ESR STUDIES OF 1,1-DITHIOL COMPLEXES WITH NIOBIUM(IV)

Dissertation for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY
KIRBY KIRKSEY
1975

This is to certify that the

thesis entitled

ESR Studies of 1,1-Dithiol Complexes with
Niobium(IV)

presented by

Kirby Kirksey

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemistry

Major professor

Date November 20, 1975

O-7639

ABSTRACT

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by

Kirby Kirksey

Eight coordinate Nb(pipdtc)$_4$ was isolated from the reaction of ammonium piperdinyldithiocarbamate (NH$_4$pipdtc) with niobium tetrahalides. The infrared spectrum indicates that pipdtc$^-$ is bidentate. The electronic spectrum exhibits four d-d transitions and supports a D_{2d} dodecahedral configuration for the complex. Esr spectra confirm this geometry with the parameters $\langle g \rangle = 1.9677$, $g_{||} = 1.9155$, $g_{\perp} = 1.9938$, and $\langle a \rangle = 0.0110$ cm^{-1}. By using molecular orbital theory developed for D_{2d} complexes, metal-ligand bonding parameters were obtained which indicate strong mixing of metal and ligand orbitals.

When two moles of NH$_4$pipdtc were allowed to react with the tetrahalides, complexes of varying stoichiometries were obtained. In each, the pipdtc$^-$ was bidentate as determined from infrared spectra. Far infrared spectra showed bands which could be assigned as ν(Nb-S) and ν(Nb-X) (X = Cl, Br, I). Two bands in the near infrared-visible region were

assigned as d-d transitions. Esr spectra of these species were unresolved single peaks at both ambient and 77°K temperatures. The chloro compound when diluted into a solution of the disubstituted zirconium complex, gave a powder esr spectrum which was indicative of an exchange-coupled dimer. The esr parameters are $g_{||} = 1.7873$ and $A_{||} = 0.00642\ \text{cm}^{-1}$. The zero field splitting is $0.05778\ \text{cm}^{-1}$ which corresponds to a niobium-niobium separation of 3.30 Å.

ESR STUDIES OF 1,1-DITHIOL COMPLEXES WITH NIOBIUM(IV)

By

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A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree

DOCTOR OF PHILOSOPHY

Department of Chemistry

1975

ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to Professor James B. Hamilton for patience, guidance, and encouragement during the course of this study.

Special thanks go to Dr. R. N. McGinnis and Mr. B. L. Wilson, whose discussions on various aspects of the universe were both invaluable and enjoyable.

Appreciation is also extended to Ms. B. L. Robbins for considerable help in the preparation of this thesis.

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INTRODUCTION

The niobium tetrahalides, which, except for the fluoride species, contain metal-metal bonded Nb_2X_8 pairs, are diamagnetic chains formed by NbX_6 octahedra sharing two opposite edges.[1-3]

This structural feature has dominated the chemistry which the tetrahalides undergo. Most of the complexes formed are either:

a) Simple addition compounds in which the metal-metal bond is cleaved. These complexes are paramagnetic.

b) Simple addition compounds in which the metal-metal interaction is only slightly altered. These compounds are usually dimeric and may by either diamagnetic or antiferromagnetic.

c) Substitution products in which the metal-metal bond is cleaved. These complexes are usually paramagnetic monomers.

d) Partially substituted products in which the metal-metal interaction may or may not be altered. These complexes may be monomers dimers, etc., and may exhibit either paramagnetic, antiferromagnetic, or diamagnetic behavior.

Relatively few of these complexes have been investigated by esr methods. The limited studies which have been done have focused upon alkoxo-complexes formed by $NbCl_4$ in alcohol solutions.[4,5]

More recently esr methods have proven to be useful in investigations of complexes of both type (a) and (c) above.

This particularly has been the case for eight coordinate complexes formed *via* reactions of type (a) and (c). Esr has been demonstrated to be a powerful tool for elucidating the structure of eight-coordinate complexes - both in solution and in the solid state. Studies of exchange coupled dimers for a number of d^1 and d^9 systems have utilized esr methods.[6]

With niobium(IV), 1,1-dithiols have proven to be quite versatile ligands, forming both paramagnetic eight-coordinate complexes,[7] and in at least one instance, exchange-coupled dimeric species.[8] In each instance, esr has proven to be a valuable tool for investigating such systems.

REVIEW OF PREVIOUS WORK

There have been several reviews on the chemistry of niobium halides and their complexes.[9-11] Reviews of the coordination chemistry of 1,1-dithiols have also been recorded.[12,13] What is lacking in these reviews are discussions of complexes formed by niobium(IV) with 1,1-dithiols and related sulfur donor ligands. This review will focus upon niobium(IV)sulfur complexes, related dithiocarbamate-metal complexes, and dimeric, niobium(IV) systems.

Hamilton and McCarley in their studies of thioether complexes[14,15] found that the thioethers would form both paramagnetic and diamagnetic complexes of the general formulations NbX_4L_2 and $[NbX_4L]_2$. Anomalous behavior was found with the methyl sulfide complexes. Under a dynamic vacuum, the diadduct which was recovered from the original reaction mixture would lose one mole of methyl sulfide over a period of twelve hours, yielding the monoadduct. The ethyl sulfide would only form a monoadduct. All of these species were weakly paramagnetic. Fowles[16] also studied these systems and obtained similar results, the one exception being the postulation of the monoadducts as antiferromagnetic exchange-coupled dimers. Further study of this system in solution by Chen and Hamilton[17] by use of esr methods, revealed that in solution both the ethyl and methyl monoadducts were strongly paramagnetic, but exhibited no resonances at g≈4 as expected for a dimeric exchange-coupled species.[18]

Fowles[16] also investigated the reactions of tetrahydrothiophene (tht) with niobium tetrahalides. This ligand formed diadducts with $NbCl_4$ and $NbBr_4$; two different forms of the bromide complex were obtained. The far infrared spectra of the chloride and α-bromide species were similar. In both $NbCl_4(tht)_2$ and α-$NbBr_4(tht)_2$, the expected ν(Nb-X) and ν(Nb-S) were observed in the region 340-240 cm^{-1}, with the appropriate shift for the change in the halide. The β-bromide complex gave only one strong band at 227 cm^{-1}. The latter complex was assigned a *trans* configuration and the other complexes *cis*. Although most bis-adducts of niobium tetrahalides have been assigned as *cis* structures, there has been a *trans* structure reported for DMF[19] complexes. Bereman,[20] on the basis of esr data, proposed a *trans* structure for certain pyridine adducts.

Douglas and Green[21] studied the product from the reaction of methyl mercaptan and bis(η^5-cyclopentadienyl)-niobium dichloride. The resulting complex, $(\eta^5\text{-}Cp)_2Nb(SCH_3)_4$ was examined by esr. The esr spectrum of the complex gave ten lines with <g> = 1.991 and <a> = 25.1 gauss. The phenylthio-derivative gave similar esr parameters. Of interest was the small <a> values reported. Except for the hexahaloniobium(IV) complexes, the usual <a> values are ~150-200 gauss. The authors made no comment as to what contributed to these lower values. These complexes could be oxidized by the addition of iodine.

Bidentate sulfur ligands typically form eight coordinate species. Hamilton and McCarley[15] used 1,2-bis(methylthio)-ethane (dth) to prepare $NbX_4(dth)_2$. Far infrared data on metal-halogen and metal-sulfur vibrations show the ligand is bidentate. Molar magnetic susceptibilities ranged from 1.28-1.60 B.M. and did obey the Curie law. Solid-state esr data of the chloride complex indicated the structure was a dodecahedron. Further investigation of the complexes in frozen solution by esr[22] supported this proposed structure. From the frozen solution spectra of the chloride and bromide complexes, the fact that $g_{||} < g_{\perp}$ was taken as evidence of an idealized triangular dodecahedron as has been found with similar complexes.[23]

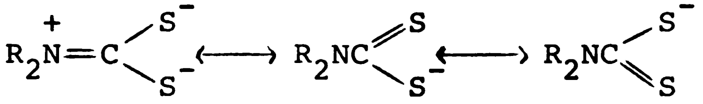
Tetrasubstituted dialkyldithiophosphate complexes were studied by esr.[7] Esr spectra of both the solid and solution gave $\langle g \rangle = 1.955$. At 77°K, $g_{||} < g_{\perp}$ was what is expected for a dodecahedron. Far ir studies assigned the strong bands at 356 and 274 cm^{-1} as ν(Nb-S) modes. The presence of two bands so assigned is further support of the structure. When the acid form of the ligand was used, only viscous oils resulted.

Machin and Sullivan[24] used a variety of ligands to study the tetrahalides. Three different compounds were formed by thiourea (TU), $NbCl_4(TU)_2$, $NbI_4(TU)_3$, and an unidentifiable $NbBr_4$ polymer. The magnetic moment of the chloride species determined by the Faraday method, 1.19 B.M., was consistent with those found for other octahedral complexes.[14] No esr work was performed. The iodide compound had a molar conductivity of 220 ohm^{-1} in a 1 x 10^{-3} molar solution in acetonitrile, in the range expected for a 1:1 electrolyte. Bands in the infrared at 695, 1510 cm^{-1} and 700, 1510 cm^{-1} for the chloride and iodide adducts respectively, as well as the absence of a band at 1080 cm^{-1}, supported sulfur bonding.

One class of sulfur donor ligands which will be treated separately is the dithiocarbamates. This ligand is readily prepared by the reaction:

$$R_2NH + CS_2 + OH^- = R_2NCS_2^- + H_2O \qquad (1)$$

This ligand has the ability to exist in the following canonical forms.



(2)

Chatt and his colleagues[25] have demonstrated the ability of this type of ligand to form complexes with a large number of metals in which it bonds bidentately.

