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THE SYNTHESIS AND CHARACTERIZATION OF SOME ALKYL SULFIDE COMPLEXES OF NIOBIUM(IV)

by

James Beclone Hamilton

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INTRODUCTION

Niobium(IV) halides are diamagnetic solids (1-4) with structures consisting of chains of $MX_2X_{4/2}$ octahedra having direct metal-metal bonds between alternate pairs of niobium atoms (2,3). They will react with various bases to form (a) paramagnetic species in which the metal-metal bonds are cleaved and (b) diamagnetic species in which these bonds are retained. Their reactions with nitrogen donor ligands or halide ions have been the most extensively studied, while reactions with other ligands have been largely neglected.

Fairbrother and coworkers (5-7) as well as Keenan and Fowles (8) have recently shown that niobium pentahalides (class "a" acids) will react with alkyl sulfides (class "b" bases) to form more stable complexes than are obtained with the class "a" oxygen analogues. This result contrasts with the predictions of Ahrland, Chatt and Davies (9) as well as Pearson (10), but is consistent with the observation of Jorgensen (11) that class "b" metals includes three disparate categories one of which is metals in high oxidation states. The possibility exists that a metal in a high or a low oxidation state will exhibit class "b" character, while in intermediate states class "a" character will be found.

In the present study the reactions of niobium(IV) halides with selected sulfur donor ligands are investigated. The possible importance of steric effects determined the choice of dimethyl- and diethylsulfide, tetrahydrothiophene, and 1,2-dithiamethylethane as potential ligands. Ligand-ligand repulsions become increasingly important in the order 1,2-dithiamethylethane < tetrahydrothiophene < dimethylsulfide < diethylsulfide. Halogen-ligand and halogen-halogen repulsions increase in the order chloride < bromide < iodide. Conceivably the stereochemical consequence of sterically hindered ligands could be stabilization of a paramagnetic trans-NbX_4L_2 species. To date only the cis isomers have been reported.

Review of Previous Work

This section shall consist of (1) a discussion of known complexes containing niobium(IV) and (2) a consideration of some alkylsulfide complexes formed by group IV and V transition elements. Bruce A. Torp (12) and F. Fairbrother (13) have recently reviewed the chemistry of niobium(IV) and a recent publication by Livingstone (14) considers metal complexes formed by sulfur donor ligands. In this review therefore only those aspects are discussed which are relevant to later discussions of results.

Complexes containing niobium(IV)

Direct reaction of niobium(IV) halides with alkali metal halides yields M_2NbX_6. Safonov and Khorschunov (15-17) studied the binary systems $NbCl_4$-MCl (M = Na, K, Rb and Cs) using the techniques of thermal analysis and found evidence for the congruently melting compounds M_2NbCl_6. Morozov and Lipatova (18) recently prepared the ammonium, rubidium, and cesium hexachloroniobate(IV) by mixing together concentrated hydrochloric acid solutions containing niobium tetrachloride and the salt MCl (M = NH_4^+, Rb^+, and Cs^+). Analytical data and x-ray powder diffraction data for the compounds were reported.

Torp (12) describes the synthesis, structure, spectra and magnetic properties of the series M_2NbX_6 (M = K^+ and Rb^+; X = Cl^- and Br^-) and Cs_2NbI_6. With the exception of Rb_2NbBr_6 the compounds were face-centered cubic. A detailed structure determination revealed that K_2NbCl_6 and K_2PtCl_6 were isomorphous. Diffuse reflectance spectra and the spectrum of $NbCl_6^{2-}$ in fused pyridinium chloride were discussed in terms of molecular orbital theory. Spectra in the visible region for M_2NbCl_6, $NbCl_6^{2-}$, and M_2NbBr_6 each exhibited two bands at 23.5 and 18.7 kK, 24.4 and 18.2 kK, and 18.9 and 14.0 kK, respectively. Average 10 Dq values were 21.1 and 16.4 kK for the chloride and bromide. The molar magnetic susceptibilities exhibited Curie-Weiss behavior. Effective magnetic moments calculated from the data ranged from a low of 1.13 B.M. for Cs_2NbI_6 to 1.40 B.M. for Rb_2NbCl_6 at room temperature.

Cozzi and Vivarelli (19) studied the visible spectra of concentrated hydrochloric acid solutions of $NbCl_4$, but no discrete complexes were isolated. A red-orange niobium(IV) complex in 13N. HCl exhibited a band at 20.8 kK.

Fedotov, Garif'yanov, and Kozyrev (20) obtained epr spectra from ethanolic solutions of hydrogen chloride and niobium pentachloride reduced by zinc, but no species was isolated from the solutions. Similarly, Lardon and Gunthard (21) studied the epr spectrum of a niobium(IV) complex in alcoholic solution. At $77^{\circ}K$ the spectrum exhibited a resonance having axial symmetry. The components of the g and A tensors of the spin-Hamiltonian were evaluated from the spectrum: $g_1 = 1.892$, $g_3 = 1.925$ and $g(ave) = 1.903$; $A_1 = 247.6$, $A_3 = 519.7$, and $A(ave) = 357.8$ gauss. In the absence of knowledge concerning the nature of the species in solution no further discussion of the bonding was presented.

Wentworth and Brubaker (22,23) prepared a new class of chlorocomplexes by electrolytically reducing niobium pentachloride in anhydrous alcoholic hydrogen chloride. Addition of an alcoholic solution of an amine hydrochloride precipitated the salts $(BH)_2Nb(OR)Cl_5$ (R = CH_3, CH_3CH_2, and $(CH_3)_2CH$) from such solutions. The molar magnetic susceptibilities of $(pyH)_2\ Nb(OCH_3)Cl_5$, $(QnH)_2Nb(OCH_2CH_3)Cl_5$, and $(QnH)_2Nb(OCH(CH_3)_2)Cl_5$ (QnH = quinolinium and pyH = pyridinium) exhibited Curie-Weiss dependence upon reciprocal temperature. Effective magnetic moments were virtually spin-only (1.73 B.M.) for one unpaired electron per niobium atom. Diffuse reflectance spectra exhibited a single band having a maximum at 19.6 kK.

Rasmussen, Kuska, and Brubaker (24) obtained epr spectra of glasses containing $Nb(OCH_3)Cl_5^{2-}$. From the spectra it was found that $g_{\parallel} = 1.965$, $g_{\perp} = 1.809$, A = 248 gauss and B = 144 gauss. A molecular orbital treatment was consistent with covalent chlorine-niobium sigma bonds and appreciable π-bonding by the chlorine atoms.

Wentworth and Brubaker (25) found that treatment of the above reduced alcoholic solutions with pyridine produced a diamagnetic species $NbCl(OCH_2CH_3)_3py$. Molecular weight determinations in chloroform established that this was a dimer. The visible spectrum of a chloroform or ethanol solution exhibited a single band at ca. 27.4 kK. When this dimer was treated with sodium ethoxide (in ethanol) the diamagnetic polymer $Nb(OEt)_4$ formed. Direct metal-metal bonds were proposed to account for the observed magnetic behavior of $Nb_2(OEt)_6Cl_2py_2$ and $Nb(OEt)_4$.

Djordjevic and Katovic (26) report the isolation of paramagnetic $Nb_2Cl_5(OCH_2CH_3)_3(bipy)_2$ (bipy = 2,2'-bipyridine) from an ethanol solution containing $NbCl_4$ and bipyridine. The magnetic moment at 20° was 1.39 B.M. Properties of the compound suggested its formulation as an ionic derivative containing the ions $(Nb(OCH_2CH_3)_2(bipy)_2)^{2+}$ and $(NbCl_5(OCH_2CH_3))^{2-}$.

Niobium(IV) halide complexes with nitrogen donor ligands can be obtained by either (1) direct reaction of the tetrahalide and the ligand, or (2) reaction of excess ligand with niobium pentahalide.

McCarley and coworkers (27) isolated $NbX_4(py)_2$ (X = Cl and Br; py = pyridine) from reactions of NbX_5 and excess pyridine. McCarley and Torp (1) obtained the same species as well as $NbI_4(py)_2$ from reactions of NbX_4 with pyridine at room temperature. Visible spectra of pyridine solutions exhibited bands with maxima at 20.6 kK for the chloride and 20.7 and 13.9 kK for the bromide. Because the extinction coefficients were larger than expected for bands due to "d-d" transitions, the bands were attributed to either pyridine-to-metal or metal-to-pyridine charge transfer. M. Albutt and coworkers (28) also report the synthesis of $NbX_4(py)_2$ (X = Cl and Br) using method (2). The visible spectra were similar to those obtained by Torp and McCarley. Effective magnetic moments at room temperature were respectively, 1.53 and 1.36 B.M. for the chloride and bromide. These were higher than the corresponding moments of 1.37 and 1.26 B.M. reported by Torp and McCarley. The latter authors studied the susceptibility as a function of temperature, Curie behavior was encountered and derived values of the TIP (temperature independent paramagnetism) constituted a significant contribution to the paramagnetic susceptibility at room temperature.

Albutt and coworkers (28) also report the synthesis of $NbX_4(\gamma\text{-pic})_2$, $NbX_4(bipy)$, and $NbX_4(O\text{-phen})$ (X = Cl and Br; γ-pic = γ-picoline and O-phen = 1,10-phenanthroline). The room temperature effective magnetic moments were lower than spin-only. Solid state and solution spectra of $NbCl_4(bipy)$ exhibited band maxima at 19.0 kK (solid) and 17.5 and 22.5 kK (in acetonitrile). Extinction coefficients for the doublet of 50 and 180 $M^{-1}cm^{-1}$ were not unreasonable for "d-d" bands, but in dilute acetonitrile molar conductance values were obtained which suggested that the complex was behaving as a weak electrolyte according to (1).

$$NbCl_4(bipy) + CH_3CN \rightleftharpoons (NbCl_3(NCCH_3)bipy)^{1+} + Cl^- \qquad (1)$$

Cognizance of this complication precluded definite assignment of the spectral bands.

With the bidentate arsenic donor ligand O-phenylenebisdimethylarsine (diars) Clark and coworker (29) obtained the eight coordinate complexes $NbX_4(diars)_2$ from reactions of niobium pentahalide, niobium tetrahalide, or niobium oxytrihalide. The chloride and bromide were isomorphous with the known eight coordinate dodecahedral complexes $MX_4(diars)$ (M = Ti, Zr, Hf or V; X = Cl and M = Ti, Zr, or Hf; X = Br) (30). Comparison of the diffuse reflectance spectra suggested the presence of a similar ligand field in $NbI_4(diars)_2$ as in the chloride and bromide analogues. Results from magnetic susceptibility investigations were complicated by decomposition of the sample during packing into a Gouy tube. Efforts to correct for the effect resulted in magnetic moments of 1.7, 1.9, and 1.6 B.M. for the respective chloro, bromo, and iodo complexes.

Torp (12) isolated the complexes $NbX_4(ac)_2$ (X = Cl, Br, and I; ac = acetonitrile) from direct reactions of the tetrahalides with acetonitrile at room temperature. Dipole moment studies of benzene solutions suggested a cis-arrangement of the ligands in the chlorocomplex. Solid state and solution (ac) spectra were consistent with the same ligand environment for niobium(IV) in each phase. Two bands in each spectrum were assigned as "d-d" bands due to transitions from an essentially nonbonding d_{xy} orbital into anti-bonding d_{z^2} and $d_{x^2-y^2}$ orbitals. These anti-bonding orbitals arise via splitting of an excited e_g level by the low symmetry ligand field. This splitting decreased in the order Cl > Br > I. Derived values of 10 Dq (here properly referred to in molecular orbital terms as Δ_1) place acetonitrile above chloride ion in the spectrochemical series for niobium(IV). The true magnetic moment of the chloro complex was 1.75 B.M., and effective magnetic moments for the bromide and iodide were 1.75 and 1.45 B.M. at 300°.

Dougherty (31) only recently reported the results of far infrared studies of $NbX_4(ac)_2$ (X = Cl and Br) as well as a structure determination of $NbBr_4(ac)_2$ using the techniques of single crystal x-ray diffraction analysis. The far infrared spectra exhibited two or more bands in the niobium-halogen stretching regions where only one band should be observed for a trans adduct. A cis arrangement of the ligands was proposed and this was confirmed for $NbBr_4(ac)_2$ by the structure analysis (31).

Brown and Newton (32) isolated the species NbX_4B (X = Cl, Br, and I; B = N, N', N", N'''-tetramethylethylenediamine) from direct reactions of the amine and the tetrahalides. No magnetic susceptibility data were obtained. Diffuse reflectance and solution spectra were similar with band maxima occurring at 19.8 and 23.3 kK, 17.9 and 22.0 kK, and 17.7 and 18.2 kK for the chloro, bromo, and iodo complexes, respectively. On the basis of extinction coefficients (<100) these were assigned as transitions from a singlet ground state to a ^2E_g state which has been split by low symmetry ligand field components. The triethylamine complexes approaching the composition $NbX_4(N(CH_2CH_3)_3)$ (X = Cl, Br, and I) were obtained. The chlorocomplex $NbCl_4 \cdot 0.9\ N(CH_2CH_3)_3$ was diamagnetic and its diffuse reflectance spectrum contained a single band at 26.3 kK. A polymeric species containing direct metal-metal bonds was proposed.

Bradley and Thomas (33) obtained $Nb(NR_2)_4$ (R = CH_3, CH_3CH_2, $CH_3(CH_2)_2$, and $CH_3(CH_2)_3$) from the direct reaction of $LiNR_2$ and $NbCl_5$. The valence state of niobium in the compounds was established by treatment of their H_2SO_4-ethanol solutions with excess $FeCl_3$ followed by titration of the $FeCl_2$ formed with standard ceric sulfate solution.

Rasmussen and Broch (34) report the synthesis of $Nb(S_2CNR_2)_4$ (R = alkyl group). On the basis of unpublished data eight coordination of niobium (IV) was proposed.

Thioether complexes of group IV and V transition elements

Titanium and vanadium complexes

Baker and Fowles (35) showed that TiX_4 (X = Cl and Br) will react with sulfur donor ligands to form TiX_4L_2 (L = $S(CH_3)_2$, $S(CH_2CH_3)_2$, SC_4H_8, and SC_5H_{10}). With di-n-propylsulfide a 2:1 (ligand: TiX_4) complex is obtained with chloride, but only a 1:1 adduct is isolated for the bromide. Molecular weight determinations established the complexes as mononuclear TiX_4L_2 species, but for $TiBr_4(S(CH_2CH_3)_2)_2$ these studies suggest that dissociation was occurring via (2).

$$TiBr_4L_2 \rightleftharpoons TiBr_4L + L \qquad (2)$$

The lower stability of the bromo bis adducts was attributed to the larger steric requirements of the bromine atoms. With less sterically hindered ligands such as tetrahydrothiophene (SC_4H_8) stable bromo bis adducts could be isolated. On the basis of their far infrared spectra the complexes were assigned as cis isomers. A report by Westland and Westland (36) confirms in part, the results of this study.

Clark and coworkers (37) tried unsuccessfully to synthesize eight coordinate complexes analogous to $TiCl_4(diars)_2$ but using bidentate sulfur donor ligands. In each case only complexes $TiCl_4B$ (B = 1,2-dithiamethylethane, 1,2-dithiaphenylethane, 1,2-dithiaethylethane, and cis-dithiamethylmaleonitrile) were obtained. Attempts to introduce an additional molecule of B were without avail. Coordination via sulfur of the one ligand was established from the spectral region 1400-600 cm^{-1}. The ligand 1,2-dithiamethylethane (sometimes referred to as 2,5-dithiahexane (dth)) exists in various conformations (cis, trans, or gauche). The infrared spectrum has been studied by several workers (38-40) and most of the bands have been assigned. In the free ligand the trans conformer predominates (30), while in the metal complexes only bands due to the gauche conformer are observed (37,38). A recent report by Cotton and coworkers (41) described a rhenium-dth complex which gives an infrared spectrum showing bands due to the trans conformer. In this case the ligand is thought to bridge different rhenium atoms.

Kharlamova and Gur'yanova (42) also prepared a series of $TiCl_4$-alkylsulfide complexes. Here complex formation was established cryoscopically and by dielectrometric titrations. For the monodentate ligands R_2S ($R = CH_3CH_2$, $CH_3(CH_2)_3$, and $CH_2C_6H_5$) and tetrahydrothiophene evidence for 1:1 and 2:1 complexes was found. The 1:1 complex $TiCl_4(SC_4H_8)$ was isolated as yellow crystals which melted at 116-120°C. The complex $TiCl_4(SC_4H_8)_2$ was isolated as an orange solid. Evidence was presented which suggested that species $TiCl_4(R_2S)_2$ are unstable with respect to $TiCl_4(R_2S)$ in the presence of excess $TiCl_4$.

Fowles, Lester, and Walton (43) found that titanium trihalides form stable solid complexes. TiX_3L_2 (X = Cl, Br, and I; $L = S(CH_3)_2$ and SC_4H_8). The presence of coordinated dimethylsulfide was established by comparing infrared spectra of the complexes with those of dimethylsulfide (44). The carbon-sulfur stretching bands were shifted by ca. 20 cm^{-1} to lower energy in the complexes relative to the free ligand. From electronic spectra of solids and solutions ligand field bands were identified at 12.0 and 15.3 kK for $TiCl_3(SC_4H_8)_2$, 12.1 and 15.6 kK for $TiCl_3(S(CH_3)_2)_2$, 11.9 and 13.8 kK for $TiBr_3(SC_4H_8)_2$, 11.8 and 14.3 kK for $TiBr_3(S(CH_3)_2)_2$, and 10.8

12.6 kK for $TiI_3(SC_4H_8)_2$. Charge transfer bands were identified in the spectra and appeared at lower energies than in the five coordinate complexes $TiX_3(N(CH_3)_3)_2$ but in the same region as they occur in the spectra of $TiCl_6^{2-}$ and $TiBr_6^{2-}$. Five coordination was thus eliminated for the bromide and chloride complexes. However, using the position of the highest metal-halogen stretching band as an index to coordination number (45), far infrared (500-200 cm^{-1}) spectra of nujol mulls were consistent with either a five-coordinate complex or a halogen bridged dimer. In tetrahydrothiophene the highest titanium-chlorine stretching occurred at 373 cm^{-1} while in nujol a band appeared at 390 cm^{-1}. Six coordination was indicated for solutions in the free ligand. The solid state and solution far infrared spectra of the bromide complexes were the same. While unambiuous stereochemical assignments could not be made, this result suggested six coordination of Ti(III) in both phases. Similar conclusions were applicable to $TiI_3(S(CH_3)_2)_2$. Magnetic susceptibility determinations of $TiX_3(R_2S)_2$ over the temperature range 47° to -193° established that the chloride complexes were antiferromagnetic. This argues against five coordination of Ti(III) in these complexes in the solid state. The bromide and iodide exhibited little, if any, antiferromagnetic behavior.

Duckworth, Fowles, and Green (46) studied the reaction of vanadium tetrachloride with dimethyl- and diethylsulfide and found that reduction to VCl_3 occurred. The species $VCl_3(R_2S)_2$ were subsequently isolated as solid products. Direct reaction of VCl_3 with dimethyl sulfide produced an identical product. Ethanethiol also reduced VCl_4, but the reddish-purple solid which formed was not fully characterized. Far infrared spectra of $VCl_3(R_2S)_2$ in benzene and as nujol mulls were distinctly different exhibiting maxima at 422 cm^{-1} in the former, and 420, 373, and 342 cm^{-1} in the latter. Five coordination was proposed for the solution species. Metal-sulfur stretching bands exhibited maxima at 262 and 259 cm^{-1} in solution and nujol mull spectra. Visible and near infrared spectra of solutions of the complexes in different solvents were reported. In non-donor solvents such as benzene or iso-octane two bands appeared in the near infrared at 5.0 and 7.0 kK. In spectra of solutions with donor solvents such as the free ligand these near infrared bands were absent. In these donor solvents six coordinate complexes formed. A detailed discussion of the spectra of the five-coordinate, d^2 complexes has recently been reported (47).

Vanadium tetrachloride was not reduced by bidentate sulfur donor ligands (37). Species VCl_4B (B = dth or cis-dimethylthiomaleonitrile) were isolated. Effective magnetic moments at room temperature ranged from 1.68 to 1.73 B.M. Far infrared spectra exhibited vanadium-chlorine stretching bands in the region expected for six coordinate vanadium(IV). Diffuse reflectance spectra showed broad asymmetric bands at 17.0-20.0 kK which were tentatively assigned as "d-d" bands. The average ligand field strength for sulfur donors was ca. 18.0 kK compared to ca. 17.8 kK for VCl_6^{2-}. The following spectrochemical series was proposed for vanadium(IV) complexes: bipy > O-phen > $(CH_3OCH_2-)_2$ > $(RSCH_2-)_2$ > Cl^-.

Zirconium and hafnium Beattie and Webster (48) report infrared spectra of $ZrCl_4(S(CH_3)_2)_2$ and find metal-chlorine stretching bands at 372 and 299 cm^{-1}. No details of the synthesis are reported. There have been no other reported examples of complex formation between zirconium or hafnium tetrahalides or trihalides with sulfur donors.

Niobium and tantalum Fairbrother and coworkers (5-7) report that thioethers form more stable adducts with MX_5 (M = Nb or Ta; X = Cl or Br) than do their oxygen analogues. The series MX_5R_2S (R = CH_3 and CH_3CH_2) was isolated. Tantalum pentachloride also formed the 1:2 adduct $TaCl_5(S(CH_3)_2)_2$. With tetrahydrothiophene the compounds $NbX_5(SC_4H_8)_2$ (X = Cl and Br) and $TaX_5(SC_4H_8)_2$ (X = Cl, Br, and I) were isolated. These are presumably seven coordinate complexes.

Keenan and Fowles (8) found that $NbX_5(SC_4H_8)$ could be obtained if the reaction of $NbCl_5$ and tetrahydrothiophene was carried out in benzene.

Safonov and coworkers (17) report the only evidence for complex formation by Nb(III). A phase corresponding to niobium trichloride was allowed to interact with alkali chlorides in melts. Time-temperature curves indicated that compounds formulated as M_2NbCl_5 were produced. The compound Rb_2NbCl_5 melts incongruently at 753° and Cs_2NbCl_5 melts congruently at 762°. The formation of the compounds (or at least new phases) was confirmed by x-ray phase analysis. Fleming, Mueller, and McCarley (49) isolate $K_4Nb_6Cl_{18}$ and K_2NbCl_6 from the high temperature reaction of KCl and Nb_3Cl_8.

EXPERIMENTAL

Extreme sensitivity to oxygen and moisture was characteristic of all the compounds synthesized during this study. It was therefore essential that all manipulations of these compounds be effected in an inert atmosphere box or under a high vacuum.

Materials

Niobium

Niobium beads of high purity and low tantalum content were purchased from the Pigments Division of E. I. Dupont Company.

Zirconium

Zirconium in block form was obtained from Laboratory stock. It was machined into turnings for use in the synthesis of zirconium(IV) chloride.

Chlorine

Chlorine in lecture bottles was purchased from the Matheson Company. It was vacuum distilled into the reaction vessel at -78^{o} and extensively outgassed at ca. 10^{-5} Torr before sealing off the vessel.

Bromine

Bromine was obtained from the J. T. Baker Chemical

Company and was dried over outgassed phosphorous(V) oxide and vacuum distilled into flasks for storage.

Iodine

Resublimed iodine crystals from the General Chemical Division, Allied Chemical were extensively outgassed in the reaction vessel at 10^{-5} Torr prior to sealing off the vessel.

Organic reagents

Dimethylsulfide purchased from Matheson, Coleman, and Bell was dried by stirring it at room temperature over porous lithium aluminum hydride followed by extensive outgassing of this mixture at ca. 10^{-5} Torr. The dimethylsulfide was subsequently vacuum distilled onto niobium(V) chloride in a clean dry 500 cc. flask for storage.

Diethylsulfide was obtained from Columbia Chemicals. It was dried over $LiAlH_4$ and stored over this solid until required.

Tetrahydrothiophene was dried using the technique applied to diethylsulfide. It was obtained from Matheson, Coleman, and Bell.

The compound 1,2-dimethylthioethane, more commonly referred to as 2,5-dithiahexane, was purchased from Columbia Chemicals. It was dried over $LiAlH_4$ and extensively outgassed at

10^{-5} Torr. Solids were removed from this mixture by filtration in the inert atmosphere box. The filtrate was stored in the inert atmosphere box in capped bottles.

Benzene was obtained as a spectro-quality chemical from Eastman Chemicals. It was dried by refluxing it over sodium beads for ca. 12 hours followed by extensive outgassing in vacuo and distillation onto dry niobium(V) chloride for storage.

Analytical Procedures

Niobium

Niobium in solids was determined gravimetrically as niobium(V) oxide. Samples were prepared by hydrolysis with ammonia solutions. These mixtures were heated to boiling to hasten the hydrolysis and after cooling to room temperature and acidification with concentrated nitric acid a white precipitate of hydrous niobium(V) oxide formed. This was collected by gravity filtration on ashless medium porosity filter paper, washed successively with three portions of dilute nitric acid, and ignited to anhydrous niobium(V) oxide in tared porcelain crucibles at 600-700°.

Niobium in dilute solutions was determined spectrophotometrically (50) by the Ames Laboratory Analytical Service Group, Iowa State University of Science and Technology, Ames, Iowa. Solutions were prepared by hydrolysis of solid samples with ammonia followed by exhaustive digestion with concentrated sulfuric acid. The sulfuric acid solutions were diluted to volume with more acid and submitted for analysis.

Halogens

These were determined by potentiometric titration with standard silver nitrate solutions. A Beckmann Expanded Scale pH Meter in conjunction with a silver indicating and saturated calomel reference electrode was used.

Zirconium was determined gravimetrically as zirconium(IV) oxide. Solid samples were dissolved in 25 cc. of 20% (by volume) hydrogen chloride solution. These solutions were diluted in turn with 50 cc. of 16% (by weight) aqueous mandelic acid and distilled water to a volume of 100 cc. After heating this mixture at 85° for 20 minutes it was filtered and the white hydrous precipitate was washed with a solution of hot 2% HCl-15% mandelic acid solution. The residue was ignited to ZrO_2 at 900°.

Carbon and hydrogen

Carbon and hydrogen determinations were made by Mr. J. J. Richards of the Ames Laboratory Analytical Service Group, Iowa State University of Science and Technology, Ames, Iowa.

Physical Measurements

Magnetic susceptibility

Magnetic susceptibility measurements were made from -196^{o} to room temperature using a Faraday Balance. The balance has been described by Converse (51).

Sample preparation entailed loading powders into Teflon containers in the inert atmosphere box. These containers were fitted with Teflon screw caps which were tightly secured before removing the containers from the box. Weights of the empty container, and container plus sample both before and after the measurement were recorded. Diamagnetic corrections included a correction for the container.

Electron paramagnetic resonance spectra

All epr spectra were obtained on powders at room temperature or -196^{o} using a Strand Model 601 spectrometer equipped with an AFC system which locked the microwave oscillator frequency to the instantaneous cavity frequency. For room temperature measurements the Strand cavity used was the cylindrical TE_{011}^{o} having the maximum of magnetic fields on the cylinder axis and the middle of the end and side walls. At -196^{o} a Varian general purpose rectangular cavity was used.

Nuclear magnetic resonance spectra

The Varian A60 and HA-100 instruments were used for the examination of N.M.R. spectra of benzene solutions. Samples were prepared in vacuum. Tetramethylsilane was added as an internal standard for runs on the A-60 spectrometer.

Electronic spectra

Solid state spectra were obtained using a Beckmann DU Spectrophotometer with reflectance attachment. Samples were mounted as dilute powders with dry $MgCO_3$ as diluent and as reference. The cell used has been previously described (12).

Solution spectra were recorded using a Cary Model 14 Spectrophotometer. Cylindrical fused silica cells 1 cm. long and adapted for use at low pressure (12) were used. Powdered samples were loaded in the dry box and the cell plus adapter was evacuated to ca. 10^{-5} Torr. Solvent was vacuum distilled onto the sample. After sealing off the cell assembly, solvent and/or solutions of different concentrations could be transferred through a medium porosity ground glass frit into the silica cell. After determining the spectra of the most concentrated solutions they were analyzed for niobium using the technique described in the analytical section.

Vibrational spectra

Solid state spectra were obtained by Miss E. Conrad using either a Beckmann IR-7 (1400-600 cm^{-1}) or Beckmann IR-11 (800-42.5 cm^{-1}) spectrophotometer. Samples were prepared in the inert atmosphere box and were mounted as nujol mulls between cesium iodide or polyethylene windows. Mulls were prepared immediately before recording the spectra. The average time to record a spectrum was *ca*. one hour. Mulls were stable over several hours in the cell.

The same instruments were used to record solution spectra. Solutions of the complexes were contained in polyethylene molded cells of 0.2 or 0.5 mm. pathlength. These cells were purchased from Barnes Engineering Company, Instrument Division, Stanford, Connecticut.

