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SYNTHESIS AND CHARACTERIZATION OF SPECIES RESULTING
FROM REDUCTION OF Nb (IV) HALIDE ADDUCTS

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Synthesis and characterization of species
resulting from reduction of Nb(IV) halide adducts

by

Edward Thomas Maas, Jr.

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Synthesis and characterization of species
resulting from reduction of Nb(IV) halide adducts

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Synthetic procedures were developed which enabled isolation of discrete thioether complexes containing niobium(III). These complexes were formulated as $\text{Nb}_2\text{X}_6(\text{SC}_4\text{H}_8)_3$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). Tetrahydrothiophene was determined to be present in two different types of chemical environment by means of proton magnetic resonance spectra. The unique tetrahydrothiophene ligand was postulated to be in a bridging configuration between two niobium atoms. Magnetic susceptibility measurements on the chloride led to the postulation of a double metal-metal bond also joining the two niobium atoms. Further characterization included both infrared and electronic spectra. Tentative assignments were made to absorptions in the far-infrared region as arising from either mainly metal-halogen or metal-sulfur stretching vibrations. The electronic spectrum of the iodide indicated that its structure may differ somewhat

from those of the chloride and bromide. The electronic spectra of the chloride in the solid state and in a benzene solution were virtually identical indicating similar species in each case.

Substitution reactions enabled the replacement of varying numbers of tetrahydrothiophenes present in $\text{Nb}_2\text{Cl}_6(\text{SC}_4\text{H}_8)_3$. The compounds isolated were formulated as $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{Nb}_2\text{Cl}_8(\text{SC}_4\text{H}_8)$ and $[(\text{C}_2\text{H}_5)_4\text{N}]_3\text{Nb}_2\text{Cl}_9$. Characterizations by means of electronic and infrared spectra and magnetic susceptibility indicated that the structure of the partially substituted salt was very similar to that of the original neutral complex. A substantial structural rearrangement during the synthesis of the completely substituted salt was thought to occur.

Possible structures for the neutral complexes were discussed in relation to their observed properties. The most appealing arrangement was a triply-bridged bioctahedral structure with the unique tetrahydrothiophene ligand acting as one of the bridges.

INTRODUCTION

Investigations of the chemistries of second and third row transition metals have been rather limited when compared with extensive studies performed on first row transition metals. The chemistry of niobium (Nb) falls into this realm of sparsely investigated phenomena. This may be the result of a general lack of understanding of the physical laws which control the behavior of second and third row transition metals as well as the high reactivity and chemical instability exhibited by compounds of niobium itself in its varied oxidation states. It would be almost superfluous to say that more knowledge, of any sort, is needed in order to better understand the position of niobium with respect to the other elements in nature.

Niobium does, in fact, as previously stated, possess the ability to form compounds in which the niobium atom or atoms may assume many varied formal oxidation states. This allows systematic studies of the effects of varying the number of valence electrons on the metal atom. The majority of the work on niobium to date has been centered primarily on Nb(V) having a valence electronic configuration $4d^0$. Fewer studies have been aimed at the elucidation of the chemistry of Nb(IV) whose valence electronic configuration is $4d^1$. Even fewer studies have been directed at Nb(III) and lower oxidation states.

The valence electronic configuration of Nb(III) is $4d^2$. Investigations of the magnetic and spectral properties associated with these electrons might give some insight into their behavior and environment. The ability of niobium to form direct chemical bonds to other niobium atoms could possibly be exhibited by compounds possessing niobium in this oxidation state since each niobium atom would have a partially filled d orbital manifold. The method and nature of bonding exhibited by niobium in this low oxidation state with other types of atoms would also be enlightening.

It was with these ideas in mind that the research described in this dissertation was undertaken. The immediate aims were to synthesize and characterize new species of Nb(III). It was hoped that these species might exhibit physical properties permitting further physico-chemical studies which would broaden the knowledge and understanding of this oxidation state of niobium and the chemistry of niobium in general.

Review of Previous Work

Two main areas of studies will be described in this section. These are: (1) niobium(III) species and compounds, and (2) some interesting alkyl sulfide adducts of niobium and other metals.

Formation of Niobium(III) by Electrochemical

Reduction.—Early attempts to study niobium(III) species were mainly done electrochemically. Cozzi and Vivarelli showed that niobic acid could be reduced in 0.1 N HNO_3 (1 N in KNO_3) and that the polarographic reduction wave was proportional to the niobium concentration.¹ Later these same workers studied the reduction of niobium(V) in highly concentrated hydrochloric acid solutions.² In this system two reduction waves were observed. The first wave which was assigned as the reduction of Nb(V) to Nb(IV) had a half-wave potential of -0.455 volts vs. a saturated calomel electrode. The wave's height was proportional to the concentration of niobium in solution. This wave remained unvaried with respect to height for a given concentration of niobium as the concentration of HCl was varied from 13 N to 9 N. However, below 9 N the wave's height decreased rapidly and was nonexistent at 6 N HCl. Postulated reactions responsible for this wave were: (a) $\text{HNbCl}_6 + e^- \rightleftharpoons \text{HNbCl}_6^-$; or (b) $\text{HNbOCl}_4 + e^- \rightleftharpoons \text{HNbOCl}_4^-$. The second reduction wave exhibited in these experiments was rather ill-defined. It was suggested that the second wave was caused by the reduction of hydrogen from one of the above products. It was noted that the addition of up to 20% by volume of ethylene glycol helped to enhance the definition of this second wave.

Later studies, again by these same researchers,³ determined that initially Nb(V) in concentrated HCl solutions was reduced to Nb(IV). This in turn disproportionated to Nb(V) and Nb(III). Reduction ceased with the formation of Nb(III). The role of ethylene glycol was investigated further during the course of these studies. It was found that in hydrochloric acid solutions containing 10-20 vol % ethylene glycol, the Nb(IV) disproportionation was greatly slowed. In this case Nb(IV) could be reduced electrochemically to Nb(II). Reaction of Nb(IV) with Nb(II) resulted in formation of Nb(III). Again reductions ceased with the formation of Nb(III).

Absorption spectra for solutions of niobium in various oxidation states were reported in a later paper.⁴ Concentrated hydrochloric acid solutions of Nb(V) were reported to be yellow. The color of Nb(IV) varied from red-orange (13 M HCl) to blue-violet (10 M HCl) to blue (8 M HCl). The differences in these colors were assigned to the presence of the ions NbCl_6^{2-} , NbOCl_4^{2-} , and NbO^{2+} respectively. Niobium(III) in 10 M HCl was reported to range in color from yellow at low concentrations ($< 10^{-3}$ M) to black at higher concentrations ($> 10^{-2}$ M). An absorption spectrum of Nb(III) in HCl solution revealed a major absorbance at 445 nm and weaker absorbances at 530 nm and 650 nm. This color was attributed to the presence of

Nb(III) in some type of anionic chloro-complexes. Finally, a solution of Nb(II) in 10 M HCl containing ethylene glycol was reported to be yellow.

The disproportionation of Nb(IV) was studied in 11-13 M HCl solutions by Cozzi, Vivarelli, and DiStefano.⁵ It was found that this disproportionation was second order with an activation energy of 26.7 ± 0.4 kcal/mole. The reaction rate was also very sensitive to the acidity of the solution. A tenfold increase in rate of the reaction $2\text{Nb(IV)} \rightarrow \text{Nb(III)} + \text{Nb(V)}$ was noted when the acidity was decreased from 12.66 M to 11.10 M HCl.

It should be noted that all of the work described thus far was performed in aqueous solutions at very low concentrations of niobium. In no case was a solid product containing niobium in any reduced oxidation state isolated from the solutions.

McCullough and Meites later reinvestigated the reduction of Nb(V) in concentrated hydrochloric acid solutions.⁶ Their interest in this system was analytical in nature with the purpose of determining small amounts of niobium in solutions. Two polarographic reduction waves were also observed. The first wave was reversible, whereas the second wave was irreversible. In dilute solutions of niobium(V), it was deduced from their data that Nb(V) was present in a monomeric species. This monomeric species

underwent a single electron reduction to form a monomeric Nb(IV) species. This Nb(IV) species was then postulated to undergo a two electron reduction to form a Nb(II) species, again monomeric in nature. The Nb(II) species reacted with a Nb(IV) species to form Nb(III) species, at which point the reduction ceased. In deference to this postulated mechanism, it was proposed that in more concentrated solutions Nb(V) was present in a dimeric species designated by a symbolism $[\text{Nb(V)} \cdot \text{Nb(V)}]$. The first of the two polarographic reduction waves in this case was a composite of waves produced by essentially three different reductions. $[\text{Nb(V)} \cdot \text{Nb(V)}]$ was reduced in two single electron steps to form $[\text{Nb(V)} \cdot \text{Nb(IV)}]$ and $[\text{Nb(IV)} \cdot \text{Nb(IV)}]$. These two reductions had very nearly equal half-wave potentials. The $[\text{Nb(IV)} \cdot \text{Nb(IV)}]$ species then underwent an intramolecular disproportionation to form $[\text{Nb(V)} \cdot \text{Nb(III)}]$. This was reduced in a one electron step to $[\text{Nb(IV)} \cdot \text{Nb(III)}]$, which gave rise to the third part of the composite first wave. At more negative potentials $[\text{Nb(IV)} \cdot \text{Nb(IV)}]$ was involved in a two electron reduction to form a species designated as $[\text{Nb(IV)} \cdot \text{Nb(II)}]$ which subsequently underwent an intramolecular oxidation-reduction and dissociation to form two equivalents of Nb(III). It was also reported that upon addition of ethylene glycol, as earlier done by Cozzi and Vivarelli,² the Nb(V) was present in a monomeric species only,

regardless of concentration, and the appropriate reduction mechanism applied. Speculation as to the nature of the dimeric species present in concentrated Nb(V) solutions, without ethylene glycol added, consisted in the postulation of an anionic binuclear species with two oxygen bridges.

A further investigation of this system by the same workers consisted of controlled potential coulometry and chronoamperometry.⁷ The electrochemical behavior of 0.01 F Nb(V) solutions in concentrated hydrochloric acid was explained by assuming the existence of several dimeric species each containing two oxygen bridges. The possibility of an intermetallic bond between the two niobium atoms in dimers containing at least one metal in less than the +5 oxidation state was postulated. This sharing of one or more electrons by two niobium atoms would facilitate disproportionation reactions such as $[\text{Nb(IV)} \cdot \text{Nb(IV)}] \rightarrow [\text{Nb(V)} \cdot \text{Nb(III)}]$. It was also postulated that dimers containing two niobium atoms in the same oxidation state could dissociate reversibly to give monomers more rapidly than could dimers containing metal atoms of differing oxidation states. The difference in these rates was attributed to the possible stabilization of the latter species by the proposed metal-metal bond. However, in this author's opinion this conclusion is not justified when one considers the possible dissociation of a postulated

species $[\text{Nb(IV)} \cdot \text{Nb(IV)}]$ which was thought by McCullough and Meites to dissociate rather rapidly.

Bosselaar, van der Heyden, and Mieras studied electrochemical reductions of Nb(V) at concentrations which would enable isolation of solid derivatives in workable quantities from the resulting solutions.⁸ The actual solutions used for reductions consisted of NbCl_5 dissolved in dry ethanol. HCl from external sources, as well as that resulting from solvolysis of NbCl_5 , was rigorously excluded at first. It was found, however, that some HCl had to be present in order that reduction occur. Reduction appeared to cease after a two electron reduction from Nb(V) to Nb(III). The amount of Nb(III) present was determined by titration with excess I_2 in ethanol followed by back titration with $\text{Na}_2\text{S}_2\text{O}_3$ in water. A solid product was isolated from a solution of reduced niobium to which had been added lactic acid. Analytical data were presented which were consistent with a formulation of niobium trilactate. No further data supporting the presence of niobium in the 3+ oxidation state were given.

Gladyshev and Rakhmatulin reported attempted reductions of Nb(V) in various media.⁹ Electrochemical reductions of Nb(V) in sulfate or phosphate media did not yield a niobium species in a definite oxidation state. In the presence of

fluoride, oxalate, tartrate, or acetate, reductions were accomplished at low acidity ($\text{pH} \geq 5$).

Use of various amalgams as reducing agents was also studied by Gladyshev and Rakhmatulin.¹⁰ Reductions were carried out in hydrochloric and sulfuric acid media, with and without the addition of fluoride ion. Zinc amalgam reduced Nb(V) to Nb(III) in both HCl and H_2SO_4 solutions. Cadmium amalgam reduced Nb(V) to Nb(IV) in H_2SO_4 and to Nb(III) in HCl. Tin amalgam reduced Nb(V) to some indeterminate reduced oxidation state in HCl solution. The degree of reduction of Nb(V) was established by titration techniques employing permanganate ion in the case of sulfuric acid solutions or ferric chloride for hydrochloric acid solutions. Reductions observed were reported quantitative if the niobium concentration was greater than one milligram per milliliter. In the presence of 0.1 - 2.0 M F^- , zinc and cadmium amalgams failed to reduce Nb(V) in either HCl or H_2SO_4 solutions. This was related to the possibility of strong complex formation between Nb(V) and F^- . It was also found that tantalum in the 5+ oxidation state was not reduced under any of the conditions employed in this work.

Discrete Compounds of Niobium(III).—Probably the most important compounds containing niobium(III) are salts of the type $\text{M}_3\text{Nb}_2\text{X}_9$ (where $\text{X} = \text{Cl}, \text{Br}, \text{I}$ for $\text{M} = \text{Cs}^+$ or $\text{X} = \text{Br}$

for Rb^+). These have been recently synthesized and studied by Broll, von Schnering, and Schäfer.¹¹ These materials were formed in a reaction between stoichiometric amounts of the appropriate alkali metal halide and Nb_3X_8 . The reactants were placed in a quartz ampule which was then evacuated and heated in a temperature gradient furnace. The reactants were placed in the higher temperature portion of the gradient while the desired product was deposited in the cooler region. The temperatures employed in these reactions were in the range 640°C to 690°C at the high temperature portion of the gradient, while the low temperature portion of the gradient was maintained in the range 600°C to 650°C . The exact temperatures used were a function of the alkali metal and halide. The chloride was reported to be dark green; the bromides and iodide were black. The structures of the niobium containing species were studied using X-ray crystallographic techniques revealing structures containing anionic species formed by two octahedra sharing a common face. This is the same structure as that for the compound $\text{Cs}_3\text{Cr}_2\text{Cl}_9$.¹² The metal-metal distance in $\text{Cs}_3\text{Nb}_2\text{Br}_9$ is reported to be $2.77 \pm 0.03 \text{ \AA}$. This short distance is indicative of a very strong direct metal-metal bond. The measured magnetic moment of this compound, 2.68 BM, is close to that expected for two unpaired electrons. It can be inferred from the communication describing this

study that there exists a double metal-metal bond between the two niobium atoms and that the highest filled molecular orbital is at least doubly degenerate. Little else is reported concerning the actual physico-chemical characteristics of the compounds.

Other discrete compounds of Nb(III) are mainly in the realm of organometallic chemistry. Nesmeyanov, et al., reported the synthesis of $(C_5H_5)Nb(CO)_2Ph_2C_2$ (where $Ph = C_6H_5$) from $(C_5H_5)Nb(CO)_4$ in a photochemical reaction.¹³ This compound contains niobium in what can be considered an oxidation state of 3+. Later, the formation of $[(C_5H_5)Nb(CO)-(C_6H_5CCC_6H_5)]_2$ from the previously mentioned compound by a simple thermal process was reported.¹⁴ This compound was reported to be diamagnetic while molecular weight determinations gave basis for formulation of a dimeric species. The structure was determined by X-ray crystallographic techniques revealing the dimeric structure as was postulated. There were two acetylenic ligands bridging between the niobium atoms. The metal-metal distance was reported to be 2.74 Å which was relatively short but in good agreement with the double bonded Nb-Nb distances of 2.70 Å in $Cs_3Nb_2Cl_9$ and 2.77 Å in $Cs_3Nb_2Br_9$.¹¹ The mass spectrum of $[(C_5H_5)Nb(CO)-(C_6H_5CCC_6H_5)]_2$ also exhibited the strength of the metal-metal bond by showing a peak at $m/e = 316$ corresponding to $[(C_5H_5)Nb]_2^+$, but no peak corresponding to $[(C_5H_5)Nb]^+$.

The compound $(\pi\text{-C}_5\text{H}_5)_2\text{Nb}(\pi\text{-C}_3\text{H}_5)$ was isolated from the reaction of $(\pi\text{-C}_5\text{H}_5)_2\text{NbCl}_2$ and $\text{C}_3\text{H}_5\text{MgBr}$ in ether.¹⁵ This compound contains formally Nb(III) but was diamagnetic as was predicted by bonding ideas formulated by Ballhausen and Dahl.¹⁶ The green-black crystalline solid was unusually stable and sublimed at 135°C (0.25 mm pressure). The C-C stretching frequency of 1480 cm^{-1} and the proton magnetic resonance spectrum were compatible with a π -bonded allyl group.