Several workers have prepared tetrakisdiethyldithiocarbamatoniobium(IV).[26-28] Bradley[26] prepared the complexes by allowing the pentakisdimethylamidoniobium(IV) to react with CS_2 while the other authors used the sodium salt of diethyldithiocarbamate. Characteristic ir bands occurring at ~1500, 1000 and 360 cm^{-1} were assigned as $\nu(C \overset{\cdot\ \cdot\ \cdot}{-\!-\!-} N)$,

ν(C —— S) and ν(Nb —— S) respectively. The magnetic data were in conflict with Bradley[26] and Machin[27] finding $\mu_{eff} \approx 0.5$ B.M. while Brown[28] found $\mu_{eff} = 1.57$ B.M. No comment was made as to the cause of the low magnetic moments. Another study of the stereochemical lability of eight-coordinate complexes[29] confirmed the equivalence of the alkyl groups by use of ^{1}H and ^{13}C nmr, and established a dodecahedral structure.

The lack of work with sulfur-donor ligands is clearly illustrated by these citations. Except when the dithiocarbamates were used as precipation reagents,[30] a similar situation exists for niobium - dithiocarbamate complexes. However, with other d^1 systems, in particular V(IV), as well as other metal systems such as Ti(IV), Zr(IV) and Cu(II), a great deal of work has been reported.

Tetrakis-N,N-dialkyldithiocarbamate complexes of Ti(IV) and V(IV) have been reported in two papers by Bradley.[26,31] These complexes were prepared *via* an insertion reaction involving CS_2 and the metal dimethylamines. Some contamination of the tetrakisdiethylvanadium(IV) compound by the presence of the tris species caused μ_{eff} to be 2.24 B.M., which is much greater than the expected value ≤ 1.73 B.M. for a V(IV) d^1 species. This contamination was due to the method of preparation which involved refluxing the reaction mixture. Esr data, which gave $g_{||} < g_{\perp}$, and $A_{||} > A_{\perp}$, supported a structure based on a dodecahedral model. When the vanadium complex was doped into the isomorphous titanium compound, the esr spectrum showed g-anisotropy corresponding to an axially symmetric species with resolved ^{51}V nuclear-hyperfine splitting. Electronic spectra, which showed a maximum at 13,600 cm^{-1}, assigned as a $^2B_1 \rightarrow {}^2E$ transition, were considered consistent with a $d_{x^2-y^2}$ ground state. In the infrared region, three bands of importance were noted for the complexes. These bands, occurring at ~1500, ~1000 and 850, and ~360 cm^{-1} were assigned as "thioureide" C · · · N, C —— S, and M —— S respectively. The tris-(N,N-diethyldithiocarbamato)vanadium(III) compound was assigned a distorted octahedral structure based on three transitions found in the electronic spectra.

Fay and his co-workers[32] prepared a seven-coordinate titanium(IV) compound, TiX(R$_2$NCS$_2$)$_3$, by the reaction of the tetrahalide with a stoichiometric amount of the anhydrous sodium dialkyldithiocarbamate. The ethyl derivative was found to be monomeric in benzene. Nmr spectra over a temperature range indicated the ligands were non-rigid on the nmr time scale. Although symmetry requirements should make some of the alkyl protons inequivalent, no splitting was found as low as -80°C. Further evidence as to the coordination was found from the infrared data. The single bands found at 1500 and 1000 cm^{-1} were indicative of bidentate coordination. The authors did not assign the compound a structure based on any idealized geometry for seven-coordination.

Additional work on the titanium(IV) dithiocarbamates by Fay[33] produced compounds of the stoichiometry $Ti(S_2CNR_2)_nCl_{4-n}$ where n = 2,3, or 4. The nature of the species formed was only dependent on the amount of dithiocarbamate allowed to react with $TiCl_4$. Conductance measurements showed the complexes were nonelectrolytes and molecular weight determinations in benzene established that they were monomers. Infrared data were indicative of bidentate coordination by the ligand. Proton nmr experiments on the isopropyl derivatives reveal the presence of two equally populated *i*-Pr sites at low temperatures.

Several investigators[12] have examined Cu(II) complexes of dialkyldithiocarbamates. The compounds were reasonably stable in water, having stability constants of ~23.0. The diethyl species was monomeric in both benzene and chloroform. However, a crystal structure[34] showed the copper to be five coordinate, a distorted tetragonal-pyramid of four sulfur atoms, at a distance ranging between 2.297 and 2.339 Å and a fifth apical sulfur atom at 2.851 Å. The solid state study determined that this species was a dimer. The importance of the canonical form, $---S_2^{-}C = \overset{+}{N}R_2$ as established from infrared study[25] was also supported.

Dimeric niobium(IV) complexes occur quite frequently due to the structure of the tetrahalides. In some cases, there is conflict concerning the nature of the compounds. Different reports[14,16,17] on the compound, $NbCl_4 \cdot S(CH_3)_2$, found it was diamagnetic[14] in the solid, and paramagnetic in solution,[17] while other authors[16] showed it was antiferromagnetic.

This type of ambiguity was found when $NbBr_4$ was allowed to react with less than four moles of sodium diethyldithiocarbamate (Na dtc).[27] A species was prepared which was formulated as $Nb_2Br_3(dtc)_5$. The molecular weight of the compound in chloroform was found to be 1240, compared to the calculated value of 1166. The infrared spectrum was similar to that of $Nb(dtc)_4$, indicating the ligands were bidentate. The molar conductance in nitromethane lead the authors to propose a formulation, $[Nb_2(dtc)_5Br_2]Br$. The magnetic susceptibility was field dependent.

Wentworth and Brubaker[35] prepared two compounds, $[NbCl(OC_2H_5)_3(C_5H_5N)]_2$ and $Nb(OC_2H_5)_4$, which were dimers. The former species had five possible isomers, two octahedra with a shared edge, bridged by two chlorine atoms. When it was allowed to react with sodium ethoxide, $Nb(OC_2H_5)_4$ was formed. The oxidation state of (IV) was demonstrated by the lability of the compound to chloride ion to form $NbCl_5(OC_2H_5)^{2-}$ which is known to contain Nb(IV). Esr studies of the same system by Gunthard[5] confirmed the existance of the latter compound, although these authors did not isolate the species.

McGinnis' study[8] of the dimethyldithiophosphates (dmtp) found that dimeric niobium(IV) species could be formed with the composition $Nb_2X_4(dmtp)_4$. The compounds were prepared by allowing stoichiometric amounts of the tetrahalides to react with sodium dimethyldithiophosphate. The chloride and bromide complexes were reported to be diamagnetic while the iodide exhibited antiferromagnetism with a singlet-triplet separation of -140 cm^{-1} and a room temperature magnetic moment of 2.32 B.M. The esr spectrum of the iodide complex showed both the normal $\Delta m_s = \pm 1$ transition and the "forbidden" $\Delta m_s = \pm 2$ transition. This is the only reported niobium(IV) electron-exchange coupled species.

The use of piperidyldithiocarbamate as a ligand has been reported in only one paper.[37] This ligand, as well as the 2-, 3-, and 4- methyl derivatives reacted with alcoholic solutions of Cr(III). Tris-substituted compounds were prepared and showed a great deal of metal-ligand covalency. Each of the compounds exhibited bands indicative of bidentate character for the ligand.

PURPOSE OF THIS WORK

Thus far in this brief review, several facts are apparent:

a) There has been relatively little study of niobium(IV) complexes with sulfur-donor ligands.

b) Of the work which has been reported, a significant trend is the formation of paramagnetic six-coordinate or paramagnetic eight-coordinate complexes.

c) Esr characterization of the paramagnetic species has been limited to a small number of systems.

d) A significant anomaly is the relative frequency of occurrence of either diamagnetic or weakly paramagnetic dimeric species or antiferromagnetic exchange-coupled species (especially when the halogens are partially substituted by 1,1-dithiols).

In view of the ability of sulfur donor ligands to stabilize low oxidation states while exhibiting a high degree of covalency with transition metals, it is surprising that the reactions of 1,1-dithiols with niobium(IV) halides have not been studied in more detail.

The preparation of dialkyldithiophosphate complexes of niobium(IV),[8] and the series of compounds, $Ti(S_2CNR_2)_nCl_{n-4}$ (where n = 2,3,4)[32] suggests that the 1,1-dithiols may be ideal ligands for investigation. In an attempt to study compounds of a similar nature, the uninegative, bidentate salt, ammonium piperdinyldithiocarbamate (NH_4pipdtc) was used. Previous studies[26-28] which used straight-chain dialkyldithiocarbamates did not include examination of the complexes by esr.

This ligand when allowed to react with the tetrahalides could form species in which

a) all of the halogens would be substituted.

b) disubstituted dimeric species with only the non-bridging halogen being substituted are formed.

c) disubstituted, monomeric species are formed.

All of these cases could, by electron spin resonance spectroscopy, provide further insight into the nature of the chemistry which characterizes niobium(IV).

EXPERIMENTAL

Due to the sensitivity of the compounds to oxygen and water, all the compounds were handled under high vacuum or in a Vacuum Atmospheres Corporation nitrogen filled drybox containing less than 1 ppm water and oxygen.

Materials. Niobium pentachloride, $ZrCl_4$, and high purity niobium metal were purchased from Alfa Inorganics. $NbBr_5$, NbI_5, and NbX_4 (X = Cl, Br, and I) were prepared by using procedures previously described.[38,39]

Practical grade piperidine (98%), 2-, 3-, and 4-methylpiperidine were obtained from Aldrich Chemical Company. Benzene, aqueous ammonia, carbon disulfide, anhydrous ethanol, and methylene chloride were standard reagent grade chemicals.

Ammonium piperdinyldithiocarbamate (NH_4pipdtc) and the methyl-substituted species were prepared by previously described methods[40] *via* the reaction:

$$RNH + CS_2 + NH_3(aq) \rightarrow NH_4(S_2CNR) \qquad (1)$$

Potassium ethyl xanthate was prepared by the reaction:

$$H_3CCH_2OH + CS_2 + KOH \rightarrow H_2O + K(H_3CCH_2OCS_2) \qquad (2)$$

Analytical. Microanalyses and molecular weight determinations were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Preliminary analyses were performed to determine niobium. The niobium was determined gravimetrically as niobium(V) oxide. Samples of the complexes were added to aqueous ammonia and heated for two hours. After the samples cooled to ambient temperature, they were acidified with dilute nitric acid. The white anhydrous niobium oxide was filtered on ashless filter paper, washed three times with dilute nitric acid, ignited at 900°C for two hours and weighed.