Molecular weight determinations

Molecular weights were determined cryoscopically in benzene. The apparatus has been described by Torp (12). A sufficient cooling rate was maintained by submersing the apparatus in a sodium chloride-ice bath and by constant stirring of the solution with a magnetic stirring bar.

Oxidation state determination

A weighed quantity of the solid was treated in the absence of air with 25 cc. of 0.1 N ferric ammonium sulfate. A white precipitate formed upon moderate heating of the mixture. Heating was continued for one hour and the mixture was then cooled to 25° and diluted with 25 cc. of 0.1 N sulfuric acid. After treating the mixture with three drops of ferroin it was titrated with a standard cerium(IV) solution. In this manner an average oxidation number of 4.00 ± 0.01 was established for niobium in pure $NbBr_4$.

Synthesis

Niobium(IV) halides

Niobium(IV) halides were synthesized in evacuated Pyrex tubes by the chemical reduction of the niobium(V) halide with niobium metal. The sealed tubes containing the reactants were heated for 4-5 days in the temperature gradient of a metal-lined double furnace. This gradient was 400°/250° for the chloride, 410°/350° for the bromide and 270°/35° for the iodide (4).

Anal. Calcd. for $NbCl_4$: Nb, 39.59; Cl, 60.41. Found: Nb, 39.74; Cl, 60.26. Calcd. for NbBr: Nb, 22.52; Br, 77.48. Found: Nb, 22.68; Br, 77.32. Calcd. for NbI_4: Nb, 15.47; I, 84.53. Found: Nb, 15.03; I, 84.97. Halide by difference.

Tetrachlorobis(dimethylsulfide)niobium(IV)

This material was obtained by the direct reaction of niobium(IV) chloride with excess dimethylsulfide. Anhydrous niobium(IV) chloride was placed on the medium porosity frit of a Soxhlet extractor which had been modified for work in high vacuum. The vessel was outgassed at ca. 10^{-5} Torr and excess dimethylsulfide was vacuum distilled into the extractor. After isolating this system from the vacuum line the solvent was warmed to initiate reflux. A violet extract formed initially which after several hours gave a dark red solution. The reaction was allowed to proceed to completion. Excess dimethylsulfide was removed in vacuum into cold traps. A dark brown solid remained which had the composition $NbCl_4(S(CH_3)_2)_2$.

Anal. Calcd. for $NbCl_4(S(CH_3)_2)_2$: Nb, 25.88; Cl, 39.50. Found: Nb, 26.08; Cl, 39.49.

If the compound $NbCl_4(S(CH_3)_2)_2$ was outgassed at 10^{-5} Torr for 12 hours a red powder formed for which niobium analysis was consistent with the composition $NbCl_4(S(CH_3)_2)$.

Anal. Calcd. for $NbCl_4(S(CH_3)_2)$: Nb, 31.30. Found: Nb, 31.06.

Tetrachloro(dimethylsulfide)niobium(IV)

Approximately 2.0 g. of $NbCl_4(S(CH_3)_2)_2$ was extracted in vacuo with anhydrous benzene. A red solution formed from which a red crystalline solid separated. Excess benzene was removed into cold traps leaving a residue of red crystals and an orange powder which was outgassed at 10^{-5} Torr for 12 hours. The crystals reduced to an orange powder upon grinding. Chemical analysis was consistent with the composition $NbCl_4(S(CH_3)_2)$.

Anal. Calcd. for $NbCl_4(S(CH_3)_2)$: Nb, 31.30; Cl, 47.77; C, 8.09; H, 2.04. Found: Nb, 31.02; Cl, 47.26; C, 8.07; H, 2.19.

Tetrachloro(diethylsulfide)niobium(IV)

Using the same technique applied for $NbCl_4(S(CH_3)_2)_2$ gave a dark red solid. The solid was outgassed at 10^{-5} Torr for twelve hours without decomposition being apparent. Chemical analysis was consistent with the composition $NbCl_4(S(CH_2CH_3)_2)$.

Anal. Calcd. for $NbCl_4(S(CH_2CH_3)_2)$: Nb, 28.59; Cl, 43.65; C, 14.79; H, 3.10. Found: Nb, 28.83; Cl, 43.65; C , 14.55; H, 3.09.

Tetrabromobis(dimethylsulfide)niobium(IV)

Essentially the same procedure was used here as has been described for the analogous chloride complex. With 2.0 g. of niobium(IV) bromide as starting material the yield was 90-95%. The final product was a dark green crystalline solid having the composition $NbBr_4(S(CH_3)_2)_2$.

Anal. Calcd. for $NbBr_4(S(CH_3)_2)_2$: Nb, 17.31; Br, 59.54;

C, 8.95; H, 2.25. Found: Nb, 17.47; Br, 59.14; C, 8.14; H, 1.75.

Tetrabromo(dimethylsulfide)niobium(IV)

A red crystalline solid having the composition $NbBr_4(S(CH_3)_2)$ was obtained by recrystallization of $NbBr_4(S(CH_3)_2)_2$ from benzene. Yield was 100 per cent.

Anal. Calcd. for $NbBr_4(S(CH_3)_2)$: Nb, 19.57; Br, 67.34; C, 5.06; H, 1.27. Found: Nb, 20.30; Br, 66.31; C, 5.15; H, 1.39.

Tetrabromo(diethylsulfide)niobium(IV)

This compound was prepared in a manner analogous to the previous description. It was isolated as a dark red solid which was stable under dynamic vacuum after *ca*. 12 hours.

Anal. Calcd. for $NbBr_4(S(CH_2CH_3)_2)$: Nb, 18.48; Br, 63.58; C, 9.56; H, 2.00. Found: Nb, 18.44; Br, 64.08; C, 9.23; H, 2.09.

Tetraiodobis(dimethylsulfide)niobium(IV)

A dark brown crystalline solid was obtained using the procedures applied for synthesis of the analogous chloride and bromide compounds. The product was dried under dynamic vacuum over a 12 hour period.

Anal. Calcd. for $NbI_4(S(CH_3)_2)_2$: Nb, 12.82; C, 6.65; H, 1.67. Found: Nb, 12.95; C, 6.01; H, 1.49.

Tetrahalobis(tetrahydrothiophene)niobium(IV)

The complexes $NbX_4(S(CH_2)_4)_2$ (X = Cl, Br and I) were prepared by placing 1 g. of NbX_4 on the medium porosity frit of a modified Soxhlet extractor. This system was evacuated to *ca*. 10^{-5} Torr and an excess of tetrahydrothiophene was distilled into the flask. After isolation of the assembly from the vacuum system, the flask containing the excess ligand was warmed to initiate reflux. Generally three to four days were required to complete the reaction. Excess solvent was removed into cold traps and the residual crystalline solids were dried under dynamic vacuum over a twelve hour period. Products were stored in capped vials in the inert atmosphere box.

With $NbCl_4$ a dark red solution rapidly formed and upon removal of excess solvent a red crystalline solid separated. Chemical analysis was consistent with the composition $NbCl_4(S(CH_2)_4)_2$.

Anal. Calcd. for $NbCl_4(S(CH_2)_4)_2$: Nb, 22.60; Cl, 34.50; C, 22.81; H, 3.83. Found: Nb, 22.72; Cl, 34.64; C, 22.34; H, 3.70.

A deep red solution from which a dark green crystalline solid was recoverable was obtained with $NbBr_4$. Analytical data were consistent with the composition $NbBr_4(S(CH_2)_4)_2$.

Anal. Calcd. for $NbBr_4(S(CH_2)_4)_2$: Nb, 15.78; Br, 54.28; C, 16.32; H, 2.74. Found: Nb, 15.80; Br, 54.48; C, 16.24; H, 2.77.

With NbI_4 a dark brown solid of composition $NbI_4(S(CH_2)_4)_2$ was obtained. This was dried, as above, under dynamic vacuum over 12 hours.

Anal. Calcd. for $NbI_4(S(CH_2)_4)_2$: C, 12.37; H, 2.07. Found: C, 11.93; H, 1.94.

Tetrachlorobis(tetrahydrothiophene)zirconium(IV)

A 1.0 g. sample of white $ZrCl_4$ was allowed to react over several days with excess tetrahydrothiophene in the manner described above for NbX_4. No color changes were observed. The final product was a white powder.

Anal. Calcd. for $ZrCl_4(S(CH_2)_4)_2$: C, 23.47; H, 3.94. Found: C, 23.56; H, 3.91.

Tetrahalobis(2,5-dithiahexane)niobium(IV)

Compounds of composition $NbX_4(dth)_2$ (X = Cl, Br, and I; dth = 2,5-dithiahexane) were obtained by direct reaction of NbX_4 with a solution of excess dithiahexane in *ca*. 50 cc. of dry benzene. A 2-3 g. quantity of NbX_4 was introduced into a 100 cc. round bottom flask to which an excess (10 cc.) of dithiahexane had been added. A magnetic stirring bar was introduced and the flask was evacuated to ca. 10^{-5} Torr, benzene was distilled in, and the flask was isolated from the vacuum system. This mixture was stirred continuously at room temperature for 4-5 days. During this period all the tetrahalide reacted.

With dark brown $NbCl_4$ a tan flocculant precipitate began forming after one hour. After about one day no unreacted tetrachloride could be observed. The reaction was allowed to proceed for three more days. Excess ligand and benzene were removed into cold traps and the residual tan solid was dried under dynamic vacuum over 12 hours.

Anal: Calcd. for $NbCl_4((CH_3SCH_2)_2)_2$: Nb, 19.39; Cl, 29.59; C, 20.05; H, 4.21. Found: Nb, 19.92; Cl, 29.61; C, 19.04; H, 3.96.

From $NbBr_4$ a green precipitate with the composition $NbBr_4(dth)_2$ was isolated.

Anal: Calcd. for $NbBr_4((CH_3SCH_2)_2)_2$: Nb, 14.14; Br, 48.65; C, 14.62; H, 3.07. Found: Nb, 14.34; Br, 48.63; C, 14.02; H, 2.98.

A brown precipitate approaching the composition $NbI_4(dth)_2$ was obtained after a total of ten days of reaction of NbI_4 and the benzene solution of dithiahexane.

Anal. Calcd. for $NbI_4((CH_3SCH_2)_2)_2$: Nb, 10.99; I, 60.07; C, 11.37; H, 2.39. Found: Nb, 11.01; I, 62.03; C, 10.61; H, 2.44.

Tetrachlorobis(2,5-dithiahexane)zirconium(IV)

Using the same procedure as has been described above a white powder having the composition $ZrCl_4((CH_3SCH_2)_2)_2$ was obtained from the reaction of dithiahexane with $ZrCl_4$.

Anal. Calcd. for $ZrCl_4((CH_3SCH_2)_2)_2$: Zr, 19.10; C, 20.14; H, 4.22. Found: Zr, 19.05; C, 20.09; H, 4.03.

RESULTS AND DISCUSSION

Preparation and Properties of Complexes

Direct reactions of excess dimethylsulfide with niobium (IV) halides proceed according to Equation 3.

$$NbX_4 + S(CH_3)_2 \rightarrow NbX_4(S(CH_3)_2)_2 \tag{3}$$

$(X = Cl, Br, \text{and } I)$

Products are isolated as powders which differ in their stability to drying under dynamic vacuum. Thus the chloride is completely converted to $NbCl_4R_2S$, the bromide is incompletely converted to $NbBr_4R_2S$, and $NbI_4(R_2S)_2$ is unaffected by exposure for twelve hours to a dynamic vacuum. Although the reactions were carried out in the presence of a large excess of dimethyl sulfide no evidence for coordination of more than two moles of the sulfide per mole of NbX_4 was indicated. Solubility studies in dimethyl sulfide and benzene indicate a low to moderate solubility in the former and a low solubility in the latter. Upon exposure to the atmosphere the compounds rapidly decomposed as indicated by color changes and the easy detection of the odor of the sulfide. Both the bromide and iodide complexes exhibited respective incongruent melting points of 91-94° and 100-103°.

Recrystallization in vacuo of $NbX_4(S(CH_3)_2)_2$ (X = Cl and

Br) from benzene gave red crystalline solids for which the analytical data were consistent with the formula $NbX_4S(CH_3)_2$. Spectral data to be subsequently discussed suggest that these are easily converted to the bis complexes in excess ligand. Equation 4 is descriptive of these observations.

$$NbX_4(S(CH_3)_2)_2 \underset{S(CH_3)_2}{\overset{C_6H_6}{\rightleftharpoons}} NbX_4(S(CH_3)_2) + S(CH_3)_2 \qquad (4)$$

(X = Cl and Br)

These monoadducts exhibited melting points of 142-144° and 134-137°, and appeared to melt with decomposition. Pure monoadducts could be obtained directly if excess diethyl sulfide was allowed to react with NbX_4 (X = Cl and Br). No evidence for solid phases having a composition $NbX_4(S(CH_2CH_3)_2)_2$ was found. The observed moderate solubility of the monoadducts in excess ligand suggests that in solution bis-adducts are present.

Only bis-adducts were obtained from reactions of NbX_4 (X = Cl, Br, and I) and $ZrCl_4$ with tetrahydrothiophene. Analytical data in every case were consistent with $NbX_4(S(CH_2)_4)_2$. These compounds melt at temperatures comparable to the dimethyl sulfide compounds. Because charring and gas formation were observed, decomposition at the melting points was evident.

Decomposition products were not investigated. Solubilities in excess ligand are moderate, and in benzene the solubilities are slightly less than 6.0 g/100 cc. at room temperature. While very pure crystalline complexes were obtained from tetrahydrothiophene, extraction of $NbCl_4(S(CH_2)_4)_2$ with benzene left a green residue on the frit of the extractor. Analytical data for this residue were consistent with the formulation $NbCl_4(S(CH_2)_4)_{1.6}$. The orange powder recovered from the extract was virtually pure $NbCl_4(S(CH_2)_4)_2$. The reason for formation of the green product is unknown. Possibly the benzene was slightly contaminated with moisture and this material is an oxygen-containing benzene-insoluble hydrolysis product. Insufficient material was obtained for further characterization via magnetic studies. It should be noted that better than 95% of the $NbCl_4(S(CH_2)_4)_2$ was recovered in the extract, and this compound will be discussed further in the section on far infrared studies. Finally, while Fairbrother (7) reports the isolation of the apparently seven-coordinate complex $NbCl_5(S(CH_2)_4)_2$, here no evidence for a coordination number greater than six for Nb(IV) was found.

With the ligand 2,5-dithiahexane (dth) complexes having compositions $NbX_4(dth)_2$ (X = Cl, Br, and I) were isolated. As described in the experimental section these reactions were performed in benzene solutions containing an excess of 2,5-dithiahexane. All the complexes were virtually insoluble in the reaction media and precipitated as fine powders. Since 2,5-dithiahexane is a bidentate ligand, eight-coordination of niobium was immediately suggested. Clark and coworkers (29) successfully prepared the eight coordinate complexes NbX_4(diarsine)$_2$ (X = Cl, Br, and I; diarsine = O-phenylenebisdimethyl arsine) from the direct reaction at high temperature of NbX_5, NbX_4, or $NbOX_3$ with diarsine. The literature contains no other reports of eight-coordinate NbX_4B_2 (B = bidentate ligand). The tetrahalides VCl_4, $TiCl_4$, and $TiBr_4$ form eight coordinate complexes with diarsine (37), but only six coordinate complexes form with dithiahexane. Zirconium(IV) chloride forms an eight coordinate dodecahedral complex with diarsine, and in this study a white powder having the composition $ZrCl_4$(dth)$_2$ was obtained from its reaction with 2,5-dithiahexane.

As described in the experimental section, all of the complexes which have been discussed decompose in air or moisture. Instability increases from the chloride to the iodide in a series, and the dimethyl sulfide complexes are less stable than the 2,5-dithiahexane species. Upon treatment of any of these solids with water a dark blue solution forms from which a white precipitate slowly deposits upon standing in air. Treatment of the blue solutions with concentrated ammonia induces immediate precipitation of a hydrous dark brown solid, probably $NbO_2 \cdot xH_2O$. This was readily oxidized by concentrated nitric acid to white $Nb_2O_5 \cdot xH_2O$. Treatment of the tetrahydrothiophene complexes with acetone in air gave red solutions which slowly lost their color and deposited white precipitates.

In order to ascertain the nature of the species in the solid and solution phases a detailed study of their infrared spectra, magnetic behavior, and electronic spectra was undertaken, and remaining sections will be concerned with those results.

Complexes of the Form MX_4L_2

The synthesis and some properties of the complexes NbX_4L_2 (X = Cl, Br, and I; L = $(CH_3)_2S$ and $(CH_2)_4S$) and $ZrCl_4L_2$ were described in the previous section. In this section the results of studies of their infrared spectra (1600-600 cm^{-1}), far-infrared spectra (400-42.5 cm^{-1}), magnetism, and electronic spectra will be given, in that order.

Infrared spectra (1300-600 cm^{-1})

Infrared spectra of the uncoordinated ligands and the complexes were recorded. Table 1 summarizes the results.

Table 1. Infrared spectra of $(CH_3)_2S$ and $NbX_4((CH_3)_2S)_n$ (n = 1 and 2; X = Cl, Br, and I)

Compound	ν(cm^{-1})			
$(CH_3)_2S$	1027m-s (CH_3 rock)	972m-s (CH_3 rock)	742w (C-S str)	692m (C-S str)
$NbBr_4(S(CH_3)_2)_2$	1028m	971m	720m	675w
$NbI_4(S(CH_3)_2)_2$	1030m	970m	722m	675w
$NbCl_4(S(CH_3)_2)$	1031m	974m	730,723w	680,670w
$NbBr_4(S(CH_3)_2)$	1026w	970w	722w	675vw

(s = strong, m = moderate, w = weak, vw = very weak)

Infrared spectra of dimethyl sulfide have been reported (44) and most of the observed bands have been assigned to fundamental modes of this molecule. In complexes containing dimethylsulfide, bands due to carbon-sulfur stretching modes are expected to be the most sensitive to coordination via sulfur, however, it has been reported (52) that these bands are usually weak and that shifts arising from coordination of sulfur are usually small. Nevertheless, Fowles *et al.* recently reported that carbon-sulfur bands at 692 (A_1) and 742 cm^{-1} (B_1) in the spectra of dimethyl sulfide were shifted, respectively, by 4-27 and 12-17 cm^{-1} in spectra of TiX_3L_2 (L = dimethylsulfide) complexes. The presence of coordinated dimethyl sulfide is also inferred for the complexes reported here, since the same bands are shifted to lower energy in spectra of the complexes by ca. 20 cm^{-1}.

The infrared spectrum of tetrahydrothiophene has not been studied in detail, but from studies of its complexes (53) it has been inferred that the band at 685 cm^{-1} in the free ligand spectrum is a ring stretching mode involving the sulfur atom. Lewis, Miller, Richards, and Thompson (53) report that this band shifts to ca. 670 cm^{-1} in spectra of the complexes $MX_3(S(CH_2)_4)_2$ (M = Al, Ga; X = Cl, Br). More recently Fowles, Lester, and Walton (43) reported shifts to lower energy of 13 to 20 cm^{-1} of the 685 cm^{-1} band in spectra of the complexes $TiX_3(S(CH_2)_4)_2$ (X = Cl, Br, and I). In the present study this band is observed to shift by ca. 24 cm^{-1} to lower energy for $NbX_4(S(CH_2)_4)_2$ (X = Cl, Br, and I) as well as $ZrCl_4(S(CH_2)_4)_2$. It is concluded then that coordinated tetrahydrothiophene is present.

Far infrared spectra (400-42.5 cm^{-1})

Far infrared spectra of the ligands, the anhydrous halides, and the complexes (solids and solutions) were recorded. These will now be discussed in turn.

Dimethyl sulfide exhibits a very broad weak band at 282 cm^{-1} which has been assigned to a C-S-C deformation mode (44). No other bands are observed in spectra of the pure ligand. Spectra of tetrahydrothiophene exhibit bands at 467(moderate), 320(weak and broad), and 300 cm^{-1}(weak and broad). As no definitive studies of tetrahydrothiophene have been done, these bands remain unassigned. Pure benzene exhibits two bands of weak-moderate intensity at 400 cm^{-1} and 300 cm^{-1}.

There appear to have been no reported far infrared spectra of niobium(IV) halides in the literature. A detailed structure determination by Dahl and Wampler (2) of α-NbI_4 has been reported as well as some of the details of a similar investigation of $NbCl_4$. McCarley and Torp (1) report the results of powder x-ray diffraction studies which indicate that $NbCl_4$ and $NbBr_4$ are isomorphous, however, it did not appear that they were isomorphous with α-NbI_4. This has been confirmed by Schäfer and Schnering (3). The α-NbI_4 structure consists of linear infinite chains formed by NbI_6 octahedra sharing opposite edges. Niobium atoms are shifted from the centers of their octahedra in pairs to form alternating metal-metal bonds. While the site symmetry is C_{2v}, Dahl (54) considered the unit $(Nb_2I_2^2)I_4^1I_{4/2}^3$ having D_{2h} symmetry in discussions of the electronic structure. It is this model which is used in this discussion of far-infrared data. Table 2 shows the assignments based on the model given in Fig. 1.

Table 2. Far infrared spectra of NbX_4 (X = Cl, Br, and I) and assignments of Nb-X stretching bands (ν in cm^{-1})

Assignment	$NbCl_4$	$NbBr_4$	NbI_4
$\nu(Nb\text{-}X^1)$	430(s)	315(s)	227(s)
	390(s)	286(s)	208,200(s)
$\nu(Nb\text{-}X^2)$	360(s)	245(w)	165(s)
	290(m,sh)	215(s)	150(m,sh)
$\nu(Nb\text{-}X^3)$	265(s)	190(s)	--
	245(s)	178(m,sh)	--
Unassigned	220(m,sh)	154(m)	110(m)
	175(w,m)	115(m,sh)	80(w,sh)
	130(w)	95(m)	65(m)
	95(s)	72(s)	57(m)

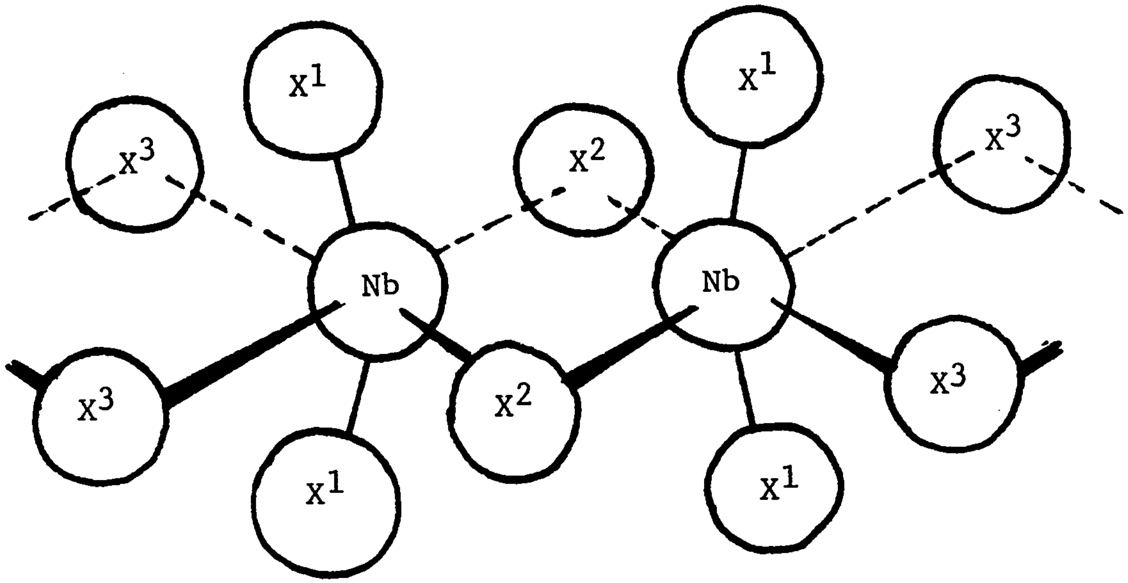

Fig. 1. Model used as basis for assignments of stretching bands in far infrared spectra of NbX_4 (X = Cl, Br, and I)

Figure 2 gives the spectra of the halides. For the model chosen, and considering stretching modes only, three different types are expected. These arise, respectively, from terminal halogens, bridging halogens (across metal bond), and bridging halogens (to adjacent octahedra). Bond distances data for $NbCl_4$ (3) and NbI_4 (2) indicate that these distances increase in the order in which they have been presented with the first two distances being shorter than the last. It is expected then that bond orders and therefore the force constants and frequencies associated with metal halogen stretching modes will decrease in the order $Nb\text{-}X^1 > Nb\text{-}X^2 > Nb\text{-}X^3$. Halogen-sensitive bands are clearly evident upon comparing the spectra. For the chloride $\nu(Nb\text{-}X^1)$ were assigned as 430 and 390 cm^{-1}, for the bromide as 315 and 286 cm^{-1}, while for the iodide three bands occurring at 227, 280, and 200 cm^{-1} are found where only two were anticipated. Bands due to $\nu(Nb\text{-}X^2)$ occur at 360 and 290 cm^{-1} for X = Cl, 245 and 215 cm^{-1} for X = Br, and 165 and 150 cm^{-1} for X = I. The intensity of the band at 245 cm^{-1} in the bromide spectrum is much lower than for corresponding bands in the chloride and iodide. For $\nu(Nb\text{-}X^3)$ bands appear at 265 and 245 cm^{-1} and 190 and 178 cm^{-1} for the chloride and bromide, respectively, but the two bands expected at approxi-

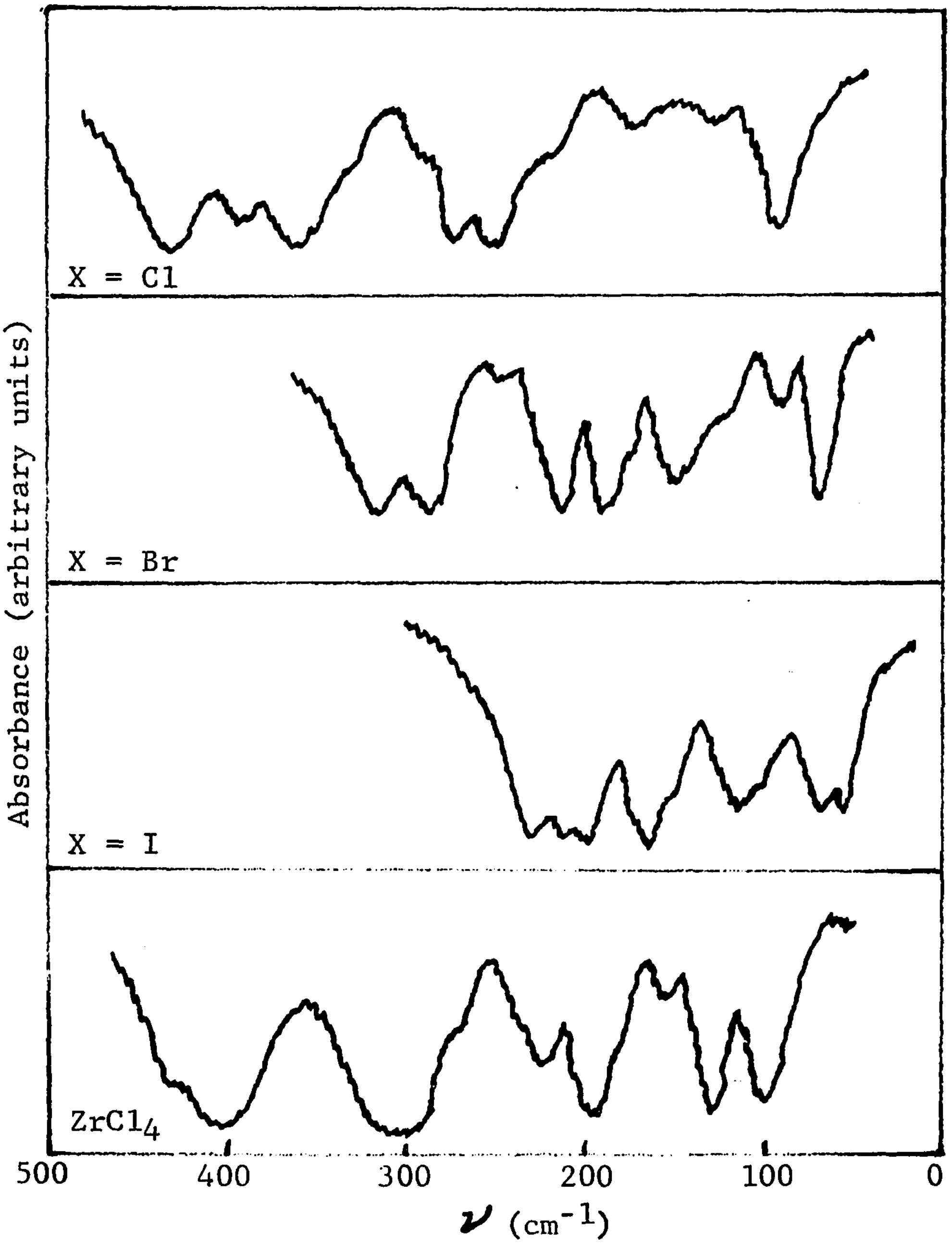

Fig. 2. Far infrared spectra of NbX_4 (X = Cl, Br, and I) and $ZrCl_4$ (nujol mulls)

mately 120-130 cm^{-1} for α-NbI_4 are not observed, instead only an ill-defined band of low intensity is observed. It should be noted that signal-to-noise ratios are small in this region resulting in loss of sensitivity. Cognizant of this fact it is concluded that the model assumed may well be applicable to all three niobium(IV) halides, however, further studies of Raman spectra would be of assistance in substantiating these conclusions.

