Cd^{2+}, and Pb^{2+},[15] it is apparent that the bromo complexes are about four times more stable than the respective chloro complexes, if other factors are equal. The destabilization of the halogen compounds upon substitution of sodium instead of lithium in the nitrate melt is apparently a polarization effect on NO_3^- by the small lithium ion, resulting in greater stability of the halogeno compound in lithium nitrate than in sodium or potassium nitrate.[19]

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Addition Compounds of Niobium(IV) Halides Formed with Monodentate Alkyl Sulfides. Synthesis, Spectra, and Magnetism[1]

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The reactions of $S(CH_3)_2$, $S(C_2H_5)_2$, and $S(CH_2)_4$ with NbX_4 (X = Cl, Br, or I) have been investigated. For the case of $S(CH_2)_4$ only paramagnetic diadducts were isolated. With $S(CH_3)_2$ paramagnetic diadducts as well as weakly paramagnetic monoadducts could be obtained. For the case of $S(C_2H_5)_2$ only weakly paramagnetic 1:1 (acceptor:donor) adducts were recoverable as stable solid phases. Infrared, far-infrared, and visible–near-infrared spectra of solid and solution phases of the compounds were recorded and the results are discussed relative to proposed molecular structures.

Introduction

While a number of adducts formed by niobium(IV) halides with nitrogen and oxygen donors have been described[2-6a] only two reports[6b,c] discuss adducts formed with different donors. The most frequently occurring ratio of acceptor to donor is 1:2 for monodentate donors and 1:1 for bidentate donors. The model expected to apply is that of an octahedral disposition of ligands about the central metal with the added possibility of *cis–trans* isomerism for monodentate ligands. Where molecular structure data have been reported[2b,6c,7] they tend to support predominance of the *cis* isomer.

Only two reports[6c,8] describe adducts in which the ratio of acceptor to donor is 1:1. The adducts are obtained *via* the direct reaction of $NbCl_4$ and triethylamine or methyl sulfide. In contrast to the known diadducts which are all paramagnetic, the triethylamine adduct is diamagnetic[8] and the methyl sulfide adduct is only weakly paramagnetic at room temperature.[6c] The magnetic behavior of $NbCl_4(N(C_2H_5)_3)$ together with other properties suggested its formulation as a dimer or higher polymer having bridging halides and niobium–niobium bonds similar to those of the anhydrous halides.[9,10] Steric effects arising from the bulky alkyl groups were thought to contribute to the destabilization of any diadduct. A similar model could be invoked to rationalize the behavior of the methyl sulfide compound, but the space requirements of a methyl group are not expected to be restrictive.

In order to more fully assess (1) the acceptor behavior of niobium(IV) halides with respect to sulfur donors and (2) the stereochemical consequences of sterically hindered ligands for the adducts formed, we chose the compounds methyl and ethyl sulfide as well as tetrahydrothiophene as potential ligands. We have also studied the electronic and vibrational spectra as well as the magnetic properties of solid and/or solution phases of the adducts.

Experimental Section

Materials.—The alkyl sulfides were purchased from commercial sources and dried prior to use by stirring them together with $LiAlH_4$ for 24 hr. After extensive outgassing *in vacuo* they were vacuum distilled onto $NbCl_5$ contained in dry, evacuated 50-ml round-bottom flasks and stored there until required.

Benzene, Spectrograde, was dried under reflux over sodium and stored *in vacuo* over anhydrous $NbCl_5$.

Niobium(IV) halides were prepared using established procedures[2a] and stored in screw-capped vials in an inert-atmosphere drybox.

Analytical Procedures.—Solid samples were hydrolyzed in the absence of air with concentrated ammonia and this mixture was heated to boiling. Heating was continued for *ca.* 1 hr and the mixture was then cooled to room temperature. This process was repeated three times to ensure complete hydrolysis and the

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(1) Work was performed in the Ames Laboratory of the USAEC.

(2) (a) R. E. McCarley and B. A. Torp, *Inorg. Chem.*, **2**, 540 (1963); (b) B. A. Torp and R. E. McCarley, to be submitted for publication.

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TABLE I

ANALYTICAL DATA FOR ALKYL SULFIDE ADDUCTS OF NIOBIUM TETRAHALIDES

Adduct	Color	% calcd				% found			
		Nb	X	C	H	Nb	X	C	H
$NbCl_4[S(CH_3)_2]_2$	Dark red	25.88	39.50	...	...	26.08	39.40	...	...
$NbBr_4[S(CH_3)_2]_2$	Green	17.31	59.54	8.95	2.25	17.47	59.14	8.14	1.75
$NbI_4[S(CH_3)_2]_2$	Dark brown	12.82	...	6.65	1.67	12.95	...	6.01	1.49
$NbCl_4S(CH_3)_2$	Red-orange	31.30	47.77	8.09	2.04	31.02	47.26	8.07	2.19
$NbBr_4S(CH_3)_2$	Red	19.57	67.34	5.06	1.27	20.30	66.31	5.15	1.39
$NbCl_4S(C_2H_5)_2$	Red-orange	28.59	43.65	14.79	3.10	28.83	43.65	14.55	3.09
$NbBr_4S(C_2H_5)_2$	Red	18.48	63.58	9.56	2.00	18.44	64.08	9.23	2.09
$NbCl_4[S(CH_2)_4]_2$	Orange	22.60	34.50	22.81	3.83	22.72	34.64	22.34	3.70
$NbBr_4[S(CH_2)_4]_2$	Green	15.78	54.28	16.32	2.74	15.80	54.48	16.24	2.77
$NbI_4[S(CH_2)_4]_2$	Dark brown	...	...	12.37	2.07	...	...	11.93	1.94

