Similar conditions compared to the two previously described experiments, except that no acid or base was used. A slow conversion of $Tc(NCS)_6^{2-}$ to a red-orange mixture (band maxima at

455 nm, 335 nm) followed by a slow bleaching to TcO_4^- was observed.

Preparation of Tetraphenylarsoniumoxopentakisisothiocyanatotechnetate(V).

To a 25 mL r.b. flask with stir bar were added 0.084 gm (0.17 mmol) $nBu_4NTcOCl_4$ and 5 mL of methanol. An ice bath was placed under the green solution to cool the solution to 0°C. Upon addition of 0.063 gm (0.84 mmol) NH_4SCN, a bright red solution rapidly developed. After one minute, 0.2 gm $Ph_4AsCl.H_2O$ were 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 $(Ph_4As)_2$-$TcO(NCS)_5$, 0.173 gm, 93% based on technetium.

Analysis, $C_{53}H_{40}As_2N_5OS_5Tc$, Calc.: 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, xs SCN^-) 450 nm (23,400 L mol^{-1} cm^{-1}),375 (9920)
(CH_2Cl_2, xs SCN^-) 462 nm, 387 nm
(CH_3CN) 450 nm, 380 (sh), 320 (sh)
(CH_2Cl_2) 455 nm, 390 (sh)
(CH_3CN, Ag^+ added) 385 nm, 320 nm

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 (v.w), 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).

Magnetic Moment μeff (298K) = 1.04 BM

Preparation of Tetraphenylarsoniumoxopentakisisothiocyanatorhenate(V).

Method A. In a beaker containing 25 mL of 2N hydrochloric acid, 0.20 gm

(0.73 mmol) $NaReO_4$ and 0.50 gm (5.14 mmol) NH_4SCN a solution consisting of 0.16 gm (0.71 mmol) $SnCl_2.2H_2O$ in 5 mL of 2N hydrochloric acid was added dropwise with stirring to produce a red solution. The solution was extracted with 100 mL of ether, the red ether layer was collected and diluted with 200 mL of ethanol. Tetraphenylarsonium-chloride monohydrate, 0.35 gm, was added and upon addition of 100 mL of ether, yellow crystals formed. The solid was collected, washed with water and ether, then dried in vacuo. Yield of $(Ph_4As)_2ReO(NCS)_5$, 0.42 gm, 46% based on rhenium.

Method B. A cherry red solution of $Ph_4AsReOBr_4.CH_3CN$, 0.38 gm (0.40 mmol) in 10 mL acetonitrile, was treated with 0.16 gm (2.76 mmol) 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 gm Ph_4AsBr. A yellow precipitate formed upon addition of isobutanol or ether. Recrystallization from hot acetone/isobutanol mixtures yielded 0.42 gm of golden orange crystals of $(Ph_4As)_2ReO(NCS)_5$, 80% based on rhenium. Recrystallizations from slow evaporation of acetone/isobutanol mixtures formed yellow green blocks of $(Ph_4As)_2ReO(NCS)_5$.

Method C. Potassium oxopentachlororhenate, K_2ReOCl_5,[23] 0.058 gm (0.13 mmol) was suspended in 5 mL of acetonitrile. Upon addition of 0.048 gm (0.63 mmol) NH_4SCN, a white precipitate formed (NH_4Cl,KCl) and a yellow solution formed. The mixture was filtered, and the filtrate treated with 0.106 gm (0.25 mmol) $Ph_4AsCl.H_2O$. The solid was precipitated with isobutanol. The solid was recrystallized as in method B. Yield of $(Ph_4As)_2ReO(NCS)_5$ was 0.134 gm, 84% based on rhenium.

Analysis, $C_{53}H_{40}As_2N_5OReS_5$, Calc.: 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 (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)

(CH_3CN) 2112 (w), 2069 (s), 2036 (m) νCN

Magnetic Moment (solid) μ eff (298K) 2.0-2.8 BM y-orange crystals

1.2-2.0 BM y-green crystals

(CH_3CN solution) diamagnetic

Conductivity 2:1 electrolyte in acetonitrile, Λ_o = 348 $cm^2 ohm^{-1} eq^{-1}$

Melting Pts. yellow orange $\xrightarrow{266°C}$ red $\xrightarrow{305°C}$ melts

yellow green $\xrightarrow{175°C}$ yellow orange $\xrightarrow{266°C}$ red $\xrightarrow{305°C}$ 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 viewing the yellow-orange crystals between crossed polarizers and a Bertrand lens.

Preparation of Tetrabutylammoniumoxopentakisisothiocyanatorhenate(V).

Use of method B for $(Ph_4As)_2ReO(NCS)_5$ but with tetrabutylammonium salts used instead yielded yellow crystals. From 0.31 gm (0.41 mmol)

$nBu_4NReOBr_4$, 0.16 gm (2.76 mmol) NH_4SCN, and 0.14 gm nBu_4NBr, 0.21 gm of yellow crystals of $(nBu_4N)_2ReO(NCS)_5$ were collected, 69% based on rhenium.

Method B. To the cathode compartment of an electrolysis cell, 1.0 gm (4.0 mmol) $NaReO_4$, 2.59 gm (34.8 mmol) NaSCN, and 12 mL of 4N hydrochloric acid were added. The anode compartment was filled with 12 mL of 4N hydrochloric acid. Platinum mesh electrodes were used to pass 1000 coulombs at 0.5 amps. The cell compartments were stirred continuously. The resultant red-brown mixture in the cathode compartment was filtered, then the filtrate was extracted with two 50 mL aliquots of ether. The combined red ether extracts were treated with a concentrated solution of nBu_4NBr in ethanol. Addition of water resulted in a phase separation and crystallization occured at the interphase. The yellow crystals were collected, washed with water and ether, then dried in vacuo. Yield of bright yellow crystals of $(nBu_4N)_2ReO(NCS)_5$, 0.61 gm, 15% based on rhenium.

Analysis, $C_{37}H_{72}N_7ORES_5$, Calc.: 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 (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).

Reaction of $TcO(NCS)_5^{2-}$ with Thiocyanate Ion.

An acetonitrile solution of $(Ph_4As)_2TcO(NCS)_5$ was treated with an approximately ten fold excess of NH_4SCN and stirred. Within one hour, the solution had visibly darkened, and 24 hours 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 darken, and the appearance of $Tc(NCS)_6^{x-}$ (x = -2,3) can be 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 2N hydrochloric acid/ethanol was treated with twenty equivalents of $SnCl_2 \cdot 2H_2O$ and ten equivalents of NH_4SCN. The yellow orange solution turned color to a rich red brown and spectrophotometrically a band at 420 nm ($Re(NCS)_6^{2-}$)[11,13] was observed. Attempts to isolate pure samples of $Re(NCS)_6^{2-}$ by this method with large univalent cations invariably also brought out tin salts (presumably $Sn(NCS)_6^{2-}$) that could not be separated from the rhenium complex.

Preparation of Tetrabutylammonium μ-(N,N')dithiocyanatooctakis-isothiocyanatodirhenate(III,IV).

This preparation is essentially identical to the preparation of $(nBu_4N)_3Re(NCS)_{10}(CO)_2$ reported by Cotton, et al.[13] A well purged 100 mL 2 neck round bottom flask with stir bar was charged

with 1.0 gm (0.88 mmol) $(nBu_4N)_2Re_2Cl_8$ and 0.9 gm (9.3 mmol) KSCN. Via a cannula, 75 mL of degassed acetone were added and the muddy brown solution stirred for 2 h. The reaction mixture was filtered to remove KCl and the filtrate was then evaporated to dryness. The brown solid was washed with aliquots of ethanol (ca. 125 mL) until the filtrate became pale yellow. It was then washed with 40 mL of water followed by THF until a very pale yellow filtrate resulted and small dark green crystals remained on the filter. These crystals were dissolved in 25 mL of acetonitrile, filtered, and the dark brown filtrate was treated with 75 mL of ether. The solution was refrigerated at -10°C. Large, well formed, dark green prisms were filtered, washed with ether and dried in vacuo. Yield of $(nBu_4N)_3Re(NCS)_{10}$, 0.48 gm, 33% based on rhenium. These crystals were of suitable quality for a single crystal X-ray structure (see below).

Optical Spectrum (CH_3CN) 1316 nm (535 $Lmol^{-1}cm^{-1}$), 670 (4075), 475 (sh), 420 (38,000), 375 (sh), 770 (sh), 231 (92,000)

Infrared Spectrum (KBr) 2950(m), 2920(m), 2900(w,sh), 2860(m), 2062(vs), 2040(vs), 2027(s), 1914(s), 1877(s), 1845(w), 1480(w), 1473(m), 1455(m), 1438(m), 1410(w), 1370(m), 1340(w), 1255(w), 1170(w), 1142(w), 1100(w), 1055(w), 1020(w), 1000(w), 960(w), 940(w), 875(w), 793(w), 731(w), 463(w), 462(w), 315(m), 286(m), 268(w)

The solid is paramagnetic[13] but no EPR signal at 77K could be detected. $\mu_{eff}(298K)$ = 2.57 BM

$E_{1/2}$(cathodic) 0.05 V vs. SCE ($1e^-$ reversible)

$E_{1/2}$(anodic) 0.45 V vs. SCE ($1e^-$ reversible)

X-Ray Data Collection

The actual X-ray crystallographic study was performed by F. A. Cotton and W. H. Ilsley at Texas A & M University. One of the large crystals of $(nBu_4N)_3(Re_2(NCS)_{10}$ was ground to a sphere with a diameter of 0.35 mm and used for preliminary examination and data collection. It was secured to the end of a thin glass fiber with epoxy cement and mounted on a Syntex P1 automatic diffractometer.

Preliminary rotation and oscillation photographs indicated that the crystal was monoclinic and examination of selected reflections indicated that it was a single crystal of good quality. ω-scans showed that several intense reflections had widths at half-height of less than 0.3°. Examination of data collected in a preliminary data set showed absences $hk\ell$, $h+k+\ell = 2n+1$, and $h0\ell$, $h = 2n+1$ consistent with the space group I2/a, which though non-standard, proved very satisfactory. Careful centering of 15 reflections in the range $25 < 2\theta < 33°$ gave unit cell parameters a = 24.016(6)Å, b = 14.340(2)Å, c = 24.798(5)Å, β = 110.5°, V = 7999(3)Å^3. This volume is consistent with Z = 4. The procedures preliminary to data collection have been described previously.[24]

All data were collected using Mo Kα (λ = 0.71073Å) radiation monochromatized in the incident beam with a graphite crystal. A total of 4263 independent reflections with $0 < 2\theta < 45°$ were collected at 22±4°C using the θ-2θ scan technique. A variable scan rate from 4-24° min^{-1} was used with a scan range of $K\alpha_1$ - 1.0° to $K\alpha_2$ + 1.0° and a scan to background time ratio of 2. The intensities of three

standard reflections were measured after every 97 reflections and showed no significant variation during the period of data collection. Lorentz and polarization corrections were applied.[25] The linear absorption coefficient for the crystal is $\mu = 34.88\ cm^{-1}$. A spherical absorption correction (min. = 2.35, max. = 2.39, av. = 2.37) was applied to the data.

Solution and Refinement.[25] The structure was solved in the monoclinic space group I2/a. The position of the independent rhenium atom was found by solution of the three-dimensional Patterson function. Subsequent Fourier and difference syntheses gave the positions of the remaining atoms. Full matrix anisotropic least-squares refinement of all atomic positional parameters and temperature factors gave final discrepancy indices of

$$R_1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o| = 0.043$$

$$R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.060$$

and a goodness of fit parameter of 1.295. The function $\Sigma w(|F_o| - |F_c|)^2$ was minimized with the weighting factor, w, equal to $4F_o^2/\sigma(F_o^2)^2$. Atomic scattering factors were those of Cromer and Waber.[6] Anomalous dispersion effects were included in the scattering factors of rhenium. A table of positional and thermal parameters is presented in Appendix II.

Results and Discussion

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 complexes, $Re(NCS)_6^-$ and $Re(NCS)_6^{2-}$.[11] Several years later, Schwochau, et al.,[15] were influenced by that study and the early work of Crouthamel,[2] who had postulated that the purple species was a technetium(V) complex. Schwochau, et al., identified the purple and yellow thiocyanate complexes as $Tc(NCS)_6^-$ and $Tc(NCS)_6^{2-}$, respectively. The technetium(V) complex was considered to be much more stable than the air-sensitive technetium(IV) complex, which readily oxidized in air to form the technetium(V) complex.

An electrochemical study on the hexahalometallate(IV) complexes of technetium and rhenium[17] revealed that oxidation of these salts to the hexahalometallate(V) species was extremely difficult and that such an oxidation was more difficult for technetium than rhenium. Thus, the apparent behavior of the pseudohalide(thiocyanate) analogues was puzzling.

The rhenium(IV) complex, $Re(NCS)_6^{2-}$, has been prepared from the disproportionation of $Re_2Cl_8^{2-}$ with thiocyanate ion,[13] and from a molten salt reaction involving K_2ReCl_6 and KSCN.[10] This material is well characterized, with an intense charge transfer absorption in the visible region at 420 nm, and a strong band at 2040 $\pm$ 10 cm^{-1} in the cyanide stretching region of the infrared found for samples from either preparation. An electrochemical

study of $Re(NCS)_6^{2-}$,[26] reveals the presence of an irreversible oxidation at 1.23 V vs. SCE in acetonitrile.[27]

Preparation of "$CsRe(NCS)_6$" from $ReCl_5$ and KSCN in a molten salt reaction produces a dark brown solid that upon dissolution in 1M sulfuric acid (in which it was reported to be stable)[11] showed a visible absorption band at 420 nm ($Re(NCS)_6^{2-}$), not at 365 nm as had been reported.[11] Although it is possible that "$Re(NCS)_6^-$" could be formed in the solid state,[28] it is apparent from the voltammetric and solution studies that such a species is not stable in solution, especially in the 2N acid solution. Thus the claim[11] 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 2N hydrochloric acid must be discounted.

