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Synthesis and Characterization of New Metal-Metal Bonded Species. I. Some Derivatives of Niobium(III)

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New metal-metal bonded niobium(III) dimers, $Nb_2X_6(SC_4H_8)_3$ (X = Cl, Br, I), have been obtained by reduction of the niobium(IV) halide-tetrahydrothiophene adducts $NbX_4(SC_4H_8)_2$ with Na(Hg) in benzene. These new compounds were soluble in nonpolar solvents, diamagnetic, and characterized by proton nmr, infrared, and uv-visible spectra. All evidence indicated the dimeric species possessed a structure based on two octahedra sharing a common face, with the sulfur atom of one SC_4H_8 molecule and two halogen atoms bridging between the two niobium atoms. The diamagnetism of the species indicates formally a double bond between the niobium atoms. Using $Nb_2Cl_6(SC_4H_8)_3$ as starting material, displacement of SC_4H_8 with Cl^- in CH_2Cl_2 solution was found to occur stepwise with formation of the anions $Nb_2Cl_8(SC_4H_8)^{2-}$ and $Nb_2Cl_9{}^{3-}$, which were isolated as crystalline $(C_2H_5)_4N^+$ salts. Based on a comparison of the electronic spectra the bridging SC_4H_8 molecule is retained in the $Nb_2Cl_8(SC_4H_8)^{2-}$ anion. In contrast to the other compounds $[(C_2H_5)_4N]_3Nb_2Cl_9$ was found to be paramagnetic, but the susceptibility was almost temperature independent.

Introduction

Little evidence can be found concerning the formation and properties of niobium(III) complexes. Although the anhydrous trihalides of niobium have been well characterized,[1-8] their inert character has unfortunately prevented their use as convenient starting materials for the synthesis of more tractable derivatives.

Among the other compounds containing at least formally niobium(III) are those of formulation M_2NbCl_5 (M = Na, K, Rb, Cs), reportedly synthesized by Safonov, *et al.*,[9-11] by means of reactions between $NbCl_3$ and alkali metal chlorides at elevated temperatures. The validity of these results may be questioned, however, since in reactions under similar conditions mixtures of KCl and $NbCl_3$ were observed to yield K_2NbCl_6 and $K_4Nb_6Cl_{18}$,[12] while RbCl or CsCl have provided the salts $M_3Nb_2Cl_9$.[13] Presumably the larger Rb and Cs ions are required to stabilize the $Nb_2Cl_9{}^{3-}$ anion in these compounds, as well as in the corresponding salts of $Nb_2Br_9{}^{3-}$ and $Nb_2I_9{}^{3-}$. These salts were actually prepared from the halides Nb_3X_8 and MX (M = Rb, Cs; X = Cl, Br, I) by means of a chemical-transport reaction under a thermal gradient at high temperatures.[13] The structure of these $Nb_2X_9{}^{3-}$ salts[13] was reported as isotypic with $Cs_3Cr_2Cl_9$.[14] From the reported Nb-Nb distances (2.70–2.96 Å) and magnetic susceptibility data, it can be inferred that the niobium atoms interact strongly, with a formal bond order of 2.

Adducts of the niobium(III) halides with nonhalide donors have not been reported previously. As a result of previous experience in this laboratory with thioether adducts of the niobium(IV) halides[15] it appeared the sulfide ligands imparted sufficient stability and solubility to the complexes that examination of reduction reactions in inert, nonpolar solvents was warranted. In this report are described some new niobium(III) halide–tetrahydrothiophene adducts which provide evidence for strong metal–metal bonding in dimeric, triply ligand-bridged species.

Experimental Section

Preparation of the niobium(IV) starting materials, namely, $NbX_4(SC_4H_8)_2$ (X = Cl, Br, I), as well as most of the physical characterization procedures, has been previously described.[15] The Nb(IV) complexes, and those obtained from the various synthetic procedures described below, were all air and moisture sensitive; hence all manipulations were carried out in a nitrogen-filled drybox or on a vacuum line using standard vacuum-line techniques.

Niobium(III) Halide Complexes. $Nb_2X_6(SC_4H_8)_3$. These compounds were synthesized *via* the reaction between sodium amalgam and the appropriate tetrahalide complex in benzene. 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. The flask was then removed from the drybox and attached to a vacuum line where it was evacuated and thoroughly outgassed. Dry benzene was then vacuum distilled into the flask in sufficient quantity completely to dissolve the tetrahalide complex. The flask then was warmed to room temperature and stirring was initiated immediately after the solvent melted. Initial color of the solution varied with the halide present and corresponded closely to the published colors of the niobium(IV) halide complexes.[15] After a few minutes the color of the solutions changed to violet, blue, and green for the chloride, bromide, and iodide, respectively. After approximately 1 hr, the reactions were terminated by removal of the solvent by vacuum distillation.