Weidlein, Müller, and Dehnicke (55) report both the Raman and infrared spectra of $ZrCl_4$. Metal halogen stretching fundamentals were assigned in Table 3 on the basis of a model having D_{2h} symmetry and consisting of a bioctahedral chlorine bridged dimer which shares axial chlorines with adjacent dimers. In the far infrared spectrum of $ZrCl_4$, which is reported in this study in Fig. 2, broad bands lacking much structure are observed where the other workers achieved resolution. It is of interest that earlier studies (56,57) support a molecular lattice of SnI_4 type for $ZrCl_4$, while the data of Weidlein _et al_. support six-fold coordination of zirconium in $ZrCl_4$.

The solid state spectra of $NbX_4(S(CH_2)_4)_2$ (X = Cl, Br, and I) and $ZrCl_4(S(CH_2)_4)_2$ are reproduced in Fig. 3. For such complexes both cis and trans isomers can be expected. Beattie,

Table 3. Far infrared spectrum and assignments of bands for $ZrCl_4$ (ν in cm^{-1})

Assignment	This work	Weidein, *et al.* (55)
$\nu_s(B_{3u})$	430(s)	431(vs)
$\nu_{as}(B_{2u})$	400(s,br)	388(s)
$\nu_{as}(B_{3u})$	300(s,br)	305(m)
$\nu_s(B_{1u})$		291(s)
$\nu_{ring}(B_{2u})$	270(m,sh)	283(m)
$\nu_{ring}(B_{3u})$		271(s)
$\delta(B_{3u})$	229(m)	233(m)
$\delta(B_{3u})$	196(s)	204(s)
$\delta(B_{2u})$		
Unassigned bands	158(w), 131(s), 101(m), 53(m-s)	154(w), 128(s), 98(m)

et al. (58) by a normal coordinate analysis, established that cis isomers should exhibit spectra having at high energy a triplet of closely spaced bands due to M-X stretching modes and transforming as the b_1, b_2, and a_1 representations of the point group C_{2v}. A fourth band (a_1) should occur at considerably lower energy. This result assumed metal-ligand force constants an order of magnitude lower than for metal-halogen. If these are comparable, for a cis complex as many as six

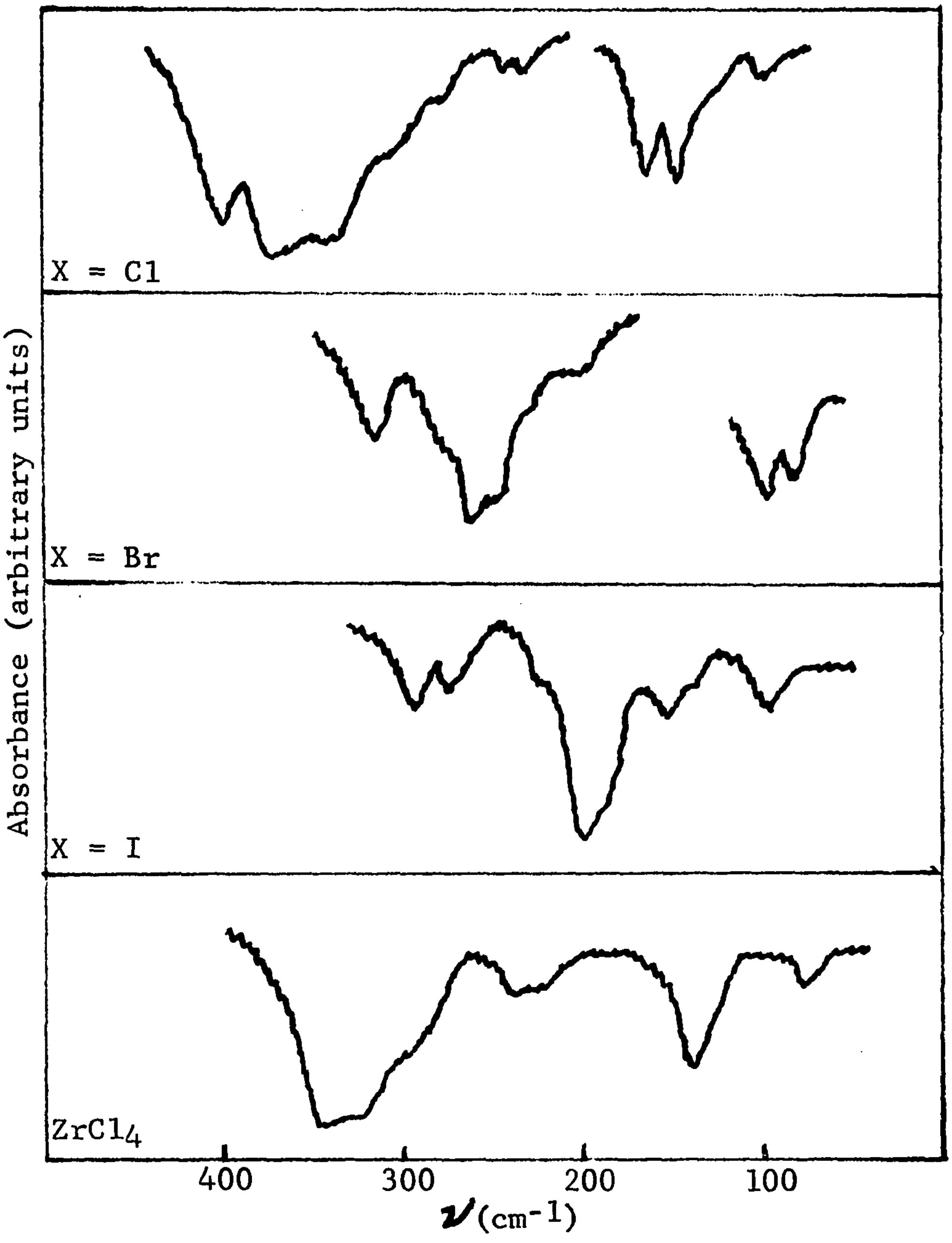

Fig. 3. Far infrared spectra (nujol) of tetrahydrothiophene complexes of NbX_4 (X = Cl, Br, and I) and $ZrCl_4$

bands could occur in these same regions. For a trans isomer when the metal-ligand force constant is low relative to metal halogen only one band (e_u) is expected in the region where three occur in the spectrum of cis-adducts. Where these force constants are comparable at least two bands can appear in this region ($e_u + a_{2u}$) with a possibility of a third if the e_u-vibration is rendered non-degenerate by solid state effects. Analysis of the present spectra proceeded initially on the assumption that metal-ligand and metal-halogen stretching force constants were very different. It quickly became evident that such was not the case for the bromide. Results are summarized in Table 4.

Several halogen-sensitive bands are evident upon comparison of the spectra of $NbX_4(S(CH_2)_4)_2$ (X = Cl, Br, and I). A closely spaced triplet occurs at 397, 372, and ~340 cm^{-1} for X = Cl and 263, 247, and 229 cm^{-1} for X = Br. These are assigned as the three higher energy Nb-X stretching bands expected for a cis isomer. Dougherty (31) reports only two very broad bands at 365 and 334 cm^{-1} for $NbCl_4(ac)_2$ (ac = acetonitrile) and a dipole moment study in benzene (12) supports a cis configuration. A closely spaced triplet at 280, 256, and 235 cm^{-1} in the spectrum of $NbBr_4(ac)_2$ (31) and

Table 4. Far infrared spectra and assignments for $NbX_4(S(CH_2)_4)_2$ (X = Cl, Br, and I) (ν in cm^{-1})

Assignment	X = Cl	X = Br	X = I
ν(Nb-X)	396(m)	263(s)	227(w)
($2a_1+b_1+b_2$)	372(s)	247(m)	200(s,br)
	340(m,sh)	229(w-m)	
	245(w)	200	148(w-m)
ν(Nb-S)[a]	302(w)	307(w-m)	297(m)
	278(w)	278(m,sh)	272(w)
ν(Nb-S-C)[a]	235(w)		
ν(X-Nb-X)	162(m-s)	96(m)	-
	148(m-s)	85(m)	-
Unassigned bands	100(w)	190(w)	98(w)
			138(ww)

[a] These assignments are tentative.

assigned as Nb-Br stretching bands also suggest a cis-stereochemistry. This has been confirmed by Dougherty (31) using the techniques of Single Crystal X-ray Diffraction Analysis. Lower energy bands at ca. 300 and 275 cm^{-1} in the spectra of the chloride, bromide, and iodide are tentatively assigned as metal-sulfur stretching bands. These are most clearly resolved in the spectrum of the iodide and support the assignment of a cis-stereochemistry for this complex. Added complications are the occurrence of a broad, weak ligand absorption at ca. 300 cm^{-1} discussed earlier, as well as the occurrence of Nb-Br and Nb-S in virtually the same region. As expected in such a case a total of six bands are observed in the region of Nb-Br stretching vibrations. A fourth Nb-X stretching is observed at ca. 245 cm^{-1} (X = Cl) and ca. 198 cm^{-1} (X = Br). Metal-halogen bending vibrations are assigned as 163 and 148 cm^{-1} (X = Cl) and 96 and 85 cm^{-1} (X = Br).

Bands assigned as M-S-C bending reportedly occur at ca. 250 cm^{-1} in spectra of cis-$PtCl_4(S(CH_3)_2)_2$ (60) though these are possibly due to torsional modes raised in the solid. In the present systems bands appear at 250 cm^{-1} in the spectra of $NbCl_4(ac)_2$ and $NbCl_4(S(CH_3)_2)_2$ and are assigned here as the fourth Nb-Cl stretching mode (a_1). The weak band at 235 cm^{-1} for $NbCl_4(S(CH_3)_2)_2$ is tentatively assigned as Nb-S-C bending. A band is expected for the bromide near the region of the fourth Nb-Br stretching band but is not observed, perhaps because of poor resolution. Additional comment is in order concerning spectra of NbI_4L_2 (L = monodentate donor) complexes. No such spectra have been reported to date. In the course of this investigation $NbI_4(ac)_2$ was prepared using the procedure of Torp (12), and its far infrared spectrum was recorded. The spectrum is reproduced in Fig. 4. Its similarity to that of

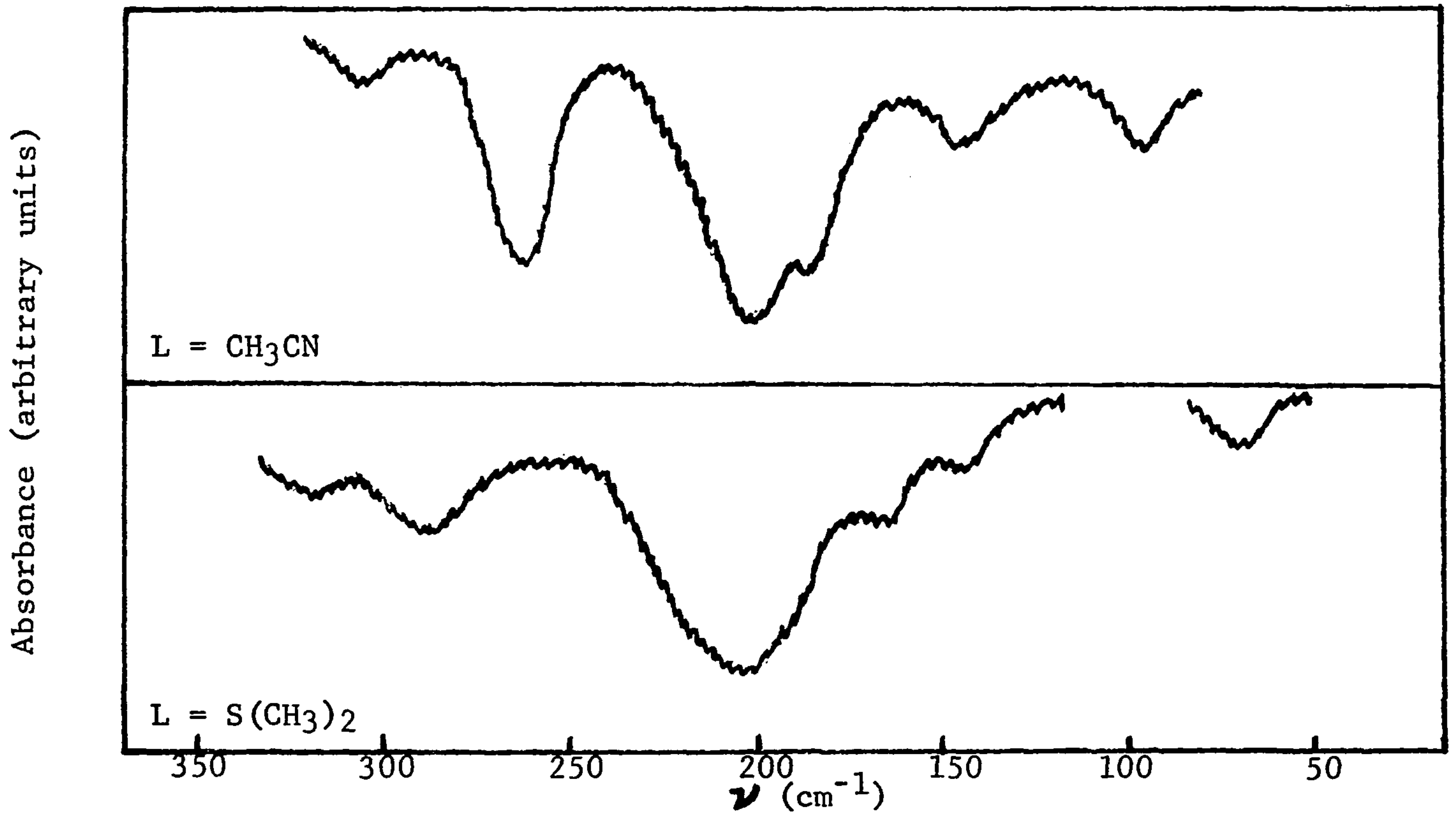

Fig. 4. Far infrared spectra of NbI_4L_2 ($L = S(CH_3)_2$ and CH_3CN) (nujol)

$NbI_4(S(CH_2)_4)_2$ is striking. Two bands at high energy in both spectra exhibit a marked sensitivity to the nature of the ligand thus supporting the conclusion that they are predominantly due to Nb-L stretching. In the acetonitrile these bands at 306 and 264 cm^{-1} are assigned as Nb-N stretching bands.

Data for $ZrCl_4(S(CH_2)_4)_2$ are given in Fig. 3 and Table 5.

Table 5. Far infrared spectrum and assignment of bands for $ZrCl_4(S(CH_2)_4)_2$ (ν in cm^{-1})

Assignment	$ZrCl_4(S(CH_2)_4)_2$
$\nu(Zr\text{-}Cl)e_u$	340(s,br)
	320(s,sh)
$\nu(Zr\text{-}S)$	290(m,sh)
$\delta(Zr\text{-}S\text{-}C)$	232(w-m)
$\delta(Cl\text{-}Zr\text{-}Cl)$	218(w,sh)
$\pi(Cl\text{-}Zr\text{-}Cl)$	140(m)
Unassigned bands	75(w-m)

Two maxima can be identified at 340 and 320 cm^{-1} on what is otherwise a very broad band. A shoulder appears at 290 cm^{-1}. By comparison with the spectra of NbX_4L_2 complexes it is expected that force constants for Zr-Cl and Zr-S will not be too different, hence a trans isomer cannot be eliminated in which Zr-Cl and Zr-S stretching frequencies are closely similar and for which the band due to the former, transforming as an e_u representation of the point group D_{4h}, is split by solid state effects. While the total number of expected infrared bands is not a highly indicative datum, it is perhaps relevant that only five to eight bands $(2a_{2u} + 3e_u)$ are expected for a trans isomer while thirteen $(6a_1 + 3b_1 + 4b_2)$ are expected for a cis form. At most seven bands are present in the spectrum of $ZrCl_4(S(CH_2)_4)_2$. The strong similarity of this spectrum to that of trans-$PtCl_4(S(CH_3))_2$ (60) is also noted.

Only the complexes $NbX_4(S(CH_3)_2)_2$ (X = Cl, Br, and I) remain to be discussed. As noted earlier, characterization of $NbCl_4(S(CH_3)_2)_2$ was totally hindered by its high instability. Far infrared spectra of $NbX_4(S(CH_3)_2)_2$ (X = Br and I) were recorded as nujol mulls. Both sets of spectra were consistent with a cis-stereochemistry. Assignment of Nb-S stretching bands in the case of the bromide was rendered difficult by the low resolution achieved, nonetheless, the occurrence of four bands in the region 220-300 cm^{-1} is inconsistent with a trans-stereochemistry for this complex. The spectrum of the iodide complex given in Fig. 4 is similar in all respects to the spectrum of $NbI_4(S(CH_2)_4)_2$. Two bands attributable to Nb-S stretching occur at 316 and 288 cm^{-1}, while a broad strong band assigned as an Nb-I stretch occurs at 205 cm^{-1} with shoulders at 164 and 144 cm^{-1}.

As described in the experimental section some investigations of solution far infrared spectra were initiated. The results of these studies are depicted in Fig. 5 and Table 6.

Table 6. Far infrared spectra of solutions of $NbX_4(S(CH_2)_4)_2$ X = Cl and Br (ν in cm^{-1})

Solvent	C_6H_6	$S(CH_2)_4$	C_6H_6	$S(CH_2)_4$
	X = Cl		X = Br	
	398(m)	396(w,sh)	400(m)[a]	
	380(m)	366(s)		
	362(s)	340(m)		
	320(w)	304(w-m)	300(m,sh)	
	300(w)			
		280(w)	266(s)	266(s)
		250(w,sh)	253(s)	253(s)
		230(w)	229(m,sh)	227(m)
			200(w)	

[a] Benzene peak.

Comparison of the spectrum of solid $NbCl_4(S(CH_2)_4)_2$ with that of the complex dissolved in tetrahydrothiophene reveals a one-to-one correspondence over the region 200-370 cm^{-1}. Above this region a band present at 306 cm^{-1} in the solid state spectrum is absent in the solution spectrum. This suggests that

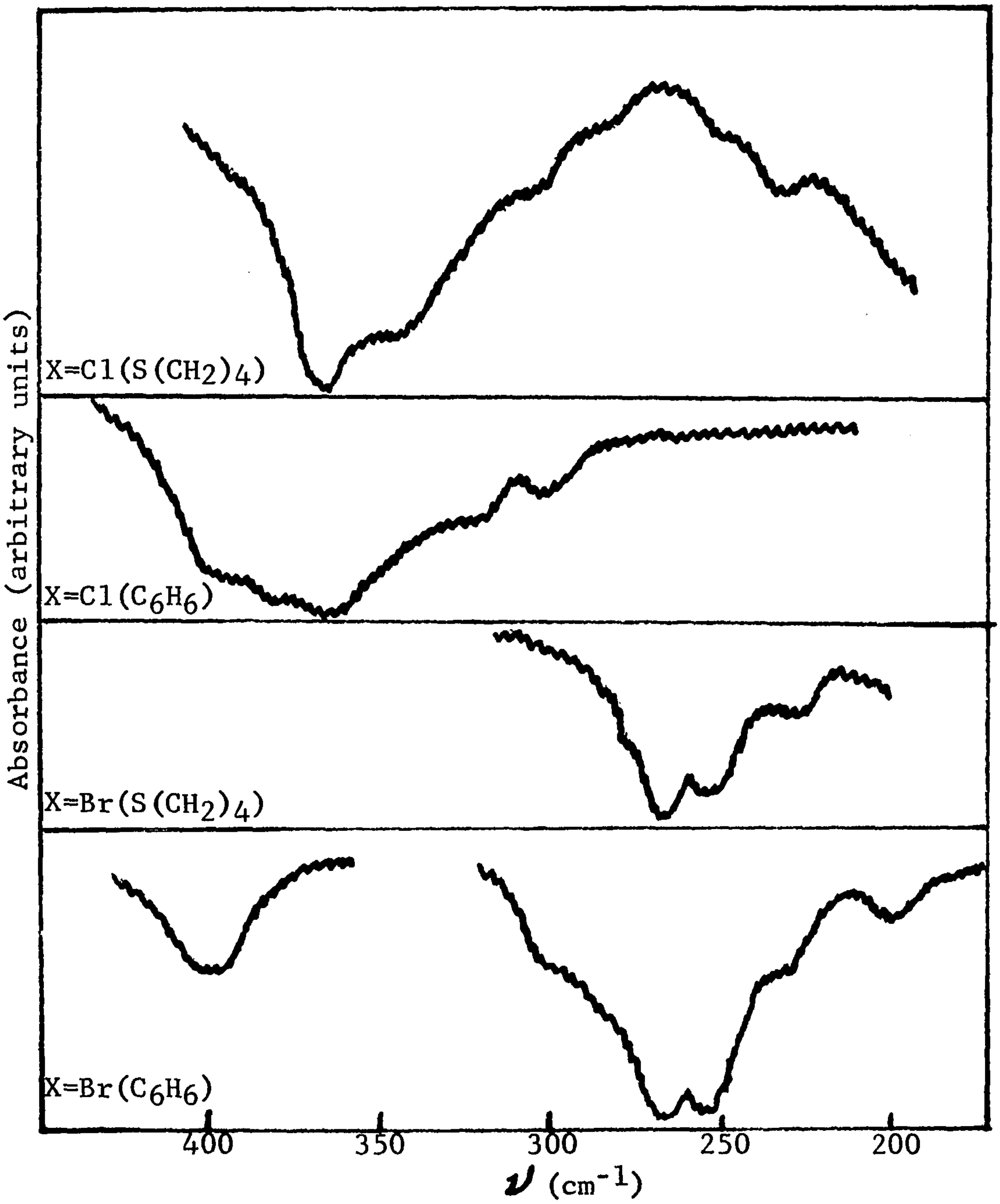

Fig. 5. Far infrared spectra of $NbX_4(S(CH_2)_4)_2$ (X = Cl and Br) in C_6H_6 and $S(CH_2)_4$

this band is due to solid state effects. Admittedly such effects are frequently introduced as explanations when one is presented with anomalous results, however, data to be subsequently presented are consistent with the same species being present in both solution and solid phases. The spectrum of the benzene solution of $NbCl_4(S(CH_2)_4)_2$ is not so easily rationalized. A group of three closely spaced overlapping bands is found at frequencies 396, 380, and 365 cm^{-1} with a lower energy doublet at 320 and 300 cm^{-1}. The number of bands in this region is consistent with a cis-complex being present in solution, however, the absence of a clearly defined band at 340 cm^{-1} and the presence of a band due to benzene at 396 cm^{-1} complicates this interpretation. Possibly some impurity bands account for the differences. Aside from solubility problems rendering difficult or impossible the detection of weak bands, the solid state and benzene and tetrahydrothiophene solution spectra of $NbBr_4(S(CH_2)_4)_2$ are virtually identical in the region of Nb-Br stretching bands (200-300 cm^{-1}). It is concluded that the same cis-isomer is present in each phase.

Discussion of solution spectra of $NbX_4(S(CH_3)_2)_2$ (X = Cl and Br) will be deferred until the monoadducts $NbX_4(S(CH_3)_2)$ are considered in a later section.

Magnetic susceptibilities

Prior to discussing the results of these studies those aspects of the theory of magnetic susceptibilities which are relevant will be considered. The molar magnetic susceptibility of a paramagnetic compound is given by Equation 5 (59), where

$$\chi_M = (NB^2\mu^2/3kT) + \chi_D + \chi_{TIP} \tag{5}$$

with

N = Avogadro number, 6.023×10^{23} mole^{-1}

B = Bohr magneton, 0.9273×10^{-20} erg gauss^{-1}

μ = magnetic moment in Bohr magnetons

k = Boltzmann constant, 1.3804×10^{-6} erg deg^{-1}

T = absolute temperature, $^{\circ}$K

χ_D = diamagnetic susceptibility, emu/mole

and

χ_{TIP} = temperature independent susceptibility, emu/mole.

Plots of the experimental molar susceptibility vs 1/T yield straight lines in cases of Curie behavior, and the intercepts on the χ_M axis are the sum of the temperature independent susceptibilities, $\chi_D + \chi_{TIP}$. Knowing the value of χ_D for specific atoms, ions, and molecules from tables, the value of χ_{TIP} can be calculated. This temperature independent susceptibility comes about by the mixing into the ground state of small amounts of some higher state under the influence of the magnetic field. The net result is a lowering of the energy of all components of the ground state by an amount proportional to the square of the magnetic field and inversely proportional to the energy separation of the upper and ground states (60). The slope of a Curie plot is used to calculate the magnetic moment via Equation 6. In this equation the constant

$$\mu(\text{B.M.}) = 2.828\sqrt{(\chi_M-\chi_D-\chi_{TIP})T} \qquad (6)$$

is obtained by substitution of the values for the constants in Equation 3. When the χ_M versus T^{-1} plots exhibit curvature it is possible to describe the behavior of χ_M as a function of T using the Curie-Weiss law described by Equation 7. Here θ is

$$\chi_M = (NB^2\mu^2)/3k(T+\theta) + \chi_D + \chi_{TIP} \qquad (7)$$

a constant which in magnetically dilute systems seldom has a basic significance. A much used procedure is to calculate an effective magnetic moment using Equation 8. Since for the

$$\mu_{eff} = 2.828\sqrt{(\chi_M-\chi_D)T} \qquad (8)$$

majority of paramagnetic compounds values of μ_{eff} are given, these are reported here and used in later discussions. Diamagnetic core corrections which were applied were obtained from the literature (61,62) and are given in Table 7, others were obtained by summing from known values.

Magnetic properties of transition metal complexes can be discussed relative to simple Kotani theory (63), or alterna-

Table 7. Diamagnetic core corrections (Units: 10^{-6} emu/mole)

Ions	χ_D	Molecules	χ_D
Nb^{4+}	14	$S(CH_3)_2$	-45
Cl^-	-26	$S(CH_2CH_3)_2$	-68
Br^-	-36	$S(CH_2)_4$	-62
I^-	-52	$(CH_3SCH_5)_2$	-90

tively the theory of Stevens (64), later modified and applied by Bleaney and O'Brien (65) to $K_3Fe(CN)_6$, can be employed. These workers found that epr data for $K_3Fe(CN)_6$ (ground state configuration t_{2g}^5, rhombic distortion) could not be correlated with theory unless an extra orbital reduction factor k was introduced into the magnetic moment operator, viz. $(kL+2S)\beta H$. This factor k accounted for modifications of the t_{2g} orbitals due to π-bonding between these orbitals and suitably oriented ligand orbitals. By varying the spin-orbit coupling constant to give the best fit with theory, k for $K_3Fe(CN)_6$ was found to be 0.87. The delocalization factor k was related to the g-factors via Equations 9. Here θ is directly related to the

$$\begin{aligned} g_z &= 2\cos^2\theta[\sin^2\alpha-(1+k)\cos^2\alpha] + 2\sin^2\theta(k-1) \\ \tfrac{1}{2}[g_x+g_y] &= -2\cos^2\theta[\cos\alpha + (k/\sqrt{2})\sin\alpha] \qquad (9) \\ \tfrac{1}{2}[g_x-g_y] &= 2\sin^2\theta[\cos\alpha+(k/\sqrt{2})\sin\alpha] \end{aligned}$$

size of the rhombic distortion. When θ approaches zero Equations 10, applicable for axial distortions, are obtained.

$$\begin{aligned} g_z = g_{\parallel} &= 2[\sin^2\alpha - (1+k)\cos^2\alpha] \\ \tfrac{1}{2}[g_x+g_y] = g_{\perp} &= -2[\sin^2\alpha + \sqrt{2}k\ \cos\alpha\sin\alpha] \qquad (10) \\ \tfrac{1}{2}[g_x-g_y] &= 0 \end{aligned}$$

Figgis (66) considered this case and its effect on magnetic properties arising from cubic field $^2T_2$ terms. The effective magnetic moment was calculated for different values of v, k, and λ with v being defined by Equation 11 as the ratio of the

$$v = \Delta/\lambda = \sqrt{2}(\cos\alpha - \tan\alpha - \sqrt{2}) \qquad (11)$$

energy difference of the split $^2T_2$ level to the spin-orbit coupling constant. When the $^2T_2$ degeneracy is removed by a low symmetry field component leaving an orbital singlet as the lowest level Δ is positive, otherwise it is negative. Results of these studies by Figgis were published as a set of tables (66), and are used later in this section.