cool mixture was then filtered. Niobium was determined gravimetrically *via* ignition of the white hydrous precipitate to Nb_2O_5. Halide ion in the filtrate was determined *via* potentiometric titration with a standard solution of $AgNO_3$. Carbon and hydrogen were determined by the Ames Laboratory Analytical Service Group.

Preparation of $NbX_4(SR_2)_2$ and $NbX_4(S(C_2H_5)_2)$.—All the compounds and starting materials were extremely sensitive to air and moisture; hence the synthesis and subsequent handling of compounds or reactants were effected under vacuum or the argon atmosphere of a drybox. The procedures used for the synthesis of all diadducts and the ethyl sulfide adducts were essentially identical. Anhydrous NbX_4 (*ca.* 4–5 g) was placed upon the medium-porosity frit of a Soxhlet extractor. Either a Teflon stopcock or a glass break-seal was incorporated into the vessel in order to allow its isolation from the vacuum line and subsequent reattachment. Excess sulfide was distilled into the extractor, frozen at $-196°$, and pumped finally to *ca.* 10^{-5} Torr. The reaction vessel was then isolated from the manifold and reflux was initiated by warming the reservoir of alkyl sulfide. A dark red extract invariably formed. The extractions were allowed to continue until all (or a substantial amount) of the tetrahalide was consumed. This usually required 3–5 days. At the end of this time excess solvent was removed through the Teflon stopcock into cold traps and the products were subsequently dried *in vacuo* for 12 hr.

Preparation of Tetrahalo(methyl sulfide)niobium(IV).—These compounds were obtained by extraction of the corresponding chloride and bromide diadducts with dry benzene. Red crystals formed during the extractions and additional crystals together with a red powder formed when benzene was removed *in vacuo*. The solid products were dried *in vacuo* and stored in screw capped vials in an inert atmosphere drybox.

Analytical data for all the adducts are summarized in Table I.

Spectra.—Absorption spectra of solutions were recorded over the range 6.0–30.0 kK using a Cary Model 14 spectrophotometer together with 1-cm cylindrical cells adapted for use under high vacuum.[2a]

Solid-state spectra were recorded in the range 10.0–30.0 kK using the Beckman Model DU spectrophotometer together with the standard Beckman reflectance attachment. Magnesium carbonate was used as the diluent and as the reference reflector.

Infrared spectra of solids and solutions were recorded using the Beckman IR-7 (1300–600 cm^{-1}) and Beckman IR-11 (800–42.5 cm^{-1}) spectrophotometers. The solids were mounted as Nujol mulls between cesium iodide or polyethylene windows. Solution spectra in the low-energy region were recorded using polyethylene cells purchased from Barnes Engineering Co.

Magnetic Measurements.—The magnetic susceptibility measurements were made using a Faraday balance. The balance has been previously described.[11] It was calibrated using nickel ammonium sulfate hexahydrate. With the more unstable adducts, principally the methyl sulfide diadducts, some loss of ligand occurred during initial evacuation of the balance housing.

Molecular Weight Measurements.—The molecular weight of $NbBr_4[S(CH_3)_2]$ was determined cryoscopically in benzene. Due to the low solubility of this and other compounds (0.1 g/100 ml or less) the precision was poor or the freezing point depression was too small to detect. For the bromide adduct the experimental molecular weight was 595 ± 100 while the calculated value for a monomer is 474.

Oxidation State Determination.—The presence of Nb(IV) in $NbCl_4[S(CH_3)_2]$ was determined using a procedure which has been previously reported.[2a]

Results

Methyl sulfide formed diadducts with all the tetrahalides and the stability of these with respect to apparent monoadducts decreased in the order $I > Br > Cl$. Pure monoadducts of the chloride and bromide could be obtained *via* extraction of the corresponding diadducts with benzene and removal of solvent under a working vacuum. This suggests that an equilibrium such as that shown in eq 1 is established in benzene solution.

$$NbX_4L_2 = NbX_4L + L \qquad (1)$$

The volatile ligand would be lost along with or more rapidly than the solvent, thus favoring the formation of the monoadduct. In the case of the chloride diadduct loss of 1 mol of methyl sulfide per mole of diadduct occurred after *ca.* 12 hr under a working vacuum. Extending this exposure time did not result in the formation of niobium(IV) chloride. With ethyl sulfide there was no evidence of diadduct formation with either the chloride or the bromide. The latter suggests that some factor in addition to eq 1 may be favoring formation of a monoadduct.