The reaction flask was then returned to the drybox and 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 remaining portion of the reaction mixture was then placed in a suitable extraction apparatus and extracted with fresh benzene to remove the highly colored soluble fraction from an insoluble gray residue. This fluffy, gray residue also was observed to be air sensitive but its exact nature was never determined. When the extraction was complete, as evidenced by a lack of color in the filtrate, the solvent was slowly vacuum distilled away yielding crystalline products of the same colors noted above for the

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various reaction mixtures. *Anal.* Calcd for $Nb_2Cl_6(SC_4H_8)_3$: 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 niobium, 3.01 ± 0.01. Calcd for $Nb_2Br_6(SC_4H_8)_3$: Nb, 19.98; C, 15.50; H, 2.60. Found: Nb, 19.54; C, 15.78; H, 2.65. Calcd for $Nb_2I_6(SC_4H_8)_3$: Nb, 15.11; C, 11.72; H, 1.97. Found: Nb, 15.19; C, 12.32; H, 2.19.

$[(C_2H_5)_4N]_2Nb_2Cl_8(SC_4H_8)$. This compound was prepared by stirring approximately 1.5 g of $Nb_2Cl_6(SC_4H_8)_3$ with 1.13 g of $(C_2H_5)_4NCl$ in CH_2Cl_2 solution. These weights give a molar ratio of $(C_2H_5)_4NCl$ to $Nb_2Cl_6(SC_4H_8)_3$ of 3.0. Little, if any, color change was noted and the reaction was terminated after 2 days by removal of the solvent by vacuum distillation. The solid products were extracted with CH_2Cl_2 to remove excess $(C_2H_5)_4NCl$, and a violet crystalline solid, insoluble in CH_2Cl_2, was isolated. *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 compound. However, in this case the $(C_2H_5)_4NCl$:Nb ratio was greater than 3.0. The violet color of the solution changed little initially and a light violet precipitate of $[(C_2H_5)_4N]_2Nb_2Cl_8(SC_4H_8)$ formed as an intermediate product. The reaction was allowed to proceed for a period of 1 day at which time the solution had assumed a bluish hue and the precipitate had also darkened. The highly crystalline precipitate was filtered out of the reaction mixture, washed with fresh dichloromethane, and then dried. Lustrous, silvery gray crystals were obtained. This compound also was conveniently prepared under similar conditions from the reaction between $[(C_2H_5)_4N]_2Nb_2Cl_8(SC_4H_8)$ and $(C_2H_5)_4NCl$ in CH_2Cl_2. *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.

Spectra. Proton magnetic resonance spectra were obtained using a Varian A-60, Varian HA-100, or Hitachi Perkin-Elmer R-20B spectrometer. Saturated solutions (25°) were prepared in a cell containing a sintered-glass frit which was used to remove undissolved solid before the solutions were decanted into the sample tubes and 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 the coordinated ligands were determined by relating the resonances in question to the solvent resonance of known position. Infrared spectra were determined on Nujol mulls with Beckman IR-7 and IR-11 spectrometers. Magnetic susceptibilities were measured on a Faraday balance by procedures previously described,[15] as were determinations of the electronic spectra.

Oxidation State Determination. The oxidation state of niobium was determined by addition of weighed samples of the solid complex to a dilute iron(III) sulfate–sulfuric acid solution. After oxidation of the sample was complete, the iron(II) formed was titrated with standard cerium(IV) solution to the ferroin end point. The ratio of Fe(II):Nb corresponded to the oxidation state change needed to oxidize Nb in the complex to Nb(V).

Results and Discussion

Syntheses. Reductions of the complexes $NbX_4(SC_4H_8)_2$ (X = Cl, Br, I) with sodium amalgam yielded at least two niobium-containing species. A relatively large amount of the highly colored species of formulation $Nb_2X_6(SC_4H_8)_3$ was isolated with yields of these materials being in the range of 60–70% of the calculated amounts. These species were soluble in benzene and other common organic solvents. Their air and moisture sensitivity, however, dictated that these solvents be thoroughly dried and outgassed before use. The other species containing niobium was a fluffy gray solid, insoluble in benzene and also air and moisture sensitive. The actual nature of this gray material was not investigated since it was less tractable and accounted for a relatively small weight fraction of the products.