Another series of compounds containing formally Nb(III) was synthesized by Tebbe and Parshall.¹⁷ These compounds, formulated as $(\pi\text{-C}_5\text{H}_5)_2\text{NbH}(\text{L})$ ($\text{L} = \text{PEt}_3, \text{PMe}_3, \text{CO}, \text{C}_2\text{H}_4$), were formed when $(\pi\text{-C}_5\text{H}_5)_2\text{NbH}_3$ was heated in the presence of the appropriate ligand. Infrared and nuclear magnetic resonance spectral data led to the postulation of a structure analogous to $(\pi\text{-C}_5\text{H}_5)_2\text{MoH}_2$.¹⁸ An alternate synthesis of the previously mentioned compound $(\pi\text{-C}_5\text{H}_5)_2\text{Nb}(\pi\text{-C}_3\text{H}_5)$ was also reported. This consisted of the heating of $(\pi\text{-C}_5\text{H}_5)_2\text{NbH}_3$ with allene. The analogous π -crotyl complex $(\pi\text{-C}_5\text{H}_5)_2\text{Nb}(\pi\text{-C}_4\text{H}_7)$ was prepared by heating $(\pi\text{-C}_5\text{H}_5)_2\text{NbH}_3$ with butadiene. The proton magnetic resonance spectrum showed nonequivalent cyclopentadienyl rings and a typical pattern for the π -crotyl group. The structure of $(\pi\text{-C}_5\text{H}_5)_2\text{Nb}(\pi\text{-C}_4\text{H}_7)$ can be thought of as being analogous to the corresponding π -allyl complex.¹⁹

Niobium Trihalides.—Various reports of niobium tri-fluorides can be found in the literature. A compound formulated NbF_3 was prepared by Ehrlich, et al., by heating a niobium hydride of uncertain composition in the presence of a mixture of hydrogen and hydrogen fluoride at $560\text{--}580^\circ\text{C}$.²⁰ The compound isolated was reported to be a crystalline substance exhibiting the ReO_3 type of structure. Other workers reported isolating a cubic product from the reaction of niobium metal and hydrogen fluoride at 225°C under pressure.²¹ This product was also formulated as NbF_3 . Gortsema and Didchenko studied the thermal decomposition of niobium tetrafluoride and reported a disproportionation to take place resulting in a black to blue-black compound.²² Analytical data for this compound indicated a formulation which approached NbF_3 but contained small amounts of oxygen which varied with material from different preparations. Freshly prepared samples of this compound were pyrophoric but could be passivated by gradual treatment with small amounts of oxygen. Schäfer, et al., concluded from their work and that of previous workers that pure NbF_3 is, at most, only a metastable compound.²³ They further asserted that it was the presence of small amounts of oxygen which allowed the so-called trifluorides of niobium, previously reported, to be isolated.

The chemistries of the other trihalides of niobium have been studied in greater detail and are understood to a higher degree. A very early report of a compound formulated NbCl_3 can be found in the literature.²⁴ This communication described a black deposit of niobium trichloride which was formed when niobium pentachloride vapor was passed through a very hot tube. Later reports indicated that hydrogen gas can reduce niobium pentachloride vapor at 550°C to niobium trichloride.²⁵⁻²⁸ Reactions between hydrogen chloride gas and niobium metal at 400°C produced similar trichlorides.^{26,29} Reductions of niobium pentachloride using metallic reducing agents have been reported as means of producing niobium trichloride. Niobium metal was used as a reducing agent at 400°C .^{30,31} Aluminum was also used with success but at a much lower temperature.²⁷ A common problem with the compounds obtained in the preceding reactions was a small deficiency of chlorine from the stoichiometric amount necessary for the actual trichloride of niobium. The properties of the above-mentioned niobium trichloride were relative inertness to air and water vapor, insolubility in common organic solvents and dilute mineral acids and nonvolatility.

Further studies of the niobium-chlorine system by Schäfer and Dohmann³² revealed that well formed crystals of niobium trichloride were obtained by the chemical transport reaction:

The desired crystals of niobium trichloride were deposited at the cooler end (355°C) of the reaction vessel while the other end of the tube was maintained at a higher temperature (390°C). It was found in these studies that the actual composition of the resulting product depended on the pressure of niobium pentachloride vapor in the reaction vessel. Compounds having formulations ranging from $\text{NbCl}_{2.67}$ to $\text{NbCl}_{3.13}$ were obtained by varying the amount of NbCl_5 in the transport tube.

A later description of a similar transport reaction provided a more convenient method of obtaining compounds having compositions within the above-mentioned limits.³³ This method consisted of enclosing weighed amounts of niobium metal and niobium pentachloride in a tube under vacuum. This tube was heated until all of the metal had been reacted and then the tube was placed in a temperature gradient at the same temperatures described for the previous transport reaction. The chemical transport then proceeded according to the equation describing the reaction between niobium tri- and pentachloride.³² It was found that compounds having Cl/Nb ratios between the limits of 2.67 and 3.13 had the same basic crystal structure. X-Ray powder diffraction data for a series of compounds in this range showed a small but progressive change in some of the

line spacings exhibited by these compounds as a function of composition. In fact, powder diffraction data were used to determine the composition of samples after suitable calibrations had been made. The color of the crystals of this homogeneity range also changed with composition, ranging from green to brown as the Cl/Nb ratio changed from 2.67 to 3.13.

A single crystal X-ray diffraction study was performed on the lower limit of this homogeneity range, namely $\text{NbCl}_{2.67}$ or Nb_3Cl_8 .³⁴ It was found to crystallize in a CdI_2 layer lattice structure with $3/4$ of the metal sites filled in a regularly ordered manner. This gave rise to a structure containing trigonal clusters of niobium atoms which were apparently bonded together by means of direct metal-metal bonds. The compound was also found to be paramagnetic with a room temperature magnetic moment of 1.86 Bohr magnetons corresponding to one unpaired electron per three metal atoms.

From all of the above evidence, it was deduced that this homogeneity range may be regarded as a solid solution between Nb_3Cl_8 and NbCl_4 (or Nb_2Cl_8).³⁵ The solubility can be described by the replacement of the Nb_3 trigonal arrays of metal in the Nb_3Cl_8 structure by Nb_2 dimeric arrays. This substitution can continue until the Cl/Nb ratio is 3.13. Between this point and Cl/Nb ratio of 4.00, the two compounds are heterogeneous. From the preceding data, it can

be deduced that true " NbCl_3 " is just an incidental composition and not really a discrete compound.

Reactions of compounds having the approximate composition NbCl_3 have also been studied in molten salts. Safonov, Korshunov, and Zimina studied NbCl_3 in both CsCl and RbCl systems.³⁶ The niobium trichloride used in these studies was prepared by high temperature reduction of NbCl_5 using a stoichiometric amount of niobium metal as a reducing agent. Evidently, the actual compound used was just one of known composition in the broad homogeneity range. The phase diagrams corresponding to the two above-mentioned salt systems were reported. Crystals of compounds having the reported formulation M_2NbCl_5 ($\text{M} = \text{Rb}^+, \text{Cs}^+$) were isolated from the respective salt systems. The rubidium compound melted incongruently at 750°C while the cesium analog melted congruently at 762°C . Both compounds were reported to be air sensitive and appeared to be red. X-Ray powder diffraction patterns for the two compounds were remarkably similar, while both patterns differed significantly from patterns of RbCl , CsCl , NbCl_3 , or Nb (metal). It was postulated that the ion $[\text{NbCl}_5]^{2-}$ was present in the melts.

In a later publication a study of the $\text{K}_2\text{NbCl}_5\text{-LiCl}$ salt system was reported.³⁷ The phase diagram corresponding

to this system was presented. A polymorphic phase transition of K_2NbCl_5 at 590°C was reported to occur.

NbCl_3 in both NaCl and KCl was the subject of a third communication.³⁸ The NbCl_3 - KCl system, which had been mentioned earlier,³⁷ was discussed more thoroughly. The compound K_2NbCl_5 , which melted congruently at 718°C , was isolated and was reported to be reddish brown and also to be air sensitive. In molten KCl , the complex anion postulated to be present was $[\text{NbCl}_6]^{3-}$. In opposition to this the anion $[\text{NbCl}_5]^{2-}$ was postulated to be present in the sodium chloride melt. The compound Na_2NbCl_5 was isolated in this case. Na_2NbCl_5 had a polymorphic transition at 362°C and melted incongruently at 450°C . X-Ray powder diffraction patterns of both isolated compounds were reported as well as the pertinent phase diagrams for the two respective systems.

The niobium-bromine system is similar to the niobium-chlorine system with regards to possessing a variable composition range for the so-called trihalide phase. An early report indicated that NbBr_3 could be obtained by the reduction of NbBr_5 using hydrogen gas at 500°C .³⁹ More recent work, however, demonstrated that this was only one composition in the range of Br/Nb ratios from 2.67 to 3.03.⁴⁰ A transport reaction, analogous to that in the NbCl_5 - $\text{Nb}(\text{metal})$ system, could be instituted between

NbBr_5 and niobium metal in a temperature gradient ranging from 450°C (for Nb metal) to 400°C (for NbBr_5). The actual composition of the resulting product was again determined by the pressure of pentahalide present in the reaction tube. The stability of the compounds over this composition range varied from air stability at the lower end ($\text{NbBr}_{2.67} = \text{Nb}_3\text{Br}_8$) to instability due to hydrolysis at the upper end ($\text{NbBr}_{3.03}$).

Two forms of Nb_3Br_8 were reported.⁴¹ The reaction described above yielded what is known as $\alpha\text{-Nb}_3\text{Br}_8$. This resembled completely the only known form of Nb_3Cl_8 in having a type of CdI_2 layer structure. If stoichiometric amounts of niobium metal and bromine were reacted at 500°C , $\beta\text{-Nb}_3\text{Br}_8$ was obtained. This differed from the alpha form in the way successive layers in the crystal lattice were arranged. The niobium atoms in each form were drawn together into triangular arrangements indicating the presence of substantial direct metal-metal bonding. $\beta\text{-Nb}_3\text{Br}_8$ appeared to be more sensitive to hydrolysis.

Seabaugh and Corbett reported that the compound Nb_3I_8 was the condensed equilibrium phase in the region of the triiodide of niobium.⁴² In an earlier report, however, they reported the thermal decomposition of NbI_5 and NbI_4 which yielded compounds having I/Nb ratios of 3.00 ± 0.05 .⁴³ This niobium triiodide could also be obtained as the

principal initial product of the reactions of excess niobium metal and higher iodides of niobium or elemental iodine. NbI_3 was reported to decompose at 513°C to Nb_3I_8 and an iodine-rich liquid ($\text{NbI}_{4.4}$). Both NbI_3 and Nb_3I_8 were shown to be diamagnetic at room temperature. Nb_3I_8 exhibited very high stability to both air oxidation and hydrolysis. Simon and von Schnering have indicated that this compound should be classified as $\beta\text{-Nb}_3\text{I}_8$ since it had the structure of $\beta\text{-Nb}_3\text{Br}_8$.⁴¹ They noted that in the structure of $\beta\text{-Nb}_3\text{I}_8$ the niobium atoms were again drawn together into a triangular arrangement exhibiting metal-metal bonds but the actual Nb-Nb distance depended on the size of the anion present. Further studies have indicated that Nb_3I_8 can be thermally decomposed to yield a still lower iodide, $\text{NbI}_{1.83}$ (Nb_6I_{11}).⁴⁴

Complexes with Thioethers.—This section will deal with the use of thioethers (organic sulfides) as ligands for the coordination of various metals. The use of sulfur-containing species (including thioethers) as coordinating agents has been the subject of a recent review by Livingstone.⁴⁵ Also Hamilton has briefly considered thioether complexes of group IV and V transition metal elements.⁴⁶ Therefore, the scope of this discussion will be limited to thioether complexes of niobium and related

metals and also to anomalous behavior exhibited by thioethers in certain coordination compounds.

Thioether complexes of niobium pentachloride and pentabromide were prepared by Fairbrother and co-workers.^{47,48} With dimethyl sulfide and diethyl sulfide simple mono adducts of formulation $\text{NbX}_5 \cdot (\text{R}_2\text{S})$ ($\text{X} = \text{Cl}, \text{Br}$; $\text{R} = \text{CH}_3, \text{CH}_2\text{CH}_3$) were isolated. However, reactions of tetrahydrothiophene (SC_4H_8) with NbCl_5 or NbBr_5 resulted in bis adducts with the possibility of seven coordinate complexes being formed. These bis adducts were found to be insoluble in excess tetrahydrothiophene. It was also noted that the stability of these thioether complexes was much greater than the corresponding diethyl ether complexes studied earlier.⁴⁹

Feenan and Fowles were able to isolate simple 1:1 adducts of niobium pentachloride and pentabromide with tetrahydrothiophene and pentamethylenesulfide.⁵⁰ In these reactions benzene was used as a diluent for the ligands. No evidence was found for the previously reported bis complexes. Another interesting compound isolated during this study was a mono adduct between NbX_5 ($\text{X} = \text{Cl}, \text{Br}$) and thioxan ($\text{SC}_4\text{H}_8\text{O}$). The ligand thioxan had two potential coordination sites, namely one sulfur atom and one oxygen atom. It was deduced from infrared and nuclear magnetic

resonance spectra that the ligand employed the sulfur atom only for bonding to the niobium.

Niobium(IV) halide complexes with thioethers were the subjects of recent studies by Hamilton and McCarley.⁵¹ The ligands studied were dimethyl sulfide, diethyl sulfide and tetrahydrothiophene. Direct reaction of NbX_4 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) with tetrahydrothiophene (SC_4H_8) yielded only discrete bis adducts which were paramagnetic with a magnetic moment corresponding to one unpaired electron per niobium atom. Vibrational spectral analysis tended to favor a cis configuration for the sulfide ligands. With dimethyl sulfide two types of complexes were isolated. A bis adduct was obtained from the direct reaction of the appropriate tetrahalide and excess ligand. This species was also paramagnetic and a cis configuration was assigned. Extraction of these bis adducts with benzene yielded a mono adduct of formulation $\text{NbX}_4 \cdot \text{S}(\text{CH}_3)_2$ ($\text{X} = \text{Cl}, \text{Br}$). These complexes were only very weakly paramagnetic and a halogen-bridged dimeric structure containing a metal-metal bond was postulated. With diethyl sulfide only mono adducts could be isolated and these also were assigned a dimeric structure in analogy to the dimethyl sulfide complexes.

Similar results were also reported by Fowles and co-workers.⁵² In addition, however, they isolated two

species having the formulation $\text{NbBr}_4 \cdot 2(\text{SC}_4\text{H}_8)$. These possessed different solubilities in the parent ligand and also different far-infrared spectra. The possibility of cis and trans isomers was discussed.

The reactions of NbX_4 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) with 1,2-dimethylthioethane (or 2,5-dithiahexane) also have been studied.⁵³ Analytical data indicated two ligand molecules per metal atom were present in the isolated species. Infrared, far-infrared and electronic spectra were consistent with eight coordination about the metal atom. Magnetic studies indicated that these compounds possessed a magnetic moment very close to the spin-only value for a d^1 ion.

Some thioether adducts of titanium(III) halides have also been studied.⁵⁴ Bis adducts of TiX_3 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) with both dimethyl sulfide and tetrahydrothiophene were isolated. All of the complexes were insoluble in all common solvents except for the parent ligand. Magnetic studies indicated that the chloride complexes were highly antiferromagnetic with Néel temperatures of ca. 320°K. The bromide and iodide complexes exhibited more conventional magnetic behavior, however, the possibility of magnetic exchange of relatively small magnitude was still present. These magnetic considerations, together with far-infrared spectral data, enabled the postulation of halide-bridged

dimers containing six coordinate titanium(III) for the bromide and iodide species in the solid state. From existing data, it was not possible to assign a definite structure to the chloride species. Evidence, however, suggested a dimeric species with a direct metal-metal bond being present.

Complexes of the type $VX_3 \cdot 2L$ ($X = Cl, Br$; $L = S(CH_3)_2$, SC_4H_8 ; $L = S(CH_2CH_3)_2$ (for $X = Cl$)) have been reported by Duckworth and co-workers.⁵⁵ Synthetic procedures for these compounds consisted of the direct reaction of the trihalides of vanadium with either an excess of the appropriate ligand (for dimethyl sulfide and diethyl sulfide) or with a benzene solution of the ligand (for tetrahydrothiophene). It was also noted that dimethyl and diethyl sulfides reduced vanadium(IV) chloride yielding the analogous product as the direct reactions of trihalide. Solution studies in benzene indicated a five coordinate trigonal bipyramidal coordination sphere about the vanadium metal with the sulfide ligands being trans-oriented. Spectral evidence suggested that in the solid state, however, dimerization has occurred yielding six coordinate vanadium atoms. Magnetic moments exhibited by these compounds were close to the spin-only values for a d^2 ion.

As is evident by the reports of the preceding work, the "normal" method of coordination of alkyl sulfides is

just simple donation of one pair of electrons from the sulfur atom to an appropriate empty orbital on the metal atom. This results in adduct formation in which the alkyl sulfide occupies a single coordination site on one metal. A few examples are known however in which one sulfur atom of an alkyl sulfide occupies one coordination site on two metal atoms simultaneously resulting in an alkyl sulfide bridge.