Spectra. Esr spectra were obtained with samples in benzene solutions at ambient temperature and 77°K by use of a Varian Model E-4 spectrometer with an operating frequency range of 8.8 to 9.6 GHz and equipped with a field-dial regulated magnet. The magnetic field was calibrated by using strong pitch ($g = 2.0028$).

Electronic spectra were recorded by using a Cary Model 17 spectrophotometer. Cylindrical fused silica cells, 1.0 cm pathlength and adapted for use at low pressure (Figure 1), were used.[38] Saturated solutions were loaded in the drybox. The cell assembly was then evacuated to *ca.* 10^{-5} torr. After sealing off the cell assembly, solvent and/or solutions of various concentrations could be drawn through a medium porosity frit into the cell.

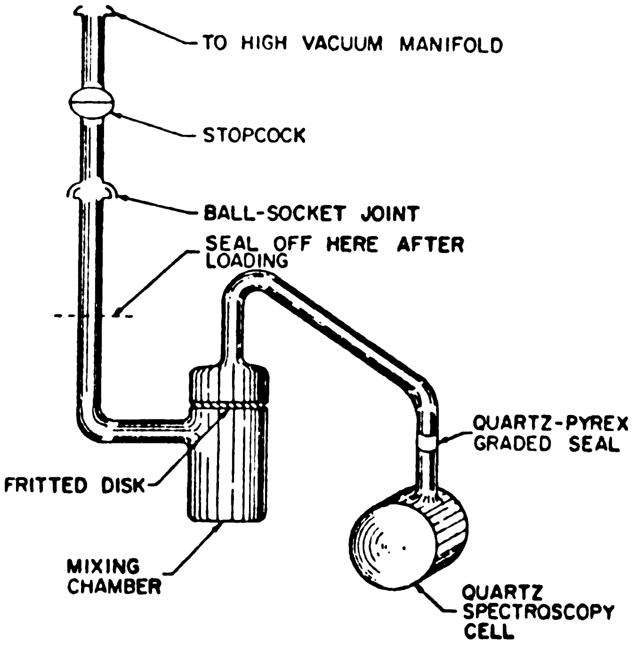


Figure 1. (Taken from Reference 38) Apparatus for Determination of Electronic Spectra

Solid state infrared spectra were obtained by use of a Perkin-Elmer 457 (4000-250 cm^{-1}) spectrophotometer. Samples were prepared in the drybox and were mounted as Nujol mulls between cesium iodide plates. Mulls were prepared immediately before measuring the spectra.

Far infrared spectra were obtained by using a Block Engineering Company Model-FTS16 (600 - 20 cm^{-1}) far infrared spectrophotometer. High density polyethylene was used for windows.

Proton nmr spectra were obtained by use of a Varian Model A56/60D spectrometer operated at 60 MHz.

Synthesis. A four to one molar ratio of NH_4pipdtc: NbX_4(X = Cl, Br, I), and a magnetic bar were introduced into a round bottom flask. The flask was evacuated to *ca.* 10^{-5} torr and 50-80 ml of benzene were vacuum distilled into the flask. The flask was isolated from the vacuum system and the mixture was stirred for 4-5 days at ambient temperature. A deep maroon solution and orangish precipitate were obtained. The precipitate was removed by filtration and the filtrate was evaporated to dryness *in vacuo*. The filtrate was extracted with benzene, and a reddish-purple solid was recovered by removal of benzene *in vacuo*. The product was then washed with dry pentane and dried *in vacuo*. Similar results were found when the acid form of the ligand was prepared *in situ* in a slurry of NbX_4 in benzene.

The methyl-substituted derivatives and ethyl xanthate species were prepared in a similar manner.

A two to one molar ratio of NH_4pipdtc: NbX_4 (X = Cl, Br, I) was placed in a round bottom flask in the same manner as above and stirred for 7-8 days. The solution, which was purple after two hours of stirring, became yellowish-brown after two days with an orangish precipitate being visible in the mixture. The species were recovered as above.

Two different two to one molar ratios of NH_4pipdtc: MCl_4 (M = Nb, Zr) were prepared. Each mixture was allowed to stir for 7-8 days. They were filtered to remove the precipitates and then mixed. The original mixtures were prepared so that the $ZrCl_4$ to $NbCl_4$ ratio was ten to one.

> *Anal.* Calculated for $NbC_{24}H_{40}N_4S_8$: Nb, 12.66; C, 39.25; H, 5.51; N, 7.64; S, 34.95. Found: Nb, 13.09; C, 39.95; H, 5.65; N, 7.61; S, 28.07. Molecular weight: Calculated, 734. Found, 698 in $HCCl_3$. MP, 128°C with decomposition.

RESULTS AND DISCUSSION

Characterization of Eight Coordinate Species

The reaction of the niobium(IV) halides with stoichiometric amounts of ammonium piperdinyldithiocarbamate in benzene proceeds according to the equation:

$$4NH_4pipdtc + NbX_4 \rightarrow Nb(pipdtc)_4 + 4NH_4X \qquad (3)$$

The complex was isolated as a reddish-purple powder which is soluble in benzene, toluene, methylene chloride, and acetonitrile. The species is either air and/or water sensitive as indicated by a color change and the distinctive odor of carbon disulfide on exposure to the atmosphere. The melting point is over the range 112-128°C with decomposition.

When the methyl-substituted species are employed as well as the ethyl xanthate salt, the reaction appears to go as stated above.

Vibrational Spectra

Infrared Spectra (4000-600 cm^{-1})

Ammonium piperdinyldithiocarbamate has not been studied in the infrared region. The spectrum of the sodium salt dihydrate is published in the Sadtler Standard Spectra.[41] Assignments were made by comparing the spectrum of the sodium salt with published correlation charts of infrared spectra.[42] The assignments for the ammonium salt were based on this information. Infrared data of the ligand and complex are presented in Tables 1 and 2 respectively.

In complexes containing pipdtc and other dithiocarbamates, two regions are of interest in the infrared, the "thiouride" band at 1490 cm^{-1} and the ν(C=S) band at 1000 cm^{-1}. The complex showed vibrations at 1490 cm^{-1} and at 997 cm^{-1}. The lower energy vibration has been used to determine whether the ligand is acting as a bidentate. Bonati and Ugo[43] in a study of organotin(IV) dithiocarbamates, compared the ir Spectra of $(Et_2NCS_2)_2Sn$ and Et_2NCS_2Et. The chelated compound showed only one strong band at 995 cm^{-1} while the ester shows a doublet (1005 and 983 cm^{-1}). An absence of a doublet in this region has been confirmed for other known chelated structures.[33] The strong band at 730 cm^{-1} is a combination of vibrations due to the δ(C-H) of both Nujol and the piperidine ring.

Far Infrared Spectra (600-100 cm^{-1})

The far infrared spectra for the ammonium salt and the complex were recorded. The data are presented in Table 3 and the spectra are shown in Figures 2 and 3 for the ligand and complex respectively. Two bands at 385 and 360 cm^{-1} were present in the spectrum of the complex and are not present in the ligand spectrum. These bands have been assigned as ν(Nb-S) vibrations. Combination bands involving ligand vibrations and ν(Nb-S) overtones were present at

Table 1

Infrared Spectral Data for pipdtc$^-$ (4000-600 cm^{-1})

Assignment	Na pipdtc·$2H_2O$		NH_4pipdtc
ν(OH)	3333 vs		*
ν(C-H)	2924 m		*
ν(N-C)	2096 w,b		*2025 m,b
δ(HOH) +	1626 m	ring deformation	1590 m
ν(C=N)	1468 s		*1430 m
ν(C-N)	1420 s		*1390 b,s
δ(CH_2)	1361 w		1305 sh
ν(C=S)	1274 m		1275 m
	1263 w		1235 m
ν(NCS_2)	1227 s		1207 s
ν(NCS_2)	1130 s		1155 w
ν(NCS_2)	1109 s		1115 s
	1070 w-m		1065 sh,b
	1024 m		1025 m
	1008 m		995 sh
	966 s		967 s
	949 m		947 m
	919 m		937 m
	884 s		883 m
	855 m		865 m
			848 m
			800 w
δ(CH_2)			730 m,b
			615 w

*Interferring vibrations from NH_4^+

b = broad, s = strong
m = moderate, w = weak
sh = shoulder

Table 2

Infrared Spectral Data for $Nb(pipdtc)_4$ (4000-600 cm^{-1})

Assignments	
ν(N-C)	2022 m,b
ring deformation	1585 m
ν(C=N)	1490 s
ν(C-N)	1390 m
δ(CH_2)	1390 sh
ν(C=S)	1275 m,sh
ν(NCS_2)	1253 m,sh
ν(NCS_2)	1232 s
	1160 w
ν(NCS_2)	1125 sh
ν(NCS_2)	1103 m,b
	1030 sh
	1015 sh
ν(C=S)	997 s
	947 m
	887 m
	850 m
	800 m
δ(CH_2)	725 s