The tetrahydrothiophene released during the reduction process was identified by means of its proton magnetic resonance spectrum. No apparent change had occurred to the liberated ligand. Sodium chloride was identified as a reduction product by means of the powder X-ray diffraction pattern of the gray insoluble material.

The average oxidation state of the niobium atoms in $Nb_2Cl_6(SC_4H_8)_3$ was determined to be 3.00. The possibility of hydrides being present was eliminated by the subsequent infrared and pmr spectral determinations which failed to show any evidence for their presence. This evidence tends to confirm the presence of Nb(III) in the complex but does not entirely rule out a mixed oxidation state compound.

Magnetic Susceptibility. The magnetic susceptibilities of $Nb_2Cl_6(SC_4H_8)_3$, $[(C_2H_5)_4N]_2Nb_2Cl_8(SC_4H_8)$, and $[(C_2H_5)_4N]_3Nb_2Cl_9$ were determined over the temperature range 77–297°K. Table I summarizes the results of these measurements. These compounds have susceptibilities which exhibit little, if any, real temperature dependence. It can be surmised that the corrected molar susceptibilities of the complexes containing tetrahydrothiophene ligands can be attributed to a temperature-independent paramagnetism. The small values effectively eliminate the possibility of these compounds possessing unpaired electrons which should be present in the ground state of simple Nb(III) (d^2) species. Also the data indicate that the neutral complex and the partially substituted salt are rather similar in structure as indicated by the corrected molar susceptibilities which are comparable in magnitude. The increase in the magnitude of the susceptibility in going to the completely substituted salt indicates that substitution of the last tetrahydrothiophene molecule results in an important structural reorganization of the anion, perhaps to a state containing unpaired electrons. Further indications of this apparent change are discussed below.

Proton Magnetic Resonance Spectra. The pmr spectrum of free tetrahydrothiophene in benzene consists of a quintet at δ 1.53 and a triplet at δ 2.58 with respect to tetramethylsilane reference. These two resonances were of equal intensity as was expected. This spectrum agreed well with that reported for a dilute solution of tetrahydrothiophene in deuteriochloroform.[16] Reported values for the chemical shifts were δ 1.93 for the protons farthest from the sulfur (labeled type "a" protons) and δ 2.82 for the protons on the carbons adjacent to the sulfur atom (labeled type "b" protons). This notation "a" and "b" type protons will be used in the following discussion.

The pmr spectrum of $Nb_2Cl_6(SC_4H_8)_3$ obtained from a saturated solution of the complex in benzene is shown in Figure 1. The spectrum consisted of three main regions of resonance other than that of the solvent. A multiplet of high order was located at approximately δ 1.50 while two triplets were located at δ 3.20 and 3.96. The relative intensities of these resonances were 3:2:1.

Interpretation of this spectrum can be simplified if one considers the possibility of having two types of chemically inequivalent tetrahydrothiophene present in the complex. The multiplet at δ 1.50 can be resolved into two overlapping quintets centered at δ 1.46 and 1.56, respectively. Although separate integration of these two 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 ligands. The triplet at δ 3.20 (relative intensity 2) was assigned as the "b" resonance associated with the "a" resonance at δ 1.56. The triplet at δ 3.96 (relative intensity 1) corresponded to the "b" resonance of a tetrahydrothiophene whose "a" resonance occurred at δ 1.46.

Chemical implications of these chemical shifts and assign-

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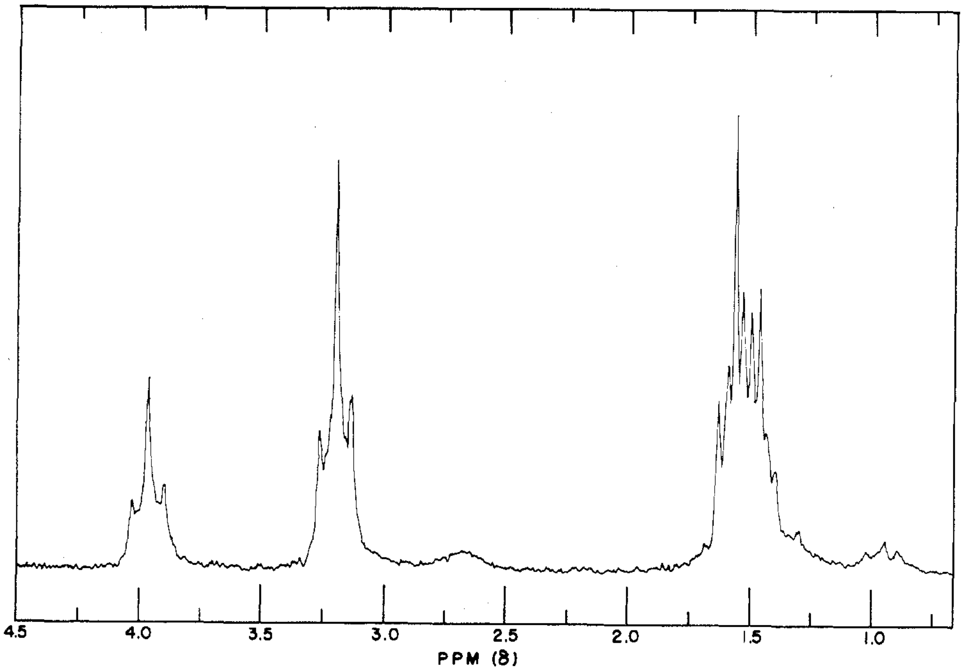