For the case of tetrahydrothiophene as ligand only diadducts were encountered. Extraction of the chloride with benzene gave two products. One of these was an orange residue recoverable from the extract and for which the analysis was consistent with a diadduct. A green residue remaining on the frit of the extractor and accounting for less than 5% of the total sample is thought to have arisen from some oxygen contamination. This was observed in only one experiment.

Melting points of diadducts and monoadducts were generally in the range 80–140° and were highest for the latter. A general darkening or charring and gas evolution at the melting points were indicative of decomposition and occurred for all the adducts. Products of decomposition were not identified. Clearly, slower heating of chloride and bromide diadducts (with methyl sulfide) would first yield the monoadducts.

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(11) J. G. Converse, Ph.D. Dissertation, Department of Chemistry, Iowa State University, 1967.

TABLE II

MAGNETIC PROPERTIES OF ALKYL SULFIDE ADDUCTS[a]

$NbCl_4[S(CH_2)_4]_2$	T	297	182	154	142	77		
	χ_M'	764	1164	1345	1444	2556		
	μ_{eff}	1.34	1.30	1.28	1.27	1.25		
$NbBr_4[S(CH_2)_4]_2$	T	298	182	166	77			
	χ_M'	802	1217	1308	2632			
	μ_{eff}	1.38	1.32	1.32	1.27			
$NbI_4[S(CH_2)_4]_2$	T	297	168	157	134	113		
	χ_M'	468	764	814	933	1077		
	μ_{eff}	1.05	1.01	1.01	1.00	0.98		
$NbBr_4[S(CH_3)_2]_2$	T	298	239	224	183	139	113	77
	χ_M'	784	877	933	1132	1427	1713	2410
	μ_{eff}	1.36	1.29	1.29	1.29	1.27	1.23	1.21
$NbI_4[S(CH_3)_2]_2$	T	293	243	233	170	131	113	77
	χ_M'	654	749	790	1040	1326	1492	2144
	μ_{eff}	1.23	1.21	1.21	1.19	1.17	1.15	1.14
$NbCl_4[S(CH_3)_2]$	T	297	236	190	163	133	83	77
	χ_M'	55	55	55	60	57	58	59
	μ_{eff}	0.36	0.32	0.29	0.28	0.24	0.19	0.19
$NbBr_4[S(CH_3)_2]$	T	299	195	162	148	77		
	χ_M'	108	135	149	162	253		
	μ_{eff}	0.50	0.46	0.44	0.44	0.38		

[a] T in degrees Kelvin; $\chi_M' = \chi_M^{cor} \times 10^6$ emu/mol; μ_{eff} in Bohr magnetons.

The diadducts were paramagnetic with molar susceptibilities exhibiting a Curie law dependence upon reciprocal temperature. Table II summarizes the magnetic data and gives the values of μ_{eff} for comparison with other data.[6c]

The chloride and bromide monoadducts were weakly paramagnetic. The small paramagnetism is independent of temperature for the chloride and only very weakly so in the case of the bromide. Because a moment of only 0.3 BM was derived from the linear plot of χ_M vs. T^{-1} for the bromide complex, the temperature dependence most likely arises from a small residue of the paramagnetic diadduct.

Electronic spectra exhibited bands in the visible and near-infrared regions. Band maxima for the solids and solutions are given in Table III, and Figures 1 and 2 depict representative solution spectra which were obtained. Temperature dependence was not investigated.

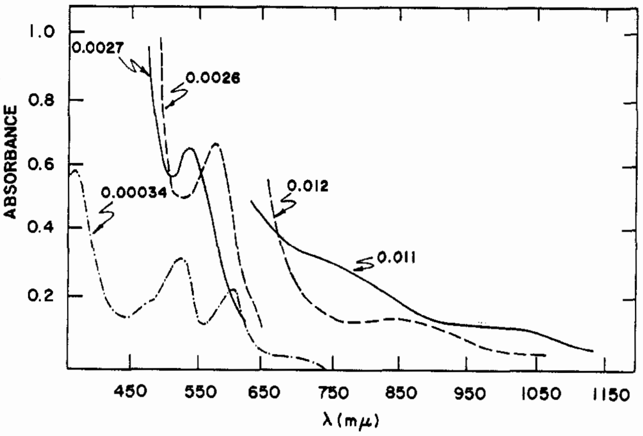

Figure 1.—Electronic spectra of $NbX_4[S(CH_2)_4]_2$ in solution: ——, X = Cl; ----, X = Br; -·-·, X = I. The numbers on the curves are molar concentrations.