All the bis-adducts which were studied here obeyed the Curie law. Figures 6 and 7 are the Curie plots, and Table 8 contains the magnetic parameters obtained from the graphs. No data were obtained for $NbCl_4(S(CH_3)_2)_2$. A compound of this composition (see experimental section) was converted to $NbCl_4(S(CH_3)_2)$ during initial evacuation of the balance

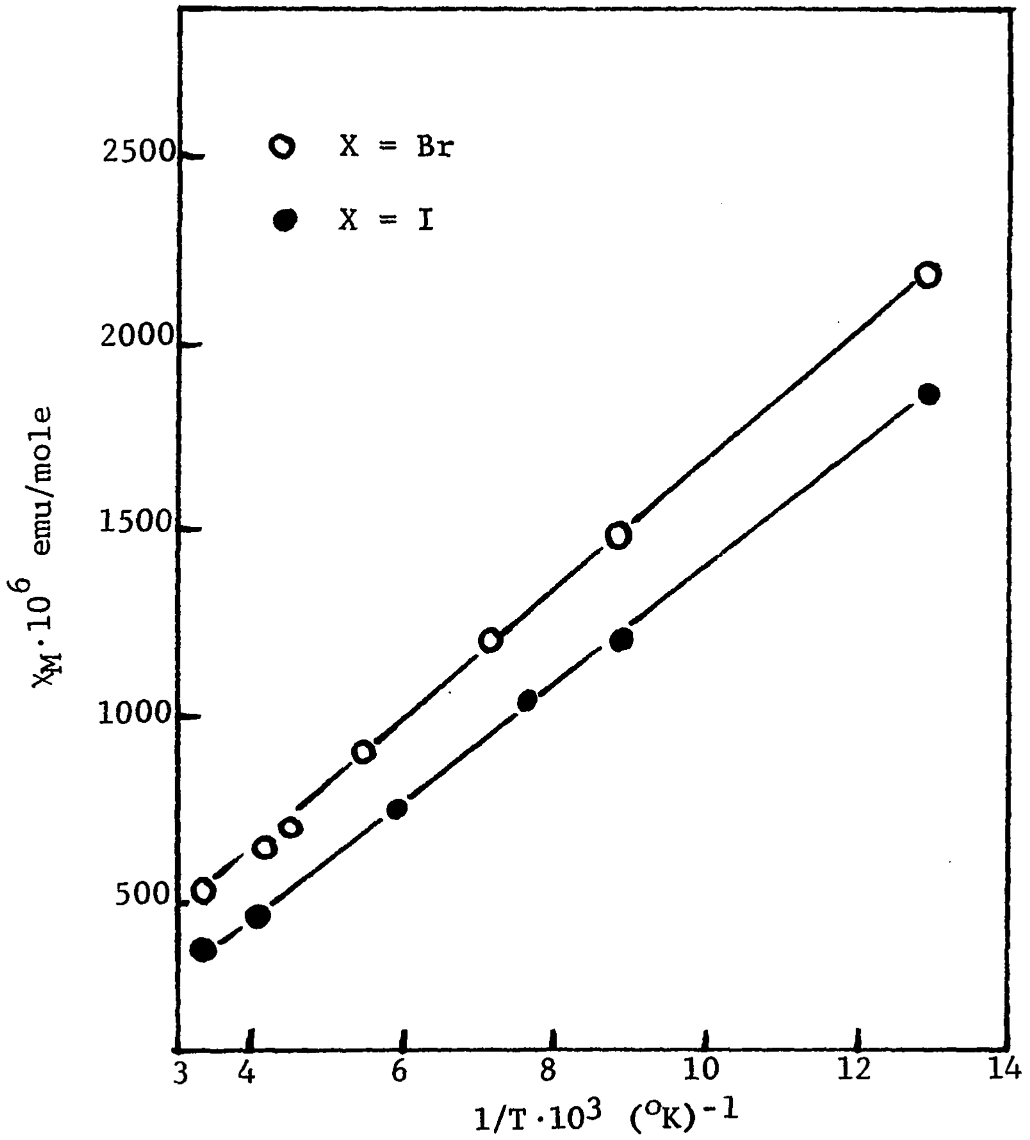

Fig. 6. Variation of molar magnetic susceptibility with reciprocal temperature for $NbX_4(S(CH_3)_2)_2$ (X = Br and I)

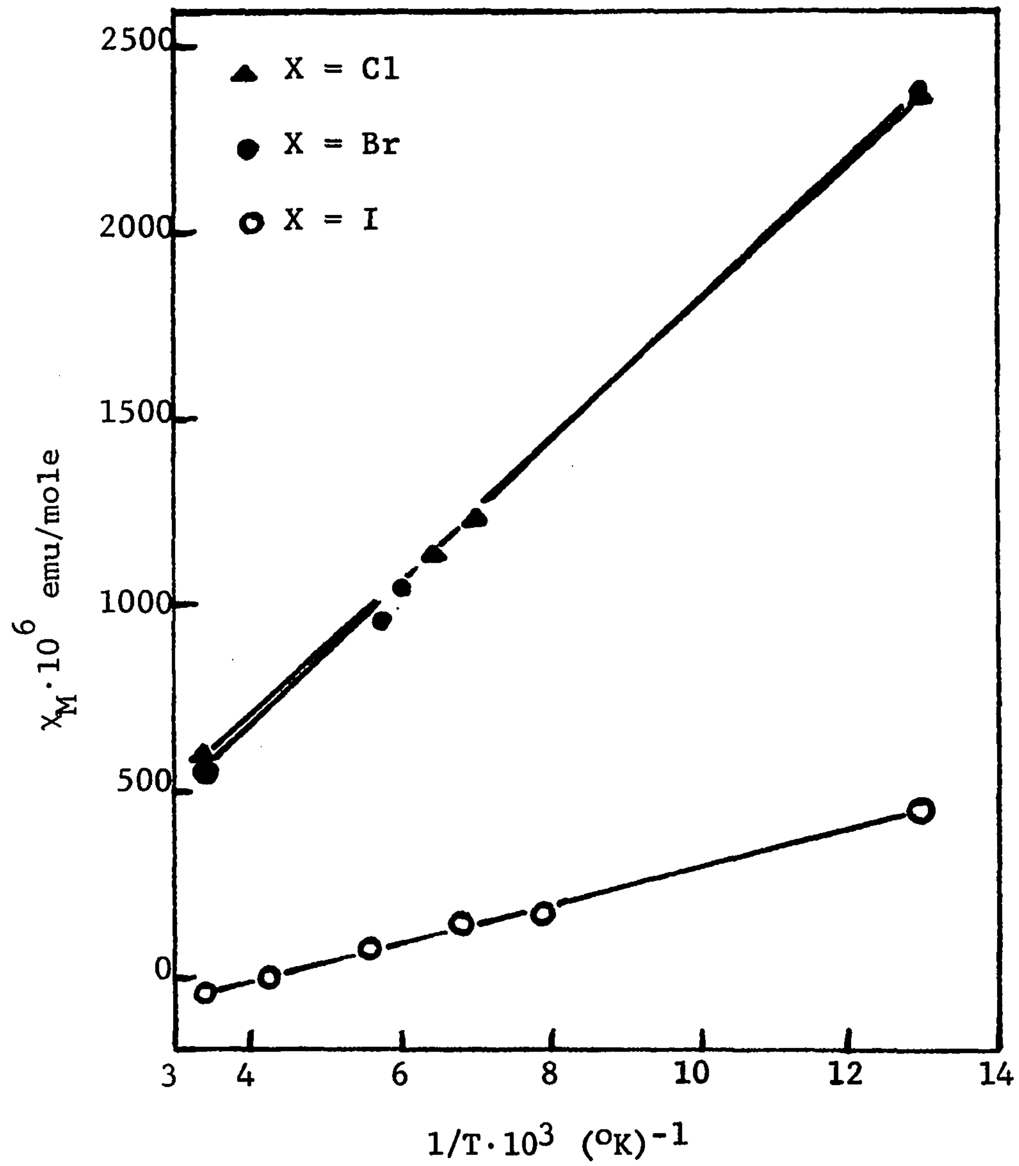

Fig. 7. Variation of molar magnetic susceptibility with reciprocal temperature for $NbX_4(S(CH_2)_4)_2$ (X = Cl, Br, and I)

housing to 10^{-5} Torr. An analysis of the material at the end of the experiment was consistent with this composition.

Anal. Calcd. for $NbCl_4(S(CH_3)_2)$: Nb, 31.30. Found: (Before) Nb, 26.10; (After) Nb, 31.06.

Table 8. Magnetic results from Curie plots

Compound	μ(B.M.)	$-\chi_D \cdot 10^6$ (emu/mole)	$\chi_{TIP} \cdot 10$ (emu/mole)
$NbCl_4(S(CH_3)_2)_2$	--	--	--
$NbBr_4(S(CH_3)_2)_2$	1.17	248	198
$NbI_4(S(CH_3)_2)_2$	1.11	314	154
$NbCl_4(S(CH_2)_4)_2$	1.21	254	180
$NbBr_4(S(CH_2)_4)_2$	1.25	294	174
$NbI_4(S(CH_2)_4)_2$	0.64	358	148

Similar difficulties were encountered with the bromide and iodide as well as with the tetrahydrothiophene complexes, but the weight losses were seldom greater than 1-2%. As indicated in Table 8 the moments as well as χ_{TIP} decreased in the order Br > I for dimethyl sulfide complexes and Br > Cl > I for tetrahydrothiophene complexes. Table 9 lists moments which have been reported for other known bis-adducts of NbX_4. For acetonitrile complexes the moments decrease in the order

Table 9. Magnetic moments of NbX_4L_2 complexes

Complex	μ(B.M.)	μ_{eff} (room temp.)	Ref.
$NbCl_4(py)_2$	1.37		1
$NbBr_4(py)_2$	1.26,1.53		1
$NbI_4(py)_2$	1.05		1
$NbCl_4(ac)_2$	1.75		12
$NbBr_4(ac)_2$		1.57	12
$NbI_4(ac)_2$		1.45	12
$NbCl_4(\gamma\text{-pic})_2$		1.18	28
$NbBr_4(\gamma\text{-pic})_2$		1.29	28
$NbCl_4$(bipy)		1.06	28
$NbCl_4$(O-phen)		1.05	28

Cl > Br > I, while for pyridine complexes two orders are found. Br > Cl > I and Cl > Br > I, where the moment of the bromide refers to that of the reported red, or green form, respectively. A complete series for γ-picoline complexes is not given, but μ_{eff} at room temperature decrease in the order Br > Cl. If the initial assumption is made that these complexes are octahedral and the effects of spin-orbit coupling and a tetragonal component in the ligand field (resulting from ligand inequivalences) upon the $^2T_{2g}$ ground term are considered, it is found (67) that this level splits into an orbital singlet and an orbital doublet level. The effect of these perturbations is depicted diagrammatically in Fig. 8. The parameter Δ is a measure of the splitting in the absence of spin-orbit coupling, while spin-orbit coupling alone generates a non-magnetic ground state (67). Figgis (66) has shown that the larger the low symmetry ligand field the more closely the moments approach spin-only values. This indicates that for dimethyl sulfide the distortions are greater for X=Br than for X=I, while for tetrahydrothiophene the distortions decrease in the order $NbBr_4(S(CH_2)_4)_2 > NbCl_4(S(CH_2)_4)_2 \gg NbI_4(S(CH_2)_4)_2$. McCarley and Torp (1) concluded from a knowledge of pyridine's position in the spectrochemical series (py > Cl > Br > I) that the observed order of decreasing magnetic moment $NbCl_4(py)_2 > NbBr_4(py)_2 > NbI_4(py)_2$ was the opposite of what would have been predicted. From studies of spectra of vanadium(IV) complexes Clark and Errington (37) place thioethers above chlorine in the spectrochemical series. This suggests a similar inversion occurs here. This will be discussed further after spectral data have been presented. The moment for $NbI_4(S(CH_2)_4)_2$ is ca. 40% lower than expected on the basis of moments reported for other iodide complexes (see Table 9). This may reflect the loss in weight prior to measurement of χ_m which inevitably occurred, but for $NbI_4(S(CH_2)_4)_2$ this amounted to only ca. 1% which seems too small to account for

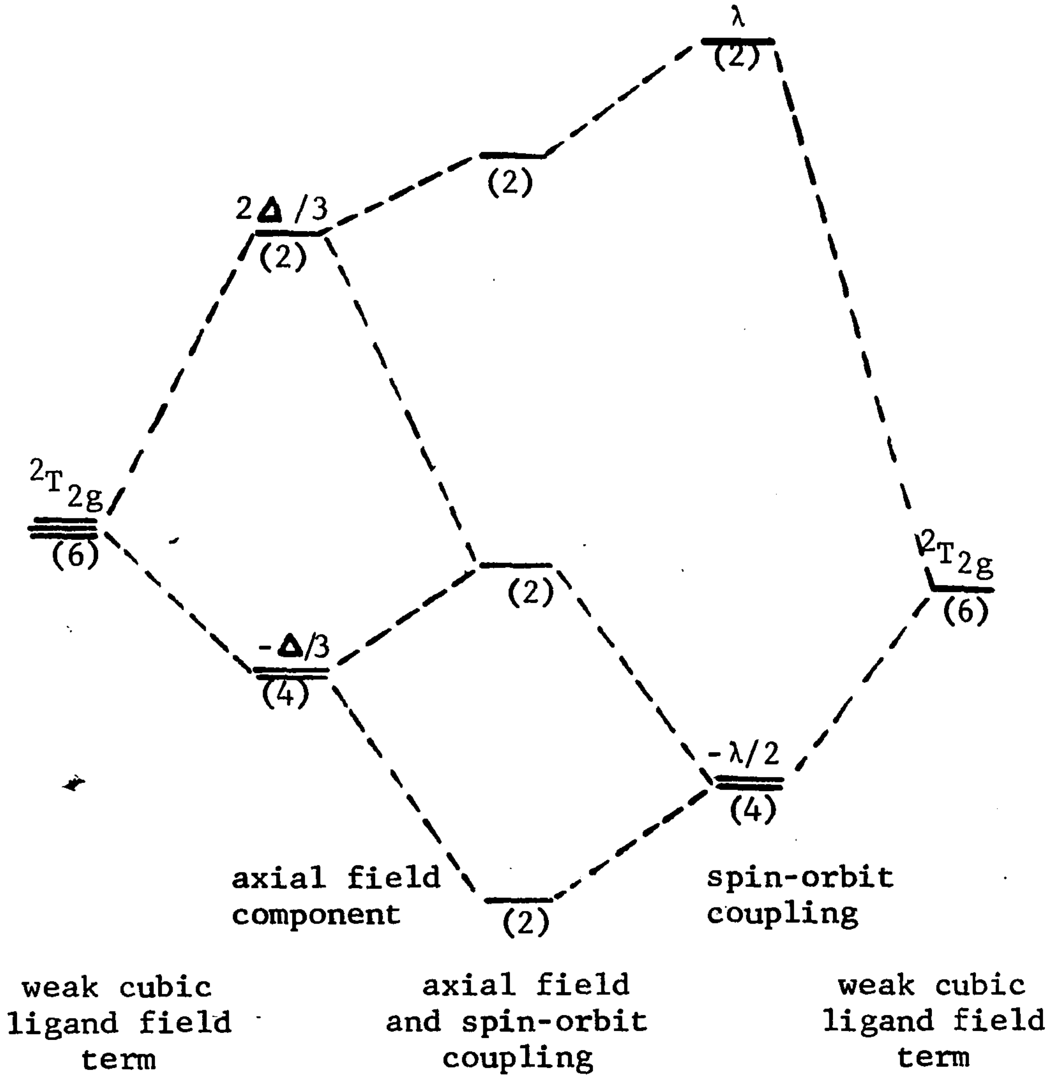

Fig. 8. The $^2T_{2g}$ term under the influence of an axial ligand field component and spin-orbit coupling.

the low moment. Far infrared spectra of this complex were consistent with a cis-MX_4L_2 configuration and showed no evidence for unreacted NbI_4. It is also noted that the carbon and hydrogen analyses were consistently low by ca. 2%, in spite of the fact that the reactions were carried out in extractors allowing filtration of the solution and isolation of products from unreacted tetrahalide. Even with the low moment for this complex χ_{TIP} is virtually identical to χ_{TIP} for $NbI_4(S(CH_3)_2)_2$ and both values are ca. 100% lower than the value of +419 emu/mole reported for $NbI_4(py)_2$. This anomaly is unresolved at this time, but will be considered further after evaluation of λ, v , and Δ for the complexes.

The value of χ_{TIP} for the bromide complexes was slightly higher than the value +155 emu/mole for $NbBr_4(py)_2$(red) but lower than the value +225 for $NbBr_4(py)_2$(green) (1). Values of +189 and +155 emu/mole for $NbCl_4(S(CH_2)_4)_2$ and $NbCl_4(py)_2$, respectively, are also not significantly different. Temperature-independent susceptibility is expected to increase as the energy separation between ground and excited states of the same symmetry decreases. In the one study of niobium(IV) complexes where this was evaluated (1) the χ_{TIP} contribution increased in the order $NbCl_4(py)_2 < NbBr_4(py)_2 < NbI_4(py)_2$ if the lowest of the two values for the bromide is taken. From the present results with the dimethyl sulfide complexes this order is I < Br and for tetrahydrothiophene complexes I < Cl < Br.

Tables 10 and 11 contain a summary of the additional magnetic data which were obtained. This includes the values of μ_{eff} used in the determination of λ, v , and Δ .

Table 10. Magnetic susceptibilities and effective magnetic moments of $NbX_4(S(CH_2)_4)_2$ (X = Cl, Br, and I)

	T^oK	$\chi_M x10^6$ (emu/mole)	$(\chi_M-\chi_D)x10^6$ (emu/mole)	μ_{eff}(B.M.)
X=Cl	297	550	774	1.36
	182	950	1174	1.31
	154	1131	1355	1.29
	142	1230	1454	1.28
	77	2342	2562	1.26
X=Br	298	548	842	1.42
	182	963	1257	1.35
	166	1054	1348	1.34
	77	2378	2672	1.28
X=I	298	-40	312	0.86
	228	0.7	338	0.81
	176	81	438	0.78
	146	140	499	0.76
	128	185	543	0.75
	77	417	775	0.69

Table 11. Magnetic susceptibilities and effective magnetic moments of $NbX_4(S(CH_3)_2)_2$ (X = Br and I)

	T^oK	$\chi_M \times 10^6$ (emu/mole)	$(\chi_M - \chi_D) \times 10^6$ (emu/mole)	μ_{eff}(B.M.)
X=Br	298	530	778	1.37
	239	653	901	1.31
	224	709	957	1.31
	183	908	1156	1.30
	139	1203	1451	1.27
	113	1489	1737	1.25
	77	2186	2434	1.22
X=I	296	370	684	1.27
	243	465	779	1.23
	233	506	820	1.24
	170	756	1070	1.21
	131	1042	1356	1.19
	129	1056	1370	1.19
	113	1208	1522	1.17
	77	1860	2174	1.16

Some comment is in order concerning the procedure used. The curve fitting was done by hand. For a given value of k the parameter v was plotted versus μ_{eff}. In this manner a family of curves, each curve associated with a particular value of kT/λ, was obtained. A total of four families were obtained covering the range k = 0.7-1.0 units in increments of 0.1 units. Experimental moments were fit to the curves and spin-orbit coupling constants calculated from knowledge of T (experimental) and kT/λ (graph). Table 12 summarizes the range of the parameters. While the range for v is not given it is

Table 12. Parameters derived from magnetic data

Compound	k	v	$\lambda(cm^{-1})$	$\Delta(cm^{-1})$
$NbBr_4(S(CH_3)_2)_2$	1.0	1.95	540-780	1050-1440
	0.8	1.65	500-600	800-1000
$NbBr_4(S(CH_2)_4)_2$	1.0	2.25	540-655	1200-1500
	0.8	1.95	520-540	1040-1050
$NbCl_4(S(CH_2)_4)_2$	1.0	2.15	540-760	1160-1640
	0.8	1.83	540-690	990-1250
$NbI_4(S(CH_3)_2)_2$	1.0	1.65	540-900	890-1480
	0.8	1.35	500-700	700-1000
$NbI_4(S(CH_2)_4)_2$	1.0	0.4	540-840	215-335

estimated as _ca_. ± 0.2 units. It is clear from the table that Δ is positive and the $^2T_{2g}$ level splits such that an orbital singlet level is lower. The range of Δ varies for each complex, but it generally has a magnitude of 1000 cm^{-1}. This is lower than was reported for acetonitrile complexes (12) where Δ varied from _ca_. 4500 cm^{-1} for the chloride to 600-1000 cm^{-1} for the iodide. The spin-orbit coupling constant decreases in the order I > Br for dimethyl sulfide and I > Cl > Br for tetrahydrothiophene complexes. Values of k = 0.8 gave the best fit and increasing or decreasing k by 0.1 unit increased the range λ to values considered too high to be reasonable. The effect of increasing k by 0.2 units is shown in Table 12.

The only decent fit obtained for $NbI_4(S(CH_2)_4)_2$ was with k = 1.0 and v = 0.4, and ranges for Δ and λ of 215-315 cm^{-1} and 540-840 cm^{-1}, respectively. Lower values of k gave spin-orbit coupling constants in excess of the reported free ion value of 748 cm^{-1} (68). The low value of k for $NbI_4(S(CH_2)_4)_2$ immediately suggests that the compound contains some diamagnetic impurity. For Δ on the order of kT a moderate temperature dependence of the moment is expected instead of the observed Curie behavior. This diamagnetic impurity is very likely niobium(IV) iodide formed during vacuum drying of the sample.

In order to obtain a check on two of the moments, epr measurements were made on $NbCl_4(S(CH_2)_4)_2$ and $NbBr_4(S(CH_3)_2)_2$ powders. The room temperature resonances were broad having halfwidths of _ca_. 1500-2000 gauss, and none of the expected anisotropy was observed. Experimental g-values of 1.72 and 1.70 for the respective chloride and bromide complexes were used in Equation 12 to calculate corresponding μ_{eff} values of

$$\mu = g\sqrt{S(S+1)} \qquad (12)$$

$$(S = \tfrac{1}{2})$$

1.47 and 1.48 B.M. Each moment was higher than the actual moments, but close to the experimental effective moments (Table 10 and 11). The measurement on powdered $NbCl_4$

$(S(CH_2)_4)_2$ was extended to ca. -196° where it was hoped that some of the expected anisotropy would be observed. Three g-values were extracted from the spectrum, $g_1 = 1.83$, $g_2 = 1.81$, and $g_3 = 1.72$ giving an average g-value of 1.75. From this average g-value a moment of 1.54 B.M. was calculated, again closer to the value for μ_{eff} than for μ. Clark and Errington (37) obtained good correlations between μ_{eff} for VCl_4B (B = $CH_3SCH_2CH_2SCH_3$) as determined from room temperature bulk magnetic susceptibility measurements and epr studies. Why values of μ_{eff} obtained from susceptibility data via Equation 8 should agree with μ from Equation 12 is not clear, since μ_{eff} (experimental) contains contributions from χ_{TIP} which, arising from the second-order Zeeman effect, are not expected to contribute to moments calculated from the g-factor.

Electronic spectra

Visible and near infrared spectra of $NbX_4(S(CH_2)_4)_2$ (X = Cl, Br, and I) and $NbX_4(S(CH_3)_2)_2$ (X = Cl, Br, and I) were studied using the techniques described in the experimental section. These studies were done with the pure solids and solutions (benzene or free ligand). It was the purpose of these investigations to determine (1) the relative position of alkyl sulfides in the spectrochemical series for niobium(IV)

(32), (2) the nature of species in solid and solution phases, and (3) the magnitude of ligand field distortions prevailing in the complexes. The representative spectra and frequency maxima of observed bands are given in Figs. 9-14 and Table 13.

Table 13. Data from electronic spectra of tetrahalobis (alkyl sulfide)niobium(IV) complexes

Compound	Medium	ν(max) (cm^{-1})	ϵ ($\ell.mole^{-1}cm^{-1}$)
$NbCl_4(S(CH_2)_4)_2$	C_6H_6	9,740	12
		13,300	29
		18,600	194
		27,800	1550
$NbBr_4(S(CH_2)_4)_2$	C_6H_6	11,950	12
		17,500	240
		27,800	~2000
$NbI_4(S(CH_2)_4)_2$	$S(CH_2)_4$	13,700	118
		16,700	1140
		19,300	1530
		21,000	1210
		27,000	2400
$NbBr_4(S(CH_3)_2)_2$	$S(CH_3)_2$	11,900	--
		17,400	--
		29,000	--
$NbI_4(S(CH_3)_2)_2$	$S(CH_3)_2$	11,100	
		17,400	
		20,800(sh)	
		22,700	
		29,000	

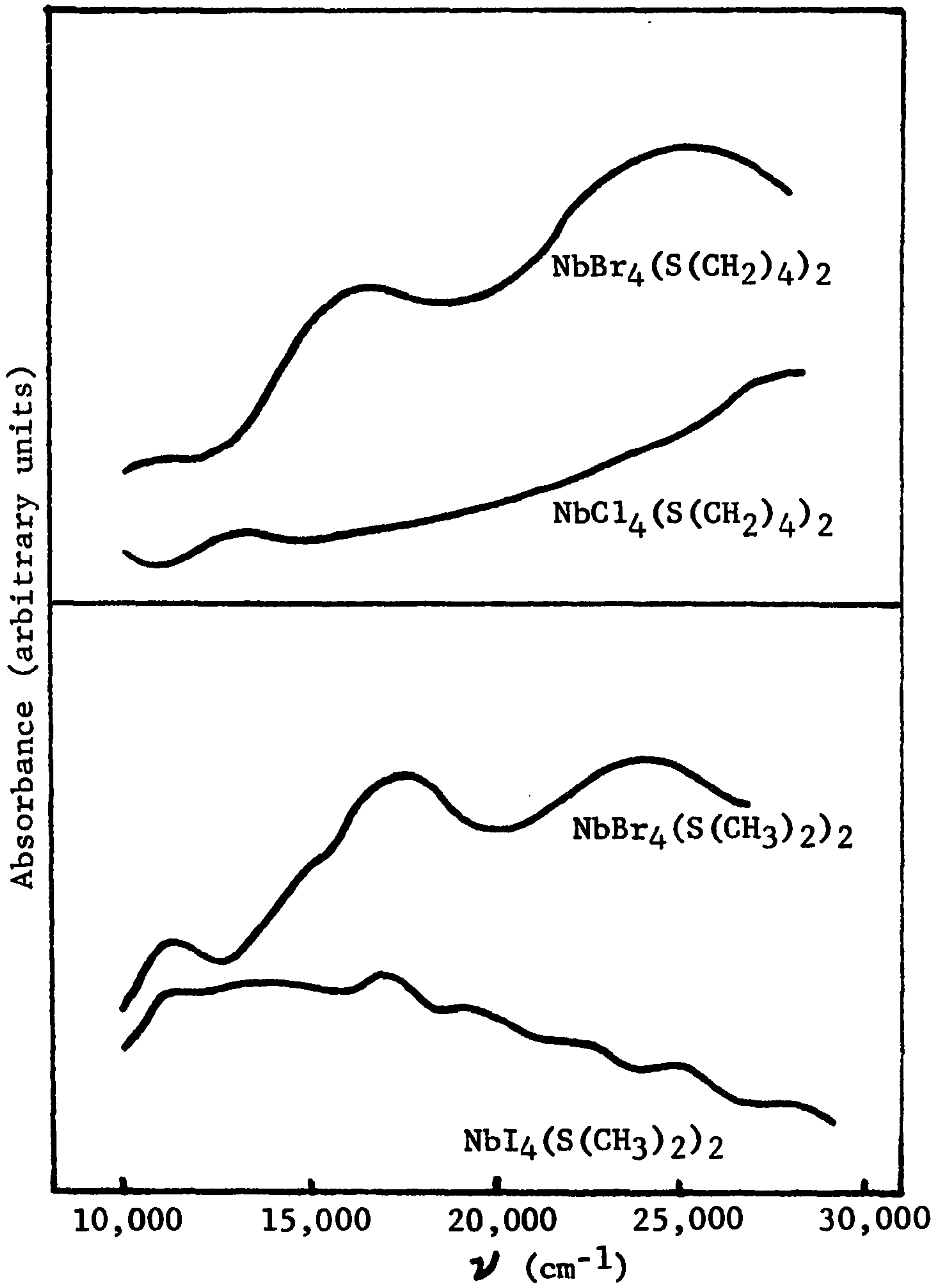

Fig. 9. Diffuse reflectance spectra of tetrahalobis(alkyl sulfide)niobium(IV) complexes