Figure 1. Proton nmr spectrum of a saturated solution of $Nb_2Cl_6(SC_4H_8)_3$ in benzene.

Table I. Magnetic Susceptibilities

Temp, °K	$10^6\chi_g$, emu/g	$10^6\chi_M$, emu/mol	$10^6\chi_M^{cor,a}$ emu/mol
	$Nb_2Cl_6(SC_4H_8)_3$		
77	−0.303	−201	179^b
249	−0.298	−198	182
295	−0.282	−187	193
	$[(C_2H_5)_4N]_2Nb_2Cl_8(SC_4H_8)$		
77	−0.340	−287	254^c
92	−0.403	−330	202
184	−0.389	−318	214
297	−0.408	−334	198
	$[(C_2H_5)_4N]_3Nb_2Cl_9$		
77	0.377	337	946^d
180	0.373	334	942
297	0.464	416	1024

^{a} $\chi_M^{cor} = \chi_M - \chi_D$. ^{b} $\chi_D = -380 \times 10^{-6}$ emu/mol. ^{c} $\chi_D = -532 \times 10^{-6}$ emu/mol. ^{d} $\chi_D = -608 \times 10^{-6}$ emu/mol.

ments show that upon coordination the "b" resonance of SC_4H_8 is shifted to lower magnetic 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. Inductive effects would then tend to deshield the protons of the ligand and their resonances are shifted to lower fields. It appears that the magnitude of the shift of resonance can be interpreted as a measure of the electron delocalization from the sulfur atom.

Using this as a basis, the tetrahydrothiophene molecules causing the "b" resonance at δ 3.20 were considered to be normally bound ligands occupying a terminal position on a niobium atom. This type of coordination utilizes only one of the two lone pairs of electrons on each sulfur atom. The ligand molecule causing the "b" resonance at δ 3.96 was assigned as being involved in a bridging configuration between two niobium atoms, where both lone pairs of electrons on the sulfur atom are used for dative-bonding purposes.

This assignment of a bridging thioether ligand is not without precedent. A binuclear complex containing two rhodium(III) ions, $Rh_2I_2(CH_3)_4[(CH_3)_2S]_3$, was found to contain dimethyl sulfide in both bridging and terminal positions.[17,18] The pmr spectrum of this compound showed that the protons on the bridging ligand resonated at lower magnetic fields than those on the terminal ligands.

Similar pmr spectra were obtained for the bromide and iodide analogs of $Nb_2Cl_6(SC_4H_8)_3$. The chemical shifts, relative intensities, and assignments are summarized in Table II. 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 decreased solubility of the bromide and iodide 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. Minor resonances of very low intensity were also present in the spectra, but these were thought to have arisen from slight decomposition of the complexes due to contaminants in the solvents. The pmr spectrum of the partially substituted salt $[(C_2H_5)_4N]_2Nb_2Cl_8(SC_4H_8)$ was not obtained owing to insolubility of this salt in common hydrocarbon solvents.