Fritz and Schwarzhans reported the synthesis of $[(\text{H}_3\text{C})_2\text{S}]_3(\text{CH}_3)_4\text{Rh}_2\text{I}_2$ from $[(\text{H}_3\text{C})_2\text{S}]_3\text{RhCl}_3$ and CH_3MgI .⁵⁶ The proton magnetic resonance spectrum of a deuterio-benzene solution of this compound indicated two types of chemically inequivalent dimethyl sulfides present. One resonance of relative intensity two was found at $\delta = 2.45$ (TMS = 0.00). Another resonance of relative intensity one was found at $\delta = 2.53$. This latter resonance was assigned as arising from a dimethyl sulfide in a bridging configuration. The former resonance was assigned as stemming from terminally bound dimethyl sulfide ligands. A dimeric structure was postulated which consisted of two octahedra sharing a common face consisting of one dimethyl sulfide and two iodide ions. The terminal dimethyl sulfide groups were assigned as trans to the bridging sulfide ligand. This structure was later confirmed using X-ray single crystal diffraction techniques.⁵⁷ The Rh-Rh distance

was reported to be 3.38 Å. Little other information concerning distances and angles in the molecule was reported.

It was noted some time ago that $\text{Pt}_2\text{Cl}_4(\text{R}_2\text{S})_2$ ($\text{R} = \text{CH}_3$, C_2H_5) displayed color and solubility properties substantially different from other platinum(II) complexes.⁵⁸ Analysis of the far-infrared spectra exhibited by these compounds indicated no band which could be assigned to the stretching of Pt-Cl bridge bonds.⁵⁹ An infrared absorption at ca. 420 cm^{-1} could only be assigned as a Pt-S bridge stretching frequency. Single crystal X-ray diffraction studies showed that $[(\text{CH}_3\text{CH}_2)_2\text{S}]_2\text{Pt}_2\text{Br}_4$ actually contained bridging alkyl sulfide groups while $[(\text{CH}_3)_2\text{S}]_2\text{Pd}_2\text{Br}_4$ contained halide bridges.^{60,61} The Pt-S bond lengths found in the platinum compound were 2.209 Å and 2.277 Å giving a weighted mean of 2.218 Å. This was noted to be much smaller than the Pd-S terminal distance of 2.30 Å found in $[(\text{CH}_3)_2\text{S}]_2\text{Pd}_2\text{Br}_4$. This was interpreted by the authors as evidence that the sulfide ligand was more strongly bound when in a bridging situation as opposed to a terminal position. This was in direct contrast to earlier opinions that bridge bonds were weaker as compared to terminal bonds to ligands when halogens were employed as ligands.

Further studies of the far-infrared spectra of $\text{M}_2\text{X}_4\text{L}_2$ ($\text{M} = \text{Pd}, \text{Pt}$; $\text{X} = \text{halogen}$; $\text{L} = \text{alkyl sulfide ligand}$) have indicated that other compounds also have this alkyl sulfide

bridge system.⁶² $\text{Pt}_2\text{X}_4(\text{SR}_2)_2$ ($\text{X} = \text{Cl}, \text{Br}$; $\text{R} = \text{CH}_3\text{CH}_2$; $\text{CH}_3\text{CH}_2\text{CH}_2$; $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$) were postulated to possess the dimeric structure composed of two square planar arrangements sharing a common edge consisting of two bridging dialkyl sulfides. This statement was based upon the fact that they all exhibited an infrared absorption at approximately $90\text{--}100\text{ cm}^{-1}$ higher than was usually observed for a normal Pt-S terminal stretching frequency. Analogous palladium compounds did not exhibit this higher absorption and were assigned a halide-bridged structure.

EXPERIMENTAL

All of the compounds used or synthesized during the course of this investigation were sensitive in varying degrees to exposure to oxygen and water vapor in the atmosphere. To minimize decomposition due to these factors, all of the compounds were prepared in vacuo and were stored in sealed vials in an inert atmosphere drybox equipped with a circulation system capable of removing water vapor from the inert atmosphere. Manipulation of solvents and reactions in general were carried out in vacuo using standard vacuum line techniques.

Materials

Niobium.—Niobium was purchased from E. I. duPont de Nemours Company. The metal was in the form of high-purity beads.

Chlorine.—Chlorine was purchased from the Matheson Company in lecture size cylinders. It was used with no further purification.

Bromine.—Bromine was purchased from J. T. Baker Chemical Company. It was dried by stirring over anhydrous phosphorus pentoxide and was thoroughly outgassed at ca. 10^{-5} Torr before use.

Iodine.—Iodine was purchased from the General Chemical Division, Allied Chemical Company. It was purified by sublimation in vacuo at elevated temperatures.

Tetrahydrothiophene.—Tetrahydrothiophene was obtained from Mathison, Coleman, and Bell. It was dried by stirring with lithium aluminum hydride. After thorough outgassing, it was stored over lithium aluminum hydride in a round-bottom flask equipped with a high vacuum Teflon needle valve.

Benzene.—Benzene was obtained as a spectroquality solvent from Eastman Chemicals. It was vigorously refluxed over sodium metal to remove traces of water and then vacuum distilled into a needle valve equipped round bottom flask containing niobium pentachloride.

Sodium.—Sodium metal was obtained from the J. T. Baker Chemical Company. Suitably sized pieces were freshly cut immediately prior to the addition of mercury to form sodium amalgam.

Mercury.—The mercury used to make sodium amalgam was obtained from laboratory stock which had previously been triply distilled. It was used without further purification.

Synthesis

Niobium(V) Halides.—Niobium(V) halides were synthesized by direct combination of the elements. The chloride and bromide were prepared by sealing the metal and the appropriate halogen (in excess) in a Pyrex tube and then heating the metal to an elevated temperature while most of the tube remained outside of the furnace. The metal was heated to 350—400°C for chloride preparations and 400—450°C for bromide preparations. The pentahalides sublimed out of the hot portions of the reaction vessels and condensed in the cooler portions of the reaction tubes.

Niobium pentaiodide was synthesized by sealing niobium metal and elemental iodine in a Pyrex tube. A temperature gradient furnace was employed to heat the metal to 450°C and the iodine to 180°C.

Niobium(IV) Halides.—Niobium(IV) halides in general were synthesized by reducing pentahalides with niobium metal in sealed Pyrex tubes. For the chloride and bromide, temperature gradients of 400°C/250°C and 410°C/350°C respectively were employed with the metallic reducing agent being held at the higher temperature.

The preparation of niobium tetraiodide was different in that no reducing agent was necessary since niobium pentaiodide was thermally unstable in a temperature gradient of 270°C/30°C. The niobium(V) iodide decomposed

into niobium(IV) iodide and elemental iodine under these conditions.

Tetrahalobis(tetrahydrothiophene)niobium(IV).—The complexes of niobium(IV) halides (chloride, bromide, and iodide) with tetrahydrothiophene were prepared by extracting the appropriate anhydrous tetrahalide with neat tetrahydrothiophene in an extraction apparatus modified to work under high vacuum.⁴⁶ The complexes were extremely soluble in excess free ligand enabling them to be removed from unreacted tetrahalide by the extraction process. After the reaction was complete, as indicated by a lack of color in the extracting liquid, the excess ligand was removed by vacuum distillation to yield highly crystalline solids of formulation $\text{NbX}_4 \cdot 2(\text{SC}_4\text{H}_8)$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$).

Sodium Amalgam.—Sodium amalgam (3.5 mole % Na) was obtained by slowly adding an appropriate amount of triply distilled mercury to a weighed amount of freshly cut sodium metal in a vessel which allowed the sodium to remain in vacuo while the mercury was added. The reaction vessel was cooled during the reaction by submerging the lower end in an ice-water bath. The reaction vessel was then taken into a drybox where it was opened and the amalgam removed and stored in stoppered bottles until needed.

Niobium(III) Halide Complexes, $\text{Nb}_2\text{X}_6(\text{SC}_4\text{H}_8)_3$.—These compounds were synthesized by reaction between sodium

amalgam and the appropriate tetrahalide complex in a suitable solvent. Typically, a 5 g. sample of the appropriate tetrahalide complex was weighed out in the drybox and placed in a round bottom flask which contained a Teflon coated stirring bar. A sufficient quantity of sodium amalgam was then added to provide a Na:Nb ratio of 1:1. The flask was then removed from the drybox and attached to a vacuum line where it was evacuated and thoroughly outgassed. Benzene was then vacuum distilled into the flask in sufficient quantity to allow all of the tetrahalide complex to go into solution. The flask was then warmed to room temperature and a magnetic stirrer was situated beneath the flask to enable the contents to be stirred by the stirring bar, which was begun immediately after the solvent melted. Initial color of the solutions of each of the different halide complexes was a reddish-brown. After a few minutes, however, a definite color change could be observed. In the case of the chloride a brilliant violet color could be observed; the bromide showed a deep blue color, and the iodide exhibited a dark green hue. These colors intensified as the reaction proceeded with the mutual decline in intensity of the original colors of the reaction mixtures. After approximately one hour, no change in intensity or shade of the color could be observed. The solvent was then removed

by vacuum distillation yielding a solid of the same color as the solution for each of the different halides. This solid contained finely divided mercury and all other solid products of the reaction. The reaction flask was then taken into the drybox where it was emptied. A large amount of the residual mercury could be removed at this point by grinding the mixture which allowed the finely divided droplets of mercury to coalesce. The mercury separated in this manner could be easily poured from the other reaction products. The remaining portion of the reaction mixture was then placed in a suitable extraction apparatus which was then attached to the vacuum line and fresh benzene was distilled into it. Extraction was begun, and a highly colored species was immediately extracted from the reaction mixture. The solution in each case had the corresponding color as noted earlier in the actual reaction flask. Extraction with benzene appeared to remove most, if not all, of the highly colored species within a few hours. The insoluble portion at this time appeared to contain the remaining mercury and also a solid whose color ranged from gray to black. This color varied from halide to halide and from one individual reaction to the next. After extraction had ceased, the benzene was removed by vacuum distillation leaving crystalline solids. The colors of these compounds were violet, blue, and green for the

chloride, bromide, and iodide respectively. Anal. Calcd for $\text{Nb}_2\text{Cl}_6(\text{SC}_4\text{H}_8)_3$: Nb, 28.02; Cl, 32.08; C, 21.74; H, 3.65; oxidation state of Nb, 3.00. Found: Nb, 27.72; Cl, 31.50; C, 21.66; H, 3.65; oxidation state of Nb, 3.01 ± 0.01 . Calcd for $\text{Nb}_2\text{Br}_6(\text{SC}_4\text{H}_8)_3$: Nb, 19.98; C, 15.50; H, 2.60. Found: Nb, 19.54; C, 15.78; H, 2.65. Calcd for $\text{Nb}_2\text{I}_6(\text{SC}_4\text{H}_8)_3$: Nb, 15.11; C, 11.72; H, 1.97. Found: Nb, 15.19; C, 12.32; H, 2.19.

$[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{Nb}_2\text{Cl}_8(\text{SC}_4\text{H}_8)$.—This compound was prepared by stirring approximately 1.5 g. of the compound formulated $\text{Nb}_2\text{Cl}_6(\text{SC}_4\text{H}_8)_3$ with 1.13 g. of $(\text{C}_2\text{H}_5)_4\text{NCl}$ in CH_2Cl_2 solution. The above weights of reactants would give a molar ratio of $(\text{C}_2\text{H}_5)_4\text{NCl}$ to $\text{Nb}_2\text{Cl}_6(\text{SC}_4\text{H}_8)_3$ of 3.0. Initial color of the reaction solution was violet which turned a more purple hue with time. A lighter colored precipitate formed rather rapidly. The reaction was terminated after two days with the removal of the solvent by distillation. The reaction vessel was taken into the drybox where the contents were removed and placed into a suitable extraction apparatus. This was subsequently evacuated on the vacuum line and fresh CH_2Cl_2 was distilled into it. Extraction yielded a very small quantity of blue soluble fraction and a large amount of very sparingly soluble violet solid. Excess tetraethylammonium chloride was also soluble in CH_2Cl_2 as was any unreacted niobium containing starting

material. The violet solid was analyzed and formulated as $[(C_2H_5)_4N]_2Nb_2Cl_8(SC_4H_8)$. Anal. Calcd for $[(C_2H_5)_4N]_2Nb_2Cl_8(SC_4H_8)$: Nb, 22.77; Cl, 34.68; C, 29.34; H, 5.91; Cl/Nb = 4.00. Found: Nb, 22.29; Cl, 34.54; C, 30.89; H, 6.09; Cl/Nb = 4.06.

$[(C_2H_5)_4N]_3Nb_2Cl_9$.—This compound was synthesized in an analogous manner to the preceding complex. However in this case the Et_4NCl/Nb ratio was greater than 3.0. The initial violet color changed little initially and a light-colored precipitate formed in analogy with the synthesis of $[(C_2H_5)_4N]_2Nb_2Cl_8(SC_4H_8)$. The reaction was allowed to continue for a period of approximately one day at which time the solution had assumed a blueish hue. The precipitate's color had also darkened. The precipitate, which was highly crystalline, was filtered out of the reaction solution, washed with fresh dichloromethane, and then dried. All of the preceding steps were undertaken in vacuo. Grayish silver crystals were obtained, analyzed, and formulated as $[(C_2H_5)_4N]_3Nb_2Cl_9$. Anal. Calcd for $[(C_2H_5)_4N]_3Nb_2Cl_9$: Nb, 20.75; Cl, 35.64; C, 32.16; H, 6.75; Cl/Nb = 4.50. Found: Nb, 20.22; Cl, 35.64; C, 31.14; H, 6.77; Cl/Nb = 4.51.

Analytical Methods

Niobium.—The niobium content of the complexes synthesized during the course of this investigation was usually determined by hydrolysis of weighed samples in aqueous ammonia solutions. The samples were digested by heating to facilitate decomposition. Acidification of the solutions precipitated hydrous niobium oxide which was filtered off and ignited in tared crucibles using a Meeker burner or muffle furnace. In some instances certain compounds resisted hydrolysis to some extent and in these cases metal analyses were performed by direct ignition of weighed samples of the compounds in tared crucibles. Small quantities of niobium in solutions prepared for spectral studies were analyzed by the Ames Laboratory Analytical Service Group, Iowa State University of Science and Technology, Ames, Iowa, according to the procedure of Telep and Blotz.⁶³

Halogens.—Halide contents were determined by potentiometric titrations with a standardized silver nitrate solution. A Photovolt Digicord pH meter was employed using a silver indicating electrode vs. a saturated calomel reference electrode.

Carbon and Hydrogen.—Carbon and hydrogen determinations were performed by Mr. J. J. Richard of the Ames Laboratory

Analytical Service Group, Iowa State University of Science and Technology, Ames, Iowa.

Physical Measurements

Magnetic Susceptibility.—Measurements of the magnetic susceptibility of complexes were made employing a Faraday balance apparatus. The construction and calibration of this apparatus have been described previously.⁶⁴ Measurements were made from liquid nitrogen temperatures (77°K) to room temperature by means of various slush baths or use of a cryostat which was equipped with a heater to warm the sample. Sample temperatures were determined by means of a copper-constantan thermocouple located within close proximity of the sample. The sample itself was loaded in a screw-top Teflon bucket in a drybox under a argon or nitrogen atmosphere. The bucket was then suspended from one arm of the electrobalance employed. Corrections for the diamagnetism of the sample bucket were made for each determination.

Nuclear Magnetic Resonance Spectra.—Proton magnetic resonance spectra were obtained using a Varian A-60, a Varian HA-100, or a Hitachi Perkin-Elmer R-20B spectrometer. Saturated solutions of samples in benzene were obtained by means of a cell containing a sintered glass frit which removed any solid before the solution was decanted into

the sample tube. The sample tubes were then sealed off under vacuum. In all cases, the position of the solvent resonance had been previously determined using tetramethylsilane as an internal standard. The chemical shifts of the proton resonances of coordinated ligands were determined by relating the resonances in question to the solvent resonance of known position.

Vibrational Spectra.—Spectra of solid samples prepared as Nujol mulls were obtained using a Beckman IR-7 spectrophotometer for the $1400\text{--}600\text{ cm}^{-1}$ range and a Beckman IR-11 spectrophotometer for the region below 600 cm^{-1} in energy. The mulls were prepared in a drybox to exclude oxygen contamination. Cesium iodide windows were used in a screw-top cell for the $1400\text{--}600\text{ cm}^{-1}$ spectra while polyethylene sheets were used in a sealed O-ring cell for the far-infrared region.

Oxidation State Determinations.—Solid samples were treated with a ferric ammonium sulfate solution in the method described by Hamilton.⁴⁶ Titration of the resulting ferrous ion with a standardized cerium(IV) solution to a ferroin endpoint enabled the determination of the average oxidation state of the metal in the compound in question.

Electronic Spectra.—Spectra of solutions were obtained using a Cary Model 14 Recording Spectrophotometer. Samples together with an appropriate solvent were sealed in

a spectral cell adaptable for use at low pressures.⁶⁵ This cell enabled the concentration of the solution being investigated to be changed at will in order to record regions of the spectra which had vastly differing intensities.

Solid state spectra were obtained by employing a Beckman DU Spectrophotometer together with an appropriate reflectance attachment. Samples were prepared by mixing and grinding the appropriate compound with anhydrous magnesium carbonate. This mixture was then loaded into a cell which fit into the spectrophotometer.⁶⁵ Magnesium carbonate was also used as a reference to determine what was considered to be 100% reflectance.