b = broad, s = strong, m = moderate, w = weak
sh = shoulder

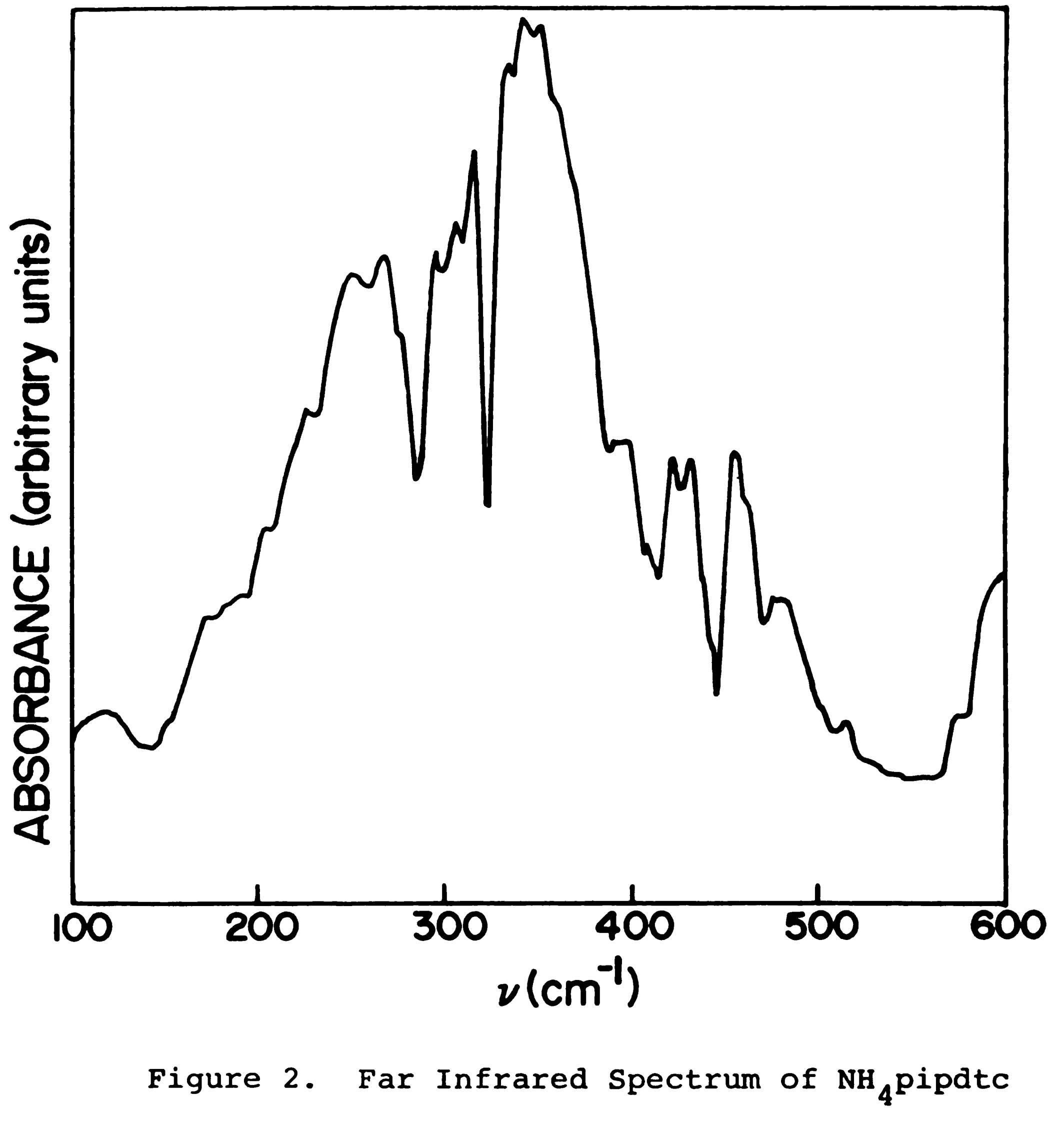


Figure 2. Far Infrared Spectrum of NH_4pipdtc

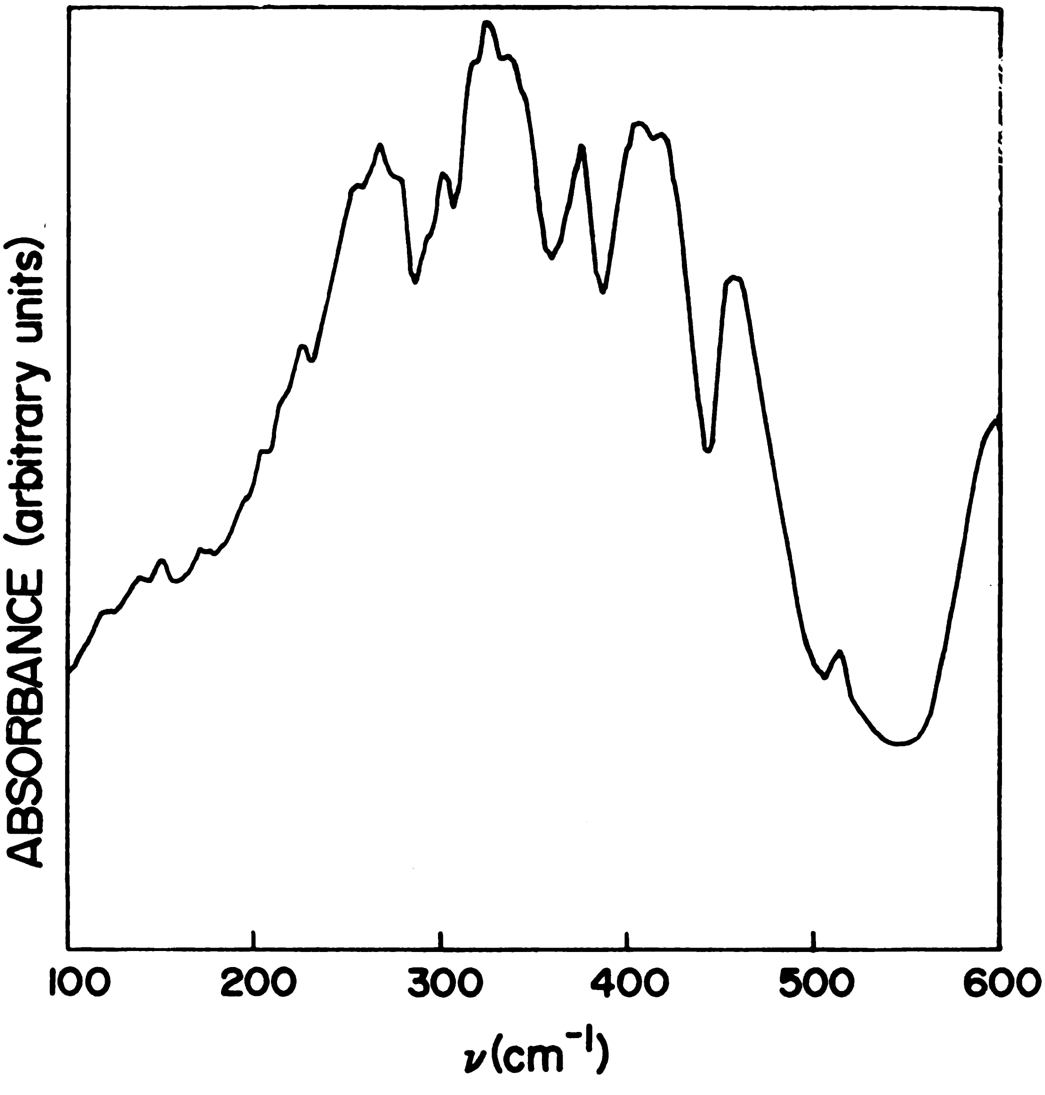


Figure 3. Far Infrared Spectrum of Nb(pipdtc)$_4$

Table 3

Far Infrared Spectral Data for pipdtc$^-$ and Nb(pipdtc)$_4$ (600-100 cm^{-1})

Assignments	NH$_4$pipdtc	Nb(pipdtc)$_4$
Combination: ν(C-S) δ(C´-N-C´), δ(C-N), ring deformation	580	
Combination: ν(M-S), ring deformation, δ(C´-N-C´)	545 s,b	550 s,b
	510 sh	510 w
δ(C´-N-C´)	445 s	443 m-s
	427 w	
δ(C´-N-C´)	415 m	
	380 sh	
ν(M-S)		385 m-s
ν(M-S)		360 m-s
	322 s	
	307 w	307 w
	297 sh	
	285 sh	
	285 s	
	260 w	260 w

b = broad, s = strong, m = moderate,
w = weak, sh = shoulder, v = very

550 and 510 cm^{-1} as were found in the Cr(III) complexes of this ligand.[37]

Electronic Spectra

Visible and near infrared spectra were recorded by using benzene solutions of the complex. The spectra and wave number maxima are given in Figure 4 and Table 4 respectively. The gross features of the spectra include four bands at 11.9, 13.7, 18.8 and 21.7 ($x\ 10^{-3}\ cm^{-1}$).

Table 4

Electronic Spectra Data for $Nb(pipdtc)_4$ in benzene

$\nu\ (x\ 10^{-3}\ cm^{-1})$	ε
11.9	52.3[†]
13.7	75.2[†]
18.8	378[‡]
21.7	340[‡]

[†] C = $7.98\ x\ 10^{-3}$ M
[‡] C = $2.50\ x\ 10^{-3}$ M

Based on the infrared data which have been discussed earlier, this complex should have either a dodecahedral or square antiprismatic structure. For a D_{4d} square antiprism, only two d-d transitions should be observed, while the D_{2d} triangular dodecahedron should exhibit three d-d transitions. The fact that this compound has four bands in the near ir-visible region is not a unique situation for niobium complexes.