Electronic Absorption Spectra. Although there was little doubt that the $Nb_2X_6(SC_4H_8)_3$ compounds had essentially the same molecular structure both in the crystalline phase and in solution, the electronic spectra of $Nb_2Cl_6(SC_4H_8)_3$ in the two phases confirm this. As indicated in Figure 2 the absorption spectrum of a dilute benzene solution showed a very close correspondence to the diffuse reflectance spectrum of the solid. Furthermore the solution spectrum of $Nb_2Br_6(SC_4H_8)_3$ is very similar to that of the chloride derivative which strongly suggests that both compounds have the same structure. As shown by the data in Table III the absorption bands of the bromide derivative are shifted to somewhat lower energies than those of the chloride. However the spectrum of $Nb_2I_6(SC_4H_8)_3$ is quite different from that of the chloride and bromide, principally in the presence of the two relatively intense bands at 27.8 and 21.1 kK. The presence of these two bands may signal a variance in the molecular structure of the iodide derivative or more likely arise from

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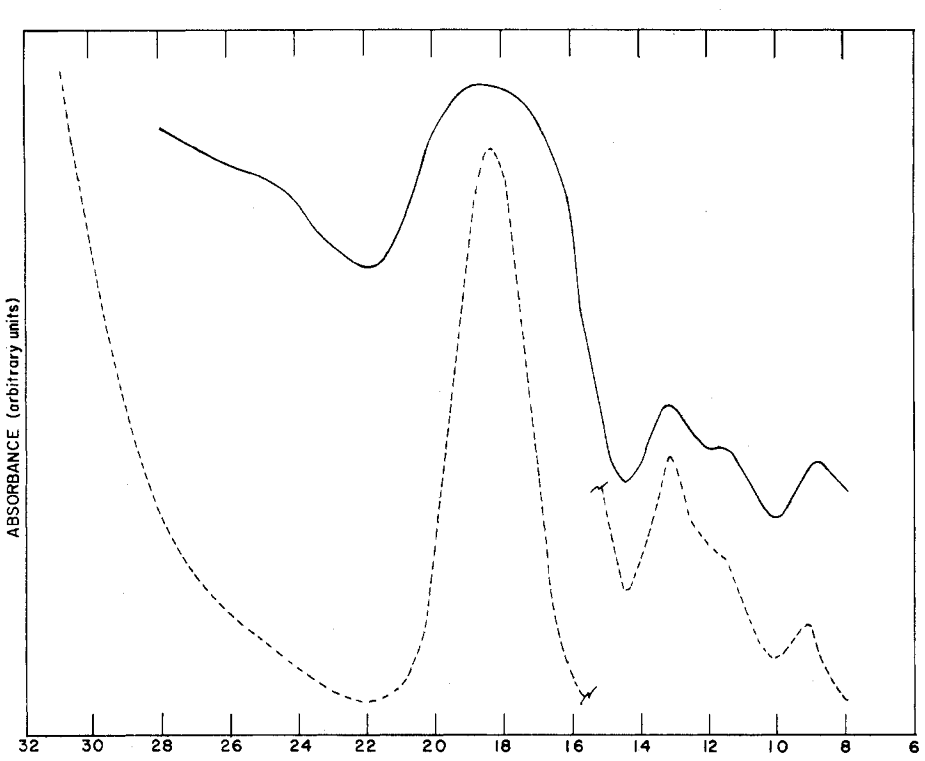

Figure 2. Electronic absorption spectrum of $Nb_2Cl_6(SC_4H_8)_3$ in benzene solution (– – –) and reflectance spectrum of the solid (——).

Table II. ^1H Nmr Data for $Nb_2X_6(SC_4H_8)_3$[a]

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

[a] Spectra obtained from saturated benzene solutions at ambient temperature. [b] Chemical shifts in ppm from TMS using benzene as internal standard. Parentheses denote relative peak intensities. [c] Quintet. [d] Triplet. [e] Unresolved multiplet.

Table III. Absorption Band Parameters for $Nb_2X_6(SC_4H_8)_3$ (X = Cl, Br, 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

[a] Spectra obtained from benzene solutions at *ca.* 25°. [b] 1 kK = 1000 cm^{-1}. [c] Estimated molar absorptivity per dimeric formulation, in l. mol^{-1} cm^{-1}. [d] Shoulder.

iodide to metal charge-transfer transitions. Intense bands of this type were previously found in the spectra of $NbI_4(SC_4H_8)_2$ and $NbI_4[S(CH_3)_2]_2$ in the range 17-27 kK.[15]

Because of their intensities it is apparent that the principal bands at 18.4 and 17.4 kK respectively for the chloride and bromide cannot arise from simple d-d transitions localized on the niobium atoms. More likely these bands arise from transitions within the molecular orbitals which result from the metal-metal interaction. Further explanation of these spectra may be attempted after a complete structure determination has been accomplished.