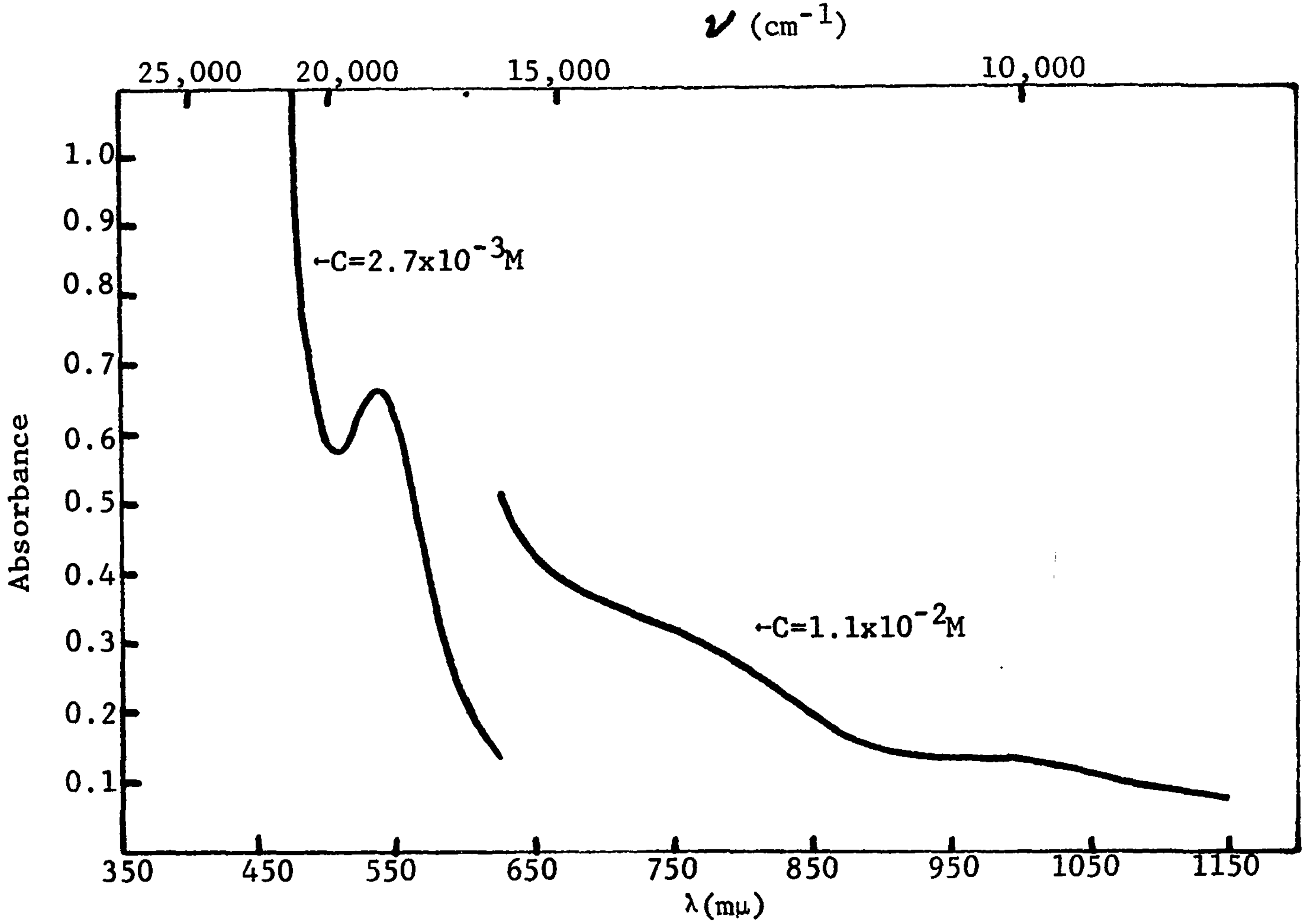

Fig. 10. Electronic spectrum of tetrachlorobis(tetrahydrothiophene)niobium(IV) in benzene

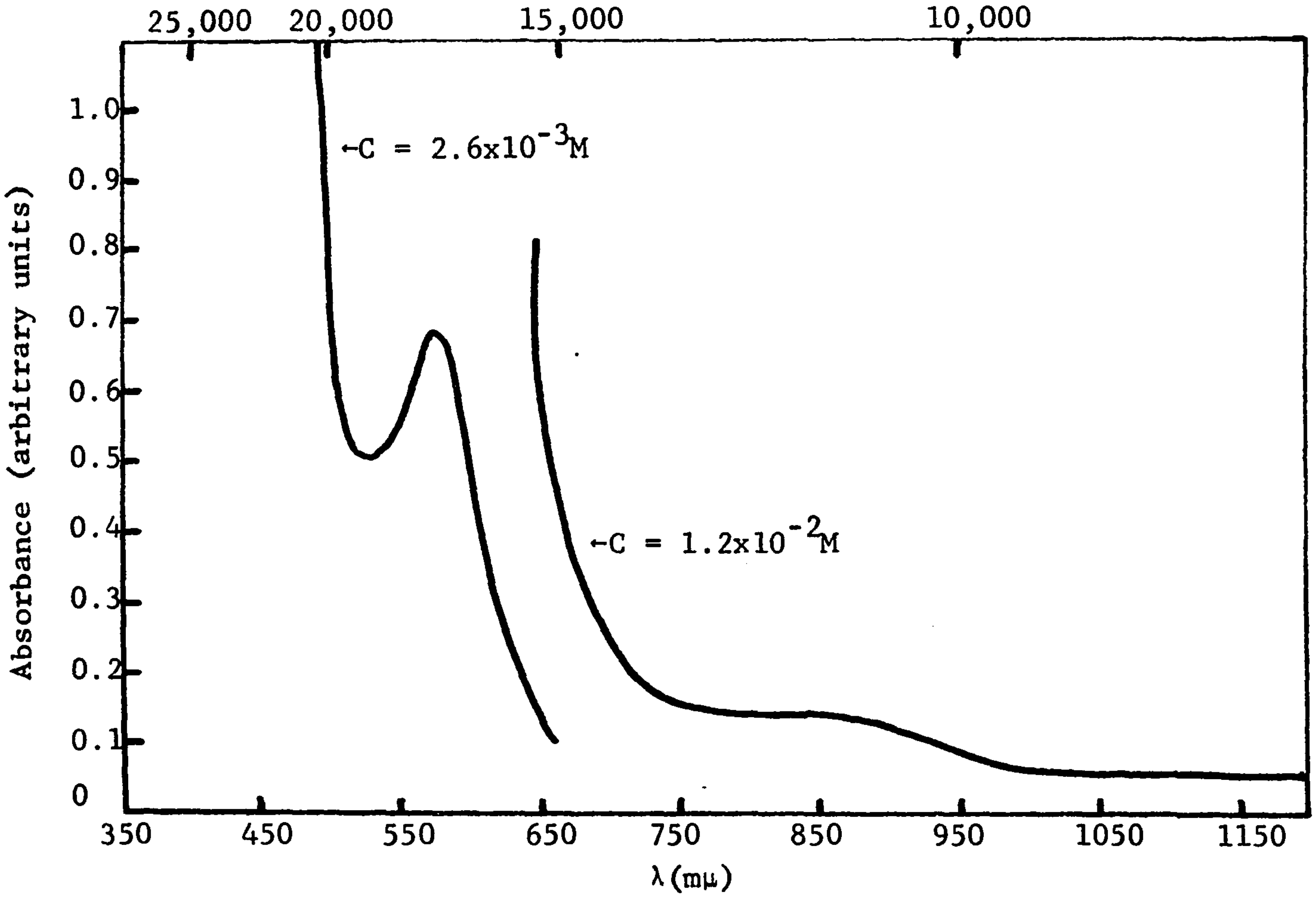

Fig. 11. Electronic spectrum of tetrabromobis(tetrahydrothiophene)niobium(IV) in benzene

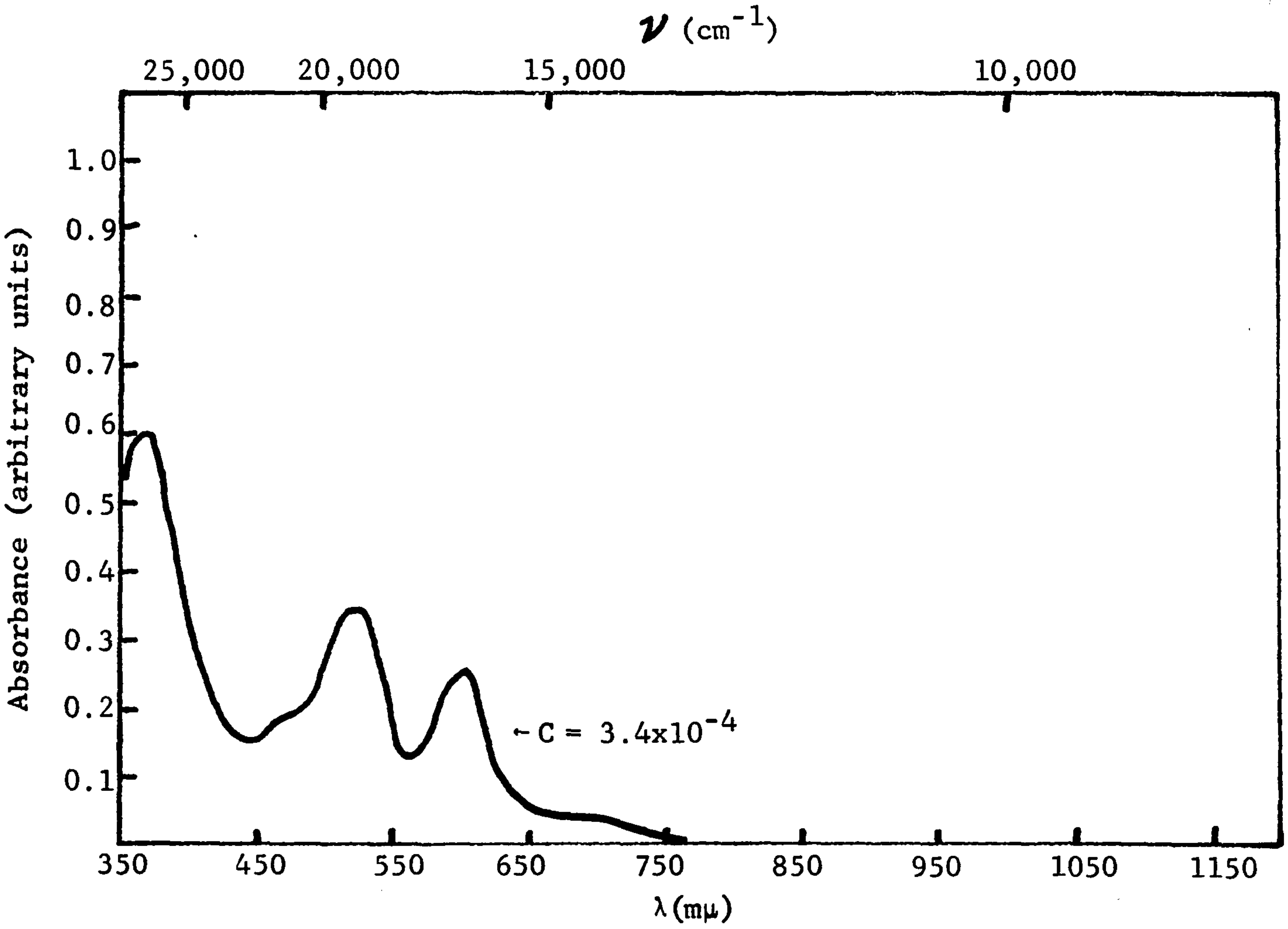

Fig. 12. Electronic spectrum of tetraiodobis(tetrahydrothiophene)niobium(IV) in tetrahydrothiophene

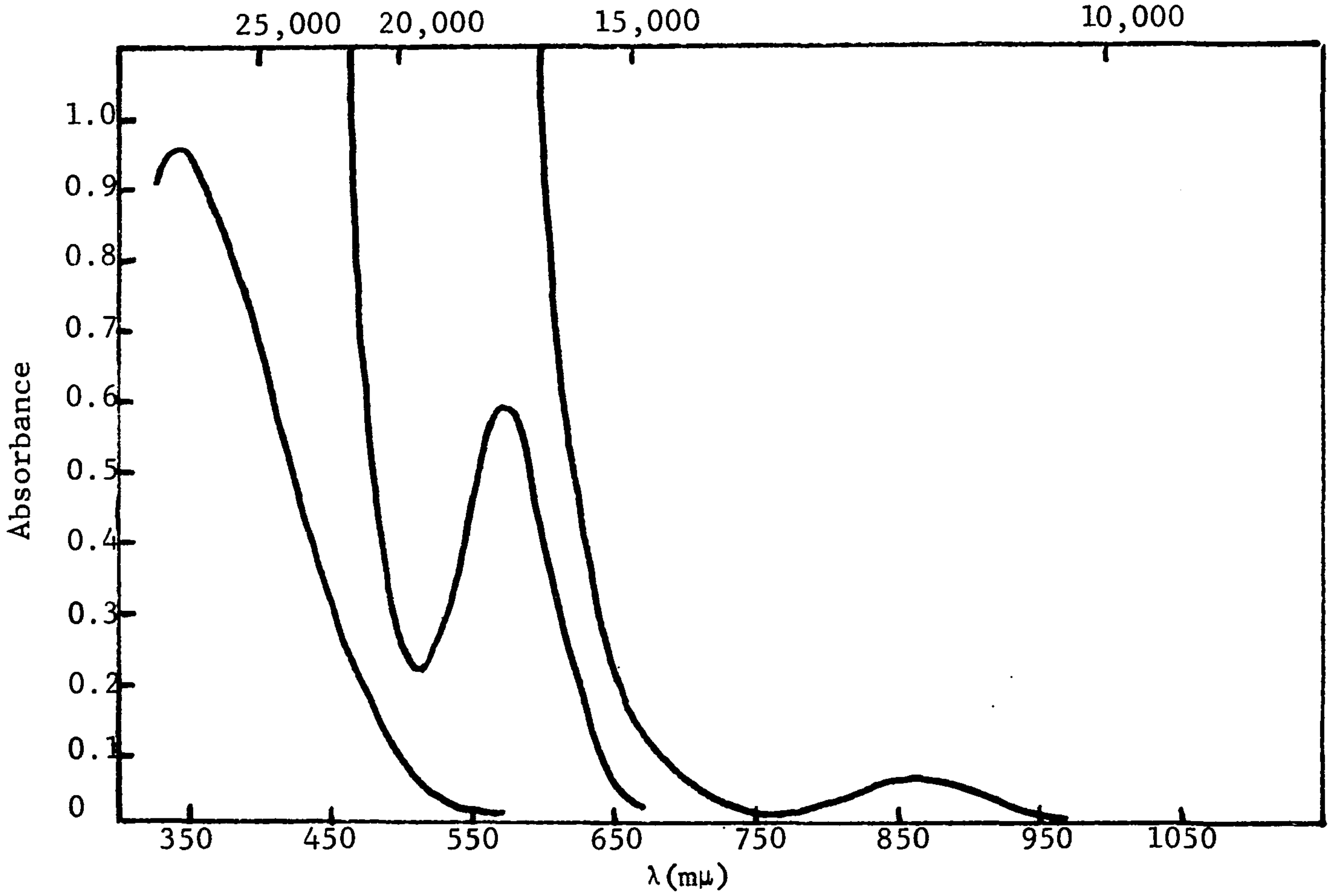

Fig. 13. Electronic spectrum of tetrabromobis(dimethylsulfide)niobium(IV) in dimethyl sulfide

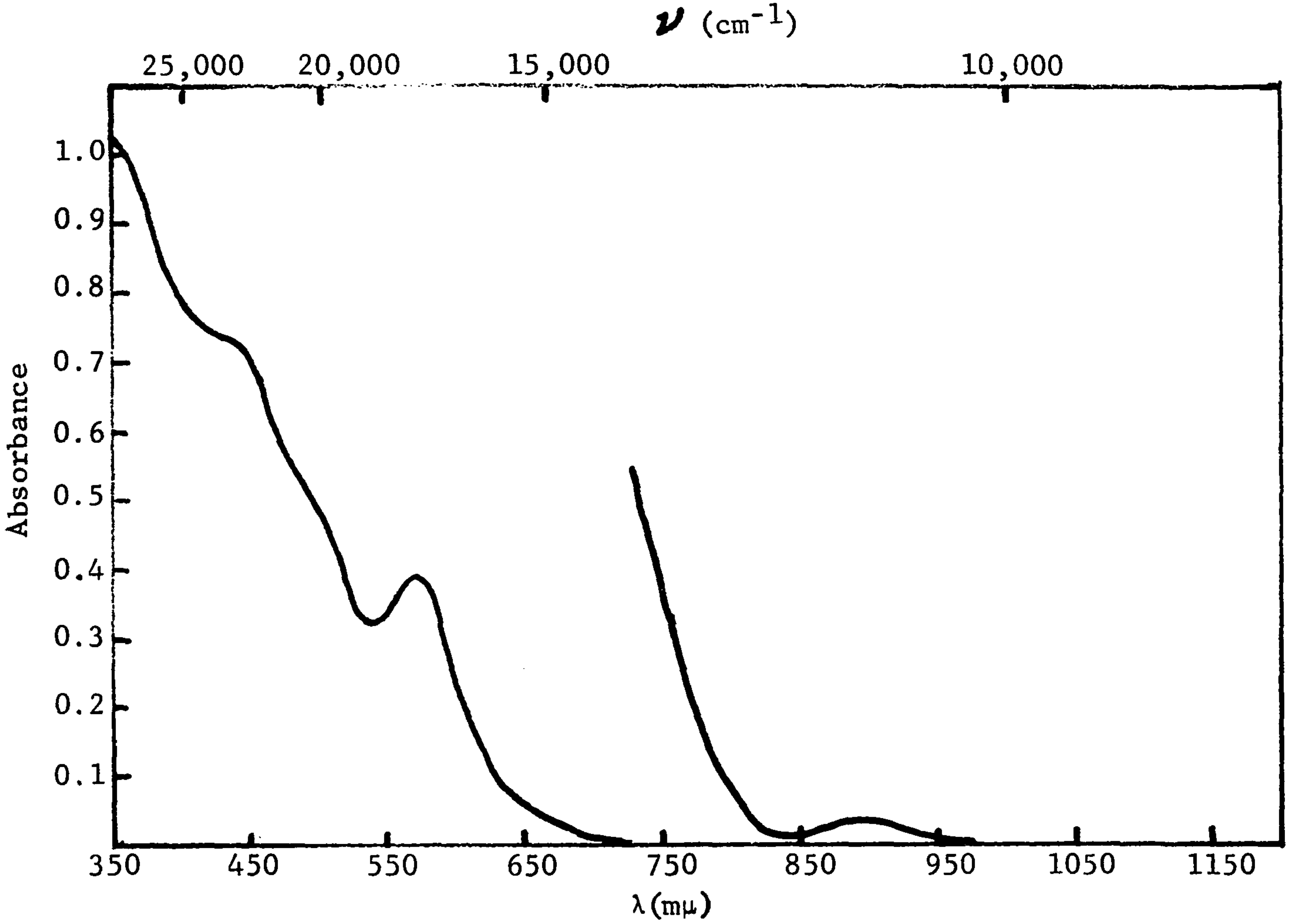

Fig. 14. Electronic spectrum of tetraiodobis(dimethyl sulfide)niobium(IV) in dimethyl sulfide

The spectra of $NbCl_4(S(CH_2)_4)_2$ in the solid state and in benzene and tetrahydrothiophene solutions were virtually identical indicating that the same species was present in each phase. Similar results were found for the complex $NbBr_4$ $(S(CH_2)_4)_2$ in solutions, but the solid state spectrum did not exhibit the band at 11,950 cm^{-1} found in the solution spectra. For $NbI_4(S(CH_3)_2)_2$ the spectra of solids and tetrahydrothiophene solutions were recorded but extremely poor resolution in the solid state spectrum rendered it valueless. A similarly poor solid state spectrum for $NbI_4(S(CH_3)_2)_2$ is shown in Fig. 9. Some band maxima are indicated and correlate roughly with solution spectra, but generally the bands are broad and poorly defined. For $NbBr_4(S(CH_3)_2)_2$ identical spectra were obtained from diffuse reflectance measurements and dimethyl sulfide solutions. It was concluded that identical species were present in each phase. The benzene solution spectrum was radically different in one respect. A band was observed at 6,900 cm^{-1}. This was later attributed to the species $NbBr_4(S(CH_3)_2)$ and will be discussed in the next section.

The spectra of cis-NbX_4L_2 complexes can be discussed relative to crystal field theory or molecular orbital theory. Torp (12) utilizes molecular orbital theory to rationalize the bonding in $NbX_4(ac)_2$ (ac = acetonitrile) complexes. Nonetheless, analysis of magnetic susceptibility data using the Figgis treatment (66) yields a delocalization parameter k of 0.8. Thus delocalization amounts to only 0.2 or 20%. Thus no great error is introduced if the spectra are viewed as if the transitions were between pure d-orbitals. Far infrared results discussed earlier were consistent with the molecular species cis-NbX_4L_2 of C_{2v} symmetry in the solid state and in solutions. If the complexes are initially considered as octahedral the effect of a low symmetry (C_{2v}) ligand field component is to remove the degeneracy of lower $^2T_{2g}$ and upper ^2E_g levels yielding, respectively, the resolved triplet ($^2B_1$, $^2B_2$, and $^2A_2$) and the doublet (a^2A_1 and b^2A_1). Here a and b coefficients are used to distinguish the two $^2A_1$ terms. Unfortunately it is not possible in this case to determine which of the three terms arising from the $^2T_{2g}$ term lies at lowest energy. In addition, as many as four absorption bands resulting from transitions between the ground level and the remaining four levels are expected and in no case are four bands observed.

Ballhausen (69) has shown, at least qualitatively, that the spectra of both cis-MX_4L_2 and trans-MX_4L_2 molecular complexes can be discussed as tetragonally (D_{4h}) perturbed complexes. The effect of a tetragonal component in the ligand field upon terms arising in O_h is depicted diagrammatically in Fig. 15. Here the $^2T_{2g}$ level is resolved into $^2B_{2g}$ and ^2E_g levels, and the excited ^2E_g level yields $^2B_{1g}$ and $^2A_{1g}$. The analogy to Fig. 8 where the effect of an axial component upon a $^2T_{2g}$ term is depicted is not fortuitous. The magnetic moments of these complexes indicate that the $^2B_{1g}$ level lies at lower energy, separated from ^2E_g by ca. 1000 cm^{-1}. Electronic spectra measurements were not extended to this low an energy, hence, only two ligand field bands are expected and they should appear in the visible region. Treating these cis complexes as if they exhibited D_{4h} symmetry the observed transitions will be from the ground $^2B_{2g}$ level to the excited $^2A_{1g}$ and $^2B_{1g}$ levels. Which of these two levels lie at lower energy is not known. Yamatera (70) and McClure (71) have shown for Co(III) complexes that the magnitude of the splitting of this upper level, $\delta(^2E_g)$ will be a function of the parameters $\delta\sigma$ and $\delta\pi$ which reflect differences in effective field strengths for σ-bonding and π-bonding as ligands denoted by L are substituted for A in a CoX_6^q ($q = \pm$ (1-3)) complex. As of this writing this theory has not been extended to d^1 systems. The results from the spectra are summarized in

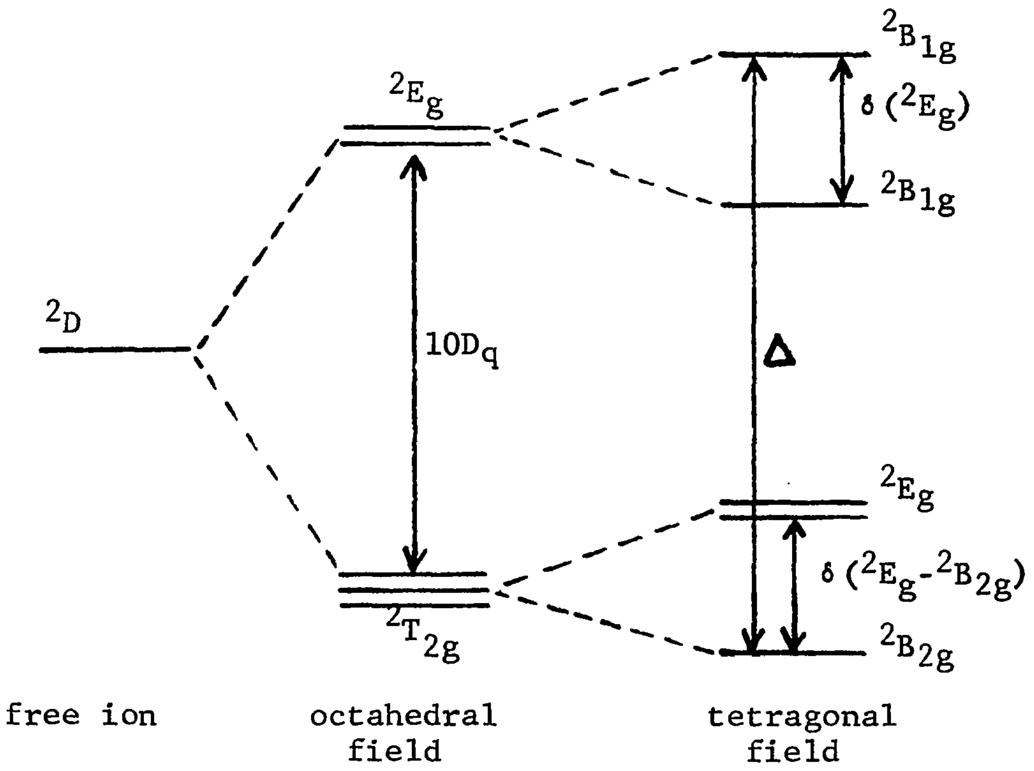

Fig. 15. Energy level diagram for a tetragonal distorted metal complex (from ref. 72 p. 261)

Table 14.

Table 14. Parameters derived from electronic spectra

Compound	Assignments ($^2B_{2g} \rightarrow {}^2E_g$) ν(cm^{-1})	Δ (cm^{-1})	δ (^2E_g) (cm^{-1})
$NbCl_4(S(CH_2)_4)_2$	18,600 13,300	18,600	5,300
$NbBr_4(S(CH_2)_4)_2$	17,500 11,950	17,500	5,550
$NbI_4(S(CH_2)_4)_2$	13,700 (16,700)	(16,700)	(3,000)
$NbBr_4(S(CH_3)_2)_2$	17,400 11,900	17,400	5,500
$NbI_4(S(CH_3)_2)_2$	(17,400) 11,100	(17,400)	(6,300)

( ) denotes uncertainty in assignment as d-d band or uncertainty in derived parameter.

The parameter Δ, which is related to 10 dQ in an octahedral complex, was taken to be the energy of the highest energy d-d band observed in the spectra. For all the complexes the extinction coefficient for this band is slightly greater than is expected for a purely d-d transition. This reflects in part the inadequacy of the assumption that purely d-orbitals can be used rather than molecular orbitals consisting of a linear combination of metal d and ligand s and p orbitals, and in part the breakdown via a vibrational-electronic interaction of the gerade-character of ground or excited levels involved in the transitions. The intensity of this higher energy d-d band decreases in the order I > Br > Cl for the present systems. With the iodides the intensity is already sufficiently high as to render very uncertain its assignment as a d-d band. From data reported for other NbX_4L_2 (L = monodentate ligand) or NbX_4B (B = bidentate ligand) complexes and the present data an order of ligand field strength $CH_3CN > C_6H_{16}N_2 > Cl > (CH_3)_2S \sim (CH_2)_4S > Br > I$ was found. The validity of Jorgensen's rule of average environment (72) was assumed. Only a few other spectrophotometric studies of complexes of sulfur ligands have been reported, hence, the position of sulfur ligands in the spectrochemical series is uncertain (14). Clark and Errington (37) studied the spectrum of $VCl_4(CH_3SCH_2-)_2$ and place this sulfur ligand above chlorine. A value of 10 Dq for VCl_6^{2-} was obtained by them from the value 7900 cm^{-1} known for VCl_4 and 9/4 relationship between octahedral and tetrahedral complexes. In addition, the sulfur ligands S^{2-} and $(CH_3CH_2O)_2PS_2^-$ reportedly lie above chloride ion (72).

Values of ~5000 cm^{-1} were found for $\delta(^2E_g)$ for all complexes except $NbI_4(S(CH_2)_4)_2$. Here a low energy band appearing at 13,700 cm^{-1} led to a value 3,000 cm^{-1} for $\delta(^2E_g)$ which contrasts with expected value of 5,600 cm^{-1} found for $NbI_4(S(CH_3)_2)_2$. This band at 13,700 cm^{-1} is attributed to an impurity, very likely diamagnetic, in the compound. The magnitude of $\delta(^2E_g)$ is considerably larger than the value 1000 cm^{-1} found for $\delta(^2E_g - {}^2B_{2g})$ from magnetic studies, but the values of $\delta(^2E_g)$ and $\delta(^2E_g - {}^2B_{2g})$ are virtually unchanged from one complex to another.