X-Ray Diffraction.—X-Ray powder diffraction patterns were obtained using a 114.59 mm. Debye-Scherrer camera. Ni-filtered copper K_{α} radiation was employed. Samples were finely ground and loaded into 0.2 mm. Lindemann capillaries in an inert atmosphere drybox. The capillaries were plugged using small amounts of silicone high vacuum stop-cock grease in order that they could be removed from the drybox and then sealed using a small flame.

Single crystal X-ray diffraction patterns were obtained using a Buerger precession camera. Crystals were mounted inside of thin-walled Lindemann capillaries in an inert atmosphere drybox. Similar sealing procedures were employed as described above. The X-rays employed were

either copper or molybdenum radiation. Zero level precession photographs were obtained using appropriate screens designed for this purpose.

Single crystal X-ray diffraction data were obtained using a Hilger-Watts X-ray Diffractometer which was completely automated and controlled by a computer. Filtered molybdenum radiation was employed. Computer programs for the analysis of single crystal X-ray diffraction data were obtained from the XTALOG library as maintained by the X-ray crystallography group directed by Professor Robert A. Jacobson of the Ames Laboratory, USAEC, Ames, Iowa.

RESULTS AND DISCUSSION

Synthesis of Niobium(III) Species

Reduction Reactions.—Derivatives of the niobium trihalides are difficult, if not impossible, to obtain directly from the so-called trihalide phases because of their relative inertness. Hence, it was thought that adducts containing niobium(III) could be obtained by the reduction of niobium(IV) species with an appropriate reducing agent. The selection of suitable complexes containing Nb(IV) was quickly narrowed to a series of complexes of formulation $\text{NbX}_4 \cdot 2(\text{SC}_4\text{H}_8)$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). These had recently been synthesized and characterized by J. B. Hamilton of this laboratory.⁴⁶ Data obtained in these studies indicated that these compounds were well-behaved examples of Nb(IV) complexes. Although they were unstable toward air oxidation and hydrolysis in the atmosphere, they could be easily handled under inert atmospheres and in vacuo. They were found to be highly soluble in common organic solvents which had been thoroughly dried and out-gassed. Although no structural data were obtained, inference from spectral data indicated a cis stereochemistry of the two sulfide ligands coordinated to the central metal atom. Another point in favor of using these thioether derivatives of the niobium tetrahalides was the behavior of the related

compounds of type $\text{NbX}_4 \cdot 2\text{R}_2\text{S}$ ($\text{X} = \text{Cl}, \text{Br}$; $\text{R} = \text{CH}_3, \text{CH}_2\text{CH}_3$). Evidence had been presented for the existence of all of these species in solutions of excess ligand. However, upon removal of excess ligand (for $\text{R} = \text{CH}_2\text{CH}_3$) or recrystallization of the solids $\text{NbX}_4 \cdot 2(\text{CH}_3)_2\text{S}$ from benzene, solids of formulation $\text{NbX}_4 \cdot \text{R}_2\text{S}$ could be obtained. These compounds exhibited properties consistent with a bioctahedral structure having two halide bridges between the niobium atoms. Magnetic susceptibility measurements indicated that the two valence electrons in this dimeric structure had coupled to form a direct metal-metal bond between the niobium atoms. In general, the properties exhibited by all of these thioether complexes were those which were thought to be advantageous in successfully accomplishing a reduction to a Nb(III) species.

The solubility and stability of these complexes in hydrocarbon solvents which do not react with strong reductants indicated that benzene would be a suitable solvent for the reduction reactions. Before use, however, the benzene was thoroughly dried and outgassed since any traces of moisture or oxygen would result in an environment of very lethal nature for the complexes being employed.

The choice of a suitable reducing agent was quickly resolved. Sodium appeared to be a logical choice due to its relatively good reducing power and also the insolubility

of its oxidation products, the sodium halides, which could easily be removed from the reaction media.

Metallic sodium was initially employed. (The use of a metallic reducing agent in elemental form had been demonstrated in the synthesis of certain niobium compounds using elemental zinc.⁶⁶ In that case the metal reacted very rapidly.) An attempt was made to coat the inside of a round bottom flask, used as the reaction vessel, with a thin coating of metallic sodium. This was done by physically swirling a flask containing molten sodium while cooling slowly through the melting point. However, the inability of molten sodium to wet the glass walls of the flask prevented a uniform coating from being deposited. An attempt to reduce $\text{NbCl}_4 \cdot 2(\text{SC}_4\text{H}_8)$ with sodium in this form resulted in the isolation of a green solid from which a brown oily residue was extracted with benzene. Analytical data obtained from the green solid were inconclusive.

In order to present a better form of sodium to the complex slated for reduction, a sodium amalgam was employed. A 3.5 mole percent amalgam of sodium was used since a known amount of reducing agent could easily be weighed out for use. Upon reacting sodium amalgam with $\text{NbCl}_4 \cdot 2(\text{SC}_4\text{H}_8)$ in benzene, a drastic color change took place very rapidly. The reddish brown solution of $\text{NbCl}_4 \cdot 2(\text{SC}_4\text{H}_8)$ turned violet and a dark precipitate formed. Removal of the solvent

yielded a violet-gray solid which also contained small droplets of mercury. It was found that grinding the reaction product would coalesce most of the mercury which could then be easily poured from the solid products of reduction. Extraction of this solid with benzene yielded a violet soluble fraction while leaving a black-to-gray residue which was insoluble in benzene. This insoluble residue, which was contaminated with the remaining mercury, accounted for a large volume of the product but a small portion of the weight. Removal of the solvent from the soluble fraction yielded a violet crystalline material having formulation $\text{Nb}_2\text{Cl}_6(\text{THT})_3$ ($\text{THT} = \text{SC}_4\text{H}_8$). The yield of this compound was maximized by using an amount of amalgam which would provide a one equivalent reduction per mole of starting complex present. It was found that employing reaction times of approximately 1 hour provided the best yield of $\text{Nb}_2\text{Cl}_6(\text{THT})_3$. Yields were normally in the range of 60-70% of the calculated amount.

Very little information was obtained concerning the nature of the grayish black benzene-insoluble residue. This was due to small amounts of mercury which remained after the violet fraction had been washed away. It was noted, however, that this residue was air sensitive and also that a dark brown solution could be obtained by extracting this residue with tetrahydrothiophene. Upon

removal of the solvent, a dark oily mass of indeterminate composition was deposited. No other studies were carried out on this material since the insoluble residue constituted only a relatively small fraction of the products of the initial reduction reaction.

The bromide and iodide analogs of the reduced chloride species were synthesized in a similar manner. In each case one mole of reducing agent was supplied for each mole of niobium present. The color change noted in the bromide reaction was from a dark reddish-brown to a royal blue. A blue crystalline solid was isolated by an extraction of the reduction mixture with benzene. The color change in the iodide reaction was from a deep brown to a dark green. In a manner similar to the procedure described above, a dark green crystalline material was isolated from the reaction mixture.

In the case of the bromide and iodide, the reaction appeared to proceed slightly slower than the analogous chloride reaction. Reaction times on the order of 1.5 hours produced yields in the range of 60-70% of the calculated amount.

The syntheses described above are summarized in reaction 1, where X = Cl, Br, or I.

In all cases the reactions were carried out at room temperature or below. The presence of free tetrahydrothiophene in solution after the reaction had taken place was ascertained by the proton magnetic resonance spectrum of the reaction solvent which had been distilled from the reaction flask. The spectrum consisted of only the resonances attributable to benzene and tetrahydrothiophene. The presence of sodium chloride was determined by means of the X-ray powder diffraction pattern of the insoluble residue. A very faint pattern which could be assigned as arising from the presence of NaCl was observed.

Metathetical Reactions.—In an attempt to generate other compounds containing niobium(III), reactions between $\text{Nb}_2\text{Cl}_6(\text{SC}_4\text{H}_8)_3$ and tetraethylammonium chloride (Et_4NCl) were studied. Two separate reactions were investigated with the only difference between the two being the relative amounts of $\text{Nb}_2\text{Cl}_6(\text{SC}_4\text{H}_8)_3$ and Et_4NCl employed. In each case dichloromethane was used as a solvent.

In the first reaction enough tetraethylammonium chloride was used so that all of the tetrahydrothiophene could be stoichiometrically replaced. Initially all of the reaction products went into solution. Gradually the violet color changed very slightly but remained a violet hue. A light colored precipitate formed rather rapidly. After two days the reaction was terminated and the solid

product obtained was washed with fresh dichloromethane which removed unreacted tetraethylammonium chloride and also a very small amount of a deep blue, rather soluble, product. The violet product was virtually insoluble in CH_2Cl_2 . This product was not the expected completely substituted material but was only a partially substituted compound as indicated in reaction 2.

The second in the series of reactions with tetraethylammonium chloride consisted of the reaction between $\text{Nb}_2\text{Cl}_6(\text{SC}_4\text{H}_8)_3$ and a quantity of Et_4NCl in excess of the amount needed to possibly form $(\text{Et}_4\text{N})_3\text{NbCl}_6$. A reaction of this type was initiated and allowed to continue for approximately 4 days. During this time the color gradually changed from the initial deep violet to a lighter violet, as in the previous reaction, and finally to a deep blue with the formation of a highly crystalline precipitate. The product was then washed with fresh dichloromethane diluted with benzene to remove any unreacted starting materials. After this extraction the obvious crystalline character of the product had been destroyed. Only a very light blue powder remained. Analytical data for this product were consistent with the formulation $(\text{Et}_4\text{N})_3\text{Nb}_2\text{Cl}_9$. From the temperature dependence of the magnetic data, however, over

the range of 77-297°K, a magnetic moment of approximately 0.4 Bohr magnetons was calculated. This value seemed to be too low for a normal paramagnetic species and too high for a normal diamagnetic species. Calculations showed that an impurity of approximately 10% (by weight) of a paramagnetic species of Nb(IV) (d^1) could cause the observed behavior. Even less contamination would be needed if the impurity was a paramagnetic d^2 ion as a simple species of Nb(III) might possibly be. One possibility was that some reaction with the solvent, CH_2Cl_2 , could have occurred, resulting in oxidation of Nb(III) to Nb(IV). Some sort of reaction was suggested by the disappearance of the highly crystalline material.

This reaction was repeated using the same ratio of starting materials. However, in this case, the reaction was terminated after a reaction time of 1 day at which time the solution was filtered to remove the highly crystalline precipitate. This filtration yielded a large amount of a gray crystalline material which was briefly washed with dichloromethane. Again analytical data were consistent with the formulation $(\text{Et}_4\text{N})_3\text{Nb}_2\text{Cl}_9$. The magnetic susceptibility of this complex was independent of temperature and hence little or no impurity was thought to

contaminate the product. The synthesis is summarized in reaction 3.

Reactions between $\text{Nb}_2\text{Cl}_6(\text{SC}_4\text{H}_8)_3$ and organic nitriles, RCN ($\text{R} = \text{CH}_3\text{CH}_2\text{CH}_3$), were also attempted. In each case the reaction proceeded rapidly with a color change from violet to dark brown. In the case of CH_3CN , a brown-to-black solid was obtained upon removal of the excess ligand by means of vacuum distillation. The solid has the consistency of a glass. Analytical data were consistent with the formulation $\text{NbCl}_3 \cdot 3\text{CH}_3\text{CN}$. Reaction of $\text{Nb}_2\text{Cl}_6(\text{SC}_4\text{H}_8)_3$ with $\text{CH}_3\text{CH}_2\text{CN}$ gave an analogous product.

The acetonitrile product was insoluble in all common organic solvents except excess ligand. A proton magnetic resonance spectrum of this product in deuterio-acetonitrile showed only a broad resonance attributable to free CH_3CN . It was concluded that rapid ligand exchange of CH_3CN with CD_3CN was taking place.

The propionitrile complex was soluble in benzene. A proton magnetic resonance spectrum of a benzene solution in the region normally expected to contain the propionitrile resonances showed nothing. It was postulated that the possible formation of a paramagnetic species had shifted the expected resonances to a different unknown region of the spectrum. Although these complexes would be of

considerable interest in themselves, no further characterization was undertaken since it was felt that efforts in other directions would help elucidate the nature of the niobium(III)-tetrahydrothiophene complexes.

Characterization of $\text{Nb}_2\text{X}_6(\text{SC}_4\text{H}_8)_3$

Introductory Observations.—Analytical data obtained from these compounds indicated an empirical formulation of $\text{NbX}_3 \cdot (1.5)\text{THT}$. Considering the fractional stoichiometry present, the initial indication was to postulate a dimeric structure of type $\text{Nb}_2\text{X}_6(\text{THT})_3$. In order to verify this, an attempt was made to determine the molecular weight of the chloride species. Two methods were tried. Measurement of freezing point depressions of benzene solutions containing known concentrations of the complex gave results of little significance since the molecular weight determined was between that of a monomer and that of a dimer. The precision of the experiments also left much to be desired. Similar results were also obtained by vapor pressure osmometry using a Thomas Isothermal Molecular Weight Apparatus. The main problem in each case appeared to stem from the inability of the apparatus being used to exclude atmospheric oxygen and water vapor from the solutions which were more susceptible to attack than were solid samples of the same compounds.

It should be noted that crystalline solid samples of these complexes exhibited a stability to the atmosphere that was in contrast to the niobium(IV) complexes which were used in the previously described synthetic procedures. The Nb(IV) complexes oxidized and decomposed so rapidly upon being exposed to the atmosphere that an obvious loss of color occurred. The Nb(III) complexes were much more stable, however, and some of their color was still apparent after exposure to the atmosphere for more than 24 hours.

The apparent oxidation state of the niobium present in the compound $\text{NbCl}_3 \cdot (1.5)\text{THT}$ was determined to be 3.01 ± 0.01 . This was not an unambiguous result since the presence of hydridic hydrogens could cause the results of the determinations to be misinterpreted. This will be considered in more detail in the discussion of the infrared and proton magnetic resonance spectra of these compounds.

The solubilities of the homologous series of compounds in benzene were not determined directly. However, from the relative ease of obtaining the proton magnetic resonance spectra of saturated solutions of the compounds, it can be inferred that the solubility decreases in the order $\text{Cl} > \text{Br} > \text{I}$ for this series of compounds.

Nuclear Magnetic Resonance Spectra.—The nuclear magnetic resonance spectrum of the protons in neat

tetrahydrothiophene was found to contain two resonances of equal intensity. The higher field resonance occurred at $\delta = 1.87$ (tetramethylsilane, TMS, $\delta = 0.00$). This resonance was assigned as arising from the protons on the carbon atoms farthest from the sulfur atom in the five-membered ring. The resonance took the form of a quintet because of the coupling of the protons in question to the two sets of two protons each on the carbon atoms adjacent to the sulfur atom. The lower field resonance occurred at $\delta = 2.74$ and was a triplet. This resonance arose from the four protons nearest the sulfur atom. The coupling was due to the protons causing the $\delta = 1.87$ resonance. It should also be noted that the shapes of both the quintet and the triplet were not ideal since the molecular skeleton of one sulfur and four carbon atoms is not planar. This nonplanarity can cause slight inequalities in the environment and attitude of the protons on each carbon atom in relation to the skeleton resulting in slightly asymmetric multiplets and also higher orders of coupling.

In a benzene solution, the resonances of tetrahydrothiophene shifted slightly to higher magnetic fields and were found at $\delta = 1.53$ (quintet) and $\delta = 2.58$ (triplet). This spectrum is reproduced in Figure 1. The same slightly asymmetric nature of the multiplets was still apparent.

These spectra agreed well with that reported for a dilute solution of tetrahydrothiophene in deuterio-chloroform.⁶⁷

Figure 1.— ^1H NMR spectrum of SC_4H_8 in benzene solution.

Reported values for the chemical shifts were $\delta = 1.93$ for the protons farthest from the sulfur (labelled type "a") and $\delta = 2.82$ for the protons on the carbons adjacent to the sulfur atom (labelled type "b"). This notation, "a" and "b" type protons, will be used in the following discussions.

The proton magnetic resonance spectrum of $\text{Nb}_2\text{Cl}_6(\text{SC}_4\text{H}_8)_3$, obtained from a saturated solution of the complex in benzene, is shown in Figure 2. The spectrum consisted of three main regions of resonance other than that of the solvent. A multiplet of high order was located at approximately $\delta = 1.50$ while two triplets were located at $\delta = 3.20$ and $\delta = 3.96$. The relative intensities of these resonances were 3:2:1.

The interpretation of this spectrum can be simplified if one considers the possibility of having two types of chemically inequivalent tetrahydrothiophene present in the molecule. The multiplet at $\delta = 1.50$ can be resolved into two overlapping quintets centered at $\delta = 1.46$ and $\delta = 1.56$ respectively. Although separate integration of these closely spaced resonances would be difficult at best, qualitatively their intensities appeared to be in a ratio of 1:2. These resonances were assigned as arising from the "a" type protons of two different types of coordinated tetrahydrothiophene. The triplet at $\delta = 3.20$ (relative intensity = 2) was assigned as the "b" resonance associated with the "a" resonance at $\delta = 1.56$. The triplet at $\delta = 3.96$ (relative

Figure 2.— ^1H NMR spectrum of a saturated solution of $\text{Nb}_2\text{Cl}_6(\text{SC}_4\text{H}_8)_3$ in benzene.

intensity = 1) corresponded to the "b" resonance of a tetrahydrothiophene whose "a" resonance occurred at $\delta = 1.46$.