Diffuse reflectance spectra of the relatively insoluble chloride-substituted salts were obtained for comparison with the spectrum of $Nb_2Cl_6(SC_4H_8)_3$. This comparison is instructive in that the three absorption bands at 18.1, 11.2, and 9.7 kK in the spectrum of $[(C_2H_5)_4N]_2Nb_2Cl_8(SC_4H_8)$ had the same general shapes and intensities as the three bands of highest energy given for $Nb_2Cl_6(SC_4H_8)_3$ in Table III. This small change in the spectrum upon replacing two of the sulfur ligands with chloride ions indicates that the energy levels in the species remain relatively undisturbed. Thus the unique, bridging tetrahydrothiophene molecule must be retained in the first substitution product, as indicated also by the magnetic susceptibility data.

By contrast to the spectra of the parent and disubstituted complexes the reflectance spectrum of $[(C_2H_5)_4N]_3Nb_2Cl_9$ is strikingly different. Relatively intense absorption bands at 18.3, 14.8, and 8.9 kK were observed, with the band at 8.9 kK the most intense. The substantial change upon replacing the last, presumably bridging, sulfur ligand with chloride might be expected. If the final chloride ion enters into the bridging position then the $Nb_2Cl_9^{3-}$ anion should have the same structure reported for $Cs_3Nb_2Cl_9$.[13] Unfortunately spectra for the latter have not been reported, and thus a direct comparison with data reported here for the tetraethylammonium salt cannot be made.

Infrared Spectra. The infrared spectra exhibited by the compounds synthesized in this study showed absorbances in the region 1400-700 cm^{-1} which were clearly assignable to vibrations arising from the organic constituents. No unusual features were noted in this spectral region and it can be concluded that all of the organic constituents retained their integrity during the course of the synthetic procedures and substitution reactions. As was noted earlier, no evidence was found at higher energies which would indicate the presence of metal hydrides.

The infrared region 100-700 cm^{-1} should be more interesting for these complexes since metal-halide and metal-sulfur vibrations should be found in this region together with a few vibrations of the tetrahydrothiophene ligands. The data obtained from this region are tabulated in Table IV.

Of particular interest in the spectrum of tetrahydrothio-

Table IV. Infrared Frequencies (cm^{-1}) for Niobium(III) Complexes and Tetrahydrothiophene (THT) (100-700 cm^{-1})[a]

Nb_2Cl_6-$(SC_4H_8)_3$	Nb_2Br_6-$(SC_4H_8)_3$	Nb_2I_6-$(SC_4H_8)_3$	$[(C_2H_5)_4]_2$-$Nb_2Cl_8(SC_4H_8)$	$[(C_2H_5)_4N]_3$-Nb_2Cl_9	THT(l)[b]
120 m-s	127 m	123m	117 w	132 m	
156 w			149 w-m	158 m	
183 m	176 m	189 s	174 w-m		
206 m-s	198 m-s	201 m			
230 m	232 s	231 s	231 s		
264 s	255 m, sh				
	266 vs	247 m-s			
282 vvw	284 s	280 vvw	278 s	303 s, sh	280 vw
318 vs, sh	320 m-s	322 m	312 vs	312 vs	
330 vs, sh	333 w-m, sh				
341 vvs					
475 w			423 w		
502 w-m	500 m	496 w-m	473 w	472 w	470 m
521 w	520 vw	516 w-m	517 w-m		520 m
	529 vvw		555 w	557 w	
673 m	669 m	664 w-m	583 vvw		
			614 vvw		683 m
			645 vw		
			663 w		
			690 w	698 w-m	

[a] Spectra obtained from Nujol mulls or as otherwise noted. Abbreviations: s, strong; m, moderate; w, weak; sh, shoulder; v, very.
[b] Reference 20.

phene is the absorbance associated with the carbon-sulfur stretching vibration. For thioethers these are normally found in the range 600-800 cm^{-1}.[19] It has been suggested that the corresponding ν(C-S) band of tetrahydrothiophene occurs at 683 cm^{-1}.[20] The frequency of this band has been reported to shift into the region 660-670 cm^{-1} upon coordination.[15,20,21] In the present study a similar shift was also noted. The ν(C-S) bands for tetrahydrothiophene in $Nb_2X_6(SC_4H_8)_3$ have been assigned as those at 673, 669, and 664 cm^{-1} for the chloride, bromide, and iodide, respectively. No evidence was found, however, for a splitting of this band due to the different types of coordinated tetrahydrothiophene, which was so evident in the resonance patterns observed in the pmr spectra of these complexes. The partially substituted chloride complex, $[(C_2H_5)_4N]_2Nb_2Cl_8(SC_4H_8)$, exhibited a band at 663 cm^{-1} which was attributable to ν(C-S) for the remaining tetrahydrothiophene. As was expected, no corresponding band was found in the spectrum of the $Nb_2Cl_9{}^{3-}$ salt.