TABLE III

ELECTRONIC SPECTRA OF ALKYL SULFIDE ADDUCTS OF NIOBIUM(IV) HALIDES

Adduct	Medium	$10^{-3}\nu$, cm^{-1} (ϵ, M^{-1} cm^{-1})
$NbCl_4[S(CH_2)_4]_2$	C_6H_6	9.74 (12), 13.3 (29), 18.6 (194), 27.8 (1550)
	$MgCO_3$	<10.0, 13.0, 18.8 sh, 22.8 sh, 27.0
	$S(CH_2)_4$	9.8, 13.3, 18.5
$NbBr_4[S(CH_2)_4]_2$	C_6H_6	11.9 (12), 17.5 (240), 27.8 (2000)
	$MgCO_3$	11.0, 16.8, 25.4
$NbI_4[S(CH_2)_4]_2$	$S(CH_2)_4$	13.7 (118), 16.7 (1140), 19.3 (1530), 21.0 (1210), 27.0 (2400)
$NbBr_4[S(CH_3)_2]_2$	$S(CH_3)_2$	11.9, 17.4, 29.0, 33.0
	C_6H_6	6.9, 11.8, 17.4, 28.6, 30.9
	$MgCO_3$	11.4, 17.5, 23.3, 24.4, 27.0, 28.6
$NbI_4[S(CH_3)_2]_2$	$S(CH_3)_2$	11.1, 17.4, 20.8 sh, 22.7, 29.0
$NbCl_4[S(CH_3)_2]$	C_6H_6	8.1, 12.4, 18.8
	$MgCO_3$	11.5, 18.2 sh, >28.6
$NbBr_4[S(CH_3)_2]$	C_6H_6	6.9, 11.8, 17.4, 28.6, 30.9
	$S(CH_3)_2$	11.9, 17.4, 29.0, 33.0
	$MgCO_3$	<10.0, 15.4 sh, ~24.0
$NbCl_4[S(C_2H_5)_2]$	C_6H_{12}	8.0, 12.1, 18.6, 26.7, 34.4, 43.5
	C_6H_6	8.1, 12.4, 18.8
$NbBr_4[S(C_2H_5)_2]$	C_6H_6	6.9 (79), 11.6 (12), 17.4 (150)
	$MgCO_3$	9.5, 14.6 sh, ~22.0 sh, ~29.1

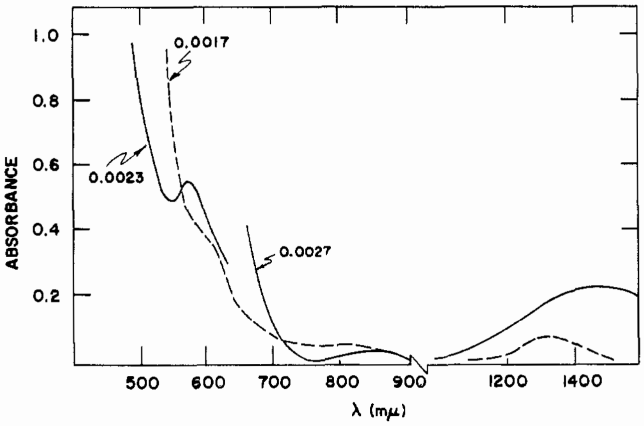

Figure 2.—Electronic spectra of $NbX_4[S(C_2H_5)_2]$ in benzene: ——, X = Br; ----, X = Cl. The numbers on the curves are molar concentrations.

Infrared spectra in the region where ν(C–S) bands

TABLE IV

FAR-INFRARED SPECTRA OF ALKYL SULFIDE ADDUCTS OF NIOBIUM(IV) HALIDES (ν IN CM^{-1})[a]

Adduct	Medium	ν(Nb–X)	ν(Nb–S)[b]	Other
$NbCl_4[S(CH_2)_4]_2$	Nujol	396 m, 372 s, 340 m, sh, 245 w	302 w, 278 w	235 w, 162 ms, 148 ms
	C_6H_6	398 m, 280 m, 362 s		320 w, 300 w
	$S(CH_2)_4$	396 w, sh, 366 s, 340 m, 250 w, sh	304 wm, 280 w	230 w
$NbBr_4[S(CH_2)_4]_2$	Nujol	263 s, 247 m, 229 wm, 200 w, sh	307 wm, 278 m, sh	190 w, 96 m, 85 m
	C_6H_6	266 s, 253 s, 229 m, sh, 200 w	300 m, sh	400 m, 300 m, sh
	$S(CH_2)_4$	266 s, 253 s, 227 m		
$NbI_4[S(CH_2)_4]_2$	Nujol	227 w, sh, 200 s, br, 148 wm	297 m, 272 wm	138 w, 98 w
$NbBr_4[S(CH_3)_2]_2$	Nujol	270 s, 256 s, 227 m, sh, 189 w	304 m, sh, 278 m, sh	
$NbI_4[S(CH_3)_2]_2$	Nujol	200 s, 164 m, sh, 144 w	316 wm, 288 m	88 w
$NbCl_4[S(CH_3)_2]$	Nujol	396 m, sh, 368 s, 340 m, sh, 250 w	304 wm, 278 w, sh	170 w, 160 w, sh, 130 w, 110 w, 76 w
	C_6H_6	396 m, 370 s, 340 m, 240 w	310 w, sh, 280 w, sh	300 w
$NbCl_4[S(C_2H_5)_2]$	Nujol	390 m, 360 s, 340 m, sh, 250 w	304 m, 280 w, sh	162 w, sh, 150 m, 132 w, sh, 110 w
	C_6H_6	398 s, 370 s, 340 m, 250 w	300 w, 280 w	
$NbBr_4[S(CH_3)_2]$	Nujol	271 s, 254 m, 227 m, 195 m	305 m, 283 m	160 w, 110 w, sh, 98 w
$NbBr_4[S(C_2H_5)_2]$	Nujol	270 s, 250 m, 227 m, 189 m	303 m, 282 s	156 m, 110 w, 92 w, 74 w