The chemical implications of these assignments must now be discussed. The "b" resonance at $\delta = 3.96$ was shifted the most upon coordination. In fact, it was shifted 1.38 δ units. This is a very large displacement when compared to the other "b" resonance which was moved only 0.62 δ units. From these considerations it can be concluded that upon coordination the "b" resonance of tetrahydrothiophene is shifted to lower fields. This is not unexpected since during coordination electron density is drawn from the sulfur atom (through donation of a lone pair of electrons) to the metal atom being complexed. Through an inductive effect electron density on the remaining portion of the tetrahydrothiophene molecule is also shifted in this direction to balance the inhomogeneous charge distribution which arises from electron donation. This results in a deshielding of the protons and their magnetic resonances are shifted to lower magnetic fields. The amount a "b" type resonance is shifted can be interpreted as a measure of the amount of electron delocalization from the sulfur atom.

Using this as a basis, the tetrahydrothiophene molecules causing the "b" resonance at $\delta = 3.20$ were considered to be normally bound ligands occupying a terminal position on a niobium atom. This type of coordination utilized only one of the two pair of electrons which the sulfur atoms

possessed for possible use in coordination. The tetrahydrothiophene causing the "b" resonance at $\delta = 3.96$ was assigned as being involved in a bridging configuration between two niobium atoms, and thus both lone pairs of electrons on the sulfur atom were being used for dative bonding purposes. This assignment of a bridging sulfide ligand is not without precedent. A dinuclear complex containing two rhodium(III) ions was found to contain dimethyl sulfide in both bridging and terminal positions.^{56,57} The proton magnetic resonance spectrum of this compound showed that the protons on the bridging ligand resonated at lower magnetic fields than those on the terminal ligands. The positions of resonance in the rhodium case differed by only 0.08 δ units. This is rather small when compared to the difference of 0.76 δ units found in this study.

It should also be noted that the "b" resonance of tetramethylenesulfone (in CDCl_3) also is shifted downfield by 0.18 δ units when compared to the corresponding resonance in tetrahydrothiophene.⁶⁷ Also in the case of $\text{C}_4\text{H}_8\text{SO}_2$, the "a" type resonance is shifted by 0.3 δ units, also downfield.

In the case of $\text{Nb}_2\text{Cl}_6(\text{SC}_4\text{H}_8)_3$, the "a" resonances shifted very little. This was also not unexpected since it would seem that these protons would be affected to a lesser degree by coordination of the sulfur atom to a metal. The shift of the "a" resonance of the bridging tetrahydrothiophene

upfield by ca. 0.06 δ units was noted, but was not understood. Therefore, little can be said about this shift, if it was, in fact, real, other than that the position of the bridging "a" resonance differed slightly from the position of the terminal "a" resonance.

The proton magnetic resonance spectra of the analogous bromide and iodide compounds corresponded very well to that of the chloride. The resonance positions, relative intensities, and assignments are tabulated in Table I. The quality of the spectra (obtained from saturated benzene solutions) declined in the order Cl > Br > I. It was felt that this was attributable to the solubility differences of the various analogs in benzene. Due to the relatively poor quality of the bromide and iodide spectra, the highest field resonance could not be resolved into the appropriate bridging and terminal components. A minor resonance of very low intensity was noted at ca. $\delta = 0.90 - 0.93$ in all of the spectra. This was not included in the tabulation of the spectra since it was thought to arise from a small amount of impurity caused by either a slight decomposition of the complexes by minute traces of water and oxygen, or by other contaminants in the solvents employed.

The proton magnetic resonance spectrum of a compound also provides a tool by which the presence of metal hydrides might be ascertained. Saturated benzene solutions of

Table I

¹H NMR Data for Nb₂X₆(SC₄H₈)₃^a

X = Cl	X = Br	X = I	
δ ^b	δ ^b	δ ^b	Assignment
1.46 (1)	1.52 (3)	1.59 (3)	"a" bridging and
1.56 (2)			terminal
3.20 (2)	3.26 (2)	3.45 (2)	"b" terminal
3.96 (1)	4.27 (1)	4.65 (1)	"b" bridging

^aSpectra obtained from saturated benzene solutions at ambient temperatures. ^bChemical shifts in ppm from TMS using benzene as internal standard. Parentheses denote relative peak areas.

$\text{Nb}_2\text{Cl}_6(\text{SC}_4\text{H}_8)_3$ and $\text{Nb}_2\text{Br}_6(\text{SC}_4\text{H}_8)_3$ were scanned up to $\delta = -20.0$ with no apparent hydride resonances. This together with the information to be presented in the discussion of the infrared spectral properties of these compounds seemed to eliminate the possibility of a hydride being present.

Magnetic Susceptibility.—Since nuclear magnetic resonance spectra were obtained and the resonances occurred in the general region where protons of this nature were expected to resonate, it was thought that these complexes were diamagnetic at least when they were in solution. In order to elucidate the magnetic properties of the solid compounds themselves, the magnetic susceptibility of $\text{Nb}_2\text{Cl}_6(\text{SC}_4\text{H}_8)_3$ was determined over the temperature range of $77-295^\circ\text{K}$. The measured susceptibility was virtually independent of temperature over this range. The value of the magnetic susceptibility (χ_M) was found to be $-195 (\pm 9) \times 10^{-6}$ emu/mole. In order to obtain a value for the true molar susceptibility, corrections for the inherent atomic diamagnetism must be applied to the measured value. These corrections were obtained from the values reported by Selwood⁶⁸ and amounted to -380×10^{-6} emu/mole. This correction was applied to the measured susceptibility by subtracting the diamagnetic correction from the measured susceptibility. This resulted in a corrected molar susceptibility (χ_M^{corr}) of ca. 185×10^{-6} emu/mole. This

value, being positive and independent of temperature, was attributed to temperature independent paramagnetism.

Since temperature independent paramagnetism does not require the presence of unpaired electrons in the ground state, it can be concluded that none were present in the chloride complex. Similar behavior was expected of the bromide and iodide analogs due to the similarity of their proton NMR spectra to that of the chloride. This will be discussed in greater detail in the following section. The actual magnetic susceptibilities of the bromide and iodide, however, were not determined.

From the observed lack of a temperature dependent magnetic susceptibility for $\text{Nb}_2\text{Cl}_6(\text{SC}_4\text{H}_8)_3$ it can be concluded that the valence electrons of the metal atoms are involved in some mechanism which effectively cancelled out any normal paramagnetic behavior which they could have possibly exhibited. One of the easiest mechanisms to visualize would be the formation of direct metal-metal bonds between the two niobium atoms. Since there were two valence electrons donated by each niobium atom, a bond order of two for this metal-metal interaction is postulated.

Electronic Spectra.—The electronic spectra of the series of complexes $\text{Nb}_2\text{X}_6(\text{SC}_4\text{H}_8)_3$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) were recorded in the range 5-32 kK ($1 \text{ kK} = 1000 \text{ cm}^{-1}$). These are reproduced in Figures 3a—3c. The absorption maxima

Figure 3a.—Electronic spectrum of $\text{Nb}_2\text{Cl}_6(\text{SC}_4\text{H}_8)_3$ in benzene.

Figure 3b.—Electronic spectrum of $\text{Nb}_2\text{Br}_6(\text{SC}_4\text{H}_8)_3$ in benzene.

Figure 3c.—Electronic spectrum of $\text{Nb}_2\text{I}_6(\text{SC}_4\text{H}_8)_3$ in benzene.

and estimated molar extinction coefficients are tabulated in Table II. Since definitive structural information concerning this series of compounds is lacking, no statements can be made as to the exact nature of their electronic configurations. This precludes any quantitative discussion and assignment of their electronic spectra.

It is worthy of note, however, that the chloride and bromide spectra corresponded very well. From the number of observed maxima, their frequencies, and estimated extinction coefficients, it could be concluded that the electronic structure of these two compounds was completely analogous. In the case of the iodide, the appearance of one more absorption band and the frequencies and intensities of the three observed highest energy transitions could have possibly indicated a difference in the electronic arrangement possessed by this molecule. The molecular structure of the iodide was thought to be very similar, if not the same, to the structure of the chloride and bromide. No data were obtained which would discount this conclusion and evidence in favor of it was obtained from the proton magnetic resonance spectra and also from the infrared spectra which will be discussed shortly.

In order to better verify the existence of similar species in solution and in the solid state, the diffuse reflectance spectrum of $\text{Nb}_2\text{Cl}_6(\text{SC}_4\text{H}_8)_3$ was determined as

Table II
Absorption Band Parameters for
 $\text{Nb}_2\text{X}_6(\text{SC}_4\text{H}_8)_3$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$)^a

Cl		Br		I	
ν , kK ^b	ϵ ^c	ν , kK ^b	ϵ ^c	ν , kK ^b	ϵ ^c
18.4	430	17.4	600	27.8	865
13.1	8	11.9	11	21.1	271
11.5 ^d	5	10.5 ^d	8	15.9	175
9.1	3	8.0	3	9.9	3
				6.6	1

^aSpectra obtained in benzene solutions at ca. 25°C.

^b1 kK = 1000 cm⁻¹. ^cEstimated molar extinction coefficients per dimeric formulation. ^dShoulder.

described in the discussion of experimental techniques. This spectrum, together with the corresponding solution spectrum, is shown in Figure 4. As is apparent from this presentation, the electronic properties of this complex changed very little upon dissolution in benzene. From this it can be concluded that no important structural change took place in going from the solid state into a solution of benzene.

Infrared Spectra (1400—700 cm^{-1}).—This region of the infrared spectrum (1400—700 cm^{-1}) is of interest since absorptions arising from vibrations directly associated with tetrahydrothiophene are usually observed here. The infrared spectra exhibited in this region by the series of compounds $\text{Nb}_2\text{X}_6(\text{SC}_4\text{H}_8)_3$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) were obtained as Nujol mulls. The frequencies and relative intensities of the absorptions observed are presented in Table III. Table IV contains data for tetrahydrothiophene as the pure liquid and in solution and for various complexes in which tetrahydrothiophene was incorporated as a ligand. As is apparent from these data the tetrahydrothiophene present in the $\text{Nb}_2\text{X}_6(\text{SC}_4\text{H}_8)_3$ complexes exhibited spectral properties analogous to those in previously reported studies. The only differences noted were the appearance of a few new absorbances as shoulders on certain bands and the apparent splitting of a few absorbances into closely-spaced

Figure 4.—Electronic spectra of $\text{Nb}_2\text{Cl}_6(\text{SC}_4\text{H}_8)_3$.

Table III
Infrared Frequencies (cm^{-1}) for
 $\text{Nb}_2\text{X}_6(\text{SC}_4\text{H}_8)_3$ (1400-700 cm^{-1})^a

X = Cl	X = Br	X = I
810 s	806 m-s	804 m
886 s	882 s	881 m
959, 964 s, s	958 m-s	958, 966 m-s, m (sh)
1027 w-m (sh)	1021 w	1023 w
1041 m	1037 w-m	1040 w
1083 m	1072, 1082 w-m, w	1078 m
1129 s	1125 m-s	1131 s
1194, 1203 w-m (sh), m	1200 w	1200 w
1214 m	1211 w-m	1213 w
1248, 1256 m (sh), s	1252 m	1254 m
1270 m-s	1267 m	1269 m
1308 s	1306 s	1307 s
1326 w	1330 vw	

^aSpectra obtained from Nujol mulls. Abbreviations: s, strong; m, moderate
w, weak; sh, shoulder; v, very.

Table IV
Infrared Frequencies (cm^{-1}) for Tetrahydrothiophene (THT)
and Complexes Containing Tetrahydrothiophene ($1400\text{--}700\text{ cm}^{-1}$)

THT (ℓ) ^b	THT (in CS_2) ^c	$\text{AlCl}_3 \cdot \text{THT}$ ^b	$\text{GaCl}_3 \cdot \text{THT}$ ^b	$\text{NbCl}_4 \cdot 2\text{THT}$ ^c
816 m-s	816 m	806 m-s	805 m	801 m
876 m	882 s	876 m-s	878 m-s	872, 881 m, m
		908 w		
957 m		947 m	950 m	960 m
	996 s			1025 w
	1035 w-m			1038 w
	1060 w-m	1076 w	1082 w-m	1075 w-m
1130 w	1129 w-m	1132 w-m	1134 w	1128 w-m
1195 w-m	1197 m	1200 w-m	1200 w (sh)	1193 w
1210 w	1215 w (sh)	1210 w-m	1210 w-m	1214 w-m
1257 m	1256 s	1259 s	1262 s	1254 m
		1275 m	1278 m-s	1267 w-m
1310 w	1308 w-m	1310 m	1313 m	1308 w-m

^aSpectra obtained from Nujol mulls or as otherwise noted. Abbreviations:

s, strong; m, moderate; w, weak; sh, shoulder. ^bReference 69. ^cReference 70.

(ca. 10 cm^{-1}) doublets. It was felt that this could possibly arise from the differences in coordination positions which tetrahydrothiophene is postulated to occupy in this new series of compounds. Since no detailed analysis of the infrared spectrum of tetrahydrothiophene has been reported to date, little else can be said as to the nature of the vibrations causing the observed absorption bands. It is felt that further discussions as to the nature and causes of the new shoulders and bands in the spectra of these complexes would be inappropriate until more detailed structural data become available. It can be concluded, however, from these infrared spectra and the previously discussed proton magnetic resonance spectra that tetrahydrothiophene was present in these complexes as simple ligands and that no apparent structural change had occurred to the ligand molecules present in the complexes.

The possibility of hydrides being present in the $\text{Nb}_2\text{X}_6(\text{SC}_4\text{H}_8)_3$ complexes was discussed briefly in the section on proton magnetic resonance. The relation between hydrides and infrared spectra will now be considered. Strong, sharp absorptions in the region $2250\text{--}1700\text{ cm}^{-1}$ are usually indicative of metallic hydrides.⁷¹ In particular, Nb-H stretching frequencies have been observed in the range $1635\text{--}1735\text{ cm}^{-1}$.¹⁷ Although no data are included in Table III which describe infrared absorption bands at

energies greater than 1400 cm^{-1} , inspection of these regions for the compounds of interest in this study revealed no absorption bands assignable to Nb-H stretching vibrations. Hence it can definitely be concluded that no metal hydrides were present.

Infrared Spectra (700 cm^{-1} — 100 cm^{-1}).—This region of the vibrational spectra of the complexes $\text{Nb}_2\text{X}_6(\text{SC}_4\text{H}_8)_3$ is of interest because absorbances attributable to metal-halogen and metal-sulfur vibrations should be found in this region together with a few vibrations of the tetrahydrothiophene ligands. Spectra obtained for these compounds in Nujol mulls are presented graphically in Figure 5 and the data are tabulated in Table V. Discussion of the vibrations arising from coordinated tetrahydrothiophene ligands will be presented first.

The frequency associated with carbon-sulfur stretching vibrations in thioethers is expected to be in the range 600 — 800 cm^{-1} .⁷² For dimethyl sulfide $\nu(\text{C-S})$ has been assigned to a band occurring at 692 cm^{-1} .⁷³ Upon coordination of dimethyl sulfide to a metal atom, this band shifted to the 660 — 690 cm^{-1} region of the spectrum.^{46,51,54} It was suggested that the corresponding $\nu(\text{C-S})$ band of tetrahydrothiophene occurs at 683 cm^{-1} .⁶⁹ The frequency of this band has been reported to shift into the region 660 — 670 cm^{-1} upon coordination.^{46,51,54} In the present

Figure 5.—Schematic representation of infrared absorption band data.

Table V
Infrared Frequencies (cm^{-1}) for
 $\text{Nb}_2\text{X}_6(\text{SC}_4\text{H}_8)_3$ and Tetrahydrothiophene (THT)
(700—100 cm^{-1})

X = Cl	X = Br	X = I	THT (ℓ) ^b
120 m-s	127 m	123 m	
156 w			
183 m	176 m	189 s	
206 m-s	198 m-s	201 m	
230 m	232 s	231 s	
	255 m (sh)		
264 m-s	266 vs	247 s	
282 vvw	284 s	280 vvw	280 vw
318 vs (sh)	320 m-s	322 m	
330 vs (sh)	333 w-m (sh)		
341 vvs			
475 w			270 m
502 w-m	500 m	496 w-m	
521 w	520 vw	516 w-m	520 m
	529 vvw		
673 m	669 m	664 w-m	683 m

^aSpectra obtained from Nujol mulls or as otherwise noted.