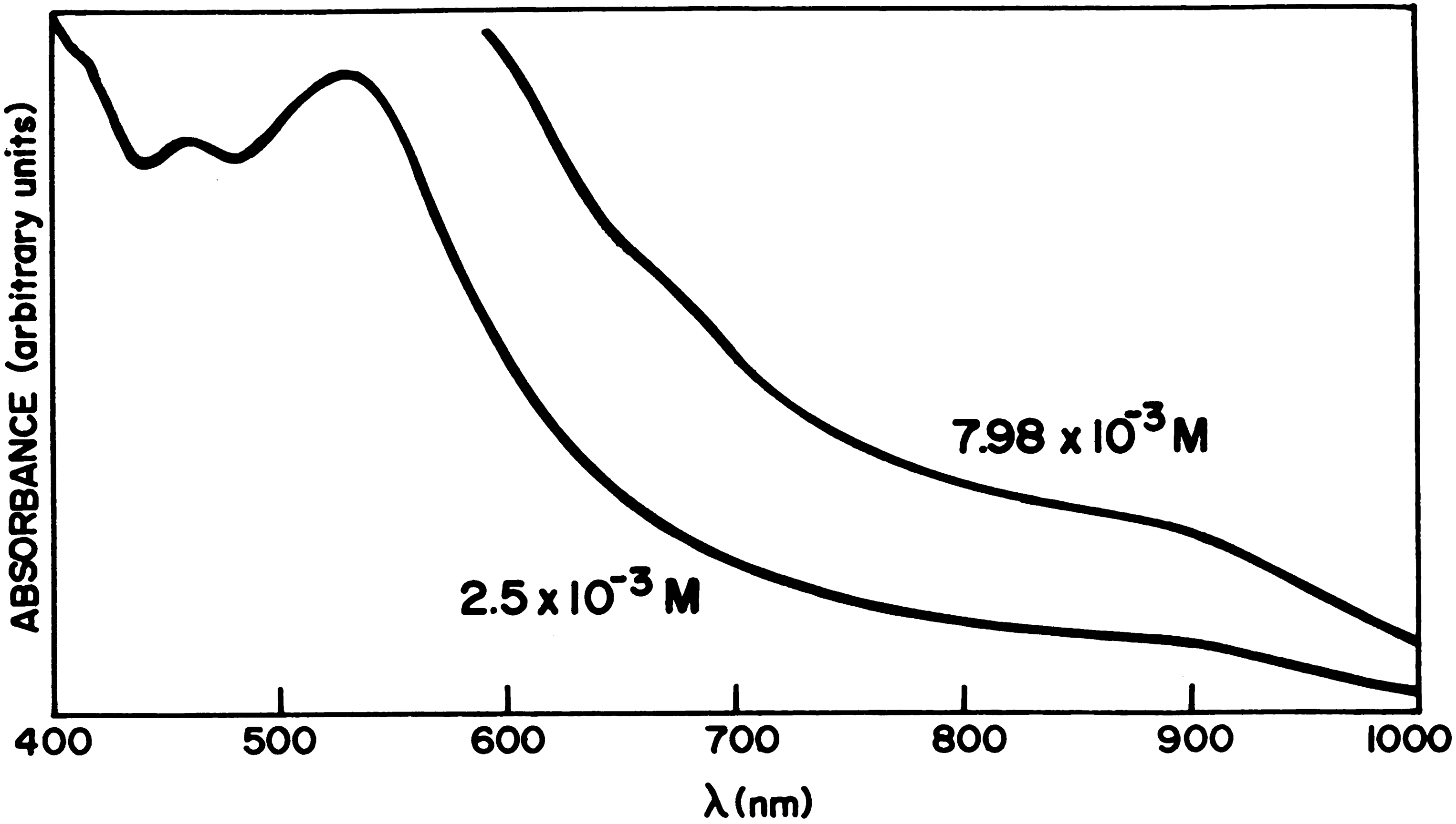


Figure 4. Electronic Spectra of $Nb(pipdtc)_4$ in Benzene

Other eight coordinate species, namely $NbX_4(dth)_2$[15] and $NbCl_4(diarsine)_2$,[44] have four bands in this region. The extinction coefficients are in the range that other authors have assigned as d-d transitions.[9]

Electron Spin Resonance Spectra

Esr studies were performed as described in the experimental section on the series of compounds NbB_4, where B = pipdtc, 2-Mepipdtc, 3-Mepipdtc, 4-Mepipdtc, and Etxan. Representative spectra are presented in Figures 5 and 6, and the esr parameters are presented in Table 5.

Examination of these data points out several features about the nature of the species. In all cases, $g_{||}$ is less than $g_{\perp}$. The significance of this observation will be discussed. For the series, pipdtc, 2-Mepipdtc, 3-Mepipdtc, and 4-Mepipdtc, the pipdtc compound had the lowest <g> value as well as the highest $A_{||}$ value. This is expected because the influence of the methyl group on the ring will cause some steric problems that will affect the amount of delocalization of the electron from the metal onto the ligand. Similar results were found in an esr study of $NbCl_4$ adducts with various substituted pyridines.[20] The spectra recorded for the 2-methyl derivative were not as well resolved as found for the other members of this series. As a result, it was not possible to extract the esr parameters at 77°K. Wasson's study[37] of this series of ligands with Cr(III) also reported anomalous behavior with 2-Mepipdtc. Clearly there

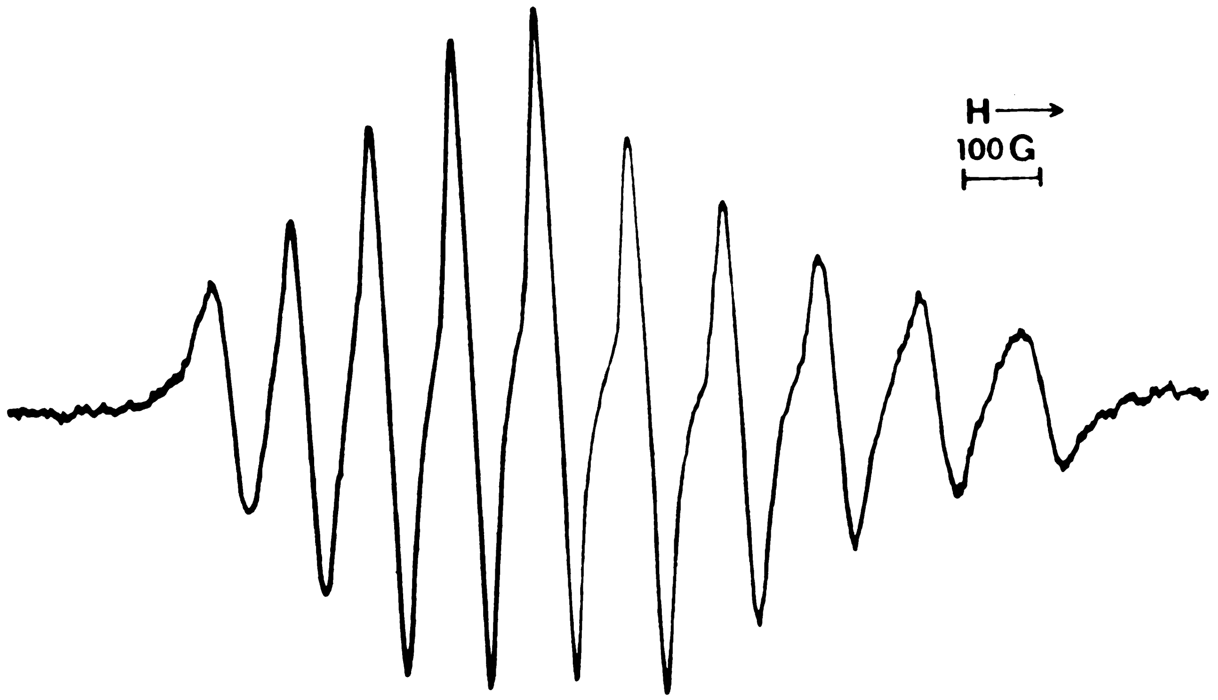


Figure 5. Esr Spectrum of NbB_4 Complexes in Benzene at Ambient Temperature

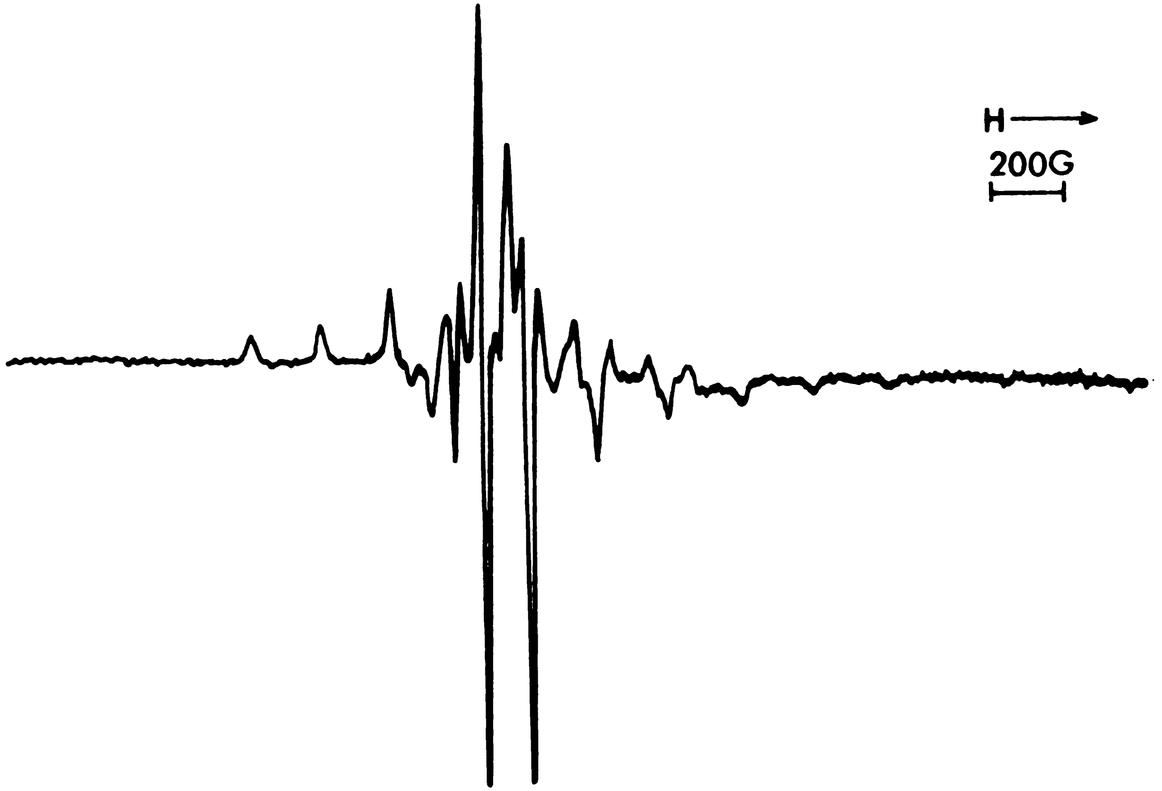


Figure 6. Esr Spectrum of NbB_4 Complexes in Benzene at 77°K

Table 5

Esr Parameters for NbB_4 Complexes

	pipdtc	2-Mepipdtc	3-Mepipdtc	4-Mepipdtc	Etxan
<a>	1.9677	1.9825	1.9848	1.9762	1.9877
$g_{\|\|}$	1.9155	------	1.9243	1.9243	1.9368
$g_{\perp}$	1.9938	------	2.0151	2.0022	2.0132
<a>*	110.0	110.1	111.2	108.9	106.2
$A_{\|\|}$*	195.2	------	177.9	174.3	171.8
$A_{\perp}$*	66.0	------	76.2	74.8	71.4

* x 10^{-4} cm^{-1}

are little or no steric effects observed in this system by the use of alkyl substituted species or bulky ligands like piperidine.