[a] Abbreviations: s, strong; m, moderate; w, weak; ms, moderately strong; wm, weakly moderate; sh, shoulder. [b] Assignments given are tentative.

are expected to occur (600–800 cm^{-1})[12] exhibited bands which for the adducts were shifted by *ca.* 15–25 cm^{-1} to lower energy relative to corresponding bands occurring in the spectra of the free ligands. Thus for methyl sulfide a band due to ν(C–S)[13] and occurring at 692 cm^{-1} appears at 670–680 cm^{-1} in spectra of the adducts. For tetrahydrothiophene a band at 685 cm^{-1}, a ring deformation very likely involving some C–S stretching,[14] is found at 660–665 cm^{-1} in spectra of the adducts.

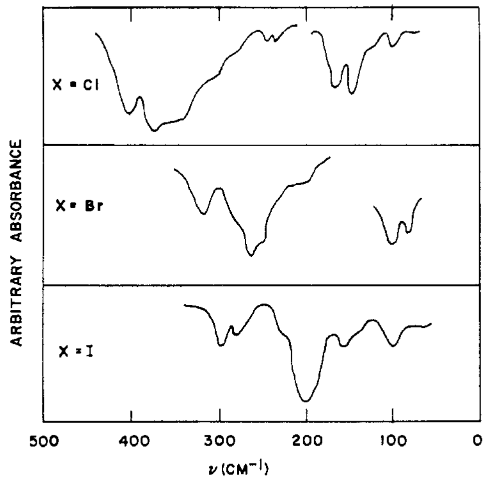

Figure 3.—Far-infrared spectra of $NbX_4[S(CH_2)_4]_2$ as Nujol mulls.

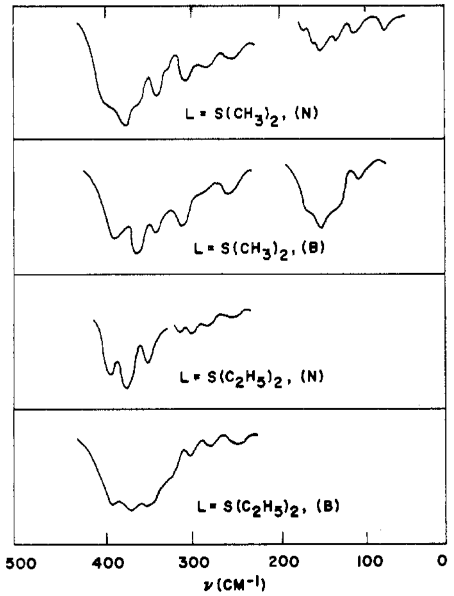

Figure 4.—Far-infrared spectra of $NbCl_4L$ in benzene solution (B) and as Nujol mull (N).

Figures 3 and 4 contain representative far-infrared spectra and Table IV summarizes the wave number maxima of bands appearing in the spectra of all the diadducts and monoadducts.

Discussion

Magnetic Properties.—Table V summarizes the data obtained from the Curie law plots. This Curie behavior of the susceptibility strongly supports an orbital singlet ground state well separated from the next excited state. The magnetic moments decrease in the order Br > Cl > I for tetrahydrothiophene and Br > Cl for methyl sulfide adducts and are of the same order of magnitude as reported for other diadducts.[2–6,8]

TABLE V

MAGNETIC PARAMETERS DERIVED FROM CURIE PLOTS

Adduct	μ, BM	$10^6(-\chi_D)$, emu/mol	$10^6\chi_{TIP}$, emu/mol
$NbCl_4[S(CH_2)_4]_2$	1.21	254	180
$NbBr_4[S(CH_2)_4]_2$	1.25	294	174
$NbI_4[S(CH_2)_4]_2$	0.96	358	148
$NbBr_4[S(CH_3)_2]_2$	1.17	248	198
$NbI_4[S(CH_3)_2]_2$	1.11	314	154

Values of χ_{TIP} obtained from the Curie law plots decreased in the order Cl > Br > I for the tetrahydrothiophene adducts and similarly for the methyl sulfide adducts. This order is different from that found for a series of pyridine adducts.[2a] The reason for this difference is not clear at present.

(12) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, N. Y., 1960.

(13) J. R. Alkins and P. J. Hendra, *Spectrochim. Acta*, **22**, 2075 (1966).

(14) J. Lewis, J. R. Miller, R. L. Richards, and A. Thompson, *J. Chem. Soc.*, 5850 (1965).