The reported stability of $Tc(NCS)_6^-$ with respect to $Tc(NCS)_6^{2-}$ is therefore opposite the expected periodic trend. The reinvestigation of the technetium thiocyanate system and its reformulation as a reversible one-electron redox couple

$$Tc(NCS)_6^{3-} \rightleftarrows Tc(NCS)_6^{2-} + e$$

are presented below.

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 nm and 500 nm.

Chromatography of the reaction 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 $(NH_4)_2Tc(NCS)_6$, a d^3-octahedral technetium(IV) complex. Metathesis of this salt with tetraphenylarsonium ion results in the formation of $(Ph_4As)_2Tc(NCS)_6$, which can be recrystallized from acetone/isobutanol 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 nm 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.

As shown in Table XVI, 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 cm^{-1} can be assigned as the Tc-N stretching frequency. There is no evidence for a Tc=O, Tc_2O_3, or TcO_2 linkage in the infrared spectrum. Equivalent conductance measurements[30] show the ammonium salt to be a 1:2 electrolyte in acetonitrile, similar to $(nBu_4N)_2TcCl_6$ (Figure IX). The visible spectrum is dominated by an intense charge transfer absorption

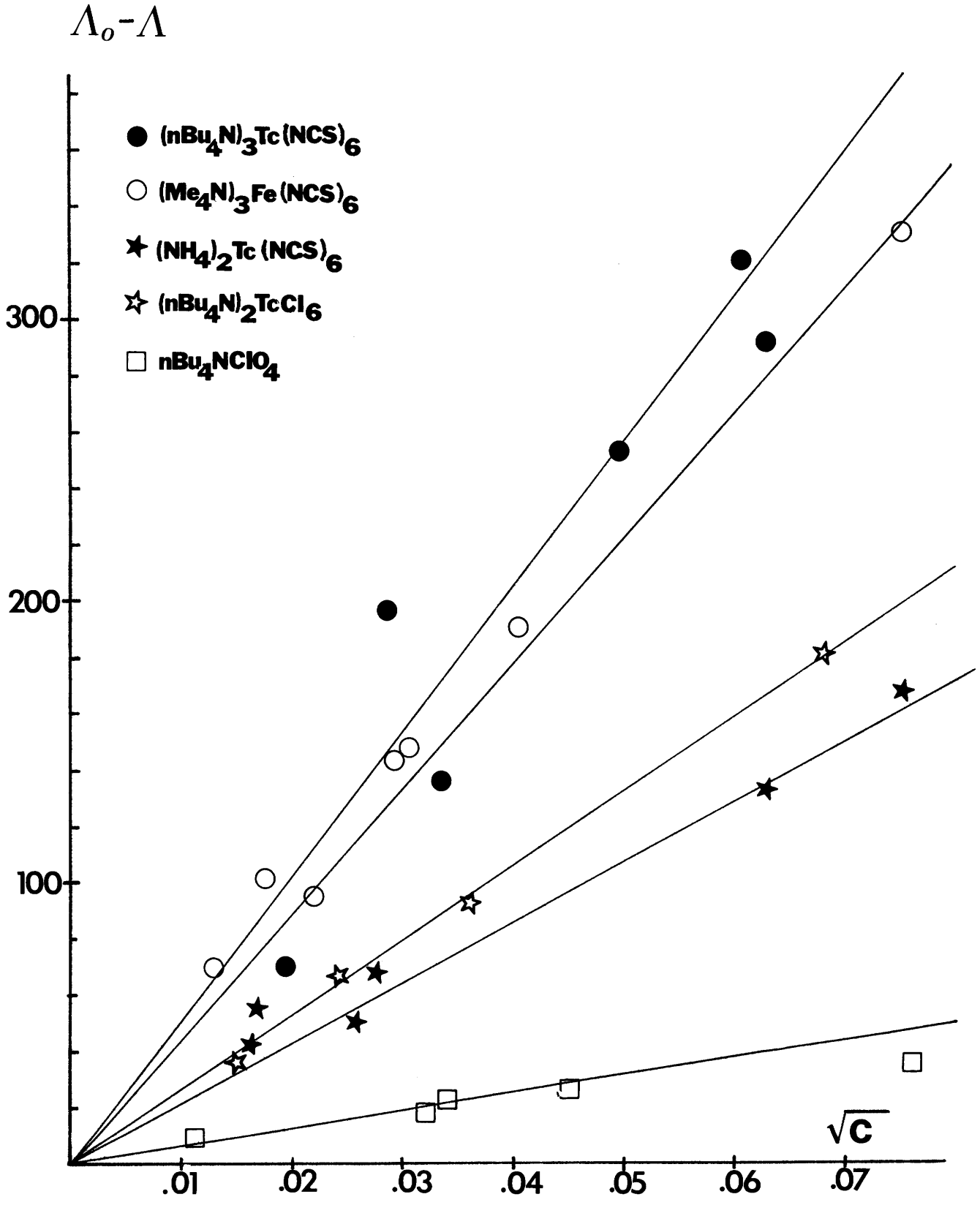
Table XVI: Infrared Spectral Data of $Tc(NCS)_6^{x-}$ Salts (cm^{-1}).

Compound	ν_{CN}[a]	ν_{Tc-N}[a]	$\nu_{NCS\ bend}$[a]
$(NH_4)_2Tc(NCS)_6$	2030(s)	320(m)	470(w)
$(Ph_4As)_2Tc(NCS)_6$	2020(s)	325(m)	460(w)
$(nBu_4N)_3Tc(NCS)_6$	2110(m) 2064(s)	318(m)	477(w)
	2050(s)[b]		
$(Ph_4As)_3Tc(NCS)_6$	2070(s)	310(m)	475(m)
Raman (solid)			
$(nBu_4N)_3Tc(NCS)_6$	ν_{CN}	2124(m), 2093(s), 2076(s)	

[a] KBr pellet.

[b] Solution spectra in methanol.

Figure IX: Equivalent conductance measurements of nBu_4NClO_4, $(nBu_4N)_2TcCl_6$, $(Me_4N)_3Fe(NCS)_6$, $(NH_4)_2Tc(NCS)_6$, $(nBu_4N)_3Tc(NCS)_6$ in acetonitrile. $\Lambda_o - \Lambda(cm^2ohm^{-1}eq^{-1})$ vs. $(eq.\ conc.)^{1/2}$.


$\Lambda_o - \Lambda$
● $(nBu_4N)_3Tc(NCS)_6$
○ $(Me_4N)_3Fe(NCS)_6$
★ $(NH_4)_2Tc(NCS)_6$
☆ $(nBu_4N)_2TcCl_6$
□ nBu_4NClO_4
300
200
100
.01
.02
.03
.04
.05
.06
.07
$\sqrt{C}$

(λ_{max} = 500 nm, ϵ = 76,200 $Lmol^{-1}cm^{-1}$ in acetonitrile).

Magnetic susceptibility measurements on the Ph_4As^+ salt (μeff(298K) = 4.1 BM) are consistent with a $^4A_{2g}$ ground state for an octahedral d^3 ion and in the range observed for the hexahalometallate salts.[31] Like salts of $TcCl_6^{2-}$, the complex does not show an EPR signal at room temperature or 77K,[32] despite the $^4A_{2g}$ ground state.

Voltammetric studies in acetonitrile (Table XVII) on either the NH_4^+ or Ph_4As^+ salt reveal an irreversible oxidation at 1.60 V vs. SCE. The analogous rhenium complex, $Re(NCS)_6^{2-}$, displays an irreversible oxidation at 1.23 V vs. SCE. As was the case with the hexahalometallate(IV) species,[17] 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 $Tc(NCS)_6^{2-}$ also show a reversible one-electron reduction at +0.18 V vs. SCE. The corresponding rhenium reduction is more difficult, occurring at -0.11 V vs. SCE. This reduction is also reversible, as shown in Figure X.

Treatment of solutions of $Tc(NCS)_6^{2-}$ with large excesses of thiocyanate ion (10^3:1; SCN^-:Tc) results in formation of orange solutions and the appearance of a band at 400 nm in the optical spectrum. Reduction of pertechnetate with $SnCl_2 \cdot 2H_2O$ 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.

Table XVII: Electrochemical Measurements of $M(NCS)_6^{x-}$ Species.

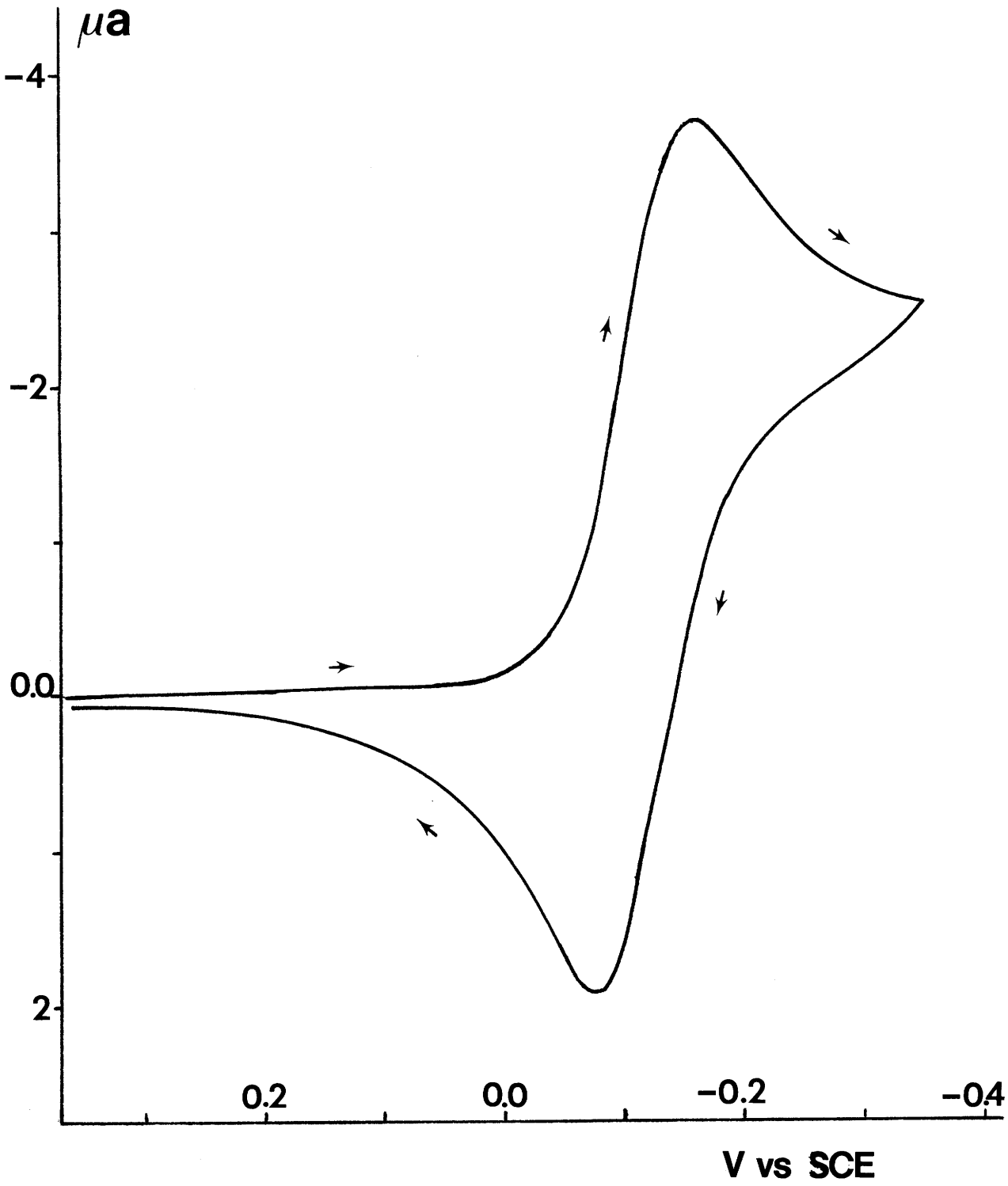
Compound	$E_{1/2}$(cathodic)[a]	$E_{1/2}$(anodic)[a]
$(NH_4)_2Tc(NCS)_6$	0.18V ($1e^-$ rev)	1.60 V (irrev)
$(Ph_4As)_2Tc(NCS)_6$	0.18V ($1e^-$ rev)	1.60 V (irrev)
$(nBu_4N)_3Tc(NCS)_6$	-1.10V (irrev)	0.18 V ($1e^-$ rev)
$(nBu_4N)_2Re(NCS)_6$	-0.11V ($1e^-$ rev)	1.23 V (irrev)