Abbreviations: s, strong; m, moderate; w, weak; sh, shoulder; v, very. ^bReference 69.

study a similar shift has also been noted. The $\nu(\text{C-S})$ bands in the chloride, bromide, and iodide have been assigned as those at 673, 669, and 664 cm^{-1} respectively. Since no band was observed at ca. 683 cm^{-1} , the conclusion that no uncoordinated tetrahydrothiophene was present was reaffirmed. No evidence was found, however, for a splitting of this band due to the different types of coordination of tetrahydrothiophene as postulated from the resonance patterns observed in the proton magnetic resonance spectra of these complexes. It is possible that donation of both lone pairs of electrons on the sulfur (as would be the case for a bridging tetrahydrothiophene) did not effect the structural aspects of the ligand skeleton enough to cause a pronounced difference in the carbon-sulfur stretching vibration. Unfortunately, data were not available for the one other known compound, $\text{Rh}_2\text{I}_2(\text{CH}_3)_4[\text{S}(\text{CH}_3)_2]_3$, which contained both terminal and bridging alkyl sulfide ligands that could show if a splitting of this band actually occurred.⁵⁶

Other bands of tetrahydrothiophene occurring in this region are found at 520, 470, and 280 cm^{-1} . The two higher frequency absorptions (520 and 470 cm^{-1}) appeared to give rise to three absorptions in both the chloride (521, 502, and 475 cm^{-1}) and the bromide (529, 520, and 500 cm^{-1}). The relatively weak absorption at 280 cm^{-1} in the spectrum of the free ligand was also evident in the chloride and

iodide. In the bromide spectrum an intense absorption at 284 cm^{-1} apparently obscured this band.

Since the homologous series of compounds has been synthesized and their infrared spectra recorded, it was possible to tentatively assign the observed absorption bands according to the nature of the vibrations involved. Inspection of the appropriate spectra quickly revealed bands at ca. 230 and 318 cm^{-1} which shifted very little with variation of the halide. These were tentatively assigned as arising from vibrations involving the metal and the sulfur atoms. Further inspection revealed one more band in each spectrum (Cl, 264 cm^{-1} ; Br, 266 cm^{-1} ; I, 247 cm^{-1}) which was also assigned as originating from some type of metal-sulfur vibration.

Since the structure of the complexes was not known, it was impossible to definitely assign these bands as to the nature of the metal-sulfur linkage which caused the observed absorptions. These complexes have been postulated to contain both bridging and terminal sulfide ligands and, therefore, it should be theoretically possible to distinguish between the bands arising from each of these different bonding arrangements. One possible solution to this problem would be to assign the lowest frequency band to the stretching of the metal-sulfur terminal vibrations. This type of argument suggesting greater

strength being present in bonds to terminally positioned ligands as opposed to bonds to bridging ligands has been made in the case of binuclear complexes of platinum, palladium and rhodium.⁶² This train of thought seemed to work well if halide bridges were present. In the case of certain compounds, namely, $\text{Pt}_2\text{X}_4(\text{SR}_2)_2$ ($\text{X} = \text{Cl}, \text{Br}$; $\text{R} = \text{CH}_2\text{CH}_3, \text{CH}_2\text{CH}_2\text{CH}_3, \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), the halogen-sensitive vibrational frequencies were easily identified but could not be fit to the normal pattern expected for Pt-X-Pt type of bridges. The spectra were consistent with that of $\text{Pt}_2\text{Br}_4[\text{S}(\text{C}_2\text{H}_5)_2]_2$ which was known to possess sulfide bridges.^{60,61} It was found in this complex that the platinum-sulfur bridge bond was significantly shorter than expected. This was also exemplified by a platinum-sulfur stretching frequency approximately $90\text{--}100\text{ cm}^{-1}$ higher than those found in cases where an organic sulfide is bonded terminally to a platinum atom. Mindful of this, it would be tempting to assign the band occurring in the range $318\text{--}322\text{ cm}^{-1}$ in the case of the Nb(III) complexes as arising from the presence of a bridging tetrahydrothiophene. Evidence against this possible assignment will be presented in the discussion of the compounds isolated from meta-thetical reactions involving $\text{Nb}_2\text{Cl}_6(\text{SC}_4\text{H}_8)_3$. Until precise structural data become available, no definite assignments will be attempted concerning the nature of the bonds

responsible for the presence of these infrared absorbances. It should be noted, however, that the stretching frequencies assigned to niobium-sulfur vibrations in the series of complexes $\text{NbX}_4 \cdot 2(\text{SC}_4\text{H}_8)$ appeared at ca. 302 cm^{-1} and 276 cm^{-1} .⁴⁶ These are located in the span of frequencies in which the absorptions assigned as arising from niobium-sulfur vibrations in this study were found. In the Nb(IV) study, the metal-sulfur vibrations were found to produce relatively weak absorptions in contrast to this work.

It is impossible to predict the maximum number of metal-halogen stretching vibrations which could arise from the compounds $\text{Nb}_2\text{X}_6(\text{SC}_4\text{H}_8)_3$. Certain bands in the spectra of the chloride, bromide, and iodide analogs definitely show a dependence on the type of halogen present. In the chloride, bands were observed at 341 cm^{-1} and 330 cm^{-1} . These appeared to have shifted to 284 and 255 cm^{-1} in the bromide. The iodide did not exhibit such obvious behavior. In this case bands of moderate to high intensity were observed at 201 and 189 cm^{-1} . Although absorptions were seen in this region in both the chloride and bromide spectra, changes in intensity of these bands going to the iodide could have indicated a coincidence in frequency of the metal-iodine stretching frequencies with vibrations associated with other aspects of the structure.

Of interest was the position of the highest frequency assignable to a metal-halogen stretching vibration in each compound. In $\text{Nb}_2\text{Cl}_6(\text{SC}_4\text{H}_8)_3$ this occurred at 341 cm^{-1} . This was much lower than the corresponding band in the spectrum of $\text{NbCl}_4 \cdot 2(\text{SC}_4\text{H}_8)$ which was seen at 397 cm^{-1} .⁴⁶ In the spectrum of $\text{NbCl}_4 \cdot 2(\text{CH}_3\text{CN})$ the highest metal-chlorine vibration was assigned at 365 cm^{-1} while in $\text{NbCl}_5 \cdot (\text{CH}_3\text{CN})$ this frequency was found to be 440 cm^{-1} .⁷⁴ The apparent decrease in metal-halogen stretching frequency with decrease in the formal oxidation state of the metal ion was not unexpected.

No conclusions can be drawn from the infrared spectra of these compounds regarding the possible existence of both bridging and terminal halides. Detailed structural analyses by means of single crystal X-ray crystallography would definitely resolve this problem. Interpretation of the complete nuclear quadrupole resonance spectra (NQR), together with variable temperature NQR studies, could also be helpful.⁷⁵

Other absorption bands are present in the infrared spectra of the $\text{Nb}_2\text{X}_6(\text{SC}_4\text{H}_8)_3$ series. These are found in the range of $100\text{--}200\text{ cm}^{-1}$. No attempt to assign these bands will be made at present.

X-Ray Crystallography.—In an effort to elucidate the exact structure of these niobium(III) complexes, a

three-dimensional X-ray crystallographic structural determination was undertaken. A sample of $\text{Nb}_2\text{Cl}_6(\text{SC}_4\text{H}_8)_3$ was recrystallized from benzene yielding rather poorly shaped crystals. A roughly cylindrically shaped crystal ca. 0.2 mm in diameter and 0.3 mm long was wedged in a thin-walled glass capillary under an argon atmosphere in a drybox. The capillary was sealed off using a small flame after it had been removed from the drybox. The crystal appeared to be stable in this environment indefinitely and no apparent decomposition took place during the course of this study.

After the capillary containing the crystal had been mounted on a suitable goniometer head, preliminary photographs of the crystal were taken using a Buerger precession camera and copper or molybdenum radiation. Initial diffraction patterns revealed no intelligible symmetry elements as being present. Subsequent photographs and adjustments allowed the determination of the three axes and corresponding angles of what was postulated to be a triclinic unit cell.

The crystal was then transferred to a completely automated Hilger-Watts four circle diffractometer which was used for the collection of diffraction data. Three non-coplanar reflections were needed to define the angle settings on the diffractometer which would allow collection and correct indexing of the remaining reflections. The

three originally chosen were the 100, 011, and 010 reflections. These low order reflections were chosen since relatively strong, higher order reflections were not observed on the original diffraction photographs. Data collection was undertaken and an initial data set consisting of ca. 250 reflections was obtained. This data set was inspected to locate three higher order reflections of moderate intensity. It should be noted that high order reflections are more desirable as standards since their positions at larger diffractometer angle settings will minimize errors in the settings needed to observe other reflections. The 003, 400, and 030 reflections were found to be suitable for this purpose. These reflections were also remeasured periodically during subsequent data collection to check for any loss of intensity due to movement of the crystal or decomposition. A hemisphere of reflections with $\theta \leq 25^\circ$ was then measured yielding ca. 1380 independent intensities. Cell dimensions were derived from the angle settings associated with the three standard reflections and were found to be: $a = 7.32$, $b = 7.23$, $c = 7.75 \text{ \AA}$, and $\alpha = 93.3$, $\beta = 106.3$, $\gamma = 100.9^\circ$. Assuming one dimeric formulation, $\text{Nb}_2\text{Cl}_6(\text{SC}_4\text{H}_8)_3$, of molecular weight 663 grams per mole, per unit cell ($383.9 \text{ \AA}^3$), the density was calculated to be 2.87 g/cm^3 . Attempts were made to measure this by the flotation method, but the compound proved to be too soluble in all of the

common organic solvents having densities in this range. It can be concluded, however, that this was a reasonable value for a compound of this type. For comparison, the density of $\text{Cs}_3\text{Nb}_2\text{Cl}_9$ was expected to be 3.60 g/cm^3 but this was also not measured.¹¹ The density of $[(\text{C}_5\text{H}_5\text{Nb}(\text{CO})-(\text{C}_6\text{H}_5)_2\text{C}_6\text{H}_5)]_2$ was found to be 1.58 g/cm^3 .¹⁴

With the postulated one dimeric molecule per unit cell, the choice of space group was limited to P1 since there was an odd number of tetrahydrothiophene ligands in each dimeric unit. The possibility of a perfectly disordered crystal of space group $\text{P}\bar{1}$ cannot be overlooked.

Initial treatment of the data consisted of the application of corrections which converted the observed data into observed intensities. These corrections were for both Lorentz and polarization phenomena. At the same time intensities considered not to be statistically above the observed background readings were rejected. All of these considerations resulted in ca. 850 observed intensities.

These observed intensities were then used as phaseless coefficients in a Fourier synthesis which resulted in the calculation of a Patterson map. This map should contain $N^2 - N$ peaks (where N = number of atoms in the asymmetric unit cell) not considering the origin. In this structure, 2162 peaks should be present. Many of

these will be lost from view, however, because of the presence of 24 hydrogen atoms in the structure. Since the Patterson map can be thought of as the collection of vectors drawn from each atom of the structure to all other atoms in the structure, when each atom is in turn placed at the origin of the map, the large number of peaks could seem overwhelming. However, it should be noted that the actual intensity of a peak is proportional to the product of the atomic numbers of the atoms causing the interaction. Hence, in this structure, peaks originating from Nb-Nb, Nb-S, and Nb-Cl interactions should have stood out. In fact the peak caused by the second niobium atom when the first was at the origin should have been immediately obvious. (There should have actually been two peaks arising from Nb-Nb interactions in the map excluding the origin since $N^2 - N$ for two atoms is two.) In the Patterson map obtained in this study, no peaks stood out to such an extent that simple assignment of one as the second niobium atom was not possible. This remained true even after the map was sharpened by means of suitable mathematical manipulations.

Since there were two niobium atoms in this structure, it was felt that phasing of the structure factors was controlled mainly by these relatively heavy atoms. Assignment of the origin as the location of one niobium

atom, followed by an appropriate structure factor calculation, resulted in a residual index (or R) of 0.459. Placing a second niobium atom at possible positions as determined from the Patterson map and again performing a structure factor calculation resulted in increases in the R value. This was felt to be rather strange behavior but considering the fact that the two niobium atoms account for only 25% of the total number of electrons in each dimeric molecule, it was thought that this observed behavior may not have been too unusual. The question of the position of the second niobium atom was still unresolved since no one location for it gave an R value significantly lower than the other positions.

At this point it was felt that the Patterson superposition technique might possibly elucidate the structure hidden in the Patterson map. Unfortunately, no intelligible array of atoms could be deduced from the application of several successive weighted Patterson superpositions.

An attempt was then made to check the correctness of certain likely positions obtained from both Patterson maps and also from electron density maps generated from structure factors obtained when one niobium atom was assigned as being located at the origin. This was done by using a discriminator function as described by Hackert and Jacobson.⁷⁶ The value of this discriminator function

depends upon the absolute value of the difference between the observed Patterson function and the calculated Patterson function arising from the structural fragment whose correctness is being tested. The originators of this testing procedure have found it to be a very useful and effective way of testing the correctness of relatively small fragments of structures at points in the process of structural determinations when the conventional R value was very insensitive to additions of one or two atoms to a known fragment of comparable size. Their studies also included the discriminator function's relation to small translations of atoms from their correct positions and also to the scaling of the observed structure factors.

In the attempt to solve the crystal structure of $\text{Nb}_2\text{Cl}_6(\text{SC}_4\text{H}_8)_3$, the discriminator function was found to be extremely sensitive to the scaling of the observed structure factor data. This was in contrast to the behavior found by Hackert and Jacobson.⁷⁶ This was not considered unusual since so little work has been done to determine the exact properties of this discriminator function. It is worthy of note, however, that the scale factor finally used in the application of the discriminator function to the niobium(III) complex structural determination closely approximated the scale factor determined previously using a Wilson plot.

A position was finally located which according to the discriminator function could be assigned to the second niobium atom. In considering the positions of the two niobium atoms, calculations showed that they were separated by ca. 2.6 Å. If this were indeed correct, the distance would be shorter than any other Nb-Nb bond in any known compound. This actual bond length could have lengthened, however, during subsequent location and insertion of the remaining atoms into the structure and various refinements in the structural determination. An increase of 0.1 Å in this distance would have brought it into close agreement with other reported niobium-niobium double bond distances.

Subsequent position testing with the discriminator function yielded positions for a number of chlorine, sulfur, and carbon atoms. A structure factor calculation at this point based on two niobiums, one sulfur, three chlorines, and six carbons resulted in an R factor of 0.439. It appeared that this process employing the discriminator had really done little in elucidating the structure since the apparent positions for these twelve atoms could not be interpreted in any chemically significant way. Also the usefulness of the discriminator function appeared to have been exhausted since any subsequent position and atom type tested was flatly rejected.

Another approach to the problem of elucidating the structure of $\text{Nb}_2\text{Cl}_6(\text{SC}_4\text{H}_8)_3$ was investigated. This consisted of the use of a series of programs called the 3-E Map Method for crystal structure determinations.⁷⁷ This method consisted of a suitable mathematical conversion of the observed structure factors to normalized unitary structure factors (E's). Three of these normalized unitary structure factors were chosen according to certain criteria (namely, magnitude and origin determining capability) and were then used to generate an electron density map, appropriately called the 3-E map. A Patterson map was then superimposed on the 3-E map both origin-to-origin and also with the origin of the Patterson map on suspected atom positions in the 3-E map. This resulted in a type of superposition map and through appropriate calculations, coefficients of the Fourier transform of the superposition map were generated. These coefficients were used to phase the aforementioned E's. The largest of the phased E's were then used to generate another electron density map of higher reliability which was used to recycle the entire process. Treatment of the observed structure factors obtained in this study, together with the use of discriminator-tested atom positions for superpositions, resulted in the generation of a final electron density map which resembled closely those obtained by other methods.

In analogy to these previous maps, this newly generated electron density map also was immune to logical interpretation.

A last attempt was made to interpret the observed diffraction data using the direct phasing program MULTAN. This program, developed by P. Main, M. W. Woolfson, and G. Germain, was described as being applicable to the automatic solution of crystal structures. It was based on the tangent formula of Karle and Hauptman.⁷⁸ MULTAN could be employed in two ways. The first consisted of inputting certain known phases of high reliability. The program would then use these to determine the phases of all of the other structure factors. The second method of usage allowed the program to choose its own starting phases and then proceed from there with the solution of the crystal structure. Both methods were tried. The known starting phases employed were those of highest reliability as determined by the 3-E program sequence.

Electron density maps generated by the phased structure factors from MULTAN in both modes of operation were identical. They were also remarkably similar to all of the other electron density maps obtained by various techniques during the course of this study. In a similar manner, they also failed to yield any chemically significant information.

It was then decided that the collection of diffraction data for the corresponding bromide compound could serve the two-fold purpose of both solving a separate analogous structure and also possibly helping with the interpretation of the diffraction data obtained from the chloride compound. Attempts to locate a suitable single crystal of $\text{Nb}_2\text{Br}_6(\text{SC}_4\text{H}_8)_3$ were all unsuccessful. All crystals inspected exhibited diffraction patterns of polycrystalline materials. Upon examination under a microscope many of these crystals had physical appearances which suggested that they might actually be discrete single crystals, but rotation photographs showed them to be made up of more than one crystal. This was evidenced by what appeared to be the start of powder rings on the films. These powder rings were actually an elongation of the spots on the films in a direction perpendicular to the direction of elongation expected from the use of unfiltered radiation.

Since the bromide analog showed a propensity for such behavior, a similar picture of the crystal used to obtain diffraction data for the chloride compound was taken at a random orientation. This picture showed a similar pattern of elongation of the spots in the wrong direction. This meant that the crystal used to collect data was not actually a single crystal. Hence, the data collected from this crystal were unreliable and useless. However, it was felt

that the unit cell parameters determined previously were reliable to some degree and the assignment of a triclinic unit cell was still reasonable.