The value of μ_{eff} found for $NbCl_4[S(CH_3)_2]$ compares favorably with the room-temperature value of 0.44 BM reported for this compound by Fowles, *et al.*[6c] However, there is no indication of the antiferromagnetic behavior anticipated by these investigators for this compound and found for the compound $TiCl_3[S(CH_3)_2]_2$.[15] When it is recalled that values of χ_{TIP} of 100×10^{-6} emu/mol or greater have been found here and elsewhere[2a] for niobium(IV) in complexes and that this can account for μ_{eff} of 0.5 BM and greater, then care must be exercised in interpreting such low moments. Cognizant of these facts we interpret the low effective moments as indicating that there are strong interactions between the unpaired electrons on adjacent niobium atoms in the solid state. Whether the interaction is direct or indirect cannot be ascertained from the present data. Other data to be subsequently discussed suggest that a doubly halogen-bridged dimer accounts for these observations.

Infrared Spectra.—This discussion of infrared data and the subsequent assignments are given in lieu of Raman studies and X-ray single-crystal structure data. Where possible both solid state and solution data were obtained. The assignments were made using a comparison method. Thus, far-infrared spectra of $NbX_4(CH_3CN)_2$ (X = Cl and Br)[6a,7] have previously been obtained and we have here recorded the spectrum of the corresponding iodide. This series plus the complete series for tetrahydrothiophene allows us to distinguish ligand-sensitive as well as halogen-sensitive bands in the spectra.

Adducts of the form MX_4L_2 (L = monodentate donor) can exist in both *cis* and *trans* forms, and Beattie, *et al.*,[16,17] have shown that in favorable cases infrared spectra can be used to distinguish the two forms. In the *cis* case the highest possible symmetry is C_{2v} while for the *trans* form this is D_{4h}. Clark, *et al.*,[18] give the symmetries of the normal modes for the two configurations. A *cis* isomer will have a maximum of four bands in the region where Nb–Cl stretching modes should absorb and a *trans* isomer will have a maximum of two (site symmetry in the solid state may be lower than D_{4h}, thus leading to a splitting of an e_u mode). Complications can occur when the metal–ligand and metal–halide stretching modes have similar force constants, as then for a *trans* isomer a maximum of three bands can occur in the region under discussion. Finally, the results of a normal-coordinate analysis by Beattie, *et al.*,[19] reveal that for a *cis* isomer a group of three metal–halogen bands should occur at high energy with a fourth band occurring at somewhat lower energy.

For the chloride diadducts the appearance of a group of three bands in the region 400–320 cm^{-1} and their absence in the spectra of the corresponding bromide and iodide diadducts support their assignment as Nb–Cl stretching modes of the *cis* isomer. A fourth band is expected at lower energy but is more difficult to identify. We observe one or more bands in the region 230–250 cm^{-1} in the spectrum of $NbCl_4[S(CH_2)_4]_2$ and the corresponding acetonitrile adduct. The highest energy of these bands is tentatively assigned as the fourth ν(Nb–Cl). Two bands above the 200-cm^{-1} region in the spectra of $NbI_4[CH_3CN]_2$ and $NbI_4[S(CH_3)_2]_2$ are clearly ligand dependent and in the two cases these are tentatively assigned as the respective Nb–N and Nb–S stretching modes. Corresponding bands in the spectrum of the chloride are observed at 307 and 278 cm^{-1}.

For the bromide diadducts complications occur since here both metal–bromine and metal–sulfur stretching modes absorb in the same region. The total number of bands occurring is however consistent with the designation of the *cis* configuration for these diadducts, and the band in the 300-cm^{-1} region in both spectra is very likely due predominantly to Nb–S stretching. A normal-coordinate analysis will be required before more definite assignments can be made.

Metal–iodine stretching bands occur at energies sufficiently low (200–150 cm^{-1}) as to make identification of metal–sulfur stretching modes easy to accomplish. These have been discussed above. Of the four expected metal–iodine bands only two are clearly identifiable and the most intense of these is the broad band at 200 cm^{-1}. There is probably more than one component under this broad band. Our tentative conclusion that the iodide diadducts have the *cis* configuration is based upon the appearance of the two niobium–sulfur bands. A *trans* isomer for the methyl sulfide diadduct is still a possibility since the free ligand does exhibit a very weak broad band in this region.[20]

Several other bands appear in the spectra at energies lower than those discussed above. No assignment of these bands is attempted. We do note the similarities in the spectra of the corresponding methyl sulfide and tetrahydrothiophene complexes in this region. Such similarities are not unexpected if the same isomers are present.

Infrared spectra for solutions of the diadducts in excess ligand were recorded and for most of these only the most intense bands were visible. The one exception was the spectrum of $NbCl_4[S(CH_2)_4]_2$ in tetrahydrothiophene. Here the correspondence between solid-state and solution spectra was excellent and indicates that the same molecular species is present in each phase. While the room-temperature magnetic moment reported here for $NbCl_4[S(CH_2)_4]_2$ is the same as that reported by Fowles, *et al.*,[6c] we observe more bands attributable to ν(Nb–Cl). This discrepancy will subsequently be considered in greater detail.