The small value of $\delta(^2E_g - {}^2B_{2g})$ from the magnetic studies indicates small deviation from O_h symmetry. It is then expected that this would be reflected in a similarity in $\delta(^2E_g)$ for NbX_6^{2-} and NbX_4L_2 (L = monodentate sulfur ligand). For salts of $NbCl_6^{2-}$ and $NbBr_6^{2-}$ this splitting amounts to *ca*. 5000 cm^{-1} (12). In the hexahalocomplexes this large splitting was attributed to Jahn-Teller distortions since x-ray powder diffraction studies, at least of K_2NbCl_6, showed that Nb(IV) occupies a lattice site having O_h symmetry (12). For acetonitrile complexes the ^2E_g splittings were 3,000, ~5,600, and 4,300 cm^{-1} for the chloride, bromide, and iodide, respectively, while splitting of the $^2T_{2g}$ level decreased from 4600 for the chloride to 600-1000 for the iodide. Clearly no correlation of

$\delta(^2E_g)$ and $\delta(^2E_g - {}^2B_{2g})$ is evident. Clark and Errington (37) took $\delta(^2E_g)$ as a measure of the deviation of the ligand field from octahedral symmetry. For vanadium(IV) chloride complexes the splitting decreased in the order $R_3N > R_2O > R_2S$ which was the same order in which the ligands occurred in the spectrochemical series. Their observation must have been a special case since here $\delta(^2E_g)$ decreased in the order I > Br for dimethyl sulfide complexes and Br $\gtrsim$ Cl for tetrahydrothiophene complexes, the opposite of the ordering in the spectrochemical series. Clark et al. (73) earlier had noted that it was not possible theoretically to correlate distortions in the ground and excited states of complexes $TiCl_3L_3$.

In the spectrum of $NbCl_4(S(CH_2)_4)_2$ an additional weak band in the near infrared region at 9,740 cm^{-1} is thought to be due to an impurity in the complex. No bands were observed at this energy or lower energy for any of the other complexes. Considering the previous discussion of this material a small amount of some other complex of $NbCl_4$ and $S(CH_2)_4$ is the likely contaminant (see page 35).

Generally the data from the visible spectra support the magnetic results. The position of the alkyl sulfides between chloride and bromide ions in the spectrochemical series is consistent with the low values, ca. 1000 cm^{-1}, for $\delta(^2E_g-^2B_{2g})$. This separation in spectra of MX_4L_2 complexes, when L is near X in the spectrochemical series, is not expected to be large (72).

Complexes of the Form MX_4L

Some properties as well as the synthesis of the complexes NbX_4L (X = Cl and Br; L = $(CH_3)_2S$ and $(CH_3CH_2)_2S$) have been presented in earlier sections. These are discussed separately since their physical properties, not unexpectedly, differ fundamentally in several respects from those of NbX_4L_2 complexes. The most desirable data for these complexes was their molecular weights, and using the techniques described in the experimental section a value of 595 ± 100 was obtained for $NbBr_4(S(CH_3)_2)$. This was not accomplished in an unambiguous manner since some apparent decomposition occurred in the dilute benzene solutions. Figure 16 shows the calibration curve for the study and the calculated molecular weight for a dimer was 949 g-$mole^{-1}$ and for a five coordinate monomer, 474 g-$mole^{-1}$. The experimental value was more consistent with a monomer, but with the uncertainty a value intermediate between monomer and dimer was not precluded.

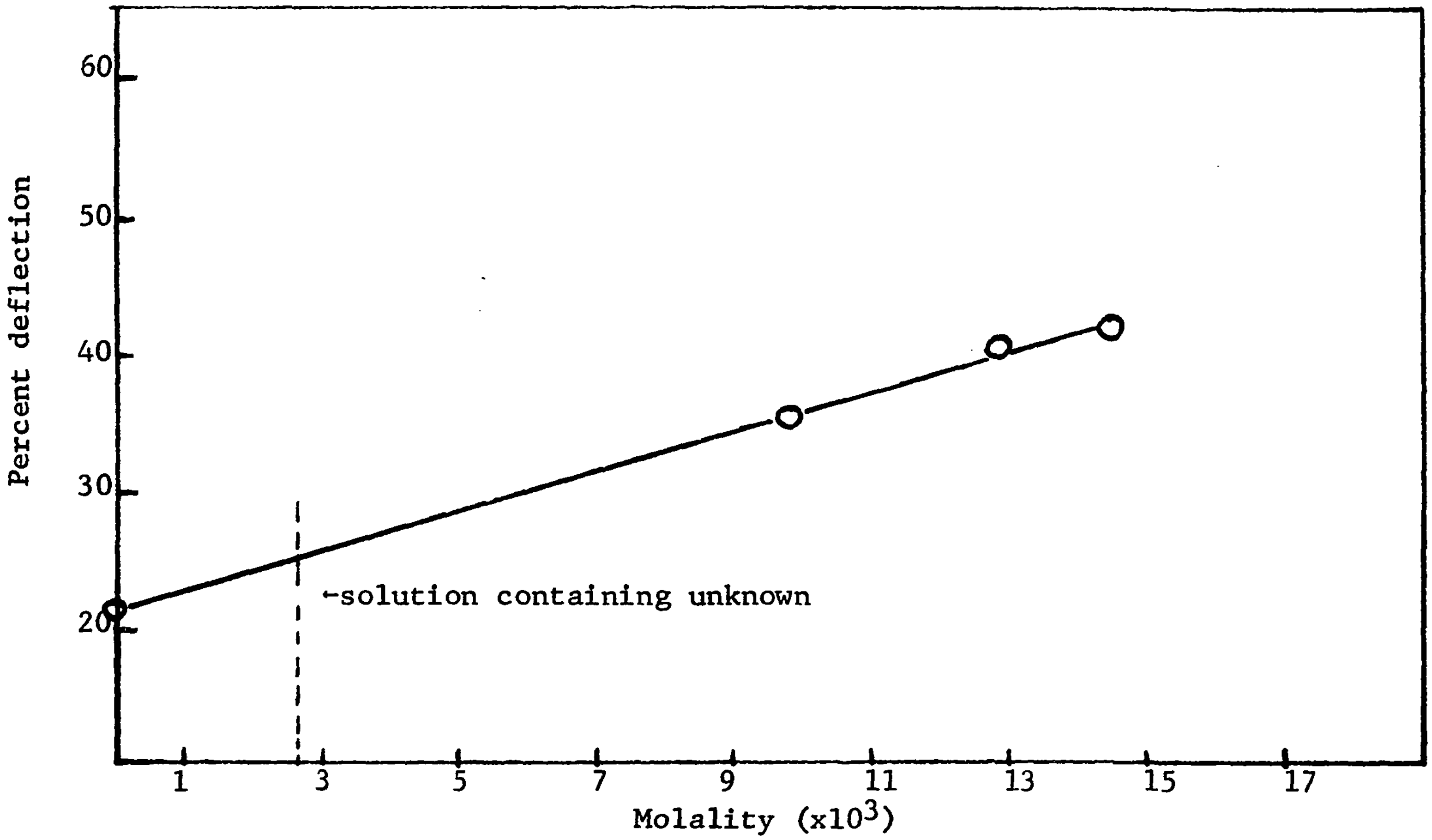

Fig. 16. Calibration curve for molecular weight determination in benzene

Using the procedure described in the analytical section an oxidation number of 4.01 ± 0.01 was established for niobium in $NbCl_4(S(CH_2CH_3)_2)$. Other properties of this and other complexes were also consistent with the presence of niobium(IV) and have been discussed earlier.

Data were also obtained using the physical methods applied to NbX_4L_2 complexes. Initially the magnetic properties were investigated, and this was followed by far-infrared and electronic spectral measurements on solids and solutions. These data and results will now be presented in that order.

Magnetic susceptibilities

Measurements of magnetic susceptibilities were made using techniques presented in the experimental section. The results are summarized in Table 15. All four compounds were diamagnetic with a very small amount of paramagnetic impurity contaminating $NbBr_4(S(CH_3)_2)$. For the latter compound a plot of χ_M vs T^{-1} shown in Fig. 7 was linear and a moment of 0.028 B.M. was obtained from the slope of the curve.

Since a single measurement of molecular weight for $NbBr_4(S(CH_3)_2)$ in benzene established the presence of monomer in this solvent, the esr spectra of benzene solutions of $NbBr_4(S(CH_3)_2)$ and of $NbCl_4(S(CH_2CH_3)_2)$ were investigated at room

Table 15. Magnetic susceptibilities for tetrahalo(dialkyl sulfide)niobium(IV) complexes

$NbCl_4(S(CH_3)_2)$		$NbBr_4(S(CH_3)_2)$		$NbCl_4(S(CH_2CH_3)_2)$		$NbBr_4(S(CH_2CH_3)_2)$	
T^oK	$\chi_M \cdot 10^6$ (emu/mole)	T^oK	$\chi_M \cdot 10^6$ (emu/mole)	T^oK	$\chi_M \cdot 10^6$ (emu/mole)	T^oK	$\chi_M \cdot 10^6$ (emu/mole)
297	-80	299	-67	298	-83	297	-555
236	-80	195	-40	177	-56	77	-111
190	-80	162	-25	77	-39		
163	-75	148	-13				
133	-78	77	78				
83	-77						
77	-76						

temperature. No resonance was detectable. This is indicative of the absence of a paramagnetic specie or the esr lines are too broad at room temperature to be detectable. In the case of $NbCl_4(S(CH_2CH_3)_2)$ nmr spectra of benzene solutions were recorded using a low resolution and a high resolution nmr spectrometer. The result of these experiments was inconclusive.

The diamagnetic behavior of the solid complexes NbX_4L contrasts with reported anti-ferromagnetic behavior of $TiCl_3L_2$ ($L = S(CH_3)_2$ and $S(CH_2)_4$) (43) as well as the slightly anti-ferromagnetic behavior of TiX_3L_2 (X = Br and I). Fowles (43) proposed a direct titanium-titanium bond in a dimeric species for $TiCl_3L_2$, and for the bromide and iodide bioctahedral halogen bridged dimers were suggested. Diamagnetic complexes of niobium(IV) have previously been reported by Wentworth and Brubaker (25) and by Brown and Newton (32). A molecular weight measurement established a dimer for $(NbCl(OCH_2CH_3)_3py)_n$ (n = 2), and it was assumed that the chloride ions were bridging groups across a metal-metal bond. The virtual insolubility of diamagnetic $NbCl_4N(CH_2CH_3)_3$ (32) in all solvents tried precluded measurement of a molecular weight, but other properties suggested its formulation as a metal-metal bonded chlorine-bridged dimer. Analogous behavior of the present complexes suggests that dimeric metal-metal bonded structures with two halide bridges are present in the solid state. In benzene solution molecular weight data suggests that the bridge Nb-X bonds are cleaved to yield five-coordinate complexes or complexes of the form $(NbX_4L\text{-solvent})$.

Far infrared spectra

Far infrared spectra of dimethyl and diethyl sulfide, solid complexes, and solutions of the complexes were recorded using procedures described in the Experimental section. The spectrum of diethyl sulfide consisted of four bands with maxima located at frequencies (rel. int.): 380(m), 342(m), 305 (w-m), and 245(w,br). The bands at 305 to 380 cm^{-1} hinder interpretation of spectra of diethyl sulfide solutions. A similar complication arises for benzene solution since bands due to the solvent appear at 400(m), and 300(s) cm^{-1}.

Spectra of solid complexes are presented in Figs. 17 and 18 and band maxima are tabulated in Table 16. There is a strong similarity between the solid state spectra of mono-adducts and bis-adducts (see Fig. 3) which is consistent with the same local symmetry for niobium(IV) in the two cases. The position of the highest energy Nb-X stretching band, taken as an index to coordination number of the metal (45), is consistent with the same coordination number of six for each complex. Far infrared data for the MX_4L_2 complexes with M = Nb were consistent with a cis-stereochemistry (C_{2v}), and indicated from the assignment of metal-sulfur and the lowest energy metal-halogen stretching frequencies that the force constants for these two types of fundamental modes are quite similar. To the extent that these assignments are valid it suggests that in a first approximation the bioctahedral halogen-bridged dimers can be considered as having pseudo-D_{2h} symmetry. For such a model a total of six infrared active Nb-X or Nb-L stretching bands are anticipated transforming according to the representations $2B_{1u} + 3B_{2u} + B_{3u}$ of the point group D_{2h}. A formal similarity between the far infrared spectrum of such a

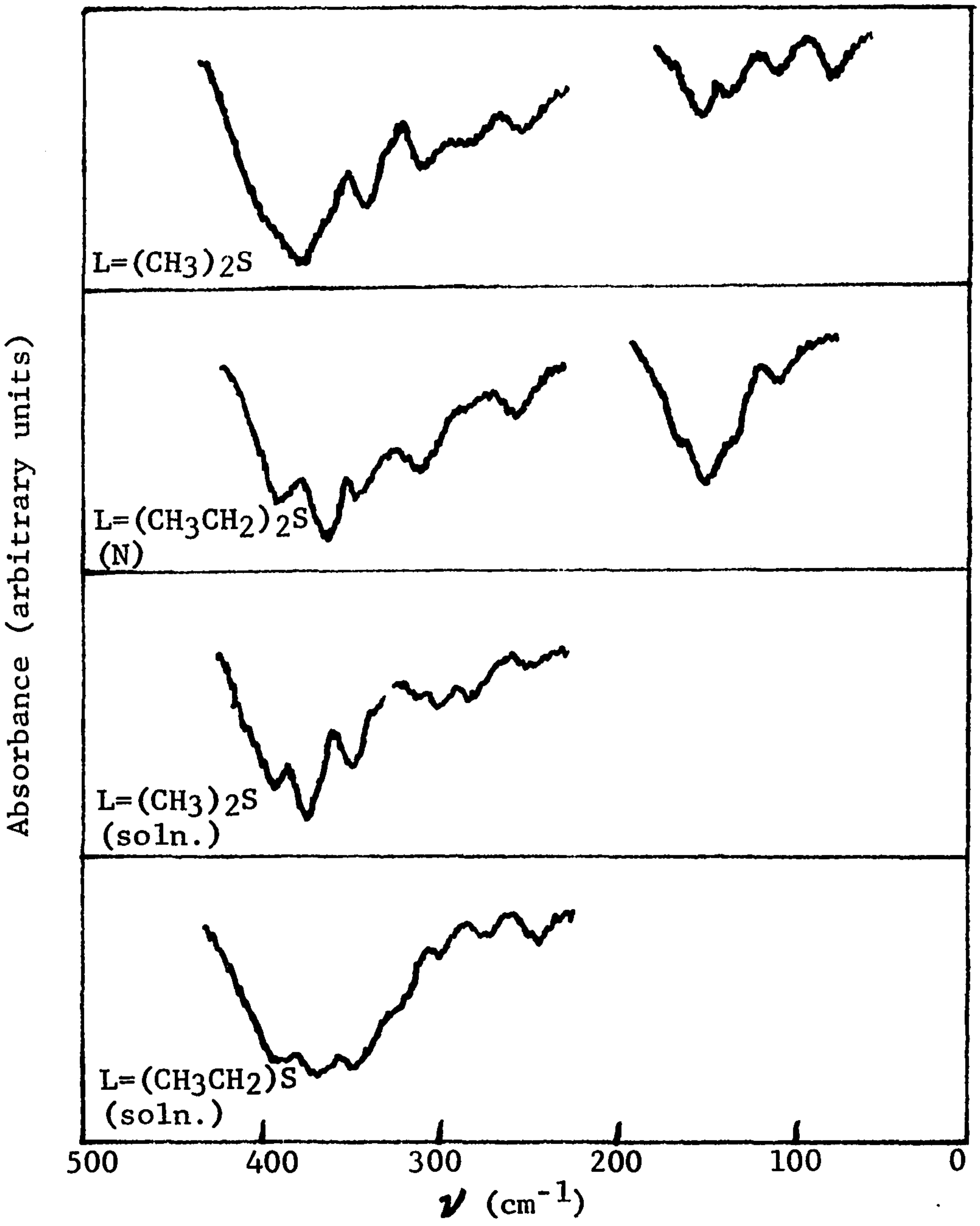

Fig. 17. Far infrared spectra of $NbCl_4L$ in benzene solutions and nujol mulls (N)

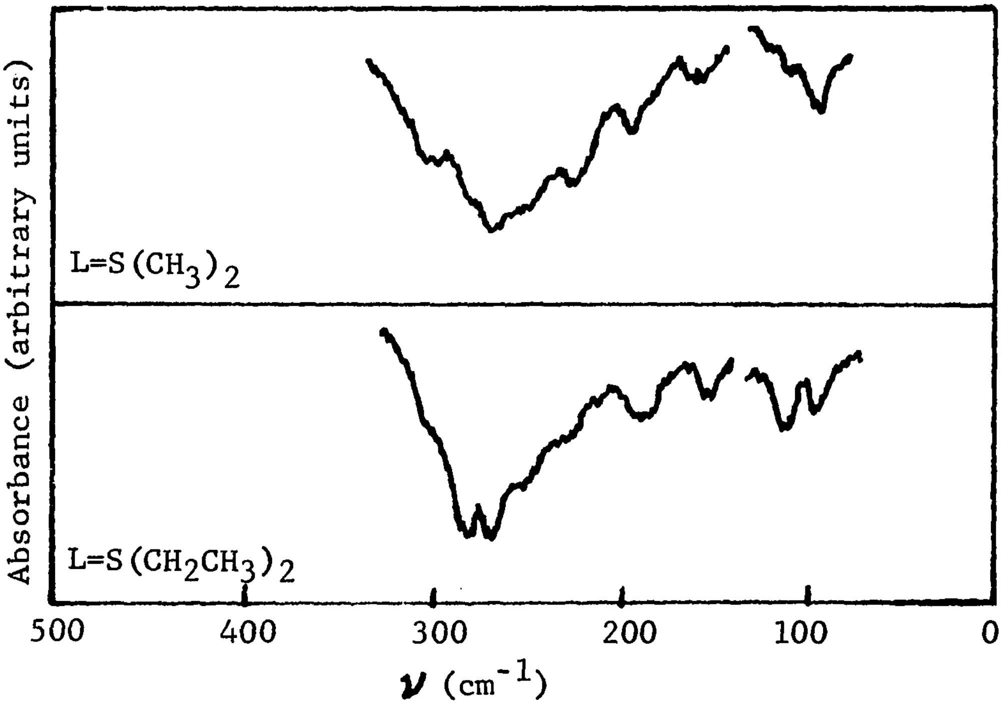

Fig. 18. Far infrared spectra of $NbBr_4L$ (L = $(CH_3)_2S$ and $(CH_3CH_2)_2S$) (nujol)

Table 16. Far infrared spectra of tetrahalo(dialkyl sulfide)niobium(IV) complexes (ν in cm^{-1})

$NbCl_4(S(CH_3)_2)$		$NbCl_4(S(CH_3CH_3)_2$		$NbBr_4$ $(S(CH_3)_2)$	$NbBr_4$ $(S(CH_2CH_3)_2)$
(Nujol)	(C_6H_6)	(Nujol)	(C_6H_6)	(Nujol)	(Nujol)
396(m,sh)	393(m)	382(m)	391(s)	305(m)	303(m,sh)
375(s)	371(s)	360(s)	367(s)	283(m)	282(s)
340(m)	346(m)	340(m)	341(s)	271(s)	270(s)
307(m)	318(w)	310(wm)	316(m,sh)	254(m)	250(m)
	300(w)		300(w,sh)		
276(w,sh)	280(w)	280(w,sh)	280(vw)	227(m)	227(m)
250	250(vw)	252(w)	250(w)	195(m)	189(m)
166(w)		162(w)		160(w)	156(w)
155(w,sh)		150(w)		110(w,sh)	110(w)
148(w)				98(w)	92(w)
132(w)		132(w)			73(w)
188(w)		108(w)			
78(w)					

($NbCl_4(S(CH_3)_2)$ in $S(CH_3)_2$: 368(m,sh), 348(s,br), 284(vw,br), 235(w-m).'

dimer and cis-NbX_4L_2 (where six M-X and M-S stretching bands are also expected) is then not unexpected. Similar conclusions follow from a comparison of reported far infrared spectra of $PdCl_2(S(CH_3)_2)_2$ (74) and $Pd_2Cl_4(S(CH_3)_2)_2$ (75) where, respectively, the bands from 400-200 cm^{-1} appear at 361(vs), 322(w), 310(m), 303(s), 295(m), 282(vw), and 220(m) cm^{-1}, and 360(vs), 340(m), 308(m), 304(sh), 283(ms), and 208(w) cm^{-1}. Beattie and Webster (48) also noted the expected similarity between the spectrum of the halogen bridged dimer Nb_2Cl_{10} and complexes of the form cis-MX_4L_2.

No further attempt at assignment of the bands is made here. Clearly a normal coordinate analysis would be required to separate bands due to $\nu(Nb\text{-}X)_t$, $\nu(Nb\text{-}X)_b$, and $\nu(Nb\text{-}S)$ since all seem to lie in the same narrow frequency range and the possibility of considerable mixing must be considered. Even for NbX_4L_2 complexes the assignments of $\nu(Nb\text{-}S)$ stretching modes were tentative.

Spectra of $NbCl_4L$ (L = $S(CH_3)_2$ and $S(CH_2CH_3)_2$) were also recorded in benzene solution, and for L = $S(CH_3)_2$ the spectrum in dimethyl sulfide was recorded. For the latter ligand bands were not expected to interfere with interpretation since dimethyl sulfide spectra exhibited only a broad weak band at ca. 282 cm^{-1}. The data are recorded in Table 16 where differences are at once apparent. The band at ca. 395 cm^{-1} in the spectrum of solid $NbCl_4(S(CH_3)_2)$ is absent in the dimethyl sulfide solution spectrum. In addition the band at 250 cm^{-1} in the solid is absent in the solution spectrum and a band at 235 cm^{-1} appears. The similarity of this spectrum of $NbCl_4(S(CH_3)_2)$ in dimethyl sulfide to that of $NbCl_4(S(CH_2)_4)_2$ in tetrahydrothiophene is consistent with the presence of six coordinate $NbCl_4(S(CH_3)_2)_2$ in dimethyl sulfide solutions. In benzene solution spectra of the chloride monoadducts the band at ca. 395 cm^{-1} is again found, in addition in the 300 cm^{-1} region two bands are observed at ca. 320 and 300 cm^{-1} instead of the one band at ca. 310 cm^{-1} observed in solid state spectra. This is very likely due to complications arising from the appearance of solvent bands, in this case benzene, at 400 and 300 cm^{-1}. The 310 cm^{-1} band in solid state spectra is shifted to ~320 cm^{-1} in solution spectra and the weak 300 cm^{-1} is probably due to benzene absorption. The relative intensity of the band at ca. 395 cm^{-1} in the benzene solution spectra suggests that it is not due entirely to solvent but instead is coincident with an Nb-Cl stretching band. This similarity between solution and solid state spectra then suggests that the same species are present in both phases, yet other data imply that possible five coordinate species are present in benzene solutions. Clark (45) observed that the frequency of the highest energy Ti-Cl vibration was a function of the coordination number of titanium decreasing from 490 cm^{-1} for tetrahedral $TiCl_4$ to ~380 cm^{-1} for six-coordinate $TiCl_4 \cdot 2L$ to 317 cm^{-1} for eight-coordinate $TiCl_42D$ (D = o-phenylenebisdiarsine). For $TiCl_3(S(CH_2)_4)_2$ in tetrahydrothiophene the highest energy TiCl band appeared at ca. 373 cm^{-1} while for five coordinate $TiCl_3(N(CH_3)_3)_2$ this band occurs at 387 cm^{-1}. The expected increase in energy of ν(Ti-Cl) with decrease in coordination number is then much sharper on going from 8-to 6-coordination or 6-to-4-coordination than from 6-to-5-coordination. It is not unreasonable then to expect the far infrared frequencies of a five-coordinate MX_4L complex to be similar in the M-X stretching region to that of a halogen bridged dimer whose M-X stretching force constants are much lower than those of the nonbridging M-X bonds.

As suggested by the preceding discussion there is clearly a need for additional study via Raman spectroscopy, and normal coordinate analysis. Ultimately a structure investigation using the techniques of single crystal x-ray diffraction analysis will be required. The data here has been discussed from various points of view, but with the great constraint of virtual identity of solid and solution phase spectra of mono-adducts, and solid state spectra of the bis-adducts NbX_4L_2. Still the conclusions are at best tentative.

Electronic spectra

Electronic spectra were recorded for solids and solutions using procedures described in the experimental section. Spectra are reproduced in Figs. 19 and 20 and Table 17 contains data o tained from the spectra. With the instrumentation available it was not possible to extend the diffuse reflectance measurements on solids to energies less than ca. 10,000 cm^{-1}. Mull spectra obtained for $NbCl_4(R_2S)$ (R = CH_3 and CH_3CH_2) using a Cary Model 14 spectrophotometer extended the measurements to 6,250 cm^{-1}, but the poor spectra each exhibited only a broad featureless band with a maximum at 330 $m\mu$. Diffuse reflectance spectra of $(NbCl(OCH_2CH_3)_3(C_5H_5N))_2$ (25) and $NbCl_4(N(CH_2CH_3)_3)$ (32) consist of a shoulder on a charge transfer band at 27,400 and 26,300 cm^{-1}, respectively. A single broad band at 25,800 cm^{-1} has also been reported for the solid state spectrum of $NbCl_4$ (32). The appearance of lower energy bands in solid state spectra of $NbX_4(SR_2)$ is not inconsistent

Table 17. Extinction coefficients and band maxima for complexes of the form NbX_4L (X = Cl and Br; L = $(CH_3)_2S$ and $(CH_3CH_2)_2S$

$NbCl_4(S(CH_2CH_3)_2)$		$NbBr_4(S(CH_2CH_3)_2$	
$\nu(cm^{-1})$	$\varepsilon(\ell.\ mole^{-1}cm^{-1})$	$\nu(cm^{-1})$	$\varepsilon(\ell.\ mole^{-1}cm^{-1})$
34,360	$14.6x10^3$		
26,310	$27x10^2$		
18,350	126	17,400	150
12,900	35	11,630	12
8,300	47	6,900	79

$NbCl_4(S(CH_2CH_3)_2)$ in C_6H_{12}: 43,478; 34,402; 26,667; 18,600; 12,100; and 8,000 cm^{-1}

$NbBr_4(S(CH_3)_2)_2$ in C_6H_6: 17,400; 11,630; and 6,900 cm^{-1}

$NbCl_4(S(CH_3)_2)$ in C_6H_6: 18,360; 12,900; and 8,300 cm^{-1}

with those findings since it has been shown in an earlier section that Dq for alkyl sulfides ligands is lower than for nitrogen donors and chlorides, hence lower energy ligand field bands for these complexes are not unexpected. The spectra of $NbX_4(SR_2)$ solids and solutions are sufficiently similar above 10,000 cm^{-1} as to suggest the presence of similar species in these phases. At energies lower than 10,000 cm^{-1} spectra of benzene solutions exhibit bands at 8,300 cm^{-1} for the chloride and 6,900 cm^{-1} for the bromide complexes. It is these low energy bands which were not observed in diffuse reflectance or nujol mull spectra.