Since the hyperfine splittings are on the order of 120 gauss, the high field approximation cannot be applied and second order corrections should be employed. The pertubation of the Zeeman transition resulting from the hyperfine interactions was corrected by means of the following equations:[45]

$$h\nu = gBH_{\circ} \tag{4}$$

$$\text{for isotropic } g \quad H'_m = H_m + \langle a \rangle m_I + \frac{\langle a \rangle^2}{2H_m}[I(I+1)-m_I^2] \tag{5}$$

$$\text{for } g_{||} \quad H_m' = H_m + A_{||}m_I + \frac{A_{\perp}^2}{2H_m}[I(I+1) - m_I^2] \tag{6}$$

$$\text{for } g_{\perp} \quad H_m' = H_m + A_{\perp}m_I + \left(\frac{A_{||}^2 + A_{\perp}^2}{4H_m}\right)[I(I+1)-m_I]^2 \tag{7}$$

where H_m' is the corrected magnetic field position, H_m is the experimental position of the esr line due to the component m_I of the nuclear spin I, ν is the kylstron frequency, and $\langle a \rangle$, $A_{||}$, and $A_{\perp}$ are the hyperfine splitting constants. The calculations are necessarily reiterative and were carried out by use of a desk calculator. Normally three iterations were sufficient. The hyperfine splitting constants were determined from the positions of the fifth and sixth, fourth and seventh, third and eighth, second and ninth, and first and tenth lines where resolution permitted. The separation of the hyperfine components in gauss is related to the energy splitting in cm^{-1} between adjacent hyperfine levels as follows:

$$A(cm^{-1}) = g \times 4.6686 \times 10^{-5} A(gauss) \qquad (8)$$

The experimental esr parameters for $Nb(pipdtc)_4$ are listed in Table 6 with the corrections due to second order effects.

Table 6

Esr Spectral Parameters of $Nb(pipdtc)_4$

	Experimental	Corrected
$\langle g \rangle$	1.9677	1.9471
$\langle a \rangle^*$	110	108
$g_{\|\|}$	1.9155	1.8969
$g_{\perp}$	1.9938	1.9722
$A_{\|\|}^*$	195	190
$A_{\perp}^*$	66	65

*Hyperfine splittings in units of 10^{-4} cm^{-1}

In benzene at 77°K, the esr spectrum may be described by the spin Hamiltonian with axial symmetry:[46]

$$\mathcal{H} = g_{||}BH_zS_z + g_{\perp}(H_xS_x + H_yS_y) + A_{||}S_zI_z + A_{\perp}(S_xI_x + S_yI_y) \qquad (9)$$

where $S = 1/2, I(^{93}Nb;\ 100\%) = 9/2$. At ambient temperature in liquid solution, the anisotropies are averaged to zero, and the Hamilton becomes:

$$H = \langle g \rangle \beta H \cdot S + \langle a \rangle I \cdot S \qquad (10)$$

Theoretical calculations of esr parameters for a D_{2d} dodecahedron and a D_{4d} square antiprism show that $g_{\perp} > g_{||}$ for a dodecahedron[23,47] and $g_{||} > g_{\perp}$ for a square antiprism.[23,48] For the series of compounds studied in this work, $g_{\perp} > g_{||}$ indicating dodecahedral symmetry in support of the electronic spectra. In comparison to other known eight coordinate complexes of Nb(IV) listed in Table 7, the data observed here fit well. Two complexes where $g_{\perp} < g_{||}$, $Nb(dpm)_4$[49] and $Nb(CN)_8^{4-}$(soln)[50] have been reported. Single-crystal x-ray studies of these compounds have determined the structure of the latter species as dodecahedral while the former is antiprismatic.

Data from the esr studies can now be used in conjunction with the electronic spectral assignments for $Nb(pipdtc)_4$ to determine the applicability of an ionic model to the present system. It can be demonstrated that while the dodecahedral model has D_{2d} symmetry, it can be considered as arising from the distortion of a cube. If a metal atom is at the center, the net effect is a tetragonal distortion. For a $d_{x^2-y^2}$ ground state, the gyromagnetic ratios are given by the equations:[47]

$$g_{||} = 2.0023 - \frac{8\lambda}{\Delta E_3} \qquad g_{\perp} = 2.0023 - \frac{2\lambda}{\Delta E_2} \qquad (11)$$

Table 7

Esr Parameters for Eight-Coordinate Niobium(IV) Species

	$NbCl_4(dth)_2$[22]	$Nb(dmtp)_4$[7]	$Nb(dpm)_4$[49]	$Nb(CN)_8^{4-}$+[50]	$Nb(CN)_8^{4-}$‡[50]
<g>	1.9969	1.9791	1.9507	1.987	1.980
$g_{\|\|}$	1.9314	1.8756	1.9967	1.976	2.000
$g_{\|}$	2.0296	2.0308	1.9278	1.992	1.970
<a>*	134.6	136.9	100.1	101	97
$A_{\|\|}$*	183.5	216.9	49.1	154	49
$A_{\perp}$*	108.9	92.0	127.0	75	121

* in units of 10^{-4} cm^{-1}
\+ solid
‡ solution

where λ is the free ion coupling constant, $\Delta E_3 = ({}^2B_2-{}^2B_1)$, and $\Delta E_2 = ({}^2E_3-{}^2B_1)$. Taking the spin-orbit coupling constant for Nb^{4+} as 748 cm^{-1}, the calculated values of $g_\perp$ and $g_{||}$ are 1.9227 and 1.7265 respectively. These values are much lower than the experimental values and this indicates the inadequacy of the ionic model. It is possible to assess qualitatively the amount of covalent bonding via the equations:[47]

$$g_{||} = 2.0023 - \frac{8\lambda\alpha^2\beta^2}{\Delta E_3} \qquad g_\perp = 2.0023 - \frac{2\lambda\alpha^2\gamma^2}{\Delta E_2} \tag{12}$$

The parameters α^2, β^2, and γ^2 are associated with B_1, E, and B_2 molecular orbitals formed by linear combinations of metal and ligand orbitals of appropriate symmetry. The range of possible values for each of the parameters is 1.0 (ionic bond) to 0.50 (covalent bond). Agreement with the experimental g values is found for $\alpha^2\gamma^2 = 0.069$ and $\alpha^2\beta^2 = 0.32$. For pure covalent bonding in the ground and excited states, $\alpha^2\gamma^2 = \alpha^2\beta^2 = 0.0625$. It therefore appears that the niobium d orbitals are strongly mixed with ligand orbitals in the formation of $Nb(pipdtc)_4$.

Although the structures of the tetrakis(dialkylamido)-niobium(IV) compounds, $Nb(NR_2)_4$,[51] are tetrahedrons, these compounds have a similar ground state of $d_{x^2-y^2}$. The esr data for $Nb(NC_5H_{10})_4$, <g> = 1.9540 and <a> = 104 x 10^{-4} cm^{-1}, are similar to the data found in this work for NbB_4.

Another guide to the delocalization of the electron from the metal to the ligand is the amount of deviation of μ_{eff} from the spin-only value of 1.73 B.M. By use of the equation

$$\mu_{eff}(\text{B.M.}) = g\sqrt{S(S+1)} \tag{13}$$

in which S is the absolute value of the spin quantum number and g is the experimental gyromagnetic ratio, a value for μ_{eff} can be obtained. Table 8 lists calculated μ_{eff} values for the compounds in this study as well as other Nb(IV) compounds. From the table, the ability of sulfur-donor ligands to form fairly covalent species with Nb(IV) is illustrated. These values which are nearly equal to the spin-only value of

Table 8

Calculated μ_{eff} Values for Eight Coordinate Nb(IV) Complexes

Ligand	μ_{eff} (B.M.)
pipdtc	1.70
2-Mepipdtc	1.72
3-Mepipdtc	1.72
4-Mepipdtc	1.71
Etxan	1.72
dth	1.73
dmtp	1.71
dpm	1.69
CN(soln)	1.72
CN(soln)	1.71

1.73 B.M. is a further indication that the electron is primarily delocalized onto the ligand.

Reports by two different authors[26,52] stated that Nb(V) could be reduced to Nb(IV) by dithiocarbamates in contrast to the experiments by Pantaleo and Johnson in which Nb(V) compounds were isolated. This prompted an investigation to determine if pipdtc would also reduce Nb(V). Four-to-one molar ratios of NH_4pipdtc: NbX_5 (X = Cl, Br, I) were prepared under conditions similar to those discussed in the experimental section for the tetrahalides. The resulting solutions were examined by esr. In each case, a spectrum which was identical to the spectrum of the four to one molar ratios of NH_4pipdtc: NbX_4 (X = Cl, Br, I) was obtained.

Characterization of Halogen Complexes

When two moles of NH_4pipdtc were allowed to react with one mole of NbX_4 (X = Cl, Br, I), several observations were made. Initially, the reaction mixture would turn purple as found in the four-to-one reaction mixtures. After two days, an orangish precipitate and yellowish-brown solution were present. In order to establish the pathway through which the reaction was proceeding, a series of experiments was performed involving two-to-one molar ratios of NH_4pipdtc: $NbCl_4$. An original mixture of a four-to-one, ligand to $NbCl_4$ molar ratio was prepared. After two days of stirring, this mixture was examined by use of esr. The resulting spectrum was a ten line niobium spectrum with esr parameters as had been found earlier. The molar ratio was then altered to two-to-one by the addition of $NbCl_4$ and the esr spectrum of this mixture was recorded. The resulting esr spectrum of this solution was the same as had been found when two-to-one molar ratios were prepared. Further discussion on this observation will be included in the esr section.