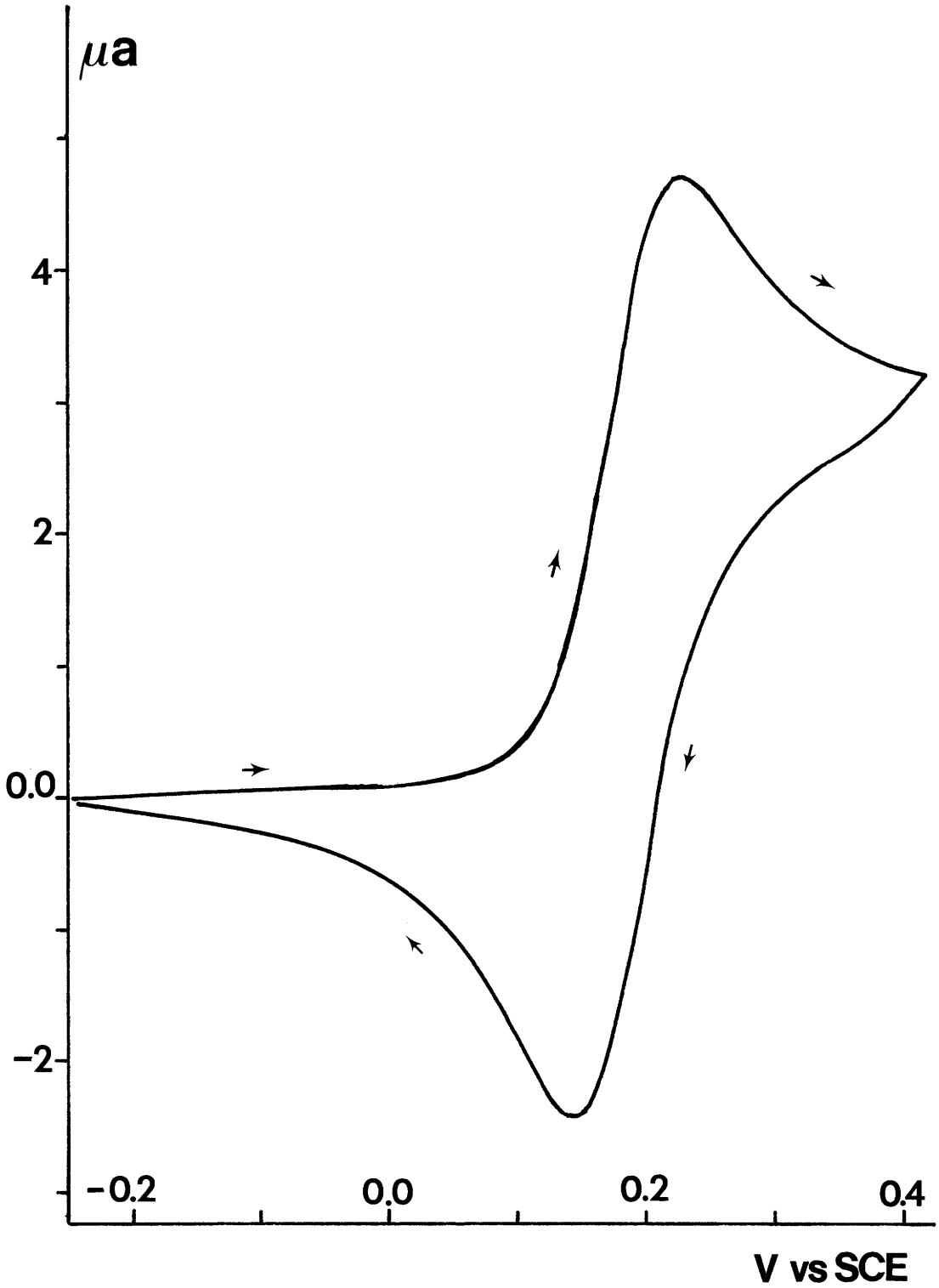
[a]Measurements taken in acetonitrile/0.1 M TBAP; all potentials vs. SCE.

The red-violet solution resulting from the reaction between $(NH_4)_2TcX_6$ and NH_4SCN in refluxing methanol can be converted to a brilliant yellow solution via the addition of $N_2H_4 \cdot H_2O$. Solutions of $(NH_4)_2Tc(NCS)_6$, 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 $M_3Tc(NCS)_6$ ($M = nBu_4N^+$, Ph_4As^+).

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 (Table XVI), consistent with octahedral symmetry. In the case of $(nBu_4N)_3Tc(NCS)_6$, 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 nBu_4N^+ salt must be due to solid state effects. Another octahedral thiocyanate complex, $(Me_4N)_3Fe(NCS)_6$, displays three bands in the cyanide stretching region of the infrared in the solid,[20] and yet, an X-ray structure has confirmed it as a generally octahedral six-coordinate complex,[33] although each of the two crystallographically distinct octahedron have markedly non-linear Fe-N-C-S moieties.

Figure X: Cyclic Voltammogram of $(nBu_4N)_2Re(NCS)_6$ in Acetonitrile/0.1M TBAP, 100 mV sec^{-1} scan rate, initially cathodic.


μa
-4
-2
0.0
2
0.2
0.0
-0.2
-0.4
V vs SCE

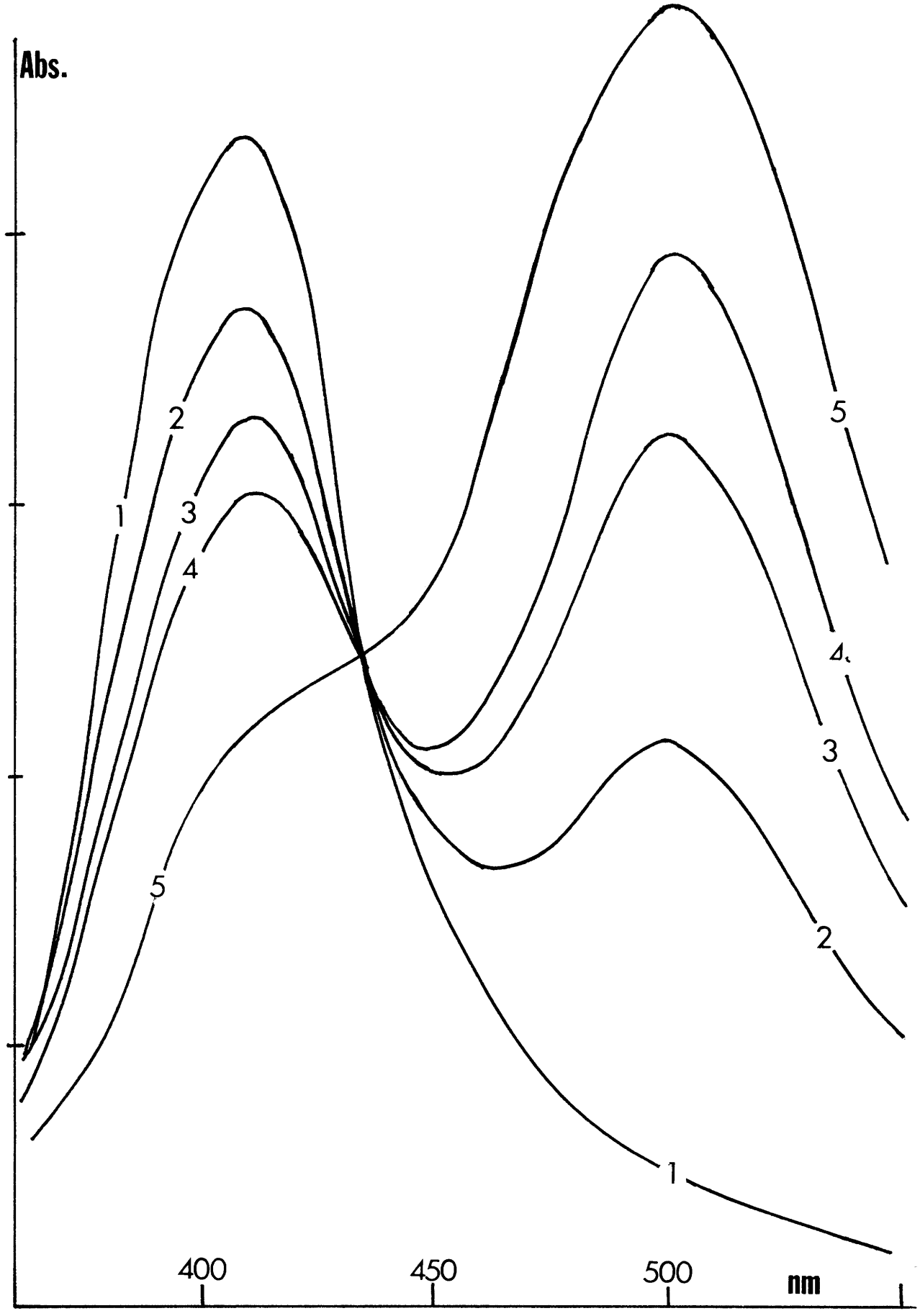

μa
4
2
0.0
-2
-0.2
0.0
0.2
0.4
V vs SCE

The observed magnetic moment of the technetium complex 3.0 - 3.3 BM at 298K, is in the range expected for a d^4 ion with two unpaired electrons.[22] No EPR spectrum was obtainable at room temperature or 77K. Equivalent conductance measurements (Figure IX) on $(nBu_4N)_3Tc(NCS)_6$ in acetonitrile are consistent with a 1:3 electrolyte (cf. $(Me_4N)_3Fe(NCS)_6$). The optical spectrum has an intense band at approximately 400 nm ($\varepsilon \sim 22{,}000$ $Lmol^{-1}cm^{-1}$) which is solvent dependent in shape and intensity.

The voltammetric behavior of hexakisisothiocyanatotechnetate(III) is summarized in Table XVII. 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 (Figure XI) 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, as shown in Figure XII. 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, $(SCN)_2$, oxidized 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:

$$Tc(NCS)_6^{3-} \rightleftarrows Tc(NCS)_6^{2-} + e \quad E_{1/2} = 0.18 \text{ V vs. SCE}$$

Figure XII: (1) Optical spectrum of $Tc(NCS)_6^{3-}$ in degassed acetonitrile/water. (2-5) After addition of one drop 1.0 M H_2SO_4 and bubbling with O_2, appearance of $Tc(NCS)_6^{2-}$.


Abs.
1
2
3
4
5
5
4
3
2
1
400
450
500
nm

The reduction of perrhenate with stannous ion in acidic thiocyanate solutions[1,6-9,11] results in formation of rich red to red-brown solutions containing optical absorptions at 365 nm and 420 nm. The species at 420 nm has been identified as $Re(NCS)_6^{2-}$;[11] however, the claim of Bailey and Kozak that the band at 365 nm was due to $Re(NCS)_6^-$ has already been dismissed (vide infra).

The careful reduction of perrhenate with one equivalent $SnCl_2 \cdot 2H_2O$ and six to seven equivalents of thiocyanate ion in 2N 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 XVIII, these salts all exhibit three bands in the cyanide stretching region of the infrared; group theory predicts that a species such as $MX(NCS)_5$ (C_{4v}) should have three infrared active vibrations ($2A_1 + E$) 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 equivalent conductance measurements (Figure XIII).

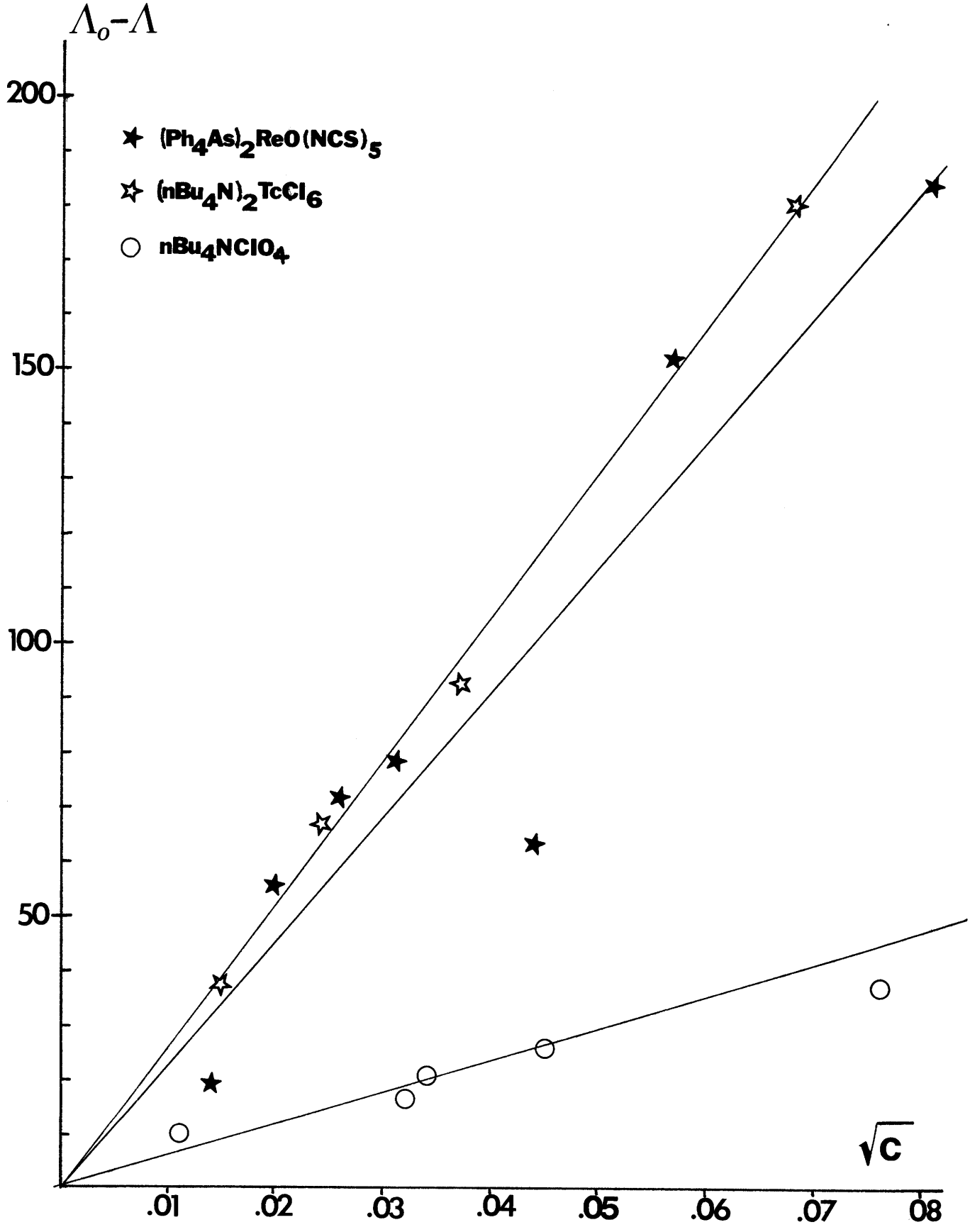
The optical spectrum reveals two bands in the ultraviolet region at 306 nm and 365 nm (ε = 14,200; 24,300 $Lmol^{-1}cm^{-1}$,

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

Compound	ν_{CN}	ν_{ReO}
$(nBu_4N)_2ReO(NCS)_5$	2105(ms) 2060(s) 2010(s)	952(s)
$(Ph_4As)_2ReO(NCS)_5$	2100(w) 2060(s)	953(m)
(yellow orange)[a]	2031(m)	
$(Ph_4As)_2ReO(NCS)_5$ (yellow green)[a]	2100(w) 2060(s) 2031(m)	961(m) 954(m)
Solution Spectra (CH_3CN)	2112(w) 2069(s) 2036(m)	

[a]Different crystal modifications.