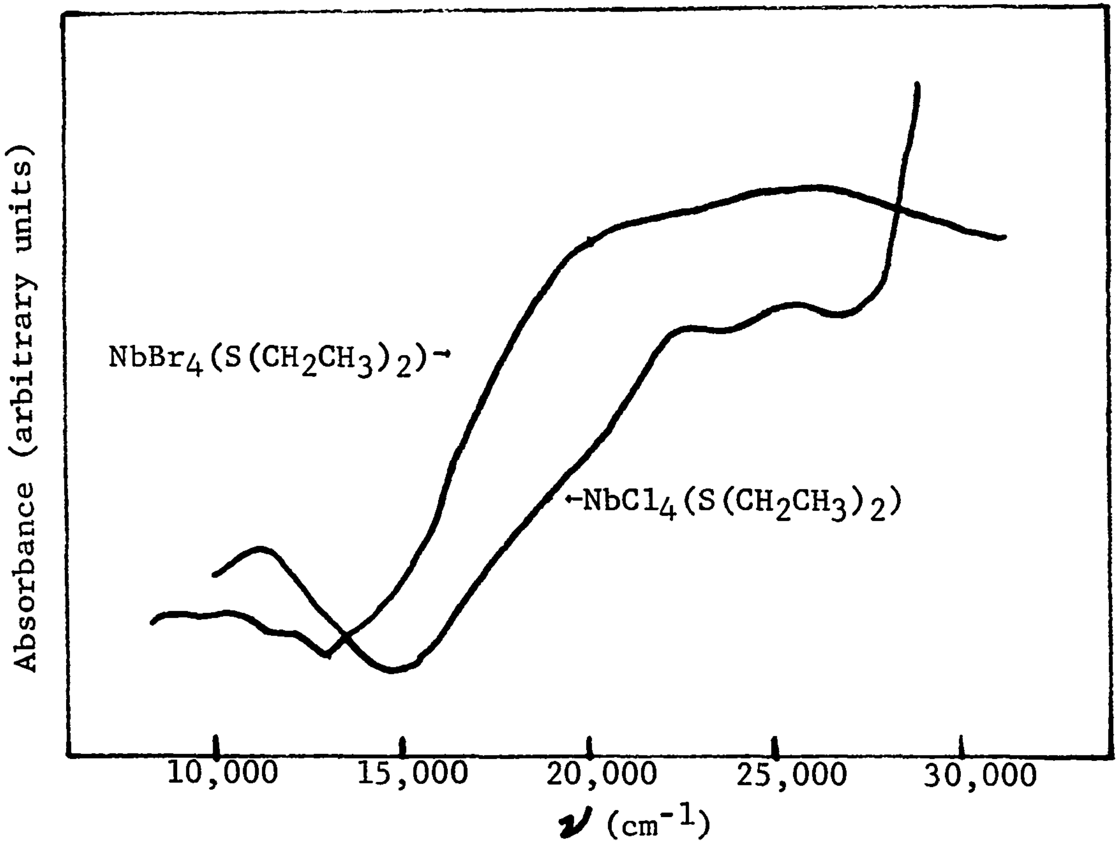

Fig. 19. Diffuse reflectance spectra of tetrahalo(alkyl sulfide)niobium(IV) complexes

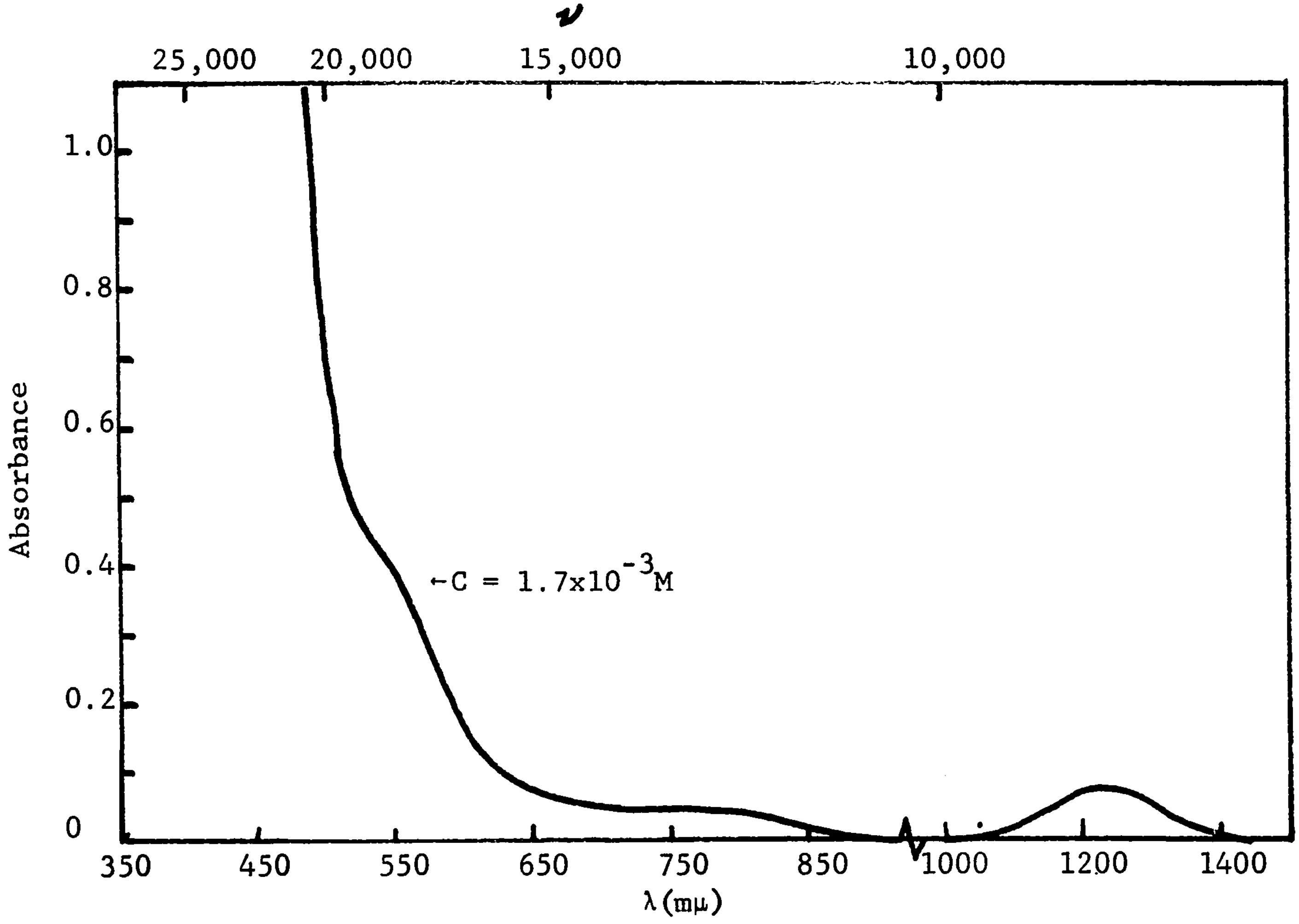

Fig. 20a. Electronic spectrum of tetrachloro(diethyl sulfide)niobium(IV) in benzene

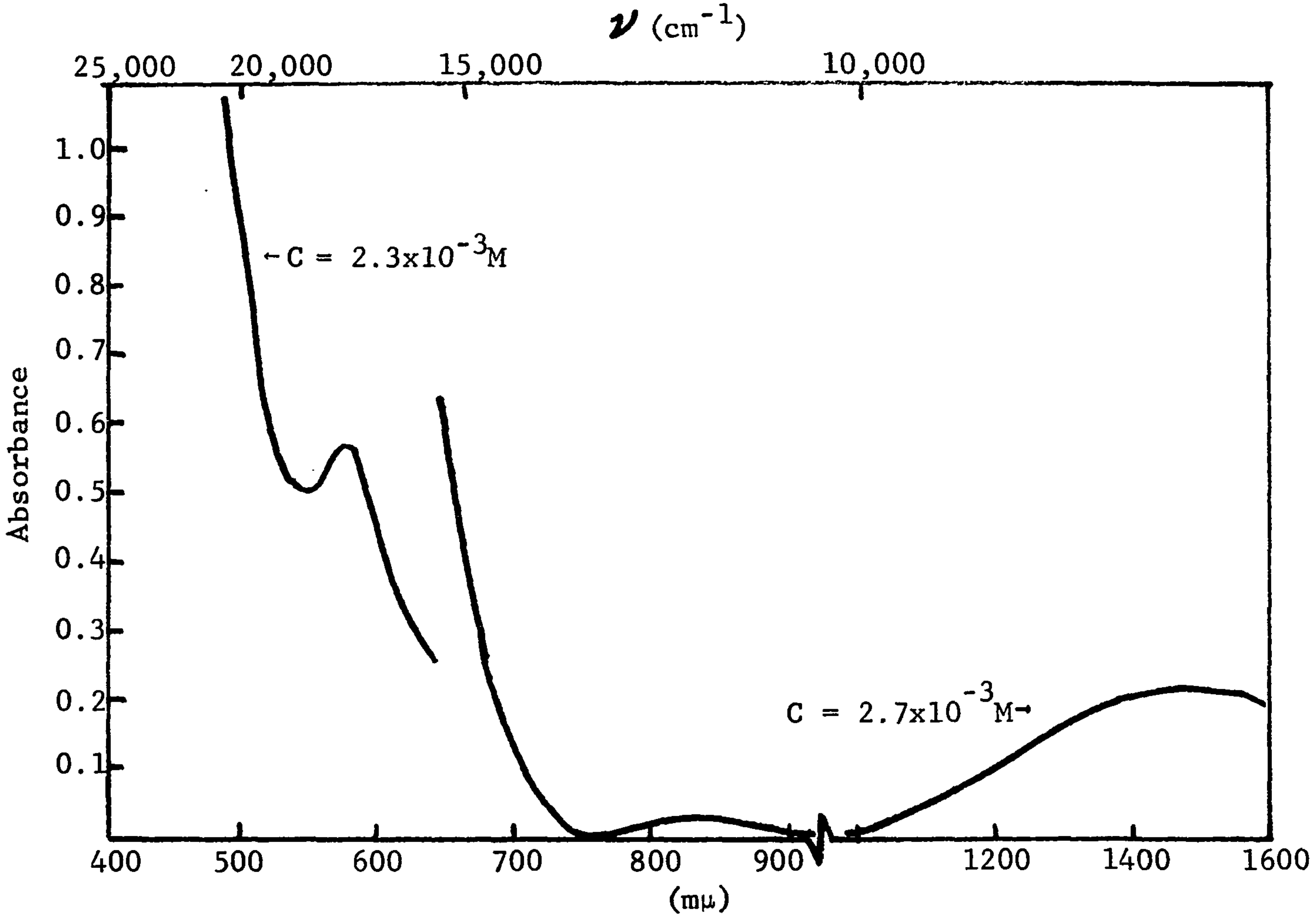

Fig. 20b. Electronic spectrum of tetrabromo(diethyl sulfide)niobium(IV) in benzene

The bonding in a dimeric metal-metal bonded complex such as has been described is not expected to differ significantly from the qualitative molecular orbital interpretation of the bonding in α-NbI_4 given by Dahl and Wampler. Octahedral symmetry about each niobium atom was assumed and the $4d_{z^2}$, $4d_{x^2-y^2}$, 5s, $5p_x$, $5p_y$, and $5p_z$ orbitals were used in σ-bonding. The $4d_{xz}$ and $4d_{yz}$ pair was used in π-bonding with suitably oriented filled π-orbitals on iodine atoms. This left a d_{xy} orbital to contain an unpaired electron. Overlap between half-filled d_{xy} orbitals on adjacent niobium atoms accounted for the diamagnetism of the compound. Bands appearing in the electronic spectrum then arise via transitions to excited levels from a filled $(d_{xy})^2$ orbital. Such a model is applicable to the dimers discussed here and accounts qualitatively for their observed magnetism and electronic spectra. Alternatively a mechanism which does not involve metal-metal bonding by direct overlap of d-orbitals, but which involves spin-coupling between chlorine-bridged niobium atoms via localized super-exchange can account for the magnetic behavior (43). However, no evidence for antiferromagnetic behavior was found, and would have been expected for such a mechanism.

Rationalization of the bonding in the solution species is more difficult since it is not certain whether a single species rather than a dimer plus its dissociation product, a five coordination monomer, is present. The appearance of the bands at low energy in the electronic spectra of solutions, the molecular weight of $NbBr_4(S(CH_3)_2)$, and the empirical composition all suggested that a five coordinate monomer was present. A spectrum of $NbCl_4(S(CH_2CH_3)_2)$ in cyclohexane solution was recorded in order to ascertain whether the band at 8,300 cm^{-1} was solvent dependent. As shown in Table 17 benzene and cyclohexane solution spectra were virtually identical. The spectra will now be discussed. Initially a trigonal bipyramidal (D_{3h}) model will be assumed.

Ciampolini (76), Allen and Hush (77), Day (78), and more recently Wood (47) have applied crystal field and/or ligand field theory to trigonal bipyramidal complexes having D_{3h} symmetry. The results were used to assign bands in the electronic spectra of a variety of complexes of the MX_5 or MX_3L_2 where X is a halide and L is a unidentate ligand. Allen and Hush (77) reported bands at ca. 8,500 and 10,000 cm^{-1} for $CoCl_5^{3-}$ which were assigned as transitions from $^2A_1'$ level to the levels $^2E'$ and $^2E''$. These levels result from a trigonal bipyramidal crystal field splitting of the d-manifold (79).

Wood (47) evaluated the one electron matrix elements within the d-manifold in terms of the tetragonality parameters D_s and D_t and obtained the orbital energies: (z^2), a_1', $2D_s+6D_t$; (xz,yz),e'',D_s-4D_t; and (xy,x^2-y^2),e',$-2D_s+D_t$. The predicted transitions are then $^2E'' \rightarrow {}^2A'$ (10 Dt+ Ds) and $^2E'' \rightarrow {}^2E'$ ($-3\ D_s + 5D_t$). (For a d' system the level sequence is inverted relative to d^9.) Using the values of D_t and D_s derived by Wood (47) for $VCl_3(S(CH_3)_2)_2$ and $VBr_3(S(CH_3)_2)_2$ the predicted energies of the expected transitions for the present system are as shown in Table 18. For chloride and bromide complexes

Table 18. Ligand field spectra and parameters for five coordinate complexes (ν in cm^{-1})

	$NbCl_4(S(CH_3CH_3)_2)$	$NbBr_4(S(CH_2CH_3)_2)$
D_s(theory)	-100	150
D_t(theory)	1,260	1,285
($^2E'' \rightarrow {}^2A_1'$)(theory)	12,300	13,000
($^2E'' \rightarrow {}^2E'$)(theory)	6,400	5,975
D_s(est.)	-520	-310
D_t(est.)	1,340	1,194
($^2E'' \rightarrow {}^2A_1'$)(exp)	12,900	11,630
($^2E'' \rightarrow {}^2E'$)(exp)	8,300	6,900

(est. denotes estimated using experimental spectra, and theory denotes estimated using D_t and D_s from $VX_3(R_2S)_2$)

the predicted energy for the $^2E'' \rightarrow {}^2A'$ transition is fairly well approximated using the parameters for the vanadium compounds, while for the $^2E'' \rightarrow {}^2E'$ there is greater disparity. New estimates of the parameters are given in Table 18 and are, for the sign convention used by Wood (47), indicative of an overall increase in the tetragonality of the ligand field. This is not unexpected since, like D_q, D_t and D_s are expected to increase on passing from a first to a second row transition element.

From this simple analysis a five coordinate trigonal bipyramidal complex can account for the spectrum. Some other species, presumably a dimer, account for the high energy bands at <u>ca</u>. 18,600 and 17,400 cm^{-1} for the chloride and bromide.

These results are by no means conclusive, but they are indicative of the formation of three types of complexes by niobium(IV) halides and unidentate alkyl sulfides. Paramagnetic cis-NbX_4L_2 species form in the presence of excess dimethyl sulfide and tetrahydrothiophene. With $NbX_4(S(CH_3)_2)_2$ (X = Cl and Br) in benzene dissociation occurs to form five coordinate complexes and dimers as evidenced by the presence of a high energy ligand field band at 17,000-19,000 cm^{-1}, and a low energy ligand field band at 7,000-8,000 cm^{-1}. Evaporation of benzene yields diamagnetic solids which exhibit bands in diffuse reflectance spectra which are similar to what is observed with cis-MX_4L_2 monomers. Spectra of $NbBr_4(S(CH_3)_2)_2$ in benzene exhibit the expected ligand field band at 6,900 cm^{-1}, while $NbBr_4(S(CH_3)_2)$ in dimethyl sulfide exhibits a spectrum virtually identical to that of $NbBr_4(S(CH_3)_2)_2$ in that solvent.

In contrast the spectrum of $NbBr_4(S(CH_2)_4)_2$ in benzene or tetrahydrothiophene is the same. Diethyl sulfide forms only the monoadduct with NbX_4 (X = Cl and Br) and its spectra are virtually identical to those of the corresponding dimethyl sulfide complexes. The similarity between the electronic spectra of solid NbX_4L and NbX_4L_2 complexes suggests that formation of a metal-metal bond does not significantly alter the σ-bonding levels of niobium. This one point is perhaps most interesting of all since such changes might have been predicted, and if not in σ-bonding levels then in π-bonding levels (79,80).

Complexes of the Form MX_4B_2

The preparation and some of the properties of the complexes MX_4B_2 (M = Nb, Zr; X = Cl, Br, and I) have been discussed in the Experimental section. At this point other data from physicochemical studies of the solids will be presented. Initially infrared and far infrared data will be discussed and this will be followed by a discussion of magnetic susceptibility data and diffuse reflectance spectra.

Infrared spectra

Several workers have investigated the spectrum of 2,5-dithiahexane (38-40) and assigned the bands observed. In the most recent study by Hayashi *et al*. (40) vibrational assignments were made in relation to rotational isomerism. A total of ten different rotational isomers are possible. Discounting rotation about C-S bonds only three rotational isomers or conformers are possible, the trans-, cis-, and gauche conformers. Studies of spectra (40) and other physical measurements (81) on the pure liquid and solid have established that in the liquid state trans and gauche forms are present, while in the solid state only the trans form is found. Similar behavior is found for other 1,2-substituted ethane derivatives (81). Mizushima *et al*. (82), Quagliano et al. (82) and Sweeney *et al*. (84) determined the conformation of 1,2-dithiocyanatoethane and 2,5-dithiahexane in metal complexes and established it as gauche. More recently Clark and Errington (37) established the gauche conformer of 2,5-dithiahexane in the com-

Table 19. Observed frequencies (in cm^{-1}) of 2,5-dithiahexane (dth) in free and coordinated states

Assignment	Liq. dth	$NbCl_4(dth)_2$	$ZrCl_4(dth)_2$	$NbBr_4(dth)_2$
CH_2wag (T,G)	1281(sh)	--	--	--
CH_2wag (G)	1268(s)	1260(m)	1267(m),1263(sh)	1257(w)
CH_2wag(T)	1208(s)	--	--	--
CH_2twist (G)	1200(sh)	1182,1170(m)	1181(m)	1182(m),1164(m)
CH_2twist (G)	1130(sh)	1142(m)	--	1139(m)
CCstr (T,G)	1030(w)	1029,1023(s)	1032(m)	1031(sh),1021(s)
CH_3rock(T,G)	972(sh)	975(w),975(sh)	982(w)	982(w)
CH_2rock (G) and CH_3rock (T,G)	960(s)	956(s)	962(m)	960(s)
CH_2rock(G)	840(w)	843(m),834(m)	843(m)	840(m),831(m)
CSstr (T)	739(s)	--	--	--
CSstr (T)	688(s)	--	--	--
CSstr (T,G)	655(vw)	644(w),640(w)	650(w)	640(w),636(w)

plexes $TiCl_4(dth)$, $TiBr_4(dth)$, $VCl_4(dth)$, $SnCl_4(dth)$, and $NiI_2(dth)_2$.

Table 19 contains absorption maxima in the spectra of the 2,5-dithiahexane complexes as well as the vibrational spectrum and assignments of the free ligand. Bands of moderate to strong intensity which are characteristic of the trans conformer appear at 1208 and 688 cm^{-1} in the solution spectrum of the free ligand, but are completely absent in the spectra of the complexes. For the gauche conformer those bands at 655, 840, and 1268 cm^{-1} in the free ligand reappear in the spectrum of the complexes, and for the weak bands, with increased intensity. These data then suggest that the ligand 2,5-dithiahexane is coordinated in the gauche form. The multiplicity of most of the bands is too complex to be associated merely with a lowering of the symmetry of the ligand, but probably also is due to the presence in the coordination sphere of two gauche-forms (39).

Far infrared spectra

Results of far infrared studies are represented diagrammatically in Fig. 21 and Table 20. The free ligand spectrum was also studied in this region and band maxima occurred at ν (rel. int.): 550(w), 510(w,sh), 415(w), and 220(m) cm^{-1}.

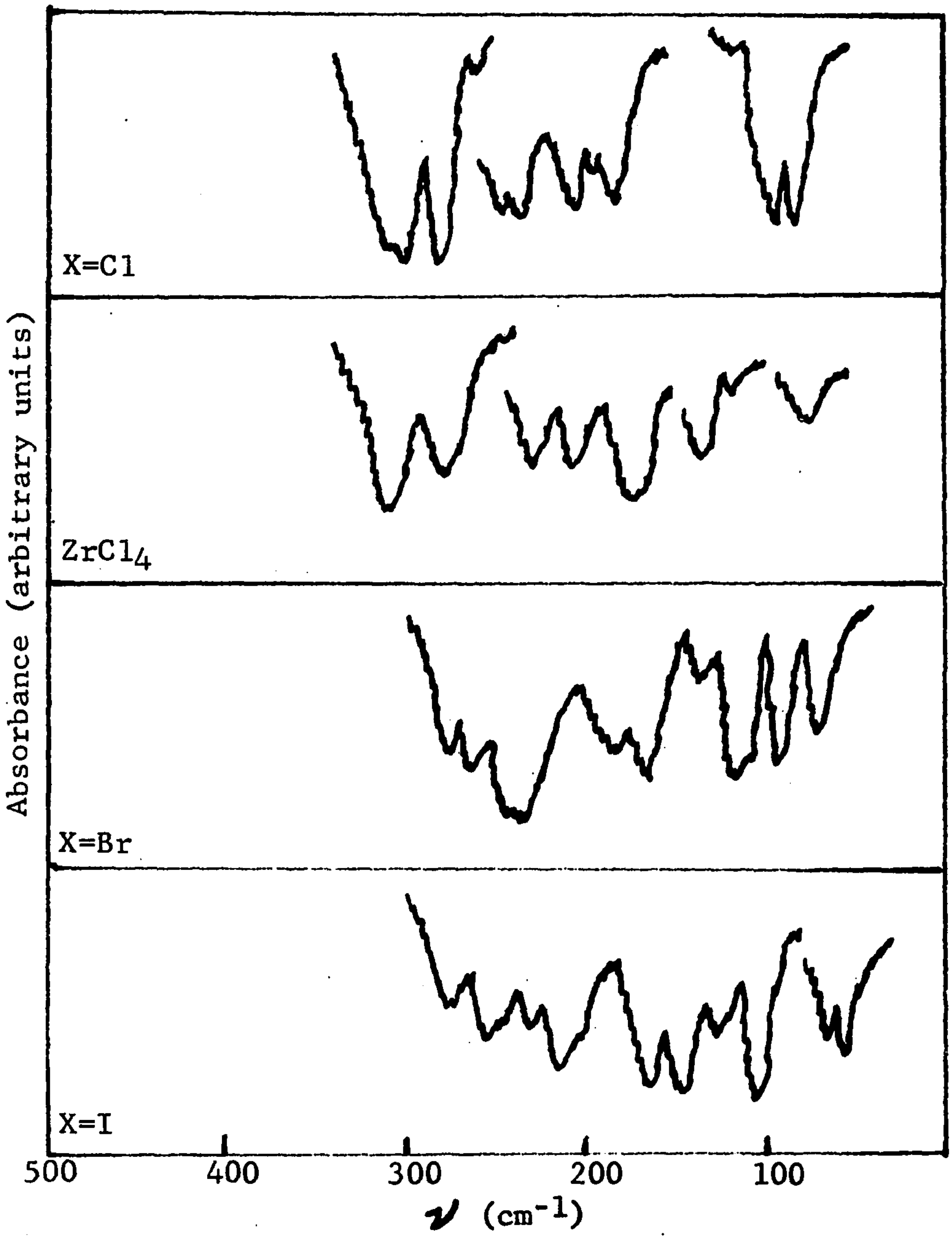

Fig. 21. Far infrared spectra of $NbX_4(dth)_2$ (X = Cl, Br, and I) and $ZrCl_4(dth)_2$ (nujol mulls)

Table 20. Vibrational frequencies and some assignments for tetrahalobis(2,5-dithiahexane)niobium(IV) complexes (ν in cm^{-1})

	$NbX_4((CH_3SCH_2-)_2)_2$			
Assignment	X = Cl	X = Br	X = I	$ZrCl_4((CH_3SCH_2-)_2)_2$
ν(M-X)	310(s,sh)	245(s,sh)	165(m)	
	303(s)	235(s)	142(m)	300(s)
ν(M-S)	281(s)	278(m)	276(m)	
	260(w)	261(m)	254(ms)	275(ms)
Unassigned bands	245(w)	194(w,sh)	230(w-m)	230(w-m)
	235(w)	185(w)	213(m)	202(w-m)
	207(w)	164(m)	123(w,sh)	175(m)
	193(w)	135(w)	108(m)	137(wm)
	180(w)	118(m)	63(w-m)	80(m)
	119(w)	113(m,ph)	59(w-m)	
	97(m)	93(m)		
	81(m)	72(m)		

($NbCl_4(CH_3SCH_2-)_2$): 460(w), 440(w), 370(s,sh), 355(s), 336(s), 320(s,sh), 280(s), 260(w), 237(w), 130(w).)

Hayashi (40) calculated vibrational frequencies of skeletal modes appearing below 500 cm^{-1} for six of ten rotational isomers. The present data are most consistent with the TTT conformer where the left hand T refers to conformation about one C-S bond, the center symbol to conformation about the C-C bond, and the right hand symbol to the conformation about the remaining C-S bond. Clearly this is consistent with the trans form (about C-C bond) predominating in solution.

The far infrared spectra of the complexes are quite rich with all of the bands appearing at *ca*. 300 cm^{-1} and below. Particularly for the chlorides this is relevant, since for six coordinate niobium(IV) chloride as well as zirconium(IV) chloride complexes the metal-chlorine stretching bands center at *ca*. 350-360 cm^{-1}. An intense band with a shoulder at 310 cm^{-1} is found at 303 cm^{-1} in the $NbCl_4(dth)_2$ spectrum and at 305 cm^{-1} in the spectrum of $ZrCl_4(dth)_2$. This represents a shift to lower energy for M-Cl of *ca*. 40-50 cm^{-1}. Clark (45) associates such shifts with increase in the coordination number of the central metal. Shifts of this magnitude were referred to earlier for six and eight coordinate complexes of $TiCl_4$. X-ray diffraction data for representative $TiCl_4L_2$ or $TiCl_4$ $(diarsine)_2$ (ophenylenebisdimethylarsine) complexes indicated a correlative increase in Ti-Cl distance with decrease in ν(Ti-Cl). Clark (45) also reports ν(M-Cl) for the authentic eight-coordinate $ZrCl_4(diarsine)_2$ and $NbCl_4(diarsine)_2$ as 295(s) and 303(sh) cm^{-1} and 299(s) and 307(sh) cm^{-1}, respectively. The present data thus are consistent with eight-coordination about the metals. Corresponding stretching bands for bromide and iodide are expected at *ca*. 235 and 170 cm^{-1}, respectively, if the ratios ν(NbBr)/ ν(Nb-Cl) = 0.76 and

and ν(NbI)/ ν(NbCl) = 0.56 derived from reported six coordinate complexes are used in their estimation. Experimentally in the spectrum of the bromide a strong doublet appears at 235 and 245 cm^{-1} and for the iodide similarly strong bands appear at 165 and 142 cm^{-1}. These bands are then assigned as ν(Nb-Br) and ν(Nb-I) and relative to six coordinate complexes are shifted to lower energy by ca. 30-40 cm^{-1}. The doublet structure of these stretching bands (except for $ZrCl_4(dth)_2$) and their similarity to ν(M-Cl) in analogous eight coordinate diarsine complexes suggests that the same molecular symmetry prevails in each. Those diarsine complexes which have been discussed are known to have local symmetry D_{2d} with the metal atom in the center of a dodecahedron (30). A model is depicted in Fig. 22. With the sulfur ligands occupying positions A and the halides positions B, and considering the ligands as point dipoles, the full D_{2d} symmetry of the dodecahedron is preserved. It is in fact this manner in which these positions are occupied in most known $MX_4(diars)_2$ complexes (30). Simple group theoretical methods reveal that nine infrared active normal vibrations are allowed. These transform according to the reduced representation $\Gamma = 4B_2 + 5E$. If it is assumed that there is negligible interaction between modes of the same

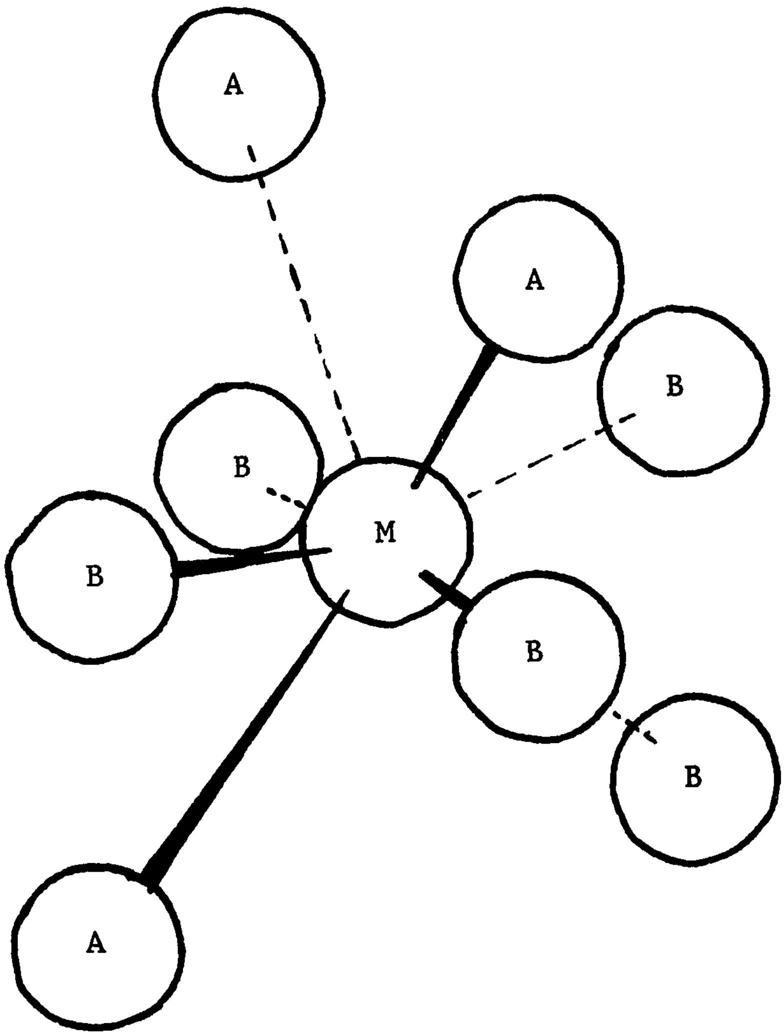

Fig. 22. Eight coordinate metal complex MA_4B_4 having D_{2d} symmetry

symmetry these can be further broken down. Thus, two M-X stretching modes transforming as B_2 + E and two M-S modes transforming similarly as B_2 + E are predicted. A cursory glance at the spectra reveals a doublet at 276(m) and 256(ms) in the iodide which is mirrored in the chloride and bromide spectra by doublets at 281(s), 260(w) cm^{-1} and 278(m), 261(m) cm^{-1}, respectively. These are assigned as the two expected metal sulfur stretching bands. For $ZrCl_4(dth)_2$ the two Zr-S bands like the two expected Zr-Cl bands seem to have merged into one band at 275(ms) cm^{-1}. Due to the possible presence of ligand skeletal bands in the remainder of the spectrum it is not possible to effectively assign the remainder of the bands. Even the assignment of the lower energy metal sulfur band is tentative since Hayashi notes that several rotational isomers of the form YGY should absorb at 257(m) cm^{-1}. Other bands due to conformers derived from the gauche (C-C) rotational isomer also introduce complications. The total number of bands observed in a given spectrum is also consistent with the number predicted since allowing for removal of the degeneracy of E, at least nine and as many as fourteen infrared active bands could appear.