Since the entire series of compounds of formulation $Nb_2X_6(SC_4H_8)_3$ had been synthesized and their infrared spectra obtained, it was possible tentatively to assign some of the observed absorption bands according to the nature of the vibrations involved. Inspection of the appropriate spectra revealed bands at *ca.* 230 and 320 cm^{-1} which shifted very little with variation of the halide. These bands were tentatively assigned as arising from Nb-S vibrations. 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 a niobium-sulfur vibrational mode.

Recent results confirm that the $Nb_2X_6(SC_4H_8)_3$ complexes contain one bridging and two terminal tetrahydrothiophene molecules.[22] It is thus desirable to consider the Nb-S stretching modes and make tentative identification of the Nb-S terminal stretching frequencies as opposed to the Nb-S-Nb bridging frequencies. The relative frequencies of these vibrational modes should depend upon whether the Nb-S-Nb bridge bonding is stronger or weaker than the Nb-S terminal bonds. We note that in at least one comparable case, that of $Pt_2Br_4[S(C_2H_5)_2]_2$,[23,24] the Pt-S-Pt bonds of the sulfur ligand bridged dimer are shorter by *ca.* 0.1 Å than in other compounds where the same sulfur ligands form only terminal Pt-S bonds. In this and similar dimeric platinum complexes the Pt-S-Pt stretching modes were assigned to bands at frequencies 90-100 cm^{-1} higher than Pt-S terminal stretching modes.

Based on these observations and preliminary results from the structure determination of $Nb_2Br_6(SC_4H_8)_3$,[22] which show that the Nb-S-Nb bridge bonds are shorter than the Nb-S terminal bonds, the band at *ca.* 320 cm^{-1} in the spectra of each of the $Nb_2X_6(SC_4H_8)_3$ complexes is assigned to a Nb-S-Nb stretching mode. In the spectrum of the $Nb_2Cl_8(SC_4H_8)^{2-}$ salt this band cannot be clearly distinguished from the bands arising from Nb-Cl stretching modes, which probably occur along with the Nb-S-Nb stretching mode at *ca.* 312 cm^{-1}. Evidently the band at *ca.* 230 cm^{-1} also arises from the Nb-S-Nb stretching modes since it occurs in the spectra of each of the $Nb_2X_6(SC_4H_8)_3$ molecules, as well as in the spectrum of the $Nb_2Cl_8(SC_4H_8)^{2-}$ anion (which is presumed to retain the bridging sulfur ligand) but not in the spectrum of the $Nb_2Cl_9{}^{3-}$ anion. Thus by a process of elimination it appears that the bands in the range 247-264 cm^{-1} may arise from Nb-S terminal stretching modes. In the case of $Nb_2Br_6(SC_4H_8)_3$ the Nb-Br terminal stretching modes also occur in this region.

Bands arising from the M-X stretching vibrations may be identified by noting the differences which appear upon comparing the spectra of the corresponding chloride, bromide, and iodide. In this case we note that the preliminary structure results show the Nb-X terminal bonds to be shorter than

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(22) Preliminary results of the structure analysis show that indeed the postulated structure is correct with the two Nb atoms bridged by one sulfur and two bromine atoms. The two terminal sulfur atoms of THT occupy positions trans to the bridging sulfur atom. Also results from the nqr spectra of both the chloride and bromide compounds clearly indicate the presence of both bridging and terminal halogen atoms in the molecules together with strong evidence for the Nb=Nb bond provided by the ^{93}Nb nqr transitions. A complete account of the structure and nqr spectra is forthcoming: W. E. Dorman, E. T. Maas, Jr., P. A. Edwards, J. C. Clardy, and R. E. McCarley, to be submitted for publication.

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the Nb-X-Nb bridge bonds.[22] Thus we expect terminal Nb-X frequencies to be greater than the bridging frequencies. On this basis the strong bands at 330-341, 255-266, and 189-201 cm^{-1} in the chloride, bromide, and iodide $Nb_2X_6(SC_4H_8)_3$ derivatives, respectively, are assigned to the Nb-X terminal stretching modes. The Nb-X-Nb bridging vibrations should have much lower frequencies and are much more difficult to identify. These probably occur in the region 150-180 cm^{-1} for the chloride derivatives and at still lower frequencies for the bromide and iodide.