Figure XIII: Equivalent conductance measurements of nBu_4NClO_4, $(nBu_4N)_2TcCl_6$, and $(Ph_4As)_2ReO(NCS)_5$ in acetonitrile. Λ_o - $\Lambda(cm^2ohm^{-1}eq^{-1})$ vs. $(eq.\ conc.)^{1/2}$.


$\Lambda_o - \Lambda$
200
150
100
50
$(Ph_4As)_2ReO(NCS)_5$
$(nBu_4N)_2TcCl_6$
nBu_4NClO_4
.01
.02
.03
.04
.05
.06
.07
.08
$\sqrt{C}$

respectively). The band at 365 nm in the spectrophotometric determination 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[34] 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 are brown to black in color, with optical spectra revealing bands at 320 nm (ε = 9800 $Lmol^{-1}cm^{-1}$) and 435 nm (ε = 13,000 $Lmol^{-1}cm^{-1}$). The existence of a strong infrared band at 2050 cm^{-1} and a rhenium-oxo stretch at ~960 cm^{-1} is also observed. Based on 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 nBu_4N^+ or Ph_4As^+ salts 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. The observations and comparisons of these two forms are listed in Table XIX. Apparently, when the complex is recrystallized rapidly, for example, from a refluxing acetone/isobutanol solution, the yellow-orange form predominates. When crystals are allowed to grow slowly from solvent mixtures, for

Table XIX: Observations on the Yellow-Orange and Yellow-Green Forms of $(Ph_4As)_2ReO(NCS)_5$.

Form	Yellow-Orange uniaxial plates	Yellow-Green biaxial blocks
Elemental Analysis		
C(50.55)[a]	51.02	50.98
H(3.20)	3.56	3.40
N(5.56)	5.69	5.57
S(12.73)	12.94	12.55
μeff (298K)	2.0 - 2.8 BM	1.2 - 2.0 BM
Infrared $\nu_{Tc=O}$	953(m)	961(m), 954(m)
Melting Pt	266°C(red) 305°(melts)	175°C (y-orange) 266°C (red) 305°C (melts)

[a]Values in parentheses are calculated %.

example, slow evaporation of acetone/isobutanol 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, 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 other 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 nBu_4N^+ salt appears to crystallize in one form only.

The colormetric 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); 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, $Re(NCS)_6^{3-}$, may be involved in the reaction, but not

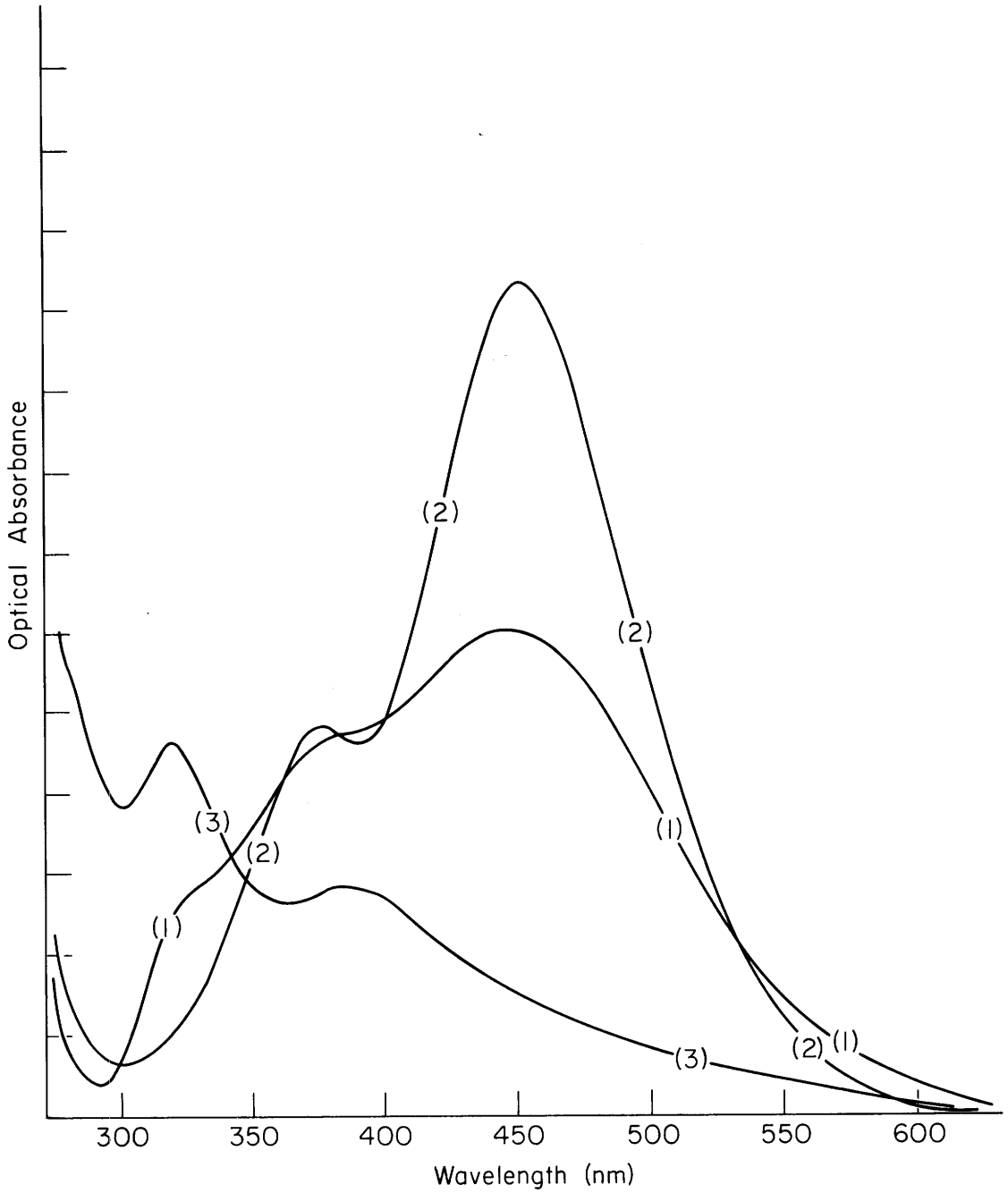
observed because it is quickly oxidized to $Re(NCS)_6^{2-}$ under the conditions of the reaction. Under the same reasoning, the existence of a technetium(V) complex, $TcO(NCS)_5^{2-}$, can be postulated, reducing rapidly to form the six-coordinate thiocyanate complexes.

The use of $TcOCl_4^-$ as a synthetic intermediate in the exploration of technetium(V) chemistry has already been described.[21] The reaction of a methanol solution of $nBu_4NTcOCl_4$ with five equivalents 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), 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 $\sim$955 cm^{-1}; the trend observed for νReO vs νTcO in the oxobis(dithiolato)metallate(V) complexes [21] is also observed here. The magnetic moment of 1.04 BM at 298K is in the range of other technetium(V),[21] rhenium(V),[21,35] and molybdenum(IV)[35] complexes.

The optical spectrum of $(Ph_4As)_2TcO(NCS)_5$ in acetonitrile has a broad band at 450 nm with shoulders at 380 nm and 320 nm (Figure XIV). This spectrum is not similar in shape to the spectrum of $(Ph_4As)_2ReO(NCS)_5$, which has well-defined bands at 365 nm and 306 nm. However, when thiocyanate ion is added to the $TcO(NCS)_5^{-2}$ solution, the band

Figure XIV: Optical spectra of $(Ph_4As)_2TcO(NCS)_5$.
(1) Acetonitrile solution; (2) same concentration as (1), but ammonium thiocyanate added; (3) same concentration as (1) but silver nitrate added.


Optical Absorbance
300
350
400
450
500
550
600
Wavelength (nm)
(1)
(2)
(3)
(1)
(2)
(3)
(2)
(3)
(1)
(2)
(1)

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 bathochromic shifted spectrum of $(Ph_4As)_2ReO(NCS)_5$. 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, $(Ph_4As)_2ReO(NCS)_5$, is a well behaved 1:2 electrolyte. This difference can be accounted for by consideration of the increased orbital overlap of 5d orbitals (Re) 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 concentra-

$$TcO(NCS)_5^{2-} \rightleftharpoons TcO(NCS)_4^{-} + NCS^{-}$$
$$\searrow ?$$

ted solutions of $TcO(NCS)_5^{2-}$ are treated with silver nitrate, pre-

cipitation of $Ag_2TcO(NCS)_5$ 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 $Tc(NCS)_6^{2-}$.

The reduction of pertechnetate ion by thiocyanate ion is quite complex, with any of the following steps going on simultaneously:

i) $TcO_4^- + 6H^+ + 7NCS^- \longrightarrow TcO(NCS)_5^{2-} + 3H_2O + (NCS)_2$

ii) $TcO(NCS)_5^{2-} + 3NCS^- + 2H^+ \longrightarrow Tc(NCS)_6^{3-} + H_2O + (NCS)_2$

iii) $Tc(NCS)_6^{3-} + 1/2\ O_2 + 2H^+ \longrightarrow Tc(NCS)_6^{2-} + H_2O$

iv) $Tc(NCS)_6^{3-} + 1/2\ (NCS)_2 \rightleftharpoons Tc(NCS)_6^{2-} + NCS^-$

v) $(NCS)_2 \longrightarrow (NCS)_x \downarrow$

It is reasonable to assume that it is even more complicated than this simple picture and that other species present in the acidic thiocyanate ion mixture could play an important role in the reaction.

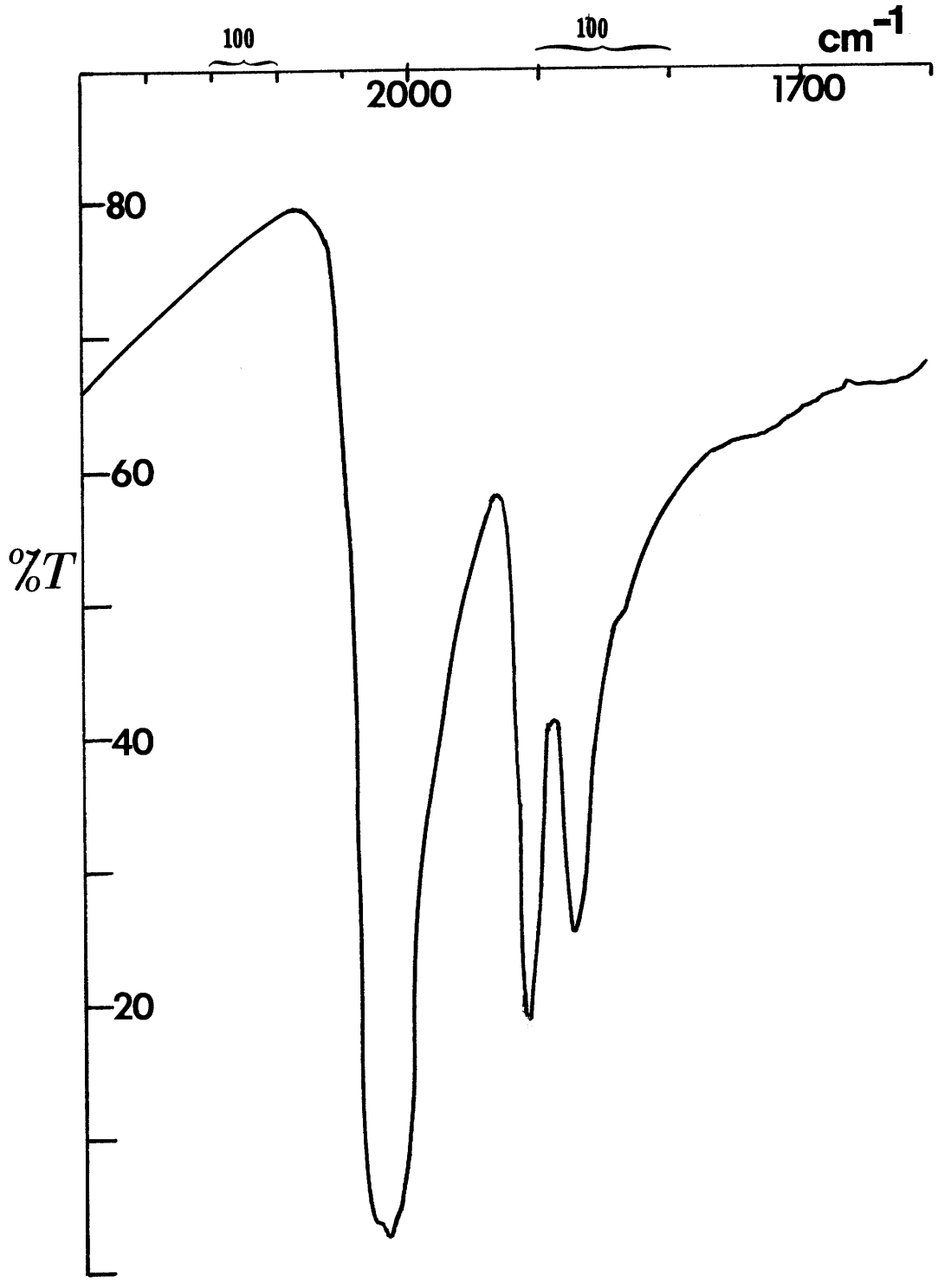
One final note about the technetium thiocyanate system deserves comment. When $(NH_4)_2Tc(NCS)_6$ solutions are oxidized to TcO_4^- by

hydrogen peroxide, spectrophotometric examination of the reaction mixture produces spectra that are strikingly similar to the spectra observed when $TcO(NCS)_5^{2-}$ decomposes in solution to form $Tc(NCS)_6^{x-}$ (x=2,3). This suggests, but does not prove, that the $TcO(NCS)_5^{2-}$ is formed in the oxidation.