The solid species were recovered from the filtrate by removing the solvent *in vacuo*. In the case of NbI_4 + $2NH_4$pipdtc the solvent, which was condensed into a liquid nitrogen trap, showed traces of iodine as well as the presence of carbon disulfide when allowed to warm to ambient temperature. It is believed that similar results are possible for the chloride and bromide when treated in this manner. Apparently, there is an oxidation-reduction occurring in the reaction mixture when less than four moles of the ligand are present. Holah and co-workers[52,54] studied the reaction of NbX_5 (X = Cl, Br, I) with diethyldithiocarbamate salts, with particular focus upon the organic products formed. These authors found that when the ligand-to-metal ratio was less than four-to-one, complexes of the type $Nb(S_2CNEt_2)_2X_3$ and $Nb(S_2CNEt_2)_2X_3 \cdot nC_6H_6$ (n = 0.85-0.95) were formed. Further studies confirmed that the ligand reacts with solvents such as methylene chloride, chloroform, and acetonitrile. Similar results could possibly occur even for reactions of NbX_4. A proposed mechanism involves the abstraction of a proton from the solvent. Although the

solvent used in this study would not undergo this type of nucleophilic attack, an excellent source of protons is NH_4^+.

In the two-to-one mixtures, the halides that would remain bonded to the metal could react with the ligand to form various organic and halo-organic species. Examples of the types of final products that could be formed are the thiuram disulfide ($C_5H_{10}NCS_4CNC_5H_{10}$) and monosulfide ($C_5H_{10}NCS_3CN$-$C_5H_{10}$). Both of these compounds would have infrared spectra similar to pipdtc. The differences between these species and the ligand could be observed in the ultraviolet region, but the metal ion in this system has charge-transfer bands that would mask this transition. Organo-halogen species such as $C_5H_{10}NHCSCl$, a thiocarbamyl, can be prepared. The precipitation of all of the halide as $NH_4^+X^-$ in the four-to-one reaction mixtures prevents the probable occurrence of these reactions. This oxidation-reduction process must only involve the ligand and not the metal, because information that will be discussed later confirms the oxidation state of niobium remains +4 in this system.

Solid species were isolated as greyish-brown, dark-brown, and light-brown powders for the chloride, bromide, and iodide respectively. The species are air and/or water sensitive as indicated by color changes when exposed to the atmosphere. The melting points are 130, 135, and 113°C respectively for the chloride, bromide and iodide.

Analyses of these species point toward a disubstituted product for the chloride for which %Nb found was 19.95 as opposed to a calculated %Nb of 19.21. The bromide and iodide analyses gave empirical formulas which can be formulated as $NbBr_4[C_5H_{10}NCS_3CNC_5H_{10}]\cdot 2C_5H_{10}NH$ and $C_5H_{10}NH_2[NbI(C_5H_{10}NCS_2)_2S]\cdot C_5H_{10}NH$.

Vibrational Spectra

Infrared Spectra (4000-600 cm^{-1})

Infrared data of these complexes are listed in Table 9. Each of these complexes had the significant bands that are expected at 1500 and 1000 cm^{-1} for dithiocarbamates. Considerable broadening of several peaks occurred in these species that was not evident in the tetra-substituted species. The unusual stoichiometries found by analyses would indicate there should be some change in the spectra. Machin and Sullivan[27] in their report of the compound $Nb_2Br_5(dtc)_3$ noted the ir spectrum of this compound did not differ from the spectrum of $Nb(dtc)_4$.

If the ligand is undergoing reduction to the thiuram monosulfide, the ir spectra would not differ very much due to the complexity of the system. This could account for the broadening of the spectra.

A band not present in the ligand nor in the tetra-substituted compound appears at 670 cm^{-1}. This band has been assigned as being due to the rocking of the CH_2 units

Table 9

Infrared Spectral Data for Halogen Complexes (4000-600 cm^{-1})

Assignments	Cl	Br	I
$\nu(N-C)$	2030 w,b	2070 w	2015 w,b
		2010-1970 w,b	
ring deformation	1575 w	1585 m	1570 w
$\nu(C=\overset{+}{N})$	1490 s	1500 s	1495 s
$\nu(C-N)$	1390 m	1390 m	1385 m
$\nu(C=S)$	1275 m	1275 w	1277 w
$\nu(NCS_2)$	1255 m	1257 sh	1260 sh
$\nu(NCS_2)$	1230 s	1238 s	1235 s
$\nu(NCS_2)$	1160 sh	1160 m	1160 sh
$\nu(NCS_2)$	1130-1050 s,b	1120-1050 m,b	1130-1050 m,b
	1018 sh	1020 sh	1018 sh
$\nu(C=S)$	995 s	1000 s	997 s
	947 m	945 m	955 w
	910 m	930 m	910 w
	885 m-s	887 m	885 m
	850 m-s	855 m-s	850 m
	800 s	800 s	795 s
	720 m	770 s	720 m
	690 m		
CH_2 rock	670 s	670 s	670 s

b = broad, s = strong, m = moderate, w = weak, sh = shoulder of the ring. Taimsala and Wood[55] found in their study of alkyl-substituted tin(IV) halides this band was much stronger for Et_2SnCl_2 than Et_4Sn. Its appearance in the spectra of these compounds is similar to that found by those authors.

Far Infrared Spectra (600-100 cm^{-1})

Far infrared data for these complexes are presented in Table 10 and the spectra are presented in Figures 7, 8, and 9 for the chloride, bromine, and iodide complexes respectively. Metal-sulfur vibrations are found in these complexes at the same positions as found in the tetrakis compound. This vibration is shifted to slightly higher frequency for the chloro complex. No significance can be attributed to this since the resolution of these bands is not very good.

A new band was present in the chloride compound at 347 cm^{-1}. Because of the intensity, general shape, and its absence from the spectra of the tetrakis compound and the ligand, this band has been assigned as ν(Nb-Cl). The triplet formed by the peaks at 303, 290, and 280 cm^{-1} may also be indicative of niobium-chloride stretching, but the appearance of this triplet in the iodide complex at a lesser intensity prevents the unambiguous assignment.

By using the ratio ν(Nb-Br)/ν(Nb-Cl) = 0.76 that was found for monodentate thioether adducts of NbX_4,[14] one expects to find a ν(Nb-Br) mode *ca.* 260 cm^{-1}. A band at 260 cm^{-1}, which is weak in the ligand, tetrakis species, and the chloride compound, and of moderate intensity in this

Table 10

Far Infrared Spectral Data for Halogen Complexes (600-100 cm^{-1})

Assignments	Cl	Br	I
Combination: ν(C-S), δ(C′-N-C′), δ(C-N), ring deformation, ν(M-S)	530 s,b	540 s,b	540 s,b
	490 w,sh	510 sh	500 s
δ(C′-N-C′)	440 m	440 s	435 m
δ(C′-N-C′)	410 w	415 sh	410 sh
ν(Nb-S)	390 m-s	390 s	395 w
	380 m-s	360 sh	370 m-s
			360 m
ν(Nb-Cl)	347 s		
		307 w	303 m
ν(Nb-Cl)	303 m		
ν(Nb-Cl)	290 m		290 m
ν(Nb-Cl)	280 m		280 m
	265 w		267 w
		ν(Nb-Br) 260 m	
	250 sh		250 m
	225 m	230 w-m	225 w-m
	207 m	210 w	203 w-m
	190 w	190 w,b	ν(Nb-I) 190 w
	180,173 w-m		175 w-m,b
	150 m	155 w	152 m
	137 w		135 w
	125 w,b		125 w,b