Characterization of Products of Metathetical Reactions

Preliminary Observations.—Exposure of $[(C_2H_5)_4N]_2Nb_2Cl_8 \cdot (SC_4H_8)$ to atmospheric oxygen and water vapor resulted in decomposition but at a much slower rate than that observed for $Nb_2Cl_6(SC_4H_8)_3$. Samples of this substituted salt left exposed to the atmosphere retained their color for a period of many days. No attempt was made to determine the exact rate of decomposition, but it was concluded that this was the most stable compound synthesized during the course of this study. Unfortunately, this compound exhibited an extremely low solubility in common hydrocarbon and chloro-carbon solvents. This precluded any possible studies of it in solution.

$[(C_2H_5)_4N]_3Nb_2Cl_9$ exhibited a much higher reactivity toward oxygen and water vapor. Samples appeared to lose most, if not all, of their color within a period of exposure to the atmosphere of one day. Although this compound appeared to be appreciably soluble in dichloromethane, no solution studies were carried out because of the possible reaction of the complex with this solvent as described earlier.

Since both of these compounds were plagued with problems concerning solution studies, characterization was carried out only in the solid state. These studies included determination of magnetic susceptibilities, electronic spectra, and infrared spectra. The results obtained will now be discussed in that order.

Magnetic Susceptibility.—The magnetic susceptibilities of both of the above-mentioned compounds were determined over the range 77—297°K. Both were found to exhibit a paramagnetic susceptibility which was independent of temperature. $[(C_2H_5)_4N]_2Nb_2Cl_8(SC_4H_8)$ possessed a measured susceptibility of $-322 (\pm 22) \times 10^{-6}$ emu/mole. Applying the diamagnetic corrections appropriate for the number and types of atoms present in the compound, a value for χ_M^{corr} was calculated to be 210×10^{-6} emu/mole. This agreed very well with the value of 185×10^{-6} emu/mole for $Nb_2Cl_6(SC_4H_8)_3$. This was a good indication that little change to the electronic skeleton of the compound had taken place upon substitution of chloride ions for two of the tetrahydrothiophene molecules previously present. It can be postulated that the substitutions which have occurred did not have a great influence on the valence electrons of the metals which were thought to be participating in direct metal-metal bonds.

It can be inferred from this observed behavior that the tetrahydrothiophene which remained intact in the compound was the one postulated to be acting as a bridge between the two metal atoms. This could probably be verified by means of the proton magnetic resonance spectrum of the compound. Unfortunately, this was not performed because of the extremely low solubility exhibited by this compound.

While the temperature dependence of the magnetic susceptibility of $[(C_2H_5)_4N]_3Nb_2Cl_9$ was analogous to that exhibited by the partially substituted compound, the actual magnitude differed considerably. The completely chloride substituted product displayed a temperature independent paramagnetic susceptibility, corrected for inherent diamagnetic effects, of ca. 960×10^{-6} emu/mole. From this value a room temperature effective magnetic moment of 1.51 BM was calculated. Obviously complete substitution of tetrahydrothiophene by chloride ions has affected the electronic structure of this compound to a greater degree than was found for partial substitution. Further evidence for this will be given in the discussion of the solid state electronic spectra exhibited by these compounds.

It would be of great interest to compare the appreciably high temperature independent paramagnetism of

$[(C_2H_5)_4N]_3Nb_2Cl_9$ with that of $Cs_3Nb_2Cl_9$. The synthesis of this compound together with pertinent structural considerations have recently been reported as was previously noted.¹¹ While this communication reported the magnetic properties of the analogous bromide and iodide compounds, it failed to discuss those of the chloride. The reason for this was not understood. The possibility exists that the chloride exhibited a susceptibility markedly different from that of the bromide and iodide and that an explanation for this was still lacking at the time of publication. It should be noted that the bromide and iodide exhibited Curie-Weiss paramagnetic behavior over the temperature range 200—500°K. Magnetic moments were in the range 2.6—2.8 BM per dimeric formulation. This is what would be expected for two unpaired electrons per dimer. Whether this relatively well-behaved magnetic susceptibility would change drastically in going to the chloride analog is a question which must be answered by further experiment.

Electronic Spectra.—During the synthesis of $[(C_2H_5)_2N]_2^- Nb_2Cl_8(SC_4H_8)$ no drastic color change from that of the starting material $Nb_2Cl_6(SC_4H_8)_3$ was noted. It can be surmised that this behavior was observed because little or no change had occurred to the chromophoric group present in this compound. If this were indeed the case, no drastic changes should have been evident in the electronic

spectrum exhibited by this compound. Inspection of the diffuse reflectance spectra of $[(C_2H_5)_4N]_2Nb_2Cl_8(SC_4H_8)$ in the region 8—28 kK revealed the presence of three obvious absorptions located at 9.7, 11.2 and 18.1 kK. The lowest frequency absorption appeared as a shoulder on the 11.2 kK absorption band. This spectrum is presented in Figure 6.

A simple correlation between this spectrum and that of $Nb_2Cl_6(SC_4H_8)_3$ (Figure 4) can be made. The three absorption bands exhibited by $[(C_2H_5)_4N]_2Nb_2Cl_8(SC_4H_8)$ in the spectral region studied appeared to be related to the three highest energy transitions observed for $Nb_2Cl_6(SC_4H_8)_3$. The relative positions and intensities of the absorption bands in each case were completely analogous. The only difference noted was the apparent shift of the entire spectral pattern to lower frequencies upon substitution of chloride ions for two of the tetrahydrothiophene molecules present in $Nb_2Cl_6(SC_4H_8)_3$. This bathochromic shift prevented the observation of the absorption band corresponding to the 8.85 kK absorption of $Nb_2Cl_6(SC_4H_8)_3$ due to the relatively small spectral region made available by the spectrometer employed. It can be concluded, however, that the electronic arrangements present in the chromophoric group in each of these compounds were quite similar. This was in complete agreement with the observed magnetic properties for these compounds and reinforced the postulation that the

Figure 6.—Diffuse reflectance spectrum of $[(C_2H_5)_4N]_2Nb_2Cl_8(SC_4H_8)$.

tetrahydrothiophene molecule which was not affected by this substitution reaction was in a bridging position between the two niobium atoms.

Complete substitution of chloride ions for the tetrahydrothiophene molecules present in the complex affected the nature of the valence electrons to a much greater degree. The variance in color between $[(C_2H_5)_4N]_2^- Nb_2Cl_8(SC_4H_8)$ and $[(C_2H_5)_4N]_3Nb_2Cl_9$ and the difference in the measured values of the magnetic susceptibilities of the two compounds tended to indicate that replacement of the last tetrahydrothiophene molecule had substantially altered the complex's electronic configuration. This fact was verified by the diffuse reflectance spectrum which the completely substituted salt exhibited. This spectrum is presented in Figure 7. The relatively intense absorption bands at 8.9, 14.8, and 18.3 kK could not be correlated with the spectra exhibited by the corresponding unsubstituted or partially substituted compounds. At present the absorption spectrum of $Cs_3Nb_2Cl_9$ has not been reported.¹¹ Comparison of the spectrum of this previously-reported compound with that of the tetraethylammonium compound of similar formulation prepared in the present study would be of great help in elucidating the nature of the anionic species present.

Figure 7.—Diffuse reflectance spectrum of $[(\text{C}_2\text{H}_5)_4\text{N}]_3\text{Nb}_2\text{Cl}_9$.

Infrared Spectra (1400—700 cm^{-1}).—The frequencies and relative intensities of the absorption bands found in this infrared region for the partially and completely chloride substituted products are tabulated in Table VI. Data for tetraethylammonium chloride are also presented. As is apparent from this listing, this spectral region was rich in absorbances arising from the various compounds being studied.

While most of the absorption bands in this region attributable to $[(\text{C}_2\text{H}_5)_2\text{N}]_2\text{Nb}_2\text{Cl}_8(\text{SC}_4\text{H}_8)$ and $[(\text{C}_2\text{H}_5)_4\text{N}]_3\text{Nb}_2\text{Cl}_9$ can be assigned as arising from the presence of tetraethylammonium cations, a few are not. A weak absorbance at 885 cm^{-1} in the spectrum of $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{Nb}_2\text{Cl}_8(\text{SC}_4\text{H}_8)$ corresponded to an absorption at 886 cm^{-1} for the unsubstituted complex, $\text{Nb}_2\text{Cl}_6(\text{SC}_4\text{H}_8)_3$ and can be assigned as arising from the presence of coordinated tetrahydrothiophene. No similar absorption for $(\text{C}_2\text{H}_5)_4\text{NCl}$ or $[(\text{C}_2\text{H}_5)_4\text{N}]_3\text{Nb}_2\text{Cl}_9$ was evident. Similar behavior could be seen for the bands at 1284 cm^{-1} and 1324 cm^{-1} in the spectrum of the partially substituted product. The band at 966 cm^{-1} might also be assignable to tetrahydrothiophene since no absorption was present in this region for the completely substituted complex. However, the presence of a band at 961 cm^{-1} in the spectrum of tetraethylammonium chloride makes this assignment questionable. A tentative assignment of this

Table VI
Infrared Frequencies (cm^{-1}) for $(\text{C}_2\text{H}_5)_4\text{NbCl}$
and Chloride-substituted Products ($1400\text{--}700\text{ cm}^{-1}$)^a

$(\text{C}_2\text{H}_5)_4\text{NbCl}$	$[(\text{C}_2\text{H}_5)_4\text{Nb}]_2\text{Nb}_2\text{Cl}_8(\text{SC}_4\text{H}_8)$	$[(\text{C}_2\text{H}_5)_4\text{Nb}]_3\text{Nb}_2\text{Cl}_9$
792 s	789 s	792 s
834 vvw		
898 vw	885 w	894 w
	909 vw	
923 vvw	931 vvw	925 m
941 vvw		
961 vw	966 w	
1009 s	999 s	1003 s
1038 m-s	1038 w	1026 s
1057 vvw (sh)	1057 m	
1083 w-m	1071 w-m	1075 m
	1092 w	
1122 w	1130 m	1124 w
1175 m (sh)	1173 s	1175 m (sh)
1186 s	1188 m (sh)	1185 s
	1248 w-m	
1275 vvw		
1305 m	1300 vw	1305 m-s
1313 m	1311 w-m	
	1324 w	
	1341 vw	
1368 m	1370 m-s	
	1390 m-s	
1396 m	1395 s (sh)	

^aSpectra obtained from Nujol mulls. Abbreviations: s, strong; m, moderate; w, weak; sh, shoulder; v, very.

same nature can be made for the absorption at 1130 cm^{-1} in the spectrum of $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{Nb}_2\text{Cl}_8(\text{SC}_4\text{H}_8)$. Because of the complexity of the vibrations of the tetraethylammonium cation which are found in this energy region, it was not possible to identify any other absorption which could be unambiguously assigned to coordinated tetrahydrothiophene molecules.

Infrared Spectra ($700\text{--}100\text{ cm}^{-1}$).—Of interest in this energy region were the absorption bands which could be assigned as arising from metal-sulfur and metal-chloride vibrations. Also of interest were the few absorbances of moderate intensity which arise from vibrations of any tetrahydrothiophene molecules which remained intact during the substitution reactions.

The spectral data in this region obtained from Nujol mulls of the partially and completely substituted products and tetraethylammonium chloride are tabulated in Table VIII. A discussion of the frequencies of vibrations involving atoms present in the tetrahydrothiophene ligands will be initially presented.

The shift upon coordination of the $\nu(\text{C-S})$ band at 683 cm^{-1} for free tetrahydrothiophene has already been discussed. As was noted, this band was found at 673 cm^{-1} for $\text{Nb}_2\text{Cl}_6(\text{SC}_4\text{H}_8)_3$. For the partially substituted complex, $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{Nb}_2\text{Cl}_8(\text{SC}_4\text{H}_8)$, a band attributable to $\nu(\text{C-S})$

Table VII

Infrared Frequencies (cm^{-1}) for $(\text{C}_2\text{H}_5)_4\text{NCl}$
and Chloride-substituted Products ($700\text{--}100\text{ cm}^{-1}$)^a

$(\text{C}_2\text{H}_5)_4\text{NCl}$	$[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{Nb}_2\text{Cl}_8(\text{SC}_4\text{H}_8)$	$[(\text{C}_2\text{H}_5)_4\text{N}]_3\text{Nb}_2\text{Cl}_9$
	117 w	132 m
	149 w-m	158 m
175 w	174 w-m	
	231 s	
	278 s	
	312 vs	303 s (sh)
		312 vs
370 vw		
394 vvw		
415 w	423 w	
460 m	473 w	472 w
	517 w-m	
	555 w	557 w
	583 vvw	
603 w	614 vvw	
	645 vw	
	663 w	
	690 w	698 w-m

^aSpectra obtained from Nujol mulls. Abbreviations: s, strong; m, moderate; w, weak; sh, shoulder; v, very.

was found at 663 cm^{-1} . As was expected, no corresponding band was found in the completely substituted complex indicating the absence of tetrahydrothiophene. While no absorptions were noted in the $500\text{--}550\text{ cm}^{-1}$ region of the spectrum of the completely substituted complex, a band of moderate intensity was observed at 517 cm^{-1} in the spectrum of the partially substituted compound. This band can be tentatively assigned as corresponding to the absorption at 520 cm^{-1} for free tetrahydrothiophene and 521 cm^{-1} for $\text{Nb}_2\text{Cl}_6(\text{SC}_4\text{H}_8)_3$.

Discussion of vibrational frequencies of metal-ligand bonds will now be presented. An absorption at $231 (\pm 1)\text{ cm}^{-1}$ has been noted in the spectra of $\text{Nb}_2\text{X}_6(\text{SC}_4\text{H}_8)_3$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). These bands had been tentatively assigned as arising from some vibration involving metal and sulfur atoms. The exact nature of this vibration was not known but is now assigned as arising from the stretching vibration of the bond between a niobium atom and the sulfur atom in the unique tetrahydrothiophene molecule. This assignment is drawn from the presence of an intense band at 231 cm^{-1} in the spectrum of $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{Nb}_2\text{Cl}_8(\text{SC}_4\text{H}_8)$. This compound was postulated as possessing a Nb-S-Nb bridge arrangement which was retained during the reaction in which the two terminally coordinated tetrahydrothiophene ligands in $\text{Nb}_2\text{Cl}_6(\text{SC}_4\text{H}_8)_3$ had been replaced. The demise of this band

upon substitution of the remaining thioether ligand tended to enforce this assignment.

Absorption bands at 312 cm^{-1} in the spectra of both substitution products can be tentatively assigned as the stretching frequencies of metal-chlorine bonds. A similar assignment for the shoulder at 303 cm^{-1} in the spectrum of the completely substituted product can be made. The partially substituted compound exhibited a band at 278 cm^{-1} of strong intensity. The exact nature of this band is unknown but it is thought that it arises from some type of niobium-chlorine vibration although no proof of this can be presented.

Other bands were present in these spectra. Some of these were readily assignable to the presence of tetraethylammonium cations. Other absorptions remained whose origins were unknown and no attempt will be made to assign these bands to possible vibrations.

CONCLUSION

Although the X-ray single crystal structural determination attempted in this study yielded no definitive information concerning the molecular geometry present in the series of complexes $\text{Nb}_2\text{X}_6(\text{SC}_4\text{H}_8)_3$, some possible structural implications can be discussed based on other observed data and physical properties.

Based mostly on the observed proton magnetic resonance spectrum, the statement has been made that there existed in these compounds what appeared to be a tetrahydrothiophene molecule in a bridging position between two niobium atoms. Assuming this is correct, two possible structural types immediately come to mind. The first of these, as shown in Figure 8a, is based on the structure of another thioether complex of a transition metal. This compound $\text{Rh}_2\text{I}_2(\text{CH}_3)_4^- [\text{S}(\text{CH}_3)_2]_3$ had been mentioned earlier in the discussion of proton magnetic spectra. As had also been noted, an X-ray crystal structure determination⁵⁷ has revealed thioethers in both bridging and terminal coordination sites. The at-present unanswerable question remains whether the niobium(III) species generated in this study could have assumed such a configuration. Some light may be thrown on this dilemma by recalling the fact that bioctahedral anions of the form $\text{Nb}_2\text{X}_9^{3-}$ have recently been reported.¹¹ Having the

Figure 8.—Some postulated structures for $\text{Nb}_2\text{Cl}_6(\text{SC}_4\text{H}_8)_3$.

some general geometry as the $\text{Cr}_2\text{Cl}_9^{3-}$ anion,¹² the $\text{Nb}_2\text{X}_9^{3-}$ anions demonstrated the ability of niobium compounds, in fact, niobium(III) compounds, to adopt the biocuboctahedral structure which possessed three bridging groups. Although the present study has uncovered some evidence for the presence of a bridging thioether, no indication as to the presence or absence of bridging halides has been made. As was noted earlier, a variable temperature NQR study might be able to differentiate between bridging and terminal halides. Photoelectron spectroscopic data could also help in distinguishing between these two types of halides if they were present. Both NQR and photoelectron spectroscopy could also furnish information concerning the chemical equality of the two niobium atoms postulated in the dimeric structure. Because of the possibility of having a rather large number of isomers of this overall structure caused by local cis and trans arrangements of thioether ligands about the individual niobium atoms, it would not be required that both niobium atoms necessarily be chemically equivalent. However, one would expect the differences to be rather slight in these cases when compared to other possible structures which would require such things as different oxidation states for each niobium atom present in the dimeric formulation. Structures of this nature will be discussed shortly.