The reaction between $Re_2Cl_8^{2-}$ and thiocyanate ion in acetone[13] yields two products: $(nBu_4N)_2Re(NCS)_6$ and a dark green solid that was formulated as $(nBu_4N)_3Re_2(NCS)_{10}(CO)_2$. By lengthening the reaction time, more of $(nBu_4N)_2Re(NCS)_6$ is produced, suggesting that the other material is an intermediate product. The formulation, $(nBu_4N)_3Re_2(NCS)_{10}(CO)_2$, was based upon elemental analysis, equivalent conductance measurements which showed it to be a 1:3 electrolyte, magnetic measurements, and interpretation of the infrared spectrum. The infrared spectrum of this material (Figure XV) reveals absorption bands at 2062 (vs), 2040 (vs), 2027 (s) cm^{-1} in the region normally observed for terminally bound thiocyanate ligands.[36,37] Also present are two bands at 1914 (s) cm^{-1} and 1877 (s) cm^{-1} which were assumed to be due to coordinated CO, arising from the solvent, acetone. No known type of thiocyanate bonding had ever been observed in that region.[36,37]

Interestingly, little notice of this complex has been made and no single crystals suitable for X-ray structural analysis had previously been grown. However, slow recrystallization from 1:3 acetonitrile/ether mixtures at -10°C affords large, well-formed blocks of this material. An X-ray diffraction study was undertaken to

Figure XV: Infrared spectrum of $(nBu_4N)_3Re_2(NCS)_{10}$ in a KBr pellet, detail on the thiocyanate stretching region. Absorptions between 2100-2000 cm^{-1} are due to terminal thiocyanates, absorptions between 1950 - 1850 cm^{-1} are assigned to symmetrically bridging thiocyanate ligands.


100
100
cm-1
2000
1700
80
60
40
20
%T

positively identify this interesting material. This study shows that there are, in fact, no CO ligands present, and the correct formulation of the mysterious dark green solid is actually $(nBu_4N)_3Re_2(NCS)_{10}$.

A computer generated drawing of the $Re_2(NCS)_{10}^{3-}$ anion, in which the atomic number scheme is defined, is shown in Figure XVI. The bond lengths and angles are listed in Table XX and XXI, respectively. Figure XVII gives schematic drawings in which the atom numbers for the two crystallographically independent tetra-n-butylammonium cations are given.

The $Re_2(NCS)_{10}^{3-}$ ions are located on crystallographic inversion centers. The ion consists of two distorted octahedra sharing an edge formed by the nitrogen atoms of the two bridging thiocyanate ions. The remaining vertices are also occupied by nitrogen atoms from the terminally bound thiocyanate ions. The anion as a whole has approximate D_{2h} symmetry. Each thiocyanate ligand, including the bridging ones, is effectively linear; angles at the carbon atoms range from 177.8° to 179.6°. For the four terminal ligands the Re-N-C angles range from 165.4° to 176.4°. The bridging thiocyanate ligands are essentially perpendicular to the Re-Re' axis with a Re-N-Re' angle of 77.4°.

Of the twelve nBu_4N^+ ions in the unit cell, eight reside on general positions and four on two-fold axes. The distances and angles within these ions are normal and require little comment.

Figure XVI: A computer generated drawing of the $Re_2(NCS)_{10}^{3-}$ ion showing the numbering system. Unlabelled atoms may be denoted by primed numbers corresponding to those of the atoms to which they are related by a center of inversion.

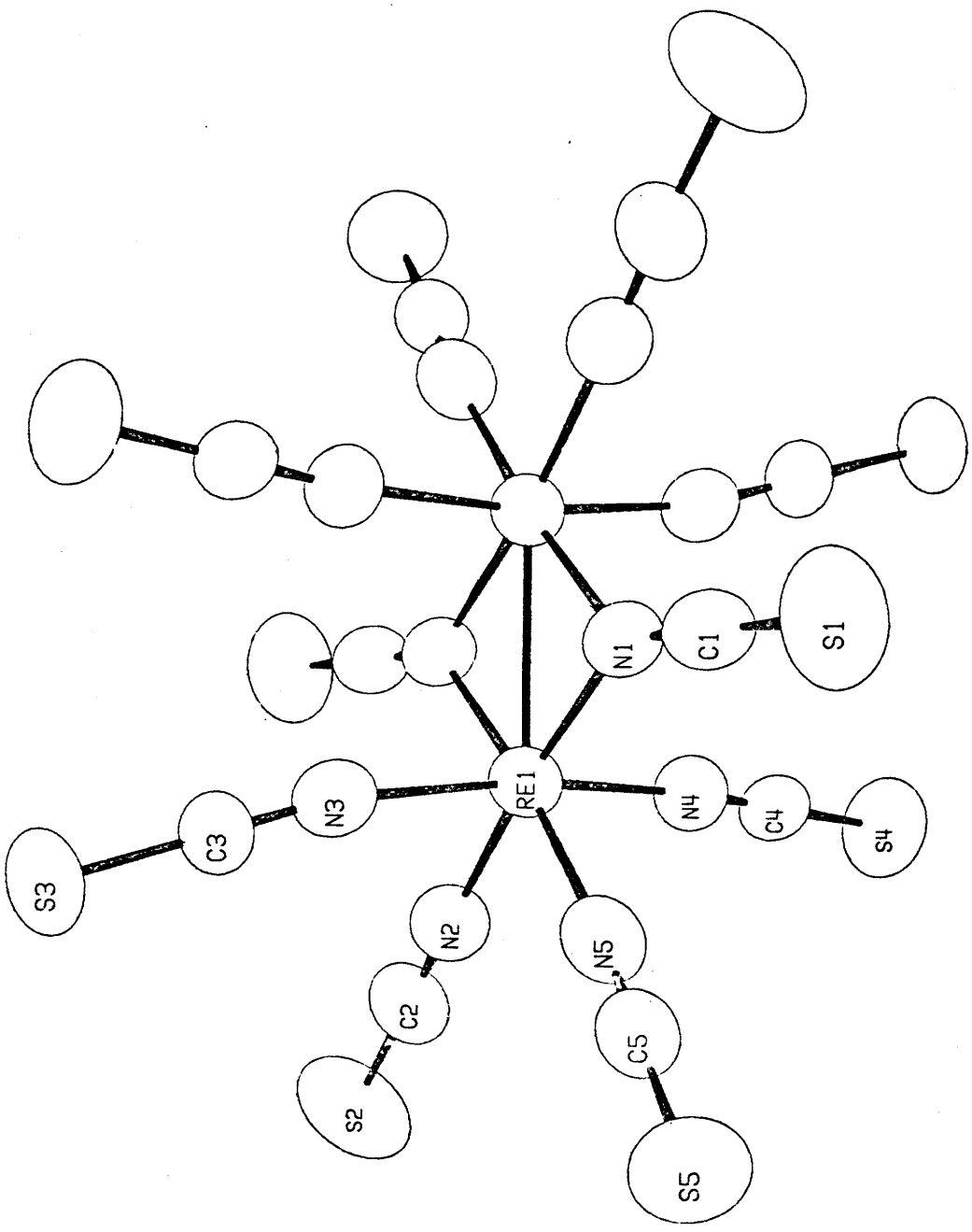
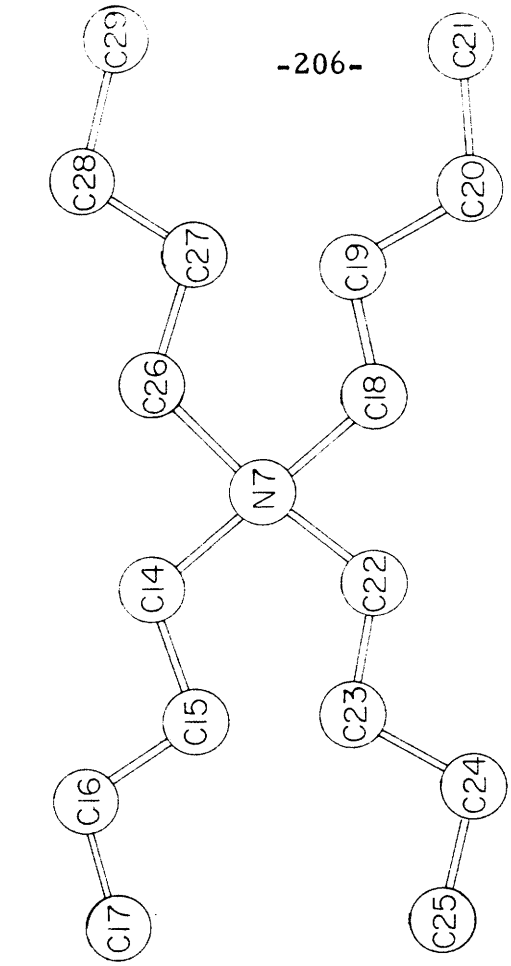

RE1
N1
C1
S1
N2
C2
S2
N3
C3
S3
N4
C4
S4
N5
C5
S5

Figure XVII: Schematic diagram of the two crystallographically different tetra-n-butylammonium ions. The figure is not intended to depict the actual geometry of the ions but only the atoms associated with the nBu_4N^+ cations. Cation I sits on a crystallographic 2-fold axis of symmetry while II occupies a general position.


C29
C21
C28
C20
C27
C19
C26
C18
N7
C14
C22
C15
C23
C16
C24
C17
C25

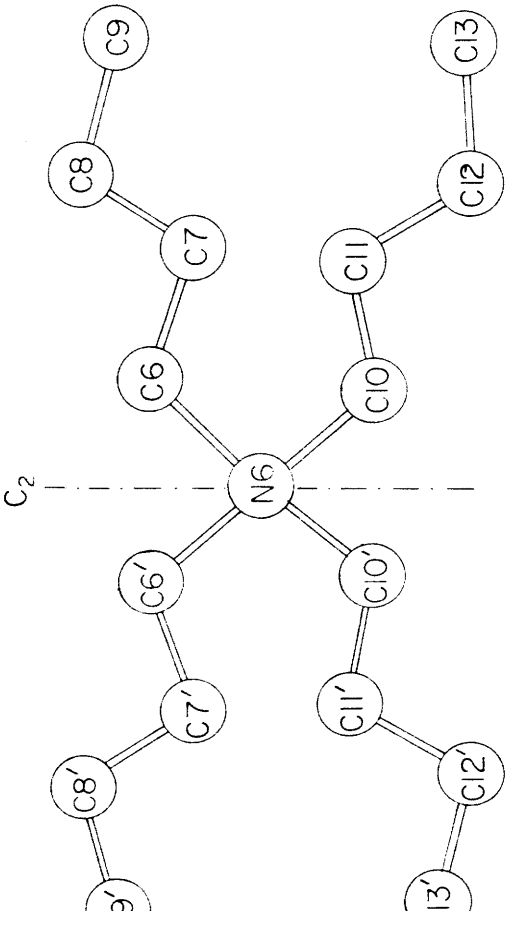

C9
C13
C8
C12
C7
C11
C6
C10
C_2
N6
C6'
C10'
C7'
C11'
C8'
C12'
C9'
C13'

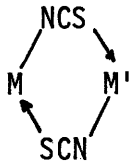
Table XX. Bond Distances

Atoms	Distance, Å	Atoms	Distance, Å
Re(1)-Re(1)	2.613(1)	N(7)-C(14)	1.52(1)
N(1)	2.087(8)	C(18)	1.52(1)
N(1)'	2.095(8)	C(22)	1.58(1)
N(2)	2.015(9)	C(26)	1.55(1)
N(3)	2.034(8)	C(6)-C(7)	1.53(1)
N(4)	2.018(8)	C(7)-C(8)	1.49(1)
N(5)	2.038(9)	C(8)-C(9)	1.51(2)
S(1)-C(1)	1.57(1)	C(10)-C(11)	1.52(1)
S(2)-C(2)	1.60(1)	C(11)-C(12)	1.50(1)
S(3)-C(3)	1.609(9)	C(12)-C(13)	1.54(2)
S(4)-C(4)	1.60(1)	C(14)-C(15)	1.54(1)
S(5)-C(5)	1.57(1)	C(15)-C(16)	1.58(2)
N(1)-C(1)	1.17(1)	C(16)-C(17)	1.50(2)
N(2)-C(2)	1.16(1)	C(18)-C(19)	1.48(1)
N(3)-C(3)	1.15(1)	C(19)-C(20)	1.52(2)
N(4)-C(4)	1.16(1)	C(20)-C(21)	1.37(2)
N(5)-C(5)	1.17(1)	C(22)-C(23)	1.53(1)
N(6)-C(6)	1.54(1)	C(23)-C(24)	1.56(2)
N(6)-C(10)	1.53(1)	C(24)-C(25)	1.55(2)
		C(26)-C(27)	1.51(2)
		C(27)-C(28)	1.55(2)
		C(28)-C(29)	1.44(2)