Table 20 also lists the bands observed in the spectrum of a substance obtained via direct reaction of $NbCl_4(dth)_2$ with excess $NbCl_4$ and benzene as the reaction medium. The reaction proceeded readily as indicated by rapid development of a red solid, however, extraction of the product with benzene proceeded extremely slowly over several days. At the end of this period the product was dried in vacuo and analyzed for niobium. This result was based on a single analysis of a small sample (<0.1 g.) and was for that reason expected to be low. In the far infrared spectrum the development of bands attributable to ν(Nb-Cl) at ca. 340-360 cm^{-1} was indicative of six-coordinate niobium.

Anal: Calcd. for $NbCl_4(CH_3SCH_2-)_2$: Nb, 26.1: Found: Nb, 23.9.

In concluding, it is clear that a dodecahedral D_{2d} ligand environment is consistent with far infrared spectra. Coordination of both molecules of 2,5-dithiahexane and the absence of free ligand are indicated by studies in the infrared. Clark and Errington's (37) conclusion that 2,5-dithiahexane would not form eight coordinate complexes with $TiCl_4$, $SnCl_4$, $TiBr_4$, or VCl_4 and the isolation here of such complexes of second row transition elements may indicate the relevance of the atomic radius of the central metal.

Magnetic susceptibilities

The magnetic susceptibilities of $NbX_4(dth)_2$ obeyed the Curie law as indicated by plots of χ_M vs T^{-1} shown in Fig. 23. Table 21 lists the values of χ_{TIP} and μ which were determined from the Curie plots. As expected χ_{TIP} is much smaller for these highly distorted complexes than was found for the six coordinate NbX_4L_2 (X = Cl, Br, and I; L = $S(CH_2)_4$) complexes. The magnitude of χ_{TIP} also increases in the order Cl < Br < I in contrast to the order Br ~ Cl > I for the six-coordinate complexes. Considering the differences in the ligand environment of niobium(IV) for these cases, analogies are not expected to be fruitful. Consistent with the greater distortion the values of μ for the chloride and bromide are only slightly (7%) less than the spin-only value for one unpaired electron.

Table 21. Magnetic data from Curie plots

Compound	$\chi_D \times 10^6$ (emu/mole)	$\chi_{TIP} \times 10^6$ (emu/mole)	μ (B.M.)
$NbCl_4((CH_3SCH_2-)_2)_2$	-298	+58	1.595
$NbBr_4((CH_3SCH_2-)_2)_2$	-338	+98	1.609
$NbI_4((CH_3SCH_2-)_2)_2$	-402	+162	1.283

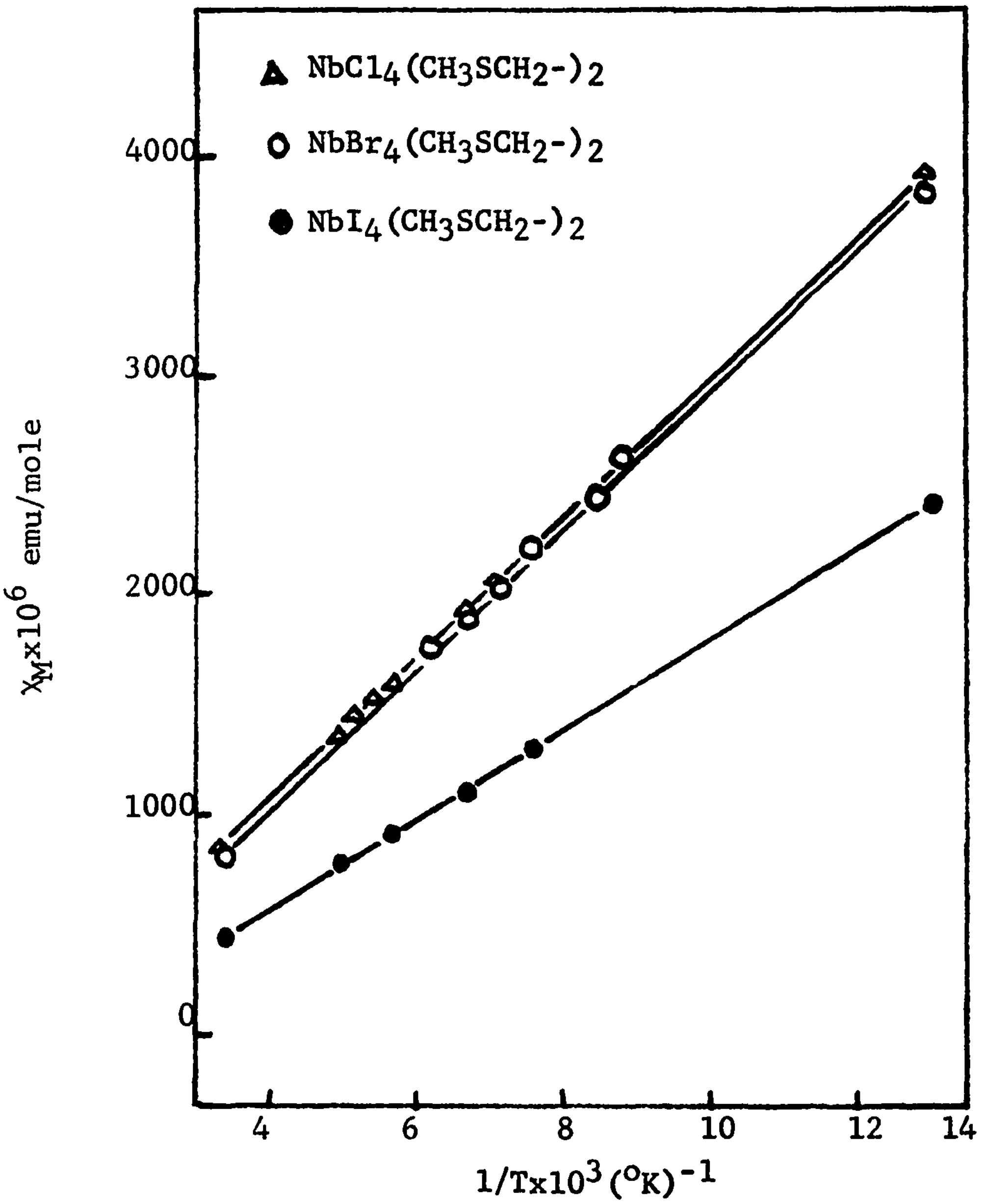

Fig. 23a. Magnetic susceptibility versus (T^{-1}) plot for tetrahalobis(2,5-dithiahexane)niobium(IV) complexes

The orbital contribution to the moment has been considerably reduced. The moments are somewhat lower than the effective moments 1.7, 1.9, and 1.6 B.M. reported for $NbX_4(diarsine)_2$ (X = Cl, Br, and I) (29). Values of μ_{eff} (R.T.) for corresponding 2,5-dithiahexane complexes (Table 22) are 1.63, 1.68, and 1.41 B.M. Problems of decomposition plagued the magnetic susceptibility measurements of Clark et al. (29), and the values of μ_{eff} which were reported are corrected for effects due to ferromagnetic decomposition products. The dithiahexane complexes, the most stable of all those studied, exhibited no weight loss during measurements and if left in air were only slowly attacked. The variation with halide of μ_{eff} for both sets of complexes is Br > Cl > I.

The esr spectrum of $NbCl_4(dth)_2$ was recorded at -196°. Figure 23 gives this spectrum of the powder. Only a very slight anisotropy was detected. The gyromagnetic ratios of $NbCl_4(dth)_2$, $g_{\parallel} = 1.985$ and $g_{\perp} = 1.804$ were derived by trial and error from the curve. These yield an average g-value of 1.864 from which a magnetic moment, μ, of 1.66 B.M. is calculated using Equation 12. This was only slightly higher than the experimental moment of 1.60 B.M. for $NbCl_4(dth)_2$.

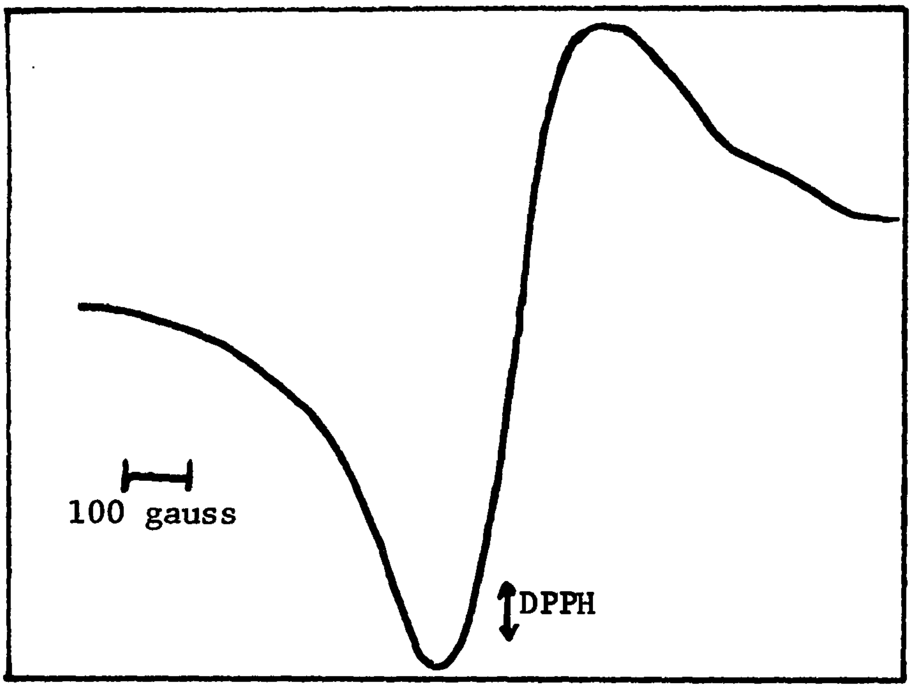

Fig. 23b.. Esr spectrum of powdered $NbCl_4(dth)_2$ at -196°

Table 22. Magnetic susceptibilities and effective magnetic moments for tetrahalo(2,5-dithiahexane)niobium (IV)

T (^{o}K)	χ_Mx10^6 (emu/mole)	$(\chi_M-\chi_D)$x10^6 (emu/mole)	$\mu_{eff.}$ (B.M.)
	$NbCl_4(DTH)_2$		
297	826	1124	1.63
161	1745	2040	1.62
150	1873	2171	1.61
140	2030	2328	1.61
131	2206	2504	1.62
118	2457	2755	1.61
113	2631	2929	1.63
77	3828	4126	1.59
	$NbBr_4(DTH)_2$		
297	855	1193	1.68
202	1374	1712	1.66
192	1457	1795	1.66
183	1537	1875	1.66
176	1601	1939	1.65
150	1917	2255	1.64
140	2046	2384	1.63
77	3936	4272	1.62
	$NbI_4(DTH)_2$		
298	437	839	1.41
200	774	1176	1.37
178	914	1316	1.37
151	1109	1511	1.35
132	1290	1692	1.34
77	2411	2813	1.32

Electronic spectra

Due to the virtual insolubility of these compounds in most solvents with which they did not react, only the spectra of the solids were investigated. These were obtained using techniques described in the Experimental section. Table 23 and Fig. 24 give the results of those studies. Each of the spectra consisted of a group of five bands. Frequencies of these decreased in the order Cl > Br > I. From these spectra it was concluded that the ligand environment of niobium(IV) in each was the same, thus confirming the conclusion presented earlier and based on far infrared data. With the exception of

Table 23. Solid state electronic spectra of tetrahalobis(2,5-dithiahexane)niobium(IV) complexes

Compound	(cm^{-1})
$NbCl_4((CH_3SCH_2-)_2)_2$	12,300, 14,000, 18,800, 24,400, 31,000 (15,300(w))*(10,700) (13,800) (17,300) (22,700)
$NbBr_4((CH_3SCH_2-)_2)_2$	11,600, 13,700, 16,900, 22,700, 28,600 (10,600) (13,800) (16,700) (21,200)
$NbI_4((CH_3SCH_2)_2)_2$	10,090, 12,700, 15,200, 18,400, 26,300 (10,250) (13,100) (15,200) 19,700

*Values in ( ) are diffuse reflectance data for corresponding diphenylbisdimethylarsine complexes. Taken from ref. 29.

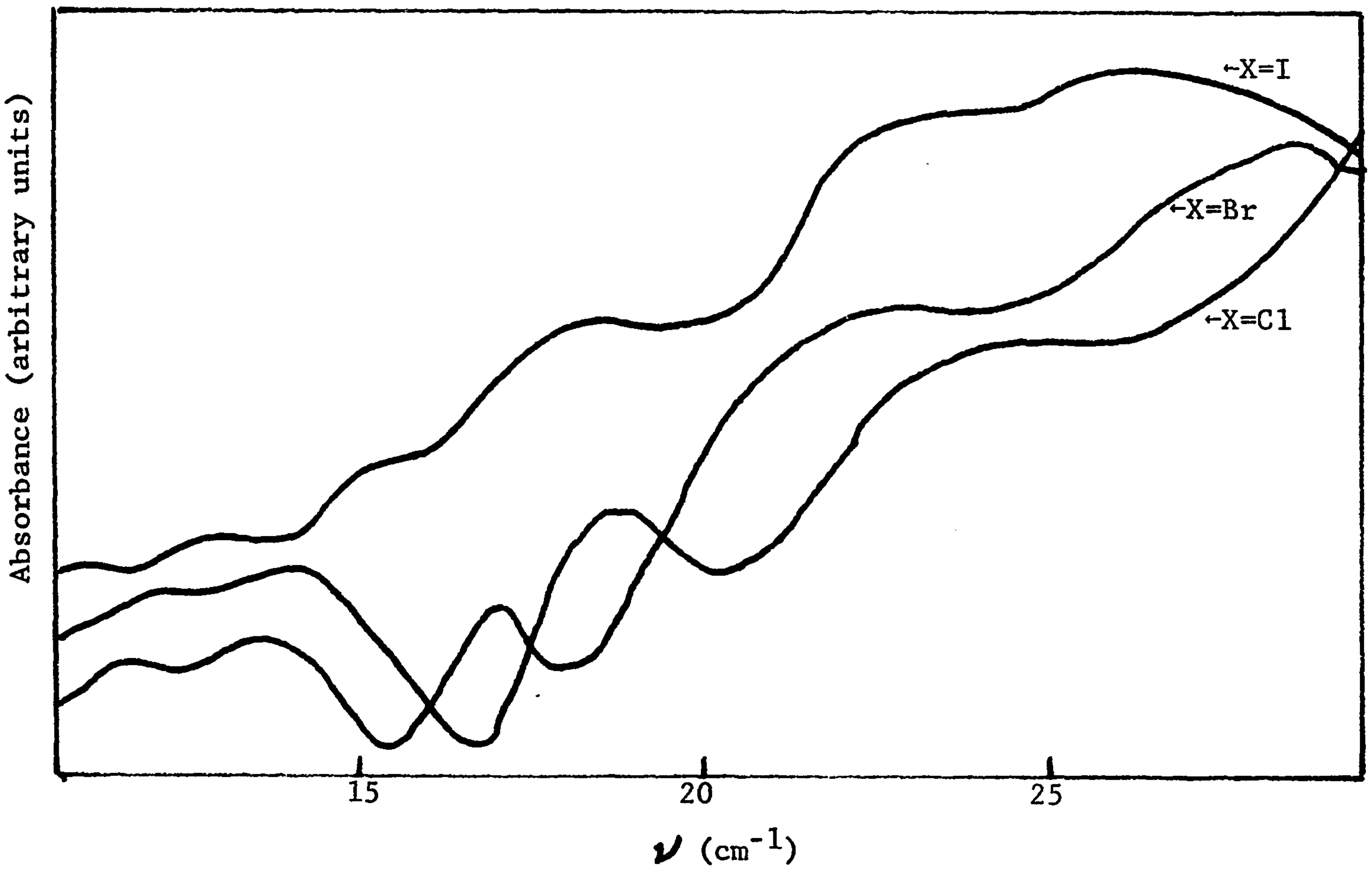

Fig. 24. Diffuse reflectance spectra of $NbX_4(dth)_2$ (X = Cl, Br, and I)

the band observed at 15,300 cm^{-1} as a weak shoulder for $NbCl_4$ $(diars)_2$ there is a fair correspondence between reported diffuse reflectance spectra for $NbX_4(diarsine)_2$ (30) and NbX_4 $(dth)_2$. The data for the former are reproduced in the table. Thus, a dodecahedral ligand environment for these dithiahexane complexes is suggested.

If the solid state spectra of $NbX_4(dth)_2$ are compared with solution spectra of the six coordinate $NbX_4(S(CH_2)_4)_2$ complexes it is not unreasonable to expect the three lowest energy bands in each to arise from transitions between the four levels which result from the splitting of the d-manifold under the influence of a dodecahedral field. From group theory these levels in order according to Ibers and Swalin (85) are $B_1(d_{x^2-y^2})$, $A_1(d_{3z^2-r^2})$, $E(d_{xz},d_{yz})$, and $B_2(d_{xy})$. The three expected transitions are then $^2B_1 \rightarrow {}^2A_1$, $^2B_1 \rightarrow {}^2E$, and $^2B_1 \rightarrow {}^2B_2$. Assignments are given in Table 24.

Table 24. Tentative assignments of ligand field bands in spectra of tetrahalobis(2,5-dithiahexane)niobium (IV) complexes (in cm^{-1})

Assignment	$NbCl_4(dth)_2$	$NbBr_4(dth)_2$	$NbI_4(dth)_2$
$^2B_1 \rightarrow {}^2A_1$	12,300	11,600	10,090
$^2B_1 \rightarrow {}^2E$	14,000	13,700	12,700
$^2B_1 \rightarrow {}^2B_2$	18,800	16,900	15,200

Data from the magnetic studies can now be used in conjunction with spectra assignments to determine the applicability of an ionic model to the present system. It has been shown that although formally the dodecahedral model has D_{2d} symmetry, it can be considered as arising from distortion of a cube. With a metal atom at the center the net effect can be considered as a tetragonal distortion. For a ground state $d_{x^2-y^2}$ the gyromagnetic ratios are given by Equations 13 (85).

$$g_{\perp} = 2(1 - \frac{4\lambda}{\Delta_2}) \qquad g_{\parallel} = 2(1 - \frac{\lambda}{\Delta_3} \qquad (13)$$

where λ = free ion spin-orbit coupling constant

$\Delta_2 = ({}^2B_{2g} - {}^2B_{1g})$

$\Delta_3 = ({}^2E_g - {}^2B_{1g})$

Taking the spin orbit coupling constant for Nb^{4+} as 748 cm^{-1} the values $g_{\perp} = 1.68$ and $g_{\parallel}$ - 1.88 are calculated. These values are much lower than the experimental quantities and this indicates the inadequacy of the ionic model. It is possible to assess the amount of covalent bonding, qualitatively, via Equations 14 (85).

$$g_{\perp} = 2(1 - \frac{\alpha^2\gamma^2\lambda}{\Delta_2}) \qquad g_{\parallel} = 2(1 - \frac{\alpha^2\beta^2\lambda}{\Delta_3}) \qquad (14)$$

The parameters α^2, β^2, and γ^2 are associated with the B_1, E, and B_2 molecular orbitals, respectively, formed by linear combinations of metal and ligand orbitals of appropriate symmetry. The coefficient of this combination for the molecular orbital of B_1 symmetry is $(1-\alpha^2)^{\frac{1}{2}}$, and analogous relations apply for E and B_2 molecular orbitals. For each of the three parameters the range of possible values is 1.0 (ionic bond) to 0.50 (covalent bond). Agreement with experiment in the present instance is found for $\alpha^2\gamma^2 = 0.65$ and $\alpha^2\beta^2 = 0.16$. The value 0.16 for $\alpha^2\beta^2$ is smaller than expected since for pure covalent bonding in the ground and excited states $\alpha^2\beta^2 = 0.25$. Thus it appears that niobium d orbitals are very strongly mixed with ligand orbitals in the formation of the complex.

SUMMARY

By direct reaction of anhydrous niobium tetrahalides with a large excess of tetrahydrothiophene or dimethyl sulfide the complexes $NbX_4(R_2S)_2$ (X = Cl, Br, and I; R_2S = dimethyl sulfide and tetrahydrothiophene) were isolated. Magnetic susceptibility measurements from -196° to 300° established the paramagnetism of the complexes. Magnetic moments calculated from the slopes of Curie plots decreased in the order Br > Cl > I for tetrahydrothiophene and Br > I for dimethyl sulfide complexes. Electron spin resonance spectra gave g-values for $NbCl_4(S(CH_2)_4)_2$ and $NbBr_4(S(CH_3)_2)_2$ from which moments were calculated which were somewhat higher than moments from bulk magnetic susceptibility measurements. Generally, the moments were considerably lower than spin-only values for one unpaired electron indicating that complete quenching of the orbital contribution to the moment by the ligand field had not occurred. Using the Figgis treatment splitting of the $^2T_{2g}$ ground state by the axial component in the ligand field was found to be ca. 1000 cm^{-1} for all the complexes except $NbI_4(S(CH_2)_4)_2$ where a much smaller splitting was observed. A low magnetic moment for $NbI_4(S(CH_2)_4)_2$ was consistent with the presence of some diamagnetic impurity. From electronic spectra estimates of

Δ for alkyl sulfide complexes placed these ligands between Cl^- and Br^- in the spectrochemical series for niobium(IV). Far infrared spectra of the complexes were consistent with a cis-configuration and some bands were assigned to normal vibrational modes.

A complex $ZrCl_4(S(CH_2)_4)_2$ was prepared and its far infrared spectrum recorded. The number of observed metal ligand vibrational frequencies was consistent with a trans rather than a cis stereochemistry and some of the observed bands were assigned on this basis.

Recrystallization of $NbX_4(S(CH_3)_2)_2$ from benzene gave the complexes $NbX_4(S(CH_3)_2)$ (X = Cl and Br) which were diamagnetic solids. From the direct reaction of diethyl sulfide and NbX_4 only the diamagnetic monoadducts $NbX_4(S(CH_2CH_3)_2)$ could be isolated. Far infrared spectra of solid dimethyl and diethyl sulfide complexes of the chloride as well as the bromide exhibited a virtual one-to-one correspondence consistent with the same ligand environment being present in each. Solid state and solution spectra of NbX_4L resembled spectra of NbX_4L_2 (L = monodentate sulfur donor ligand). A direct metal-metal bond in a bioctahedral halogen bridged dimer was proposed to account for the observed diamagnetism. Relative stability of bis-adducts in a dynamic vacuum was I > Br >> Cl and $S(CH_2)_4 > S(CH_3)_2 >> S(CH_2CH_3)_2$ indicating the influence of electronic as well as steric effects. Thus, structural studies of anhydrous NbX_4 indicate the following order of increasing strength of the metal-metal bond: I < Cl. The greater strength of the metal-metal bond in $NbCl_4$ is expected to stabilize a discrete metal-metal bonded dimer. Steric crowding of the ligands increases in the order $S(CH_2)_4 < S(CH_3)_2 < S(CH_2CH_3)_2$, and discrete solid bis-complexes of diethyl sulfide were not encountered in these studies. A molecular weight determination of $NbBr_4(S(CH_3)_2)$ in benzene indicated considerable dissociation of any dimeric species into monomers. Spectra of chloride and bromide complexes in benzene exhibited near infrared bands at 8,300 and 6,900 cm^{-1}, respectively, not far from positions predicted by current theory for a trigonal bipyramidal complex.

With 2,5-dithiahexane (dth) evidence for the complexes $MX_4(dth)_2$ (M = Nb; X = Cl, Br, and I: M = Zr; X = Cl) was obtained. Magnetic moments of the niobium complexes determined from Curie plots were only slightly lower than spin-only for the chloride and bromide indicating considerable quenching of any orbital contribution to the moment by the low symmetry ligand field. An esr spectrum of $NbCl_4(dth)_2$ at -196° exhibited anisotropy from which $g_{\parallel}$, $g_{\perp}$ and therefore g(ave) were derived. The moment calculated using g(ave) was in reasonable agreement with the bulk magnetic susceptibility result. Comparison of solid spectra of $NbX_4(dth)_2$ with those of corresponding $NbX_4(diarsine)_2$ complexes (known to have a dodecahedral ligand environment) indicated a similar ligand environment in each case. A dodecahedral ligand field formed by coordination of four halides and four sulfur atoms about Nb(IV) was proposed. Far infrared data were consistent with such a ligand field, and the expected two Nb-X and Nb-S stretching bands were identified in the spectra. Bands in the visible spectra were assigned as transitions between essentially pure d-orbitals in a D_{2d}-dodecahedral ligand field. From an interpretation of the electronic spectrum and g-values of $NbCl_4(dth)_2$ considerable mixing of metal and ligand orbitals was proposed.

Far infrared data confirm the prediction of Clark that ν(M-X) is sensitive to coordination number of the metal since ν(Nb-X) decreased by ca. 40-50 cm^{-1} on passing from six coordinate to eight-coordinate complexes. Comparison of far infrared spectra of NbX_4L and NbX_4L_2 (solid and solution) suggests that a change of coordination number from six to five has a small to negligible effect upon the highest observed Nb-X stretching frequency.

SUGGESTIONS FOR FURTHER WORK

While only cis isomers were encountered with niobium(IV) clearly small amounts of a trans isomer would have gone undetected. These studies should be extended to other solvents where trans isomers may have an enhanced stability.

Magnetic susceptibility data is not so useful in these systems as epr and electronic spectra. Such studies should be extended to single crystals as structure data becomes available. The relevance of current theories of bonding in these d^1 complexes could then be clearly assessed.

The dissociation of discrete paramagnetic bis-complexes in vacuo to yield stable diamagnetic solids should be investigated further. Crystals of these monoadducts can be obtained from hot benzene and used in structure determinations. Additional insight into the nature of the niobium-niobium bond would be the direct result.

Structure data could also provide the basis for a normal coordinate analysis of vibrational spectra of solid monoadducts of niobium(IV). The similarity of spectra of both solid bis-adduct and solid mono-adduct complexes of niobium(IV) suggests that metal-halogen (bridging) stretching modes have force constants not very different from the lowest energy terminal

Nb-X stretching force constant in discrete cis-NbX_4L_2 complexes.

In benzene and cyclohexane evidence for discrete, and very likely paramagnetic five coordinate complexes of niobium (IV) should be sought using the techniques of nmr spectroscopy.

Structure data will ultimately be required to confirm eight coordination for niobium(IV) in $NbX_4((CH_3SCH_2-)_2)_2$ and would also provide a basis for esr study of single crystals as well as normal coordinate analysis of vibrational spectra of these complexes. In conjunction with a similar study for a six coordinate niobium(IV) complex the variation of the force constant for Nb-X stretching modes with increase in coordination number could be ascertained.

Extension of these studies to other metals should also be fruitful. Thus an $MoX_4(R_2S)$ complex may or may not be diamagnetic. Extension to third row transition elements (d^1 or d^2) will be fruitful where starting materials are available which are more reactive than the anhydrous halides themselves.

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