It should be noted, however, that a triply-bridged bioctahedral structure would allow for octahedral coordination, albeit possibly distorted, around each niobium atom. From the propensity that niobium has exhibited to be six-coordinate in such compounds as NbCl_5 ,⁷⁹ NbOCl_3 ,⁸⁰ and $\alpha\text{-NbI}_4$,⁸¹ it would not be at all surprising that Nb(III) would also prefer a six-coordinate environment in the type of complexes synthesized in this study. The triply-bridged bioctahedral structure would also appear to be advantageous in allowing direct metal-metal bonding to occur. This was evident in $\text{Nb}_2\text{X}_9^{3-}$ and $\text{K}_3\text{W}_2\text{Cl}_9$ which also had this structural type and exhibited a very short W-W distance of 2.41 Å.⁸² Considering the increased stability of $\text{Nb}_2\text{X}_6(\text{SC}_4\text{H}_8)_3$ toward air oxidation and hydrolysis when compared to the niobium(IV) complexes from which they were prepared, it could be concluded that the triply-bridged bioctahedral structure may prevent oxygen, water, or other contaminants from easily entering the coordination spheres about the metal atoms. Also the triply-bridged arrangement of atoms may also "protect" the electrons present in the postulated double metal-metal bond from attack by electrophilic reagents. Hence this increased stability may be attributable to a steric rather than a thermodynamic effect. Other possible structures that will be discussed appear to be more "open" in that they provide easier pathways for

attacking atoms or molecules to enter the coordination spheres about the metals. This idea would tend to bolster the possibility that the triply-bridged bioctahedral structure is correct whereas other postulated structures are less likely to be found.

Another type of geometric arrangement in which each niobium atom could assume an octahedral coordination sphere is pictured in Figure 8b. Six-coordination in this structure would be attained by means of a direct metal-metal bond in each dimeric unit. Although no structure of this type with only one bridging group between the metal atoms has apparently been reported to date in the literature, several are known which contain two bridging groups. One is $\text{Co}_2(\text{CO})_8$ in which six-coordination about each cobalt atom was attained by the apparent formation of a metal-metal bond which was evidenced by a Co-Co distance of 2.52 Å.⁸³ Further information concerning this compound was obtained from NQR spectra which enforced the postulation of a metal-metal bond being present.⁸⁴

Two other compounds which explicitly show the effects of direct metal-metal interactions are $[\text{RhCl}(\text{CO})_2]_n$ and $\text{Rb}_3\text{Mo}_2\text{Cl}_8$. $[\text{RhCl}(\text{CO})_2]_n$ has been shown to be a polymer in the solid state.⁸⁵ In the polymer, two planar $[\text{RhCl}(\text{CO})_2]$ units were joined together by chlorine bridges. These dimeric units were not planar but were bent along the line

joining the two bridging chlorides. The cause of this bending has been attributed to some type of direct interaction between electrons in rhodium orbitals perpendicular to the planes of coordination. In $\text{Rb}_3\text{Mo}_2\text{Cl}_8$ the anionic component assumed a configuration similar to $\text{W}_2\text{Cl}_9^{3-}$ but with one of the bridging chlorides missing.⁸⁶ The lack of this one bridge atom seemed to allow distortions in the structure to occur. The shared triangular face was splayed out with a corresponding decrease in Mo-Cl-Mo bridge bond angle. The metal atoms were drawn together to a distance of 2.38 Å, well short of the distance between centers of the octahedral coordination spheres. A very strong metal-metal bond was obviously present but not as strong as that present in $\text{Mo}_2\text{Cl}_8^{4-}$ where the Mo-Mo distance was reported to be 2.14 Å.

More examples of structures affected and effected by metal-metal bonds in ligand-bridged systems have been described together with considerations of bonding implications by Dahl and co-workers.⁸⁷

Considering the effects of metal-metal bonding on these structures in relation to the niobium(III) complexes, it seems that the structure type as pictured in Figure 8b is possible. It should be noted again that the possible positions of the terminal thioether ligands would generate a large number of plausible isomers owing to cis and trans local environments. All of the data obtained in this study

cannot deny the existence of this structural type. However, from spacial considerations about the metal-metal core of this type of molecule, it would appear that the molecule in this configuration would be very susceptible to attack by such contaminants as atmospheric oxygen and water. This would result in a very low stability in the atmosphere. In fact, this stability might even be lower than that of the octahedrally coordinated complexes $\text{NbX}_4 \cdot 2(\text{SC}_4\text{H}_8)$ from which these niobium(III) compounds were synthesized. However, the observed higher stabilities of the $\text{Nb}_2\text{X}_6(\text{SC}_4\text{H}_8)_3$ complexes toward atmospheric decomposition when compared to those of the $\text{NbX}_4 \cdot 2(\text{SC}_4\text{H}_8)$ complexes may indicate that this singly-bridged structure is not correct.

Other possible structures are those that do not contain a bridging tetrahydrothiophene ligand. An example of one such structure is given in Figure 8c. This structure is similar to that reported for $\text{Re}_2\text{Cl}_5(\text{DTH})_2$ (DTH = $\text{CH}_3\text{SCH}_2\text{CH}_2\text{SCH}_3$).⁸⁸ This was better formulated as $\text{ReCl}_4\text{Re}(\text{DTH})_2\text{Cl}$ and contained rhenium in two formal oxidation states. For the niobium complexes synthesized in this study to adopt this type of structure, the two niobium atoms present in the postulated dimeric unit would also necessarily be in different oxidation states. The observed 3+ oxidation state would then be only the mean of the individual oxidation states.

Another mixed oxidation state structure would be that of a bioctahedral arrangement with three chloride bridges as shown in Figure 8d. This type of structure was postulated for the product of the reaction between $K_3W_2Cl_9$ and pyridine (py) and had the formulation $W_2Cl_6(py)_3$.⁸⁹

For the niobium(III) complexes to have any type of mixed oxidation state structure, the unique tetrahydrothiophene, as seen in the NMR spectra, would have to be coordinated to one niobium while the other two thioether ligands would be bonded to the second niobium atom. In fact, the unique tetrahydrothiophene would probably be required to be coordinated to the metal of highest formal oxidation state. This would provide a simple electrostatic rationale which could be used to explain the larger downfield shift of the protons of this tetrahydrothiophene as observed in the NMR spectra.

While there were no observed data which discounted the triply-chloride bridged structure, there was also no apparent reason to invoke a mixed oxidation state compound to explain the observable properties. The unbridged structure as pictured in Figure 8c could also be discounted on the grounds of stability as described for the structure in Figure 8b. Another factor which would tend to negate the possibility of this unbridged structure would be the lack of an octahedral environment about each niobium atom.

In the rhenium compound cited,⁸⁸ a pseudo-octahedral arrangement was accomplished by means of the packing of molecular units in the crystal which enabled the unique terminal halide to approach the empty sixth coordination position on the opposite rhenium atom of an adjacent molecular unit. In the niobium(III) complexes this type of pseudo-coordination would be impossible unless the unique thioether ligand were not in the apical coordination position as pictured. This is a possibility which cannot be ruled out.

Until conclusive structural data are obtained, the bioctahedral structure having one thioether and two chloride bridges seems most appealing. This conclusion is fortified by the results of the metathetical reactions between $\text{Nb}_2\text{Cl}_6(\text{SC}_4\text{H}_8)_3$ and $(\text{C}_2\text{H}_5)_4\text{NCl}$.

While not being instantaneous, the synthesis of the partially substituted product, $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{Nb}_2\text{Cl}_8(\text{SC}_4\text{H}_8)$, was fairly rapid. The properties of this compound, associated with the electronic structure of the complex, were almost unchanged from those of the original complex $\text{Nb}_2\text{Cl}_6(\text{SC}_4\text{H}_8)_3$. This result would be compatible with the proposed bioctahedral structure since substitution of terminal thioethers with chlorides should have little effect on the molecular framework. Substitution of the remaining tetrahydrothiophene was observed to be a more difficult reaction to

accomplish and it was obvious from the spectral and magnetic data observed from this product that a relatively drastic structural change had taken place. It should also be noted that if the original tris tetrahydrothiophene complexes were, in fact, compounds which contained niobium in mixed oxidation states, the unique tetrahydrothiophene would probably be the easiest to be substituted. The basis of this statement is purely electrostatic in nature since the unique tetrahydrothiophene was required to be on the metal of highest formal positive charge and that coordination site would be preferred by an incoming negative ion. Whether this resulting compound, $[(C_2H_5)_4N]_3Nb_2Cl_9$, was analogous to the previously reported $Cs_3Nb_2Cl_9$ remains undecided since no data were presented for the latter to be compared with that obtained in this study. It should be noted that if the three neutral complexes and the partially substituted salt synthesized in this study actually do have the proposed triply-bridged bioctahedral structure with one bridging thioether, the completely chloride substituted derivative probably has a structure significantly different from $Cs_3Nb_2Cl_9$. A single crystal X-ray structure determination of $[(C_2H_5)_4N]_3Nb_2Cl_9$ would be the ultimate means of elucidating this apparent structural change.

Some discussion of the significance of this work in relation to the previously known chemistry of niobium seems

to be in order. Of note in this regard is the fact that a facile synthetic route to a stable niobium(III) species was discovered. Whereas all previously reported syntheses of niobium(III) halides or halide-containing compounds have been at elevated temperatures, this synthetic route appears to be usable at ambient temperatures or below. Interesting also is the fact that the species generated during the course of this study were isolated as discrete crystalline compounds whose properties made them conducive to further physical studies. This has been sought after in the chemistry of niobium(III) for some time. The existence of new compounds containing postulated direct niobium-niobium bonds of apparent bond order greater than one has also been demonstrated. Of notable importance is the fact that the series of compounds $\text{Nb}_2\text{X}_6(\text{SC}_4\text{H}_8)_3$ contains the first known example of what is postulated to be a tetrahydrothiophene molecule simultaneously bonded to two metal atoms. The significance of this is increased by noting that thioethers have been found to act as bridging ligands in only two other reported systems.

SUMMARY

Reduction reactions of the series of compounds $\text{NbX}_4 \cdot 2(\text{SC}_4\text{H}_8)$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) were investigated using sodium amalgam as the reducing agent, and compounds having the general formulation $\text{Nb}_2\text{X}_6(\text{SC}_4\text{H}_8)_3$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) were isolated from these reactions. Proton magnetic resonance spectra of these niobium(III) complexes in benzene indicated that there were two types of chemically inequivalent tetrahydrothiophene molecules present in the molecule. One of these was postulated to be acting as a bridge between two niobium atoms. Magnetic susceptibility measurements performed on $\text{Nb}_2\text{Cl}_6(\text{SC}_4\text{H}_8)_3$ indicated the presence of no unpaired electrons in the complex. Electronic absorption spectra were obtained for the series of three compounds in dilute benzene solutions. The chloride and bromide exhibited similar spectra whereas the iodide showed some anomalous behavior. The diffuse reflectance spectrum of solid $\text{Nb}_2\text{Cl}_6(\text{SC}_4\text{H}_8)_3$ was virtually identical to the solution spectrum indicating similar species being present in both cases. Infrared spectra in the region $1400\text{--}100\text{ cm}^{-1}$ were recorded for the three compounds and some tentative assignments of the observed absorptions to ligand vibrations and to niobium-sulfur and niobium-halide stretching vibrations were discussed. An unsuccessful attempt was made

to solve the three-dimensional crystal structure of $\text{Nb}_2\text{Cl}_6(\text{SC}_4\text{H}_8)_3$.

Metathetical reactions involving $\text{Nb}_2\text{Cl}_6(\text{SC}_4\text{H}_8)_3$ and $(\text{C}_2\text{H}_5)_4\text{NCl}$ were investigated resulting in the isolation of two products, formulated as $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{Nb}_2\text{Cl}_8(\text{SC}_4\text{H}_8)$ and $[(\text{C}_2\text{H}_5)_4\text{N}]_3\text{Nb}_2\text{Cl}_9$. Infrared and electronic spectra as well as magnetic susceptibility measurements indicated that $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{Nb}_2\text{Cl}_8(\text{SC}_4\text{H}_8)$ possessed the same general structural characteristics as $\text{Nb}_2\text{Cl}_6(\text{SC}_4\text{H}_8)_3$. In the formation of $[(\text{C}_2\text{H}_5)_4\text{N}]_3\text{Nb}_2\text{Cl}_9$, a major structural change has apparently occurred as inferred by a drastic change in both the electronic spectra and measured magnetic susceptibility.

Some possible structures for $\text{Nb}_2\text{X}_6(\text{SC}_4\text{H}_8)_3$ were discussed taking into account their physical properties measured during the course of this study. The most appealing geometric arrangement was concluded to be one of a triply-bridged bioctahedral structure which contained tetrahydrothiophene molecules in both bridging and terminal positions. This is similar to the structure previously reported for $\text{Rh}_2\text{I}_2(\text{CH}_3)_4[\text{S}(\text{CH}_3)_2]_3$.⁵⁷

SUGGESTIONS FOR FUTURE WORK

In order to fully understand the significance of this study, one would need to have complete and accurate structural data for all of the compounds synthesized. Of primary interest would be the structures of $\text{Nb}_2\text{X}_6(\text{SC}_4\text{H}_8)_3$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). This would verify the presence of the postulated bridging tetrahydrothiophene and also the postulated metal-metal double bond. The structure of the iodide would also clarify the questions raised because of the difference of its electronic absorption spectrum when compared with those of the bromide and chloride. The structure of $[(\text{C}_2\text{H}_5)_4\text{N}]_2^-\text{Nb}_2\text{Cl}_8(\text{SC}_4\text{H}_8)$ would show if, in fact, it was the bridging tetrahydrothiophene which remained coordinated during the initial substitution reaction. Finally, determination of the structure of $[(\text{C}_2\text{H}_5)_4\text{N}]_3\text{Nb}_2\text{Cl}_9$ would demonstrate its relation to $\text{Cs}_3\text{Nb}_2\text{Cl}_9$ which has recently been synthesized. All of these structural determinations are possible since all of the compounds noted appeared to be crystalline. The method of attack would of course be single crystal X-ray diffraction.

It should also be noted that more information is needed concerning $\text{Cs}_3\text{Nb}_2\text{Cl}_9$. Magnetic and infrared spectral studies seem most pressing at the present time.

Further characterization of the nitrile complexes which were briefly mentioned would be of interest to determine if

these were truly monomeric six-coordinate complexes containing Nb(III) as indicated by the preliminary observations. If this were the case, the magnetic properties of these d^2 species would be especially interesting.

The synthesis of $Nb_2X_6(SC_4H_8)_3$ should be expanded to include complexes of other thioethers. The reduction reactions should also be attempted in excess ligand as a solvent. Both of these reactions could possibly show what part the tetrahydrothiophene plays in determining the structure.

Other reactions of interest would be analogous reductions of thioether complexes of tantalum(IV) halides and also possible reduction of similar complexes of niobium(V) and tantalum(V) by the means employed in this study.

Finally, in order to determine by what mechanism the formation of $Nb_2X_6(SC_4H_8)_3$ species takes place, it would be of interest to characterize the other products of the reduction reactions. Of primary interest would be the dark insoluble product which remained after the $Nb_2X_6(SC_4H_8)_3$ species were extracted from the reaction mixtures.

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APPENDIX

Table VIII
Magnetic Susceptibility Data

a. $\text{Nb}_2\text{Cl}_6(\text{SC}_4\text{H}_8)_3$			
Temp	$10^6 \chi_g$	$10^6 \chi_M$	$10^6 \chi_M^{\text{corr}, a, b}$
°K	emu/gram	emu/mole	emu/mole
77	-0.303	-200.9	179.1
249	-0.298	-197.6	182.4
295	-0.282	-187.0	193.0
b. $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{Nb}_2\text{Cl}_8(\text{SC}_4\text{H}_8)$			
Temp	$10^6 \chi_g$	$10^6 \chi_M$	$10^6 \chi_M^{\text{corr}, a, c}$
°K	emu/gram	emu/mole	emu/mole
77	-0.340	-287.4	253.6
92	-0.403	-329.8	202.2
184	-0.389	-318.0	214.0
297	-0.408	-333.5	198.5
c. $[(\text{C}_2\text{H}_5)_4\text{N}]_3\text{Nb}_2\text{Cl}_9$			
Temp	$10^6 \chi_g$	$10^6 \chi_M$	$10^6 \chi_M^{\text{corr}, a, d}$
°K	emu/gram	emu/mole	emu/mole
77	0.377	377.8	945.8
180	0.373	331.3	942.3
297	0.464	415.6	1023.6
$\text{}^a \chi_M^{\text{corr}} = \chi_M - \chi_D$ $\text{}^b \chi_D = -380 \times 10^{-6} \text{ emu/mole.}$ $\text{}^c \chi_D = -532$ $\times 10^{-6} \text{ emu/mole.}$ $\text{}^d \chi_D = -608 \times 10^{-6} \text{ emu/mole.}$			