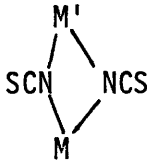
Table XXI. Bond Angles

Atoms	Angle, Deg.	Atoms	Angle, Deg.
Re(1)'-Re(1)-N(1)	51.4(2)	C(14)-N(7)-C(18)	105.3(7)
N(1)'	51.2(2)	C(22)	111.7(7)
N(2)	135.3(2)	C(26)	112.3(7)
N(3)	94.5(2)	C(18)-N(7)-C(22)	112.2(7)
N(4)	93.0(2)	C(26)	112.7(7)
N(5)	135.1(2)	C(22)-N(7)-C(26)	102.8(7)
N(1)-Re(1)-N(1)'	102.7(3)	S(1)-C(1)-N(1)	178.7(8)
N(2)'	84.1(3)	S(2)-C(2)-N(2)	179(1)
N(3)	95.1(3)	S(3)-C(3)-N(3)	177.8(9)
N(4)	92.1(3)	S(4)-C(4)-N(4)	179.6(8)
N(5)	83.7(3)	S(5)-C(5)-N(5)	178.9(9)
N(2)-Re(1)-N(3)	85.3(3)	N(6)-C(6)-C(7)	113.1(7)
N(4)	87.1(3)	C(6)-C(7)-C(8)	111.4(9)
N(5)	89.5(3)	C(7)-C(8)-C(9)	113(1)
N(3)-Re(1)-N(4)	171.9(3)	N(6)-C(10)-C(11)	113.3(7)
N(5)	87.1(3)	C(10)-C(11)-C(12)	108.0(8)
N(4)-Re(1)-N(5)	89.9(3)	C(11)-C(12)-C(13)	113(1)
Re(1)-N(1)-Re(1)'	77.4(3)	N(7)-C(14)-C(15)	113.8(8)
C(1)	143.0(7)	C(14)-C(15)-C(16)	108.3(9)
C(1)'	140.0(7)	C(15)-C(16)-C(17)	110.8(1.0)
Re(1)-N(2)-C(2)	176.4(8)	N(7)-C(18)-C(19)	115.6(9)
Re(1)-N(3)-C(3)	165.4(7)	C(18)-C(19)-C(20)	113(1)
Re(1)-N(4)-C(4)	174.1(7)	C(19)-C(20)-C(21)	118(2)
Re(1)-N(5)-C(5)	171.2(8)	N(7)-C(22)-C(23)	114.4(9)
C(6)-N(6)-C(6)	110(1)	C(22)-C(23)-C(24)	105(1)
C(10)	106.2(5)	C(23)-C(24)-C(25)	109(1)
C(10)'	111.2(5)	N(7)-C(26)-C(27)	114.8(9)
C(10)-N(6)-C(10)	112(1)	C(26)-C(27)-C(28)	107.2(9)
		C(27)-C(28)-C(29)	115(1)

The structure found accounts for the experimental evidence observed previously.[13] The infrared absorptions at 1914 cm^{-1} and 1877 cm^{-1} can be assigned to νCN in the bridging thiocyanate ions rather than to νCO in carbonyl moities. The symmetrically bridging thiocyanate ion has no precedent,[37] thus it is not surprising that the infrared absorptions were initially thought to be due to coordinated CO. In all known cases of bi- or polynuclear transition metal complexes [37] with bridging thiocyanate ions, the bridges are bonded to one metal atom by nitrogen and to the other by sulfur, as depicted schematically in 1.[38,39] The arrangement found here, 2, is unique among transition metal complexes, although the closely similar azide ion is known [40] to form



1



2

bridges in the same way.

There are only three cases in which the nitrogen atom of a thiocyanate is flanked by two metal atoms in a broadly similar way,[41-43] but in each case this seems to be the result of ionic packing. Thus, in $[Cu(1,3\text{-diaminopropane})_2](NCS)(ClO_4)$,[41] the square CuN_4 units are linked through the nitrogen atoms of interleaved thiocyanate ions by very long (2.73Å) Cu-N distances. In the alkali metal macrocycle complex, $[K_2C_{24}H_{32}O_8](NCS)_2$,[42] the pairs of K^+ ions are spanned by weakly attached (2.48Å, 2.89Å) thiocyanate ions. In the case of

$Sn(NCS)_2$[43] there are pairs of Sn^{+2} ions close to nitrogen atoms of half the thiocyanate ions, but there are also several close tin-sulfur contacts, and the whole arrangement is essentially the result of the best packing of ions, rather than of discreet covalent bonds.

The linearity and distances (N-C, 1.17Å; C-S, 1.57Å) in the bridge scarcely distinguish them from the terminal ones. The terminal thiocyanate ligands in this structure conform to the usual structural pattern.[41-53] The near linearity of each Re-N-C-S group and the short N-C distances (which average 1.16 Å) are indicative of an electron distribution like that represented by formal structure 3. The C-S distances, however, are too short, 1.59Å on average, to

$$: N{\equiv}C\text{-}S^{-} \qquad\qquad {}^{-}\ddot{N} = C = S$$

3 4

be consistent with the carbon-sulfur single bond implied by 3. Of course, π-overlap with suitable sulfur orbitals can account for this behavior; whatever explanation is preferred, it is entirely typical behavior for terminal thiocyanate ligands.

While for the terminal thiocyanates the nitrogen-carbon but not the carbon-sulfur distances could be easily correlated with the simple Lewis structure 3, the bridging thiocyanate ion observed here would seem to correspond to Lewis structure 4. Such a structure accounts for linearity, directs electron pairs on the nitrogen atom toward the rhenium atoms and is consistent with a double bond between

the carbon and sulfur atoms. However, the N-C distance of 1.17 (1) Å is too short for a double bond; it is more consistent with a triple bond.

The Re-N distances are longer for the bridging thiocyanate ligands (2.091(8)Å) than the terminal thiocyanate ligands (2.027Å(ave)), which is reasonable and expected.

A centrosymmetric structure would be expected to have only one band for the bridging thiocyanates, and the presence of two, even in solution,[13] requires some comment. In the solid state, intermolecular coupling could account for the appearance of two bands. In the solution spectrum, the presence of ion pairs of lower symmetry or distortion of the inner Re_2N_2 ring from planarity when not in a crystal environment could result in the appearance of two absorption bands instead of one.

The Re-Re distance of 2.613 (1) Å and the bridging angles of 102.7(3)° for N-Re-N and 77.4 (3)° for Re-N-Re clearly indicate the presence of a metal-metal bond in this molecule. A detailed description of the bonding is not possible presently, in part because the magnetic properties do not clearly indicate the number of unpaired electrons, in view of the large spin orbit coupling for the two rhenium atoms.

An approximate indication of the degree of bonding between the two rhenium atoms can be obtained through correlation of the observed

bond length to a plot of bond length to bond order in complexes with rhenium-rhenium bonds. The basis for such a correlation has been presented by Cotton,[55] where he compared the degree of bonding in $Re_2Cl_8^{2-}$, Re_3X_9, $Re_2Cl_5(DTH)_2$, $Ta_6X_{12}^{2+}$, and Pt_6Cl_{12}, etc. to the observed metal-metal bond length in each case. A smooth curve could be drawn through the points, indicating that within a first-order treatment, such a correlation can be used.

Fortunately, many rhenium complexes are known that contain double, triple, and quadruple bonds between rhenium atoms.[54-56] In Table XXII the bond lengths and bond orders of several polynuclear rhenium complexes are tabulated. In Figure XVIII, a plot of bond order vs bond length for these complexes and $(nBu_4N)_3Re_2(NCS)_{10}$ is presented, showing a bond order of 1.5, not unreasonable considering the odd number of electrons present in the complex.

The virtual D_{2h} symmetry of the inner Re_2N_{10} set of atoms implies that the unpaired electron(s) in this formally mixed-valence (+3, +4) complex is delocalized equally over both metal atoms. In the near-infrared region of the optical spectrum a broad band(λmax= 1316 nm, ε=535 L mol^{-1} cm^{-1}) attributable to an intervalence charge transfer absorption is observed. Whether this complex represents a Type II or Type III mixed valence system[69] has not yet been determined. An EPR signal was not observed at temperatures as low as 77K, a feature prevalent among technetium and rhenium (III and IV) complexes (vide infra).

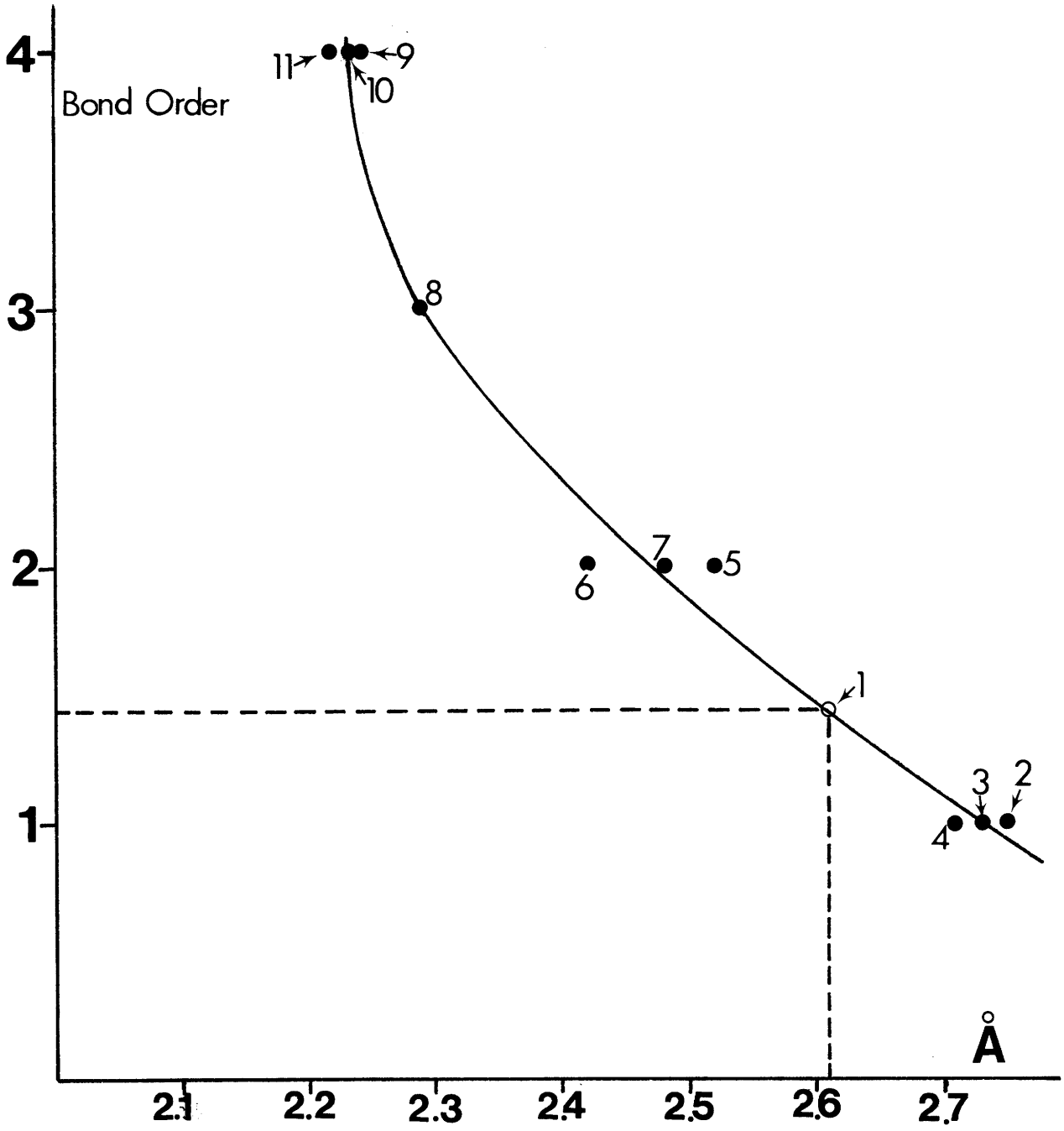
Electrochemical measurements on $Re_2(NCS)_{10}^{3-}$ in acetonitrile

Table XXII: Rhenium-Rhenium Bond Lengths and Bond Orders.

	Re-Re(Å)	Bond Order	Point No.[a]
$(nBu_4N)_3Re_2(NCS)_{10}$	2.61		1
Re metal[57]	2.75	1	2
$ReCl_4$ (fac-bridged octahedra)[58]	2.73	1	3
$nBu_4NRe_2Cl_9$[59]	2.71	1	4
$Re_2OCl_5(O_2CEt)(PPh_3)_2$[60]	2.52	2	5
$La_4Re_6O_{19}$[61]	2.42	2	6
Re_3X_9[62-64]	2.47-2.49	2	7
$Re_2Cl_5(DTH)_2$[65]	2.29	3	8
$K_2Re_2Cl_8 \cdot 2H_2O$[66]	2.24	4	9
$Re_2Cl_2(O_2CPh)_4 \cdot 2CHCl_3$[67]	2.235	4	10
$Re_2I_4(O_2CPh)_2$[68]	2.20	4	11

[a]Point in Figure XVIII.

Figure XVIII: Plot of Re-Re bond lengths vs. bond order for several di- tri-, and poly-rhenium complexes. The numbering scheme corresponds to the complexes in Table XXII . Estimation of the bond order in $(nBu_4N)_3Re_2(NCS)_{10}$.

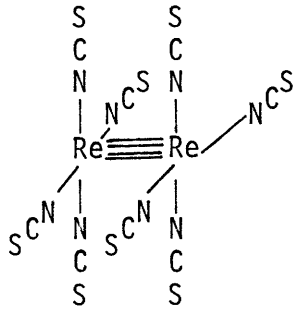

4
3
2
1
Bond Order
11
9
10
8
7
6
5
1
3
2
4
Å
2.1
2.2
2.3
2.4
2.5
2.6
2.7

(Figure XIX) reveal both a reversible one-electron reduction and a reversible one-electron oxidation at 0.05V and 0.45V vs. SCE, respectively. Such a result, implies that the Re_2N_{10} core is

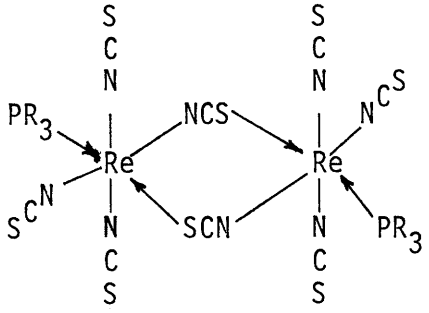
$$Re_2(NCS)_{10}^{4-} \rightleftharpoons Re(NCS)_{10}^{3-} \rightleftharpoons Re_2(NCS)_{10}^{2-}$$

reasonably robust and that electrochemical changes occur without large structural changes.