For the monoadducts the spectra exhibit striking similarities to those of the diadducts. Thus, for chloride adducts a triplet of bands due to ν(Nb–Cl) appears at *ca.* 395, 370, and 340 cm^{-1} with corresponding bands

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for the bromide occurring at *ca.* 270, 250, and 230 cm^{-1}. Fowles, *et al.*,[6c] did not observe a band as high as 395 cm^{-1} for $NbCl_4[S(CH_2)_4]_2$ but they found such a band for the monoadduct $NbCl_4[S(CH_3)_2]$. This suggested to them that in the solid state the coordination number of niobium in the monoadduct was less than 6. Since we observe the band at 395 cm^{-1} for solid $NbCl_4[S(CH_2)_4]_2$ as well as for this compound in a solution of excess ligand, we must conclude that the coordination number of niobium in the two phases is the same. Since bands in this region are further observed for both monoadducts formed by $NbCl_4$ with methyl and ethyl sulfide, the coordination number here must also be 6 (as would be the case for diadducts).[21] In the crystalline compounds formation of dimeric molecules with two bridging atoms is a likely model. Using the simple approximation that the force constants of Nb–X and Nb–S stretching modes are not very different the general features of the spectra of the chloride monoadducts should be similar to that of Nb_2Cl_{10}. Here four bands due to $\nu(Nb–Cl)_t$ and two bands due to $\nu(Nb–Cl)_b$ are found. The terminal stretching modes have been assigned as a group of three bands at higher energy with a fourth at somewhat lower energy.[22] The doublet due to bridging chlorides reportedly appears at 250 and 223 cm^{-1}.[22b] For the methyl and ethyl sulfide monoadducts a group of three bands appears at 400–350 cm^{-1} with a fourth appearing at 310 cm^{-1}. A doublet is observed at 280 and 250 cm^{-1}. All these bands are also observed in the spectra of benzene solutions. As shown in Table IV a similar analysis of the spectra of bromide monoadducts is possible. These results suggest that our approximation is perhaps a good one. Finally the strong similarity between the spectra of *trans*-$PdCl_2[S(CH_3)_2]_2$[23a] and *trans*-$Pd_2Cl_4[S(CH_3)_2]_2$[23b] over the region 400–200 cm^{-1} is noted.

The infrared spectra of benzene solutions of the monoadducts are strikingly similar to those of the solid compounds. As shown below the electronic spectra of these solutions provide evidence for the presence of five-coordinate monomers. Thus the benzene solutions probably consist of an equilibrium mixture of both monomer and dimer monoadduct species.

Electronic Spectra.—Where both solid-state and solution spectra of diadducts were obtained the reasonable correspondence between them supported the conclusion based on far-infrared studies that the same species was present in each phase. On the basis of extinction coefficients one to three bands in the spectra of the solutions of these adducts are assigned as d–d bands. For both bromide diadducts two bands observed can be associated with the transition $^2T_{2g} \rightarrow {}^2E_g$ in a ligand field approximating tetragonally perturbed O_h symmetry. On the other hand, the appearance of three bands attributable to d–d transitions in the spectrum of $NbCl_4[S(CH_2)_4]_2$ (solid and solution) indicates the presence of a lower symmetry ligand field. Fowles, *et al.*,[6c] also reported seeing bands in this region for all of their diadduct compounds and assigned them as probable d–d transitions. The band which we have observed at *ca.* 9.7 kK in the solid-state spectrum and the spectra of benzene and tetrahydrothiophene solutions of the adduct may be attributed to a transition within the split $^2T_{2g}$ manifold in a ligand field approaching rhombic symmetry (as expected if the complexes have the *cis* (C_{2v}) configuration). The bands at 13.3 and 18.6 kK thus may arise from splitting of the ^2E_g state in the field of C_{2v} symmetry. Assignment of the bands in this way is questionable because splitting of the $^2T_{2g}$ state by more than that of the ^2E_g state is unusual. To the extent that Curie behavior was found, the magnetic susceptibility data are consistent with the large splitting of the $^2T_{2g}$ ground term; however, as noted by Fowles, *et al.*,[6c] the moment is lower than might have been expected. Further studies of such d^1 complexes with *cis*-MX_4L_2 stereochemistry have been undertaken in order to clarify this problem.

For the iodide diadducts charge-transfer bands occur at sufficiently low energies that it is only possible to discern one band which can be assigned as a d–d band. For the tetrahydrothiophene and methyl sulfide adducts these occur, respectively, at 13.7 and 11.1 kK. By analogy with the chloride and bromide at least a doublet would be expected at *ca.* 11.0 and 17.0 kK. The differences in the energies of these two bands may reflect the presence of different isomers in the two cases. It is recalled that there was some ambiguity associated with the interpretation of far-infrared spectra of the iodide adducts.