From the above assignments, and those established from previous work, it is possible to compare the change in maximum M-X terminal stretching frequency with change in oxidation state of niobium. For example these bands occur at 440, 397, and 341 cm^{-1} respectively for $NbCl_5(CH_3CN)$,[25] $NbCl_4(SC_4H_8)_2$,[15] and $Nb_2Cl_6(SC_4H_8)_3$. Thus for such neutral complexes the maximum M-X stretching frequency decreases by *ca.* 50 cm^{-1} per unit decrease in formal oxidation state of the niobium atom.

Conclusion

The compounds $Nb_2X_6(SC_4H_8)_3$ (X = Cl, Br, I) and $[(C_2H_5)_4N]_2Nb_2Cl_8(SC_4H_8)$ are among the few compounds of this type where thioether ligands have been found in bridging positions between two metal atoms. Other comparable examples are $Rh_2I_2(CH_3)_4[S(CH_3)_2]_3$,[17,18] which has the confacial bioctahedral structure with two iodine atoms and one methyl sulfide as bridging ligands, and $Pt_2Br_4[S(C_2H_5)_2]_2$, which has only the two ethyl sulfide ligands bridging between the platinum atoms.[23,24] In the latter two examples there is no evidence for metal-metal bonding in the dimers. The factors which favor selection of a bridging sulfur ligand over other available ligands are not understood. In the rhodium compound the methyl ligands cannot furnish the necessary two-electron pairs to form the two-bridge bonds so the selection of the thioether bridging ligand seems natural. However in the platinum compound either the bromine atoms or sulfur ligands have the necessary two-electron pairs and the reason for choice of the bridging sulfur ligand is not obvious. In the niobium(III) derivatives reported here we can only suggest that in order for the formal oxidation state of the two niobium atoms of the dimer to be the same the selection of at least one SC_4H_8 bridging ligand in the confacial bioctahedral arrangement is necessary.

The observed diamagnetism of the compounds containing the tetrahydrothiophene bridging ligand as opposed to the paramagnetism of $[(C_2H_5)_4N]_3Nb_2Cl_9$ is interesting. This behavior can be accounted for in terms of either direct metal-metal bonding with resultant formal double bond between the niobium atoms or spin-spin exchange coupling which could result from electron spin delocalization on the bridging ligands. The former possibility is the more plausible because of the short metal-metal distance, 2.73 Å, determined in $Nb_2Br_6(SC_4H_8)_3$.[22] Also Nb-Nb bonds of order 2 have been postulated for other known species.[13,26,27]

Discounting the conformation of the tetrahydrothiophene rings the maximum symmetry attainable by either the $Nb_2X_6(SC_4H_8)_3$ molecules or the $Nb_2Cl_8(SC_4H_8)^{2-}$ anion is C_{2v}. In this point group all of the molecular orbitals belong to nondegenerate representations; hence with four electrons to be accommodated in the metal-metal bonding orbitals, the electrons must occupy two nondegenerate MO's and the complexes should be diamagnetic. In these cases paramagnetism may result only if empty MO's are sufficiently near in energy that they may become thermally populated in the observed temperature range. No evidence for this behavior was found from the magnetic susceptibility data.

The data obtained on $[(C_2H_5)_4N]_3Nb_2Cl_9$ are much more difficult to correlate with its possible structure. Although it might be supposed that the $Nb_2Cl_9{}^{3-}$ ion would have the confacial bioctahedral structure found for the salts $M_3Nb_2X_9$[13] (M = Rb, Cs; X = Cl, Br, I) the magnetic properties reported here for $[(C_2H_5)_4N]_3Nb_2Cl_9$ are not consistent with those reported for the alkali metal salts of $Nb_2Br_9{}^{3-}$ and $Nb_2I_9{}^{3-}$. The magnetic susceptibilities of the latter compounds were reported to conform to Curie-Weiss behavior and to exhibit effective magnetic moments consistent with two unpaired electrons per dimeric ion.[13] However corresponding data were not reported for the $M_3Nb_2Cl_9$ salts; thus a direct comparison of data on the chloride anions cannot be made. Additional work on salts containing the $Nb_2X_9{}^{3-}$ anions is planned to resolve this anomaly.

Registry No. $Nb_2Cl_6(SC_4H_8)_3$, 38531-73-6; $Nb_2Br_6(SC_4H_8)_3$, 38531-74-7; $Nb_2I_6(SC_4H_8)_3$, 38585-03-4; $[(C_2H_5)_4N]_2Nb_2Cl_8(SC_4H_8)$, 38531-75-8; $[(C_2H_5)_4N]_3Nb_2Cl_9$, 38531-76-9.

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