This result is interesting in light of the observed chemistry of $Re_2Cl_8^{2-}$ and thiocyanate ion. When the reaction between $Re_2Cl_8^{2-}$ and thiocyanate ion is carried out in methanol,[13] the product is the quadruply bonded dimer, $Re_2(NCS)_8^{2-}$, 5. By adding phosphine to the mixture, the species $(nBu_4N)_2Re_2(NCS)_8(PR_3)_2$ is isolated, 6,[13,14] with unsymmetrically bridging thiocyanate ligands and no metal-metal bond. When acetone is used as the solvent rather than



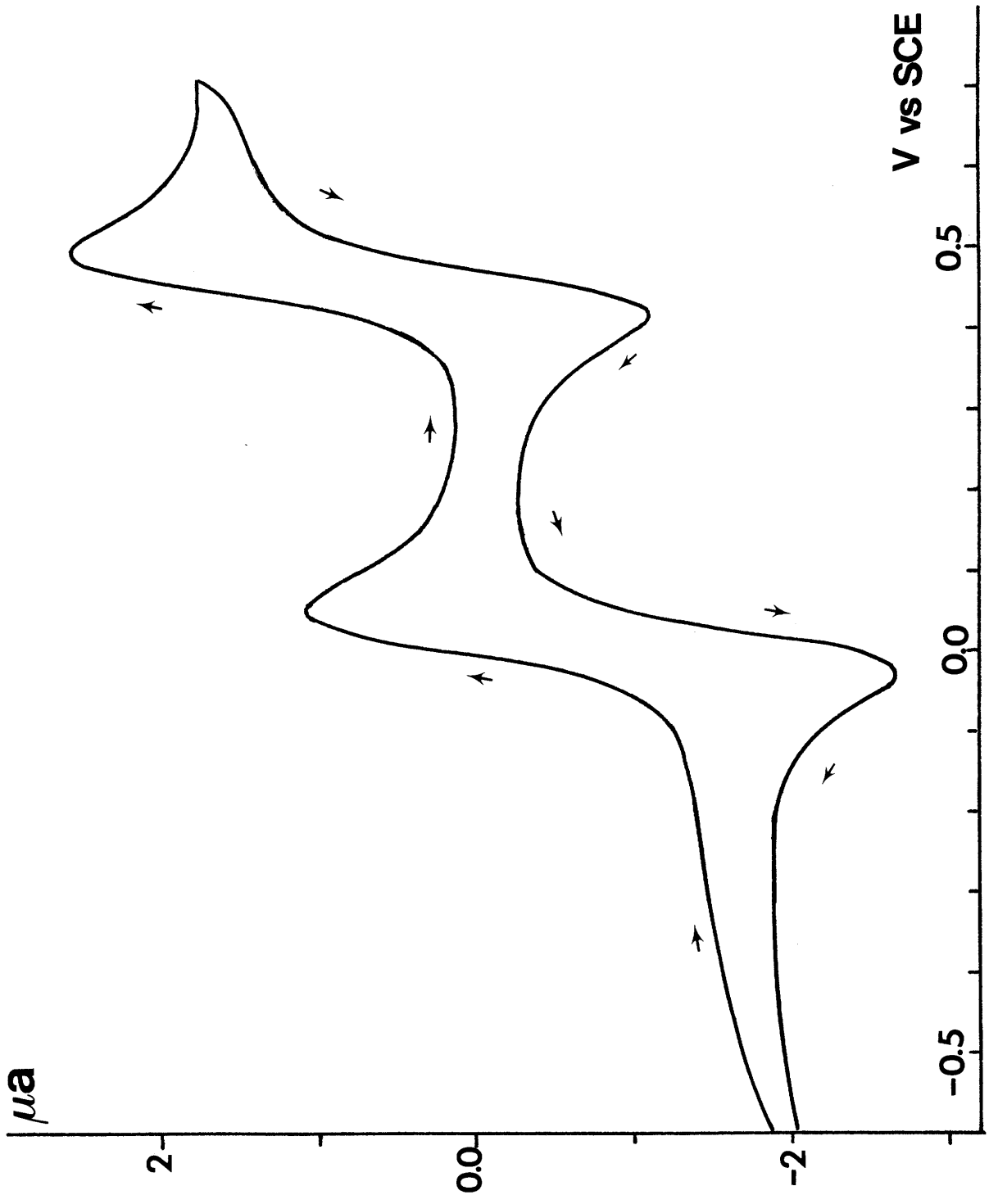
5



6

methanol, both $Re_2(NCS)_{10}^{3-}$ and $Re(NCS)_6^{2-}$ are formed. The complete disruption of the metal-metal bond is not achieved in the case of $Re_2(NCS)_{10}^{3-}$, but is seems apparent that the appearance of $Re(NCS)_6^{2-}$ arises from further degradation of $Re_2(NCS)_{10}^{3-}$ by thiocyanate ion

Figure XIX: Cyclic Voltammogram of $(nBu_4N)_3Re_2(NCS)_{10}$ in Acetonitrile/0.1 M TBAP, 100 mV sec^{-1} scan rate, initially anodic.


μa
2
0.0
-2
-0.5
0.0
0.5
V vs SCE

and oxidation to form $Re(NCS)_6^{2-}$.

Based on the variety of complexes and the interesting chemistry represented by the technetium and rhenium thiocyanate complexes, it will be some time before the last page is written about them.

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APPENDIX I

Atomic Coordinates and Thermal Parameters in $[PPN][TcOCl_4]$

Table I. Atomic Coordinates in Crystalline $[Ph_3PNPPh_3][TcOCl_4]$.[a]

Atom type[b]	Fractional Coordinates 10^4x	10^4y	10^4z	Isotropic Thermal Parameter, B,A^2[c]
		Anion		
Tc	1813.2(2)	1190.4(2)	2500.0[d]	3.7
Cl_1	1183 (1)	1063 (1)	606(2)	5.6
Cl_2	941 (1)	1683 (1)	3598(2)	5.9
Cl_3	2008 (1)	556 (1)	4562(3)	6.8
Cl_4	2400 (1)	198 (1)	1504(3)	6.7
O	2252 (2)	1958 (2)	2375(7)	5.7
		Cation		
P_1	4561 (1)	1236 (1)	810(1)	2.5
P_2	4000 (1)	2717 (1)	-387(2)	2.7
N	4315 (2)	1883 (3)	-207(5)	3.2
C_{111}	4403 (2)	1455 (2)	2602(6)	2.7
C_{112}	3776 (2)	1510 (3)	2995(6)	3.5
C_{113}	3632 (3)	1745 (4)	4320(7)	4.2
C_{114}	4096 (3)	1927 (4)	5245(7)	4.2
C_{115}	4706 (3)	1878 (4)	4854(7)	4.3
C_{116}	4856 (3)	1639 (3)	3522(6)	3.6
C_{121}	4202 (2)	296 (3)	440(6)	2.8
C_{122}	3972 (3)	147 (3)	-880(6)	3.6
C_{123}	3696 (3)	-577 (4)	-1159(7)	4.2
C_{124}	3652 (3)	-1143 (4)	-155(8)	4.2
C_{125}	3889 (3)	-1006 (4)	1141(7)	4.3
C_{126}	4165 (3)	-284 (3)	1448(7)	3.8
C_{131}	5385 (2)	1119 (3)	562(5)	2.6
C_{132}	5656 (2)	382 (3)	394(6)	3.5
C_{133}	6281 (3)	337 (4)	83(7)	4.1
C_{134}	6630 (3)	1000 (4)	-41(7)	4.1
C_{135}	6370 (2)	1728 (4)	174(7)	4.1
C_{136}	5748 (2)	1796 (3)	455(7)	3.7
C_{211}	3812 (2)	3229 (3)	1195(6)	3.1
C_{212}	3202 (3)	3417 (5)	1516(8)	4.6
C_{213}	3078 (3)	3808 (5)	2748(9)	5.5
C_{214}	3547 (4)	4009 (4)	3639(9)	5.3
C_{215}	4156 (4)	3796 (4)	3340(7)	4.7

Table I. Atomic Coordinates in Crystalline $[Ph_3PNPPh_3][TcOCl_4]$[a] (cont).

Atom type[b]	Fractional Coordinates 10^4x	10^4y	10^4z	Isotropic Thermal Parameter, $B_{,A^2}$[c]
C_{216}	4284(3)	3429(4)	2107(6)	3.7
C_{221}	3300(2)	2588(3)	-1380(6)	3.0
C_{222}	3110(2)	3142(3)	-2345(8)	4.0
C_{223}	2592(3)	2992(5)	-3148(8)	4.9
C_{224}	2268(3)	2301(5)	-2987(8)	4.6
C_{225}	2442(3)	1756(4)	-2011(8)	4.9
C_{226}	2960(3)	1898(4)	-1195(7)	4.0
C_{231}	4513(2)	3349(3)	-1352(6)	3.1
C_{232}	4997(3)	3026(4)	-2070(6)	3.7
C_{233}	5393(3)	3491(4)	-2859(7)	4.7
C_{234}	5283(4)	4293(5)	-2929(8)	5.5
C_{235}	4796(3)	4625(4)	-2219(9)	5.1
C_{236}	4411(3)	4165(4)	-1419(8)	4.3
	10^3x =	10^3y =	10^3z =	
H_{112}	345(2)	139(3)	234(6)	0(1)
H_{113}	313(3)	184(4)	467(10)	5(2)
H_{114}	402(2)	202(3)	616(6)	1(1)
H_{115}	504(3)	205(3)	554(7)	2(1)
H_{116}	526(2)	168(3)	321(6)	1(1)
H_{122}	396(3)	49(4)	-163(8)	3(1)
H_{123}	354(2)	-70(3)	-196(6)	1(1)
H_{124}	342(3)	-169(3)	-34(7)	2(1)
H_{125}	381(3)	-136(4)	181(7)	3(1)
H_{126}	435(2)	-18(3)	231(7)	1(1)
H_{132}	541(3)	-6(4)	46(7)	2(1)
H_{133}	648(3)	-14(4)	-5(7)	2(1)
H_{134}	699(3)	96(3)	-30(7)	2(1)
H_{135}	660(2)	224(3)	14(5)	0(1)
H_{136}	552(3)	231(3)	61(7)	2(1)
H_{212}	291(4)	332(4)	90(9)	5(2)
H_{213}	261(3)	404(4)	291(8)	4(2)
H_{214}	348(3)	424(4)	434(8)	4(2)
H_{215}	448(2)	399(3)	389(6)	1(1)

Table I. Atomic Coordinates in Crystalline $[Ph_3PNPPh_3][TcOCl_4]$[a] (cont).

Atom type[b]	10^3x	10^3y	10^3z	Isotropic Thermal Parameter, [c] B, A^2
H_{216}	468(2)	331(3)	186(5)	0(1)
H_{222}	335(2)	363(3)	-237(8)	2(1)
H_{223}	246(3)	344(4)	-371(8)	4(2)
H_{224}	197(3)	230(3)	-348(6)	1(1)
H_{225}	222(3)	122(4)	-192(7)	3(1)
H_{226}	311(2)	155(3)	-66(7)	2(1)
H_{232}	508(3)	257(3)	-194(6)	2(1)
H_{233}	574(3)	323(4)	-329(7)	2(1)
H_{234}	557(4)	460(5)	-353(9)	6(2)
H_{235}	477(2)	513(3)	-232(7)	2(1)
H_{236}	411(3)	434(3)	-89(7)	2(1)

[a] Figures in parentheses are the estimated standard deviation for the last significant digit. [b] Atoms are labelled in agreement with Figure 1. [c] For nonhydrogen atoms, this is the equivalent isotropic thermal parameter calculated from $B=4[V^2\det(\beta_{ij})]^{1/3}$ where the β_{ij} are the dimensionless anisotropic temperature factors employed during refinement; for hydrogen atoms, this is the isotropic thermal parameter actually refined. [d] This coordinate was held constant and used to fix the unit cell origin, it is therefore listed without an estimated standard deviation.

Table II. Thermal Parameters for Nonhydrogen Atoms in Crystalline $[Ph_3PNPPh_3][TcOCl_4]$.[a]