Above 10.0 kK the spectra of benzene solutions of the monoadducts were not very different from those of the diadducts (in excess ligand), but at lower energies a band appeared at *ca.* 8.3 and 6.9 kK for the chloride and bromide, respectively. The extinction coefficients given in Table III are based upon monomer concentrations. Solid-state spectra could not be extended to energies lower than 10.0 kK with available instrumentation. As shown in Table III when $NbBr_4[S(CH_3)_2]$ is dissolved in excess methyl sulfide the band at 6.9 kK disappears from its electronic spectrum, and when the diadduct is dissolved in benzene this band reappears. Wood[24] and Fowles[25] have studied a number of five-coordinate trigonal-bipyramidal complexes of d^1 metal ions and have concluded that bands in this region of the near-infrared spectrum are diagnostic for this type of complex. In the present system substantial dissociation of methyl sulfide diadducts in nondonor solvents as depicted earlier in eq 1 provides the route to the five-coordinate species. In an attempt to confirm this for the bromide we measured its molecular weight with the result as given in the Experimental Section. In spite of the uncertainty in the result it is consistent with a substantial concentration of monomer species being present.

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For a trigonal-bipyramidal complex having full D_{3h} symmetry two d–d bands due to transitions $^2E'' \rightarrow {}^2E'$ and $^2E'' \rightarrow {}^2A_1'$ are expected, and the former should occur well into the near-infrared region. The five-coordinate species proposed here are of the form MX_4L and could have either C_{3v} or C_{2v} symmetry. In the latter case both E levels will be split and as many as four d–d bands could be observed; only three of these would appear at energies above *ca.* 5.0 kK. In each case we observe three such bands, but these cannot be interpreted unambiguously as transitions of only the five-coordinate species since bands arising from undissociated dimer may also be present.

Conclusions

Clearly three different types of adducts are formed between alkyl sulfides and niobium(IV) halides. Diadducts are formed by the cyclic thioether tetrahydrothiophene and by methyl sulfide. Vibrational spectra are consistent with a *cis* arrangement of the ligands. It is important to note however that small amounts of a *trans* isomer would be difficult to detect using the procedures described here. With the bulkier ethyl sulfide as well as with methyl sulfide, monoadducts could be obtained. These are very likely metal–metal-bonded and halogen-bridged dimers in the solid state, but in nondonor solvents extensive dissociation to monomeric five-coordinate species occurs. Such species should be paramagnetic. We attempted to measure the epr spectra of such solutions but observed no signals. It is perhaps significant that when we attempted to observe the nmr spectrum of methyl and methylene protons in $NbCl_4[S(C_2H_5)_2]$ only very broad ill-defined spectra were obtained as would be expected if the solutions contained paramagnetic species. Since the order of increasing space requirements of the ligands, $S(CH_2)_4 < S(CH_3)_2 < S(C_2H_5)_2$, corresponds with the order of decreasing stability of diadducts, the operation of a steric effect as earlier suggested by Brown and Newton[8] is definitely indicated. It is significant however that with respect to formation of the diadducts the qualitative order of stability of the proposed dimers, $Nb_2Cl_8[SR_2]_2 > Nb_2Br_8[SR_2]_2 \gg$ "$Nb_2I_8[SR_2]_2$," is inconsistent with the steric requirement of the halogen atoms. This suggests the importance of the metal–metal bond strength when it is further noted that *d*(Nb–Nb) for bonded niobium atoms in $NbCl_4$ and NbI_4 are 3.10[9] and 3.31 Å,[10] respectively.

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Addition Compounds of Niobium(IV) Halides and Zirconium(IV) Chloride Formed with 1,2-Dimethylthioethane. Synthesis, Spectra, and Magnetism[1]

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The reactions of 1,2-dimethylthioethane with NbX_4 (X = Cl, Br, or I) and $ZrCl_4$ gave complexes of stoichiometry $MX_4[(CH_3SCH_2-)_2]_2$. Infrared and far-infrared spectra of the solids are consistent with coordination of two molecules of the bidentate sulfide ligand per molecule of MX_4, eight-coordination, and a triangular dodecahedral configuration about the niobium atom. Solid-state electronic spectra exhibit correspondences with reported spectra of dodecahedral $NbX_4(diars)_2$ (X = Cl, Br, or I; diars = *o*-phenylenebis(dimethylarsine)). The adducts are paramagnetic with magnetic moments of the chloride and bromide only slightly lower than the spin-only value for a d^1 ion.

Introduction

In a previous paper[2] a series of adducts formed by monodentate alkyl sulfides with niobium(IV) halides was described. In conjunction with that study an investigation of reactions of these halides with the bidentate donor 1,2-dimethylthioethane (more commonly referred to as 2,5-dithiahexane or dth) was undertaken. Clark and coworkers[3] had earlier established that the bidentate arsenic donor *o*-phenylenebis(dimethylarsine) formed eight-coordinate adducts with NbX_4 (X = Cl, Br, or I). A triangular dodecahedral configuration for $NbX_4(diars)_2$ (X = Cl or Br) was indicated by their isomorphism with $MX_4(diars)_2$ (M = Ti, Zr, Hf, or V and X = Cl; M = Ti, Zr, or Hf and X = Br). Clark and Errington[4] studied the reactions of several bidentate sulfur donors, including dth, with TiX_4 (X = Cl or Br), VCl_4, and $SnCl_4$. In each case only adducts in which the ratio of acceptor to donor was 1:1 were obtained.

We report here the synthesis of paramagnetic adducts

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