Atom type[b]	Anisotropic Parameters						Equivalent Isotropic Thermal Parameter,[c] B, A^2
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	
				Anion			
Tc	3.14(1)	3.10(1)	5.23(2)	-.25(1)	0.02(2)	-.18(2)	3.7
Cl_1	6.2 (1)	6.2 (1)	4.8 (1)	0.1 (1)	-.8 (1)	-.6 (1)	5.6
Cl_2	5.1 (1)	7.6 (1)	6.2 (1)	1.4 (1)	1.0 (1)	-1.4 (1)	5.9
Cl_3	7.7 (1)	7.1 (1)	6.9 (1)	0.0 (1)	-2.7 (1)	1.4 (1)	6.8
Cl_4	5.7 (1)	5.6 (1)	11.1 (2)	1.6 (1)	1.0 (1)	-1.9 (1)	6.7
O	5.1 (2)	4.1 (2)	9.8 (4)	-1.2 (2)	-.4 (3)	0.6 (3)	5.7
				Cation			
P_1	2.41(4)	2.58(4)	2.44(4)	0.15(4)	-0.02(4)	-.13(4)	2.5
P_2	2.40(4)	2.82(5)	2.89(5)	0.26(4)	-.11(5)	-.04(4)	2.7
N	3.5 (2)	3.5 (2)	2.8 (2)	0.6 (1)	-.3 (2)	-.1 (2)	3.2
C_{111}	3.1 (2)	2.7 (2)	2.3 (2)	0.1 (1)	-.1 (2)	-.2 (2)	2.7
C_{112}	3.1 (2)	4.2 (2)	3.3 (2)	-.2 (2)	0.3 (2)	-.4 (2)	3.5
C_{113}	4.1 (3)	5.0 (3)	3.9 (3)	0.0 (2)	1.3 (2)	-.3 (2)	4.2
C_{114}	6.4 (3)	5.2 (3)	2.6 (2)	0.8 (3)	0.7 (2)	-1.1 (2)	4.2
C_{115}	5.3 (3)	5.5 (3)	3.1 (3)	0.4 (3)	-.5 (2)	-1.3 (2)	4.3
C_{116}	3.7 (2)	4.1 (2)	3.1 (2)	0.0 (2)	0.1 (2)	-.5 (2)	3.6
C_{121}	2.8 (2)	2.7 (2)	3.2 (2)	-.3 (2)	0.5 (2)	-.5 (2)	2.8
C_{122}	3.6 (2)	4.0 (2)	3.5 (2)	-.6 (2)	-.3 (2)	-.7 (2)	3.6
C_{123}	3.7 (2)	5.6 (3)	4.6 (3)	-1.3 (2)	0.2 (2)	-2.0 (3)	4.2
C_{124}	4.5 (3)	3.9 (3)	6.4 (4)	-1.6 (2)	2.3 (3)	-1.9 (3)	4.2
C_{125}	5.4 (3)	3.9 (3)	4.7 (3)	-1.4 (2)	1.6 (3)	-.6 (2)	4.3
C_{126}	4.7 (3)	3.2 (2)	3.7 (3)	-.4 (2)	0.4 (2)	-.2 (2)	3.8
C_{131}	2.6 (2)	3.0 (2)	2.4 (2)	0.0 (2)	0.1 (2)	-.4 (2)	2.6
C_{132}	2.9 (2)	3.9 (2)	4.1 (3)	0.1 (2)	0.0 (2)	-.6 (2)	3.5
C_{133}	3.5 (2)	4.7 (3)	5.3 (3)	0.8 (2)	-.2 (2)	-2.0 (3)	4.1
C_{134}	2.6 (2)	6.9 (4)	4.3 (3)	0.1 (2)	0.6 (2)	-1.6 (3)	4.1
C_{135}	2.7 (2)	5.1 (3)	5.2 (3)	-.8 (2)	0.5 (2)	-.2 (3)	4.1
C_{136}	3.3 (2)	3.5 (2)	4.3 (3)	-.4 (2)	0.1 (2)	-.1 (2)	3.7
C_{211}	3.3 (2)	2.8 (2)	3.3 (2)	0.2 (2)	0.6 (2)	-.2 (2)	3.1

Table II. Thermal Parameters for Nonhydrogen Atoms in Crystalline $[Ph_3PNPPh_3][TcOCl_4]$[a] (cont).

Atom type[b]	Anisotropic Parameters						Equivalent Isotropic Thermal Parameter,[c] $B, Å^2$
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	
				Cation			
C_{212}	3.7 (2)	6.6 (3)	4.4 (3)	1.6 (3)	0.5 (2)	-.5 (3)	4.6
C_{213}	5.1 (3)	7.7 (4)	6.0 (5)	1.8 (3)	2.2 (3)	-1.1 (4)	5.5
C_{214}	7.8 (4)	5.1 (3)	4.8 (3)	-.1 (3)	2.2 (4)	-1.7 (3)	5.3
C_{215}	6.1 (3)	5.1 (3)	4.2 (3)	-2.1 (3)	0.7 (3)	-1.2 (3)	4.7
C_{216}	3.7 (2)	4.0 (3)	3.6 (3)	-.6 (2)	0.1 (2)	-.7 (2)	3.7
C_{221}	2.6 (2)	3.6 (2)	3.1 (2)	0.4 (2)	-.3 (2)	-.2 (2)	3.0
C_{222}	3.5 (2)	4.4 (2)	4.7 (3)	0.0 (2)	-1.1 (3)	0.7 (3)	4.0
C_{223}	3.5 (3)	5.9 (3)	6.6 (4)	0.3 (2)	-1.6 (3)	0.9 (3)	4.9
C_{224}	2.7 (2)	6.9 (4)	5.7 (4)	0.3 (2)	-1.1 (2)	-1.3 (3)	4.6
C_{225}	3.9 (2)	4.9 (3)	6.5 (4)	-.9 (2)	-.6 (3)	-.1 (3)	4.9
C_{226}	3.4 (2)	4.3 (3)	4.6 (3)	-.3 (2)	0.0 (2)	0.6 (2)	4.0
C_{231}	3.2 (2)	3.1 (2)	3.2 (2)	-.2 (2)	-.5 (2)	0.1 (2)	3.1
C_{232}	4.1 (2)	4.0 (2)	3.1 (2)	0.1 (2)	0.2 (2)	-.2 (2)	3.7
C_{233}	4.6 (3)	6.2 (3)	4.1 (3)	-1.0 (3)	1.2 (2)	-.1 (3)	4.7
C_{234}	6.2 (4)	6.4 (4)	5.8 (4)	-2.5 (3)	1.1 (3)	1.3 (3)	5.5
C_{235}	6.2 (3)	3.7 (2)	6.7 (4)	-1.4 (2)	-.1 (3)	1.0 (3)	5.1
C_{236}	3.9 (2)	3.9 (2)	5.4 (3)	-.1 (2)	0.3 (2)	0.0 (2)	4.3

[a]Figures in parentheses are the estimated standard deviation for the last significant digit. Anisotropic temperature factors are of the form: $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$; the B_{ij} in $Å^2$ are related to the dimensionless β_{ij} employed during refinement as $B_{ij} = 4\beta_{ij}/a_i^* a_j^*$. [b]Atoms are labelled in agreement with Figure 1. [c]Isotropic thermal parameter calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$.

APPENDIX II

Atomic Coordinates and Thermal Parameters in $(Bu_4N)_3Re_2(NCS)_{10}$

Table I. POSITIONAL AND THERMAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS.[a]

ATOM	X	Y	Z	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
Re(1)	0.02119(2)	0.04530(3)	0.04867(2)	5.14(1)	3.85(1)	4.02(1)	-0.88(2)	1.70(1)	-0.18(2)
S(1)	0.1640(1)	-0.1615(3)	0.0424(2)	7.1(1)	7.2(2)	10.8(2)	1.1(1)	3.4(1)	1.6(2)
S(2)	-0.0479(2)	0.2783(3)	0.1480(2)	9.5(2)	7.1(2)	12.9(2)	-0.2(1)	6.1(1)	-3.2(1)
S(3)	0.0813(1)	0.3296(2)	-0.0139(1)	6.2(1)	4.1(1)	7.2(1)	-0.4(1)	1.5(1)	1.3(1)
S(4)	-0.0495(1)	-0.1692(2)	0.1569(1)	7.4(1)	7.1(2)	7.3(1)	-0.8(1)	3.51(9)	2.1(1)
S(5)	0.2144(1)	0.0700(3)	0.1920(1)	5.7(1)	8.7(2)	7.3(2)	-0.6(1)	1.1(1)	-0.8(1)
N(1)	0.0632(3)	-0.0549(5)	0.0152(3)	4.6(3)	4.6(4)	3.7(3)	-1.1(3)	1.0(2)	-0.1(3)
N(2)	-0.0106(3)	0.1418(6)	0.0894(3)	5.0(3)	5.1(4)	4.8(3)	-1.0(3)	1.8(2)	-0.1(3)
N(3)	0.0497(3)	0.1560(5)	0.0141(3)	5.4(3)	5.1(4)	4.0(3)	-0.6(3)	1.3(3)	-0.1(3)
N(4)	-0.0073(3)	-0.0519(5)	0.0919(3)	6.3(3)	4.5(4)	4.4(3)	-0.7(3)	2.1(2)	0.2(3)
N(5)	0.1011(4)	0.0501(5)	0.1144(3)	6.2(4)	4.5(4)	5.7(4)	-0.8(3)	2.2(3)	-0.3(3)
N(6)	0.2500(0)	0.3549(8)	0.5000(0)	3.7(4)	6.0(6)	4.9(4)	0	1.7(3)	0
N(7)	0.5896(3)	0.0669(5)	0.6492(3)	5.1(3)	4.8(4)	5.5(3)	0.5(3)	2.1(3)	0.7(3)
C(1)	0.1059(4)	-0.1014(7)	0.0267(4)	5.6(4)	5.1(5)	4.1(4)	-0.9(4)	2.0(3)	-0.5(4)
C(2)	-0.0260(4)	0.1992(7)	0.1142(4)	5.5(4)	4.6(5)	6.3(5)	-0.8(4)	2.2(3)	-0.3(4)
C(3)	0.0621(4)	0.2992(6)	0.0027(4)	4.4(4)	4.8(4)	4.6(4)	-0.4(4)	1.0(3)	0.5(3)
C(4)	-0.0249(4)	-0.1014(7)	0.1192(4)	5.1(4)	4.5(4)	3.6(4)	0.3(4)	0.7(3)	-0.1(3)
C(5)	0.1496(4)	0.0592(6)	0.1471(4)	5.5(4)	4.3(4)	5.1(4)	-0.5(4)	2.6(3)	-0.1(3)
C(6)	0.3035(4)	0.4166(7)	0.5339(4)	4.2(4)	6.0(5)	5.3(4)	-1.2(4)	1.4(3)	-0.3(4)
C(7)	0.2902(5)	0.4819(8)	0.5769(5)	6.0(5)	8.1(6)	6.8(5)	-2.4(5)	2.4(4)	-3.3(5)
C(8)	0.3413(5)	0.5146(8)	0.6057(5)	7.1(5)	7.2(6)	6.7(5)	-1.8(5)	2.1(4)	-1.6(5)
C(9)	0.3299(7)	0.6114(11)	0.6475(6)	10.4(8)	11.1(9)	9.4(7)	-3.0(8)	3.9(6)	-4.0(7)
C(10)	0.2707(4)	0.2952(7)	0.4593(4)	5.4(4)	5.1(5)	5.9(4)	0.7(4)	2.7(3)	-1.0(4)
C(11)	0.2246(5)	0.2348(8)	0.4253(4)	6.5(5)	6.5(5)	6.2(5)	-0.3(5)	2.3(4)	-2.4(4)
C(12)	0.2512(5)	0.1681(9)	0.3894(5)	7.0(6)	8.0(7)	8.0(6)	-0.5(6)	1.9(5)	-2.8(5)
C(13)	0.2129(6)	0.0832(10)	0.3604(6)	8.7(7)	8.5(7)	8.3(6)	-0.6(6)	2.3(5)	-4.2(5)
C(14)	0.6251(5)	-0.0191(6)	0.6765(4)	5.8(5)	3.6(4)	6.0(5)	1.0(4)	1.7(4)	1.3(4)

C(15)	0.5951(6)	-0.1113(8)	0.6501(5)	11.1(7)	4.6(5)	6.5(5)	0.4(5)	2.8(5)	0.1(5)
C(16)	0.6358(6)	-0.1942(8)	0.6833(5)	14.0(8)	4.2(5)	8.5(6)	2.2(5)	5.8(5)	1.4(5)
C(17)	0.6318(7)	-0.2062(10)	0.7420(6)	11.9(8)	8.4(8)	8.2(6)	0.5(7)	3.8(6)	2.5(6)
C(18)	0.6263(5)	0.1491(7)	0.6814(5)	6.3(5)	4.2(5)	7.4(5)	0.7(4)	2.2(4)	0.1(4)
C(19)	0.6010(6)	0.2423(8)	0.6618(6)	10.6(8)	4.3(5)	10.7(8)	0.3(6)	3.4(6)	1.3(6)
C(20)	0.6420(9)	0.3213(10)	0.6922(8)	18(2)	5.8(7)	11(1)	-0.8(9)	0(1)	0.6(7)
C(21)	0.6619(12)	0.3230(13)	0.7511(9)	28(2)	7.4(9)	16(1)	1(1)	6(1)	3(1)
C(22)	0.5775(5)	0.0715(8)	0.5826(4)	6.1(4)	8.0(7)	5.6(4)	1.0(5)	3.0(3)	1.1(4)
C(23)	0.6336(5)	0.0726(8)	0.5668(5)	8.9(5)	6.4(6)	8.7(5)	1.6(5)	5.3(4)	2.1(5)
C(24)	0.6113(6)	0.0358(10)	0.5002(5)	9.9(7)	8.8(7)	5.6(5)	0.2(6)	3.6(4)	0.5(5)
C(25)	0.6647(7)	0.0762(13)	0.4792(7)	13.0(8)	12(1)	12.2(7)	2.5(8)	8.4(5)	1.0(8)
C(26)	0.5261(4)	0.0657(8)	0.6518(5)	5.1(4)	7.5(6)	7.4(5)	0.1(4)	3.1(3)	0.8(5)
C(27)	0.5230(5)	0.0598(8)	0.7117(5)	6.0(5)	8.0(7)	6.9(5)	-0.1(5)	3.0(4)	0.9(5)
C(28)	0.4573(5)	0.0560(9)	0.7054(5)	6.8(5)	9.8(8)	7.5(5)	1.6(6)	3.2(4)	2.4(6)
C(29)	0.4464(7)	0.0524(12)	0.7589(6)	9.9(7)	15(1)	6.3(5)	2.4(8)	3.7(5)	2.6(7)

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[a] The form of the anisotropic thermal parameter is:

$\exp[-1/4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

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Biographical Note

Harvey Stewart Trop was born on December 31, 1953, in Artesia, New Mexico, to Abraham and Caryl Trop. He grew up in the Southwest, living in Albuquerque, N.M., and El Paso, TX., prior to moving to California at age 9. He spent his adolescent years in Taft, California, and graduated from Taft Union High School with High Honors and as a Life Member of the California Scholastic Federation. Continuing his education, he went to the University of California, Berkeley as a California State Scholar and graduated with a B. S. in Chemistry in June, 1975. During the summer months he worked as a seasonal fireman for the Kern County Fire Department for five consecutive years, rising to the rank of Seasonal Firemen III. Coming to M. I. T. in September, 1975, he pursued the doctoral program in inorganic chemistry under Professor Alan Davison. During this time, he held seats on the Institute Committee on Radiation Protection, the Chemistry Department Safety Committee, and was the Chemistry Department representative on the Graduate Student Council for three years. He completed the requirements for the degree of Doctor of Philosophy in Chemistry in May, 1979. According to informed sources, he is now serving a two to ten year sentence for flagrant lunacy.