b = broad, s = strong, m = moderate, w = weak, sh = shoulder

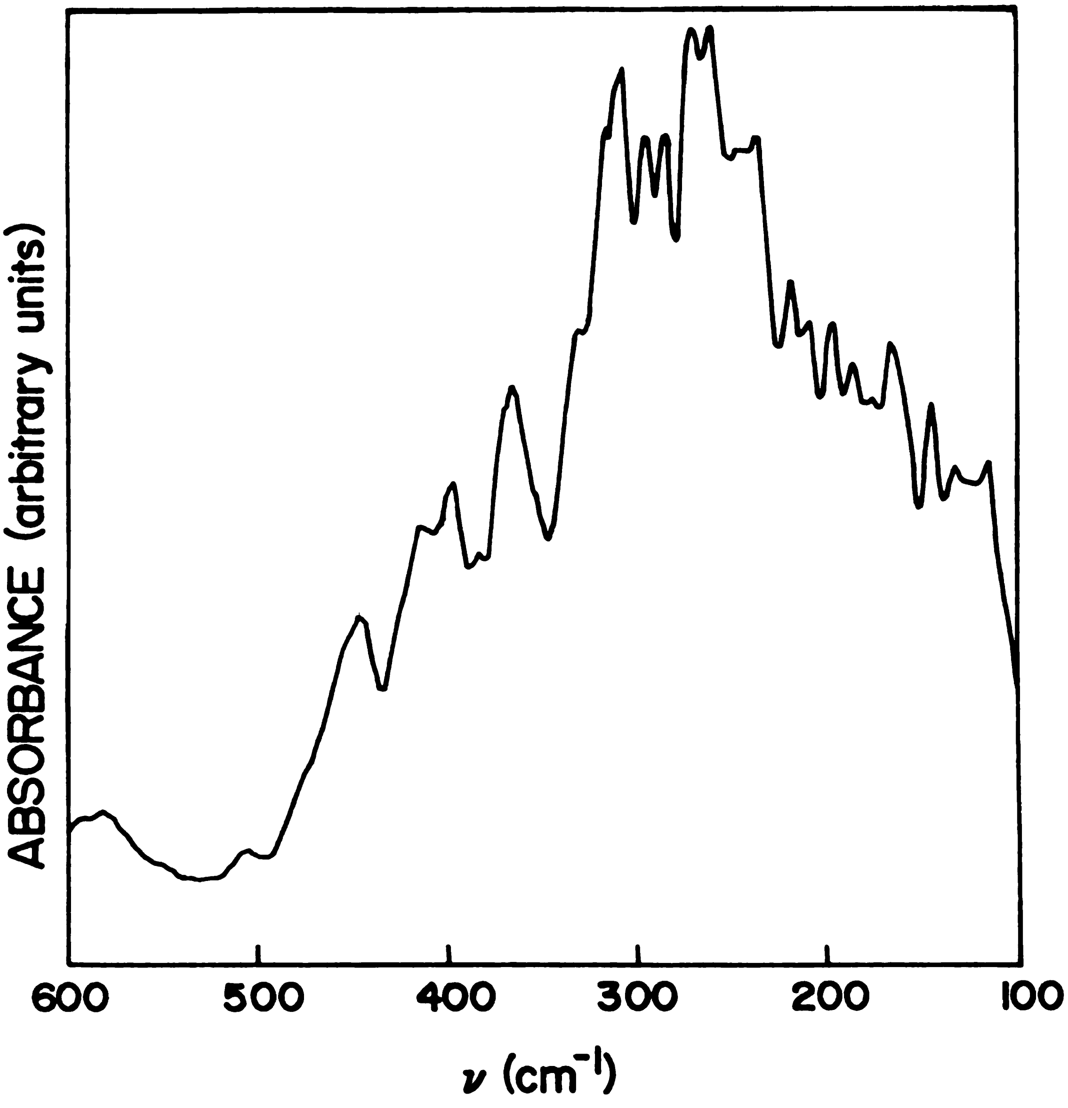


Figure 7. Far Infrared Spectrum of Chloride Complex

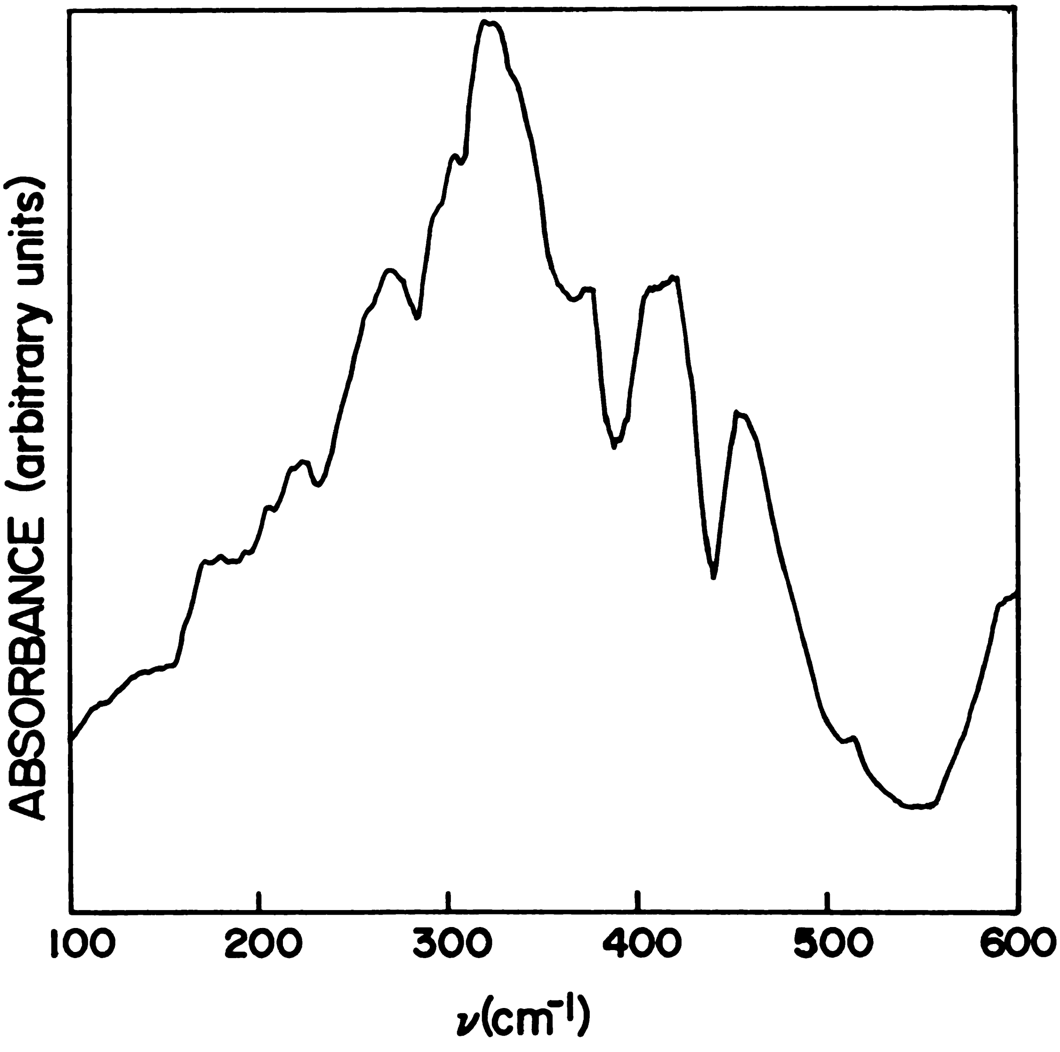


Figure 8. Far Infrared Spectrum of Bromide Complex

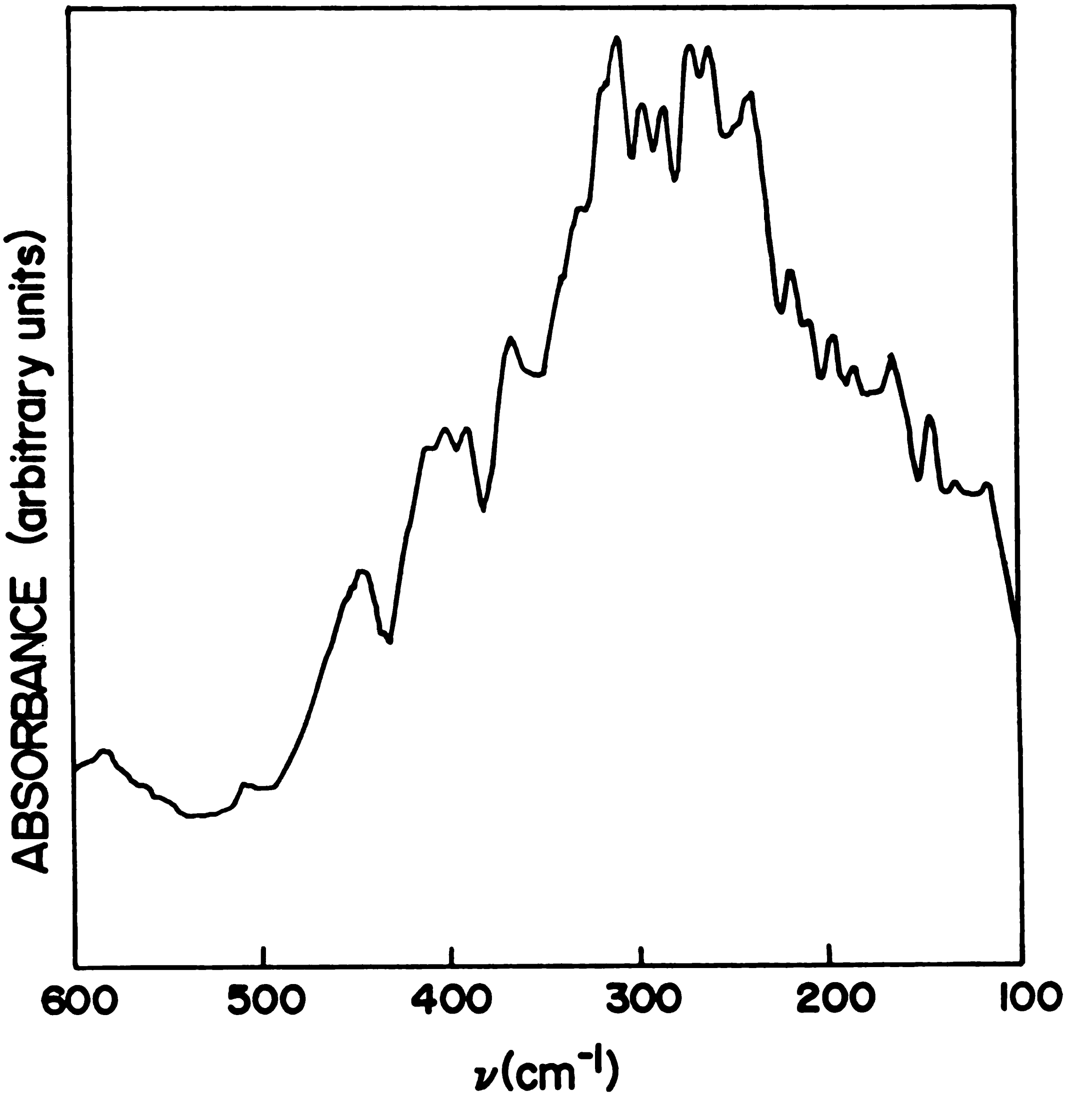


Figure 9. Far Infrared Spectrum of Iodide Complex

complex is assigned as ν(Nb-Br).

Broadening of the peaks for these compounds is most evident for the iodide complex. The ratio of ν(Nb-I)/ν(Nb-Cl), calculated as 0.56,[14] predicts a ν(Nb-I) mode *ca.* 194 cm^{-1}. A peak at 190 cm^{-1} is present in this compound. Due to peaks at 203 cm^{-1} and 175 cm^{-1} the intensity of this vibration may have been lessened. This factor, coupled with the presence of a similar peak in the chloride, prevents this band from being positively assigned as ν(Nb-I).

The information gained by this far ir study can be used in conjunction with the analytical data found for the compounds to confirm the nature of bonding between the metal, ligand, and halogen. Interaction between the ligand's sulfur atoms and niobium has been maintained. Evidence that some of the halogen has remained coordinated to the metal is supported by the appearance of bands that are due to niobium-halogen vibrations.

Electronic Spectra

Visible and near infrared spectra were studied for these species in benzene solutions as described earlier. The spectra and wave number maxima are presented in Figures 10, 11, and 12 and Table 11. Four bands are observed for the chloride and iodide containing species and iodide containing species and five bands for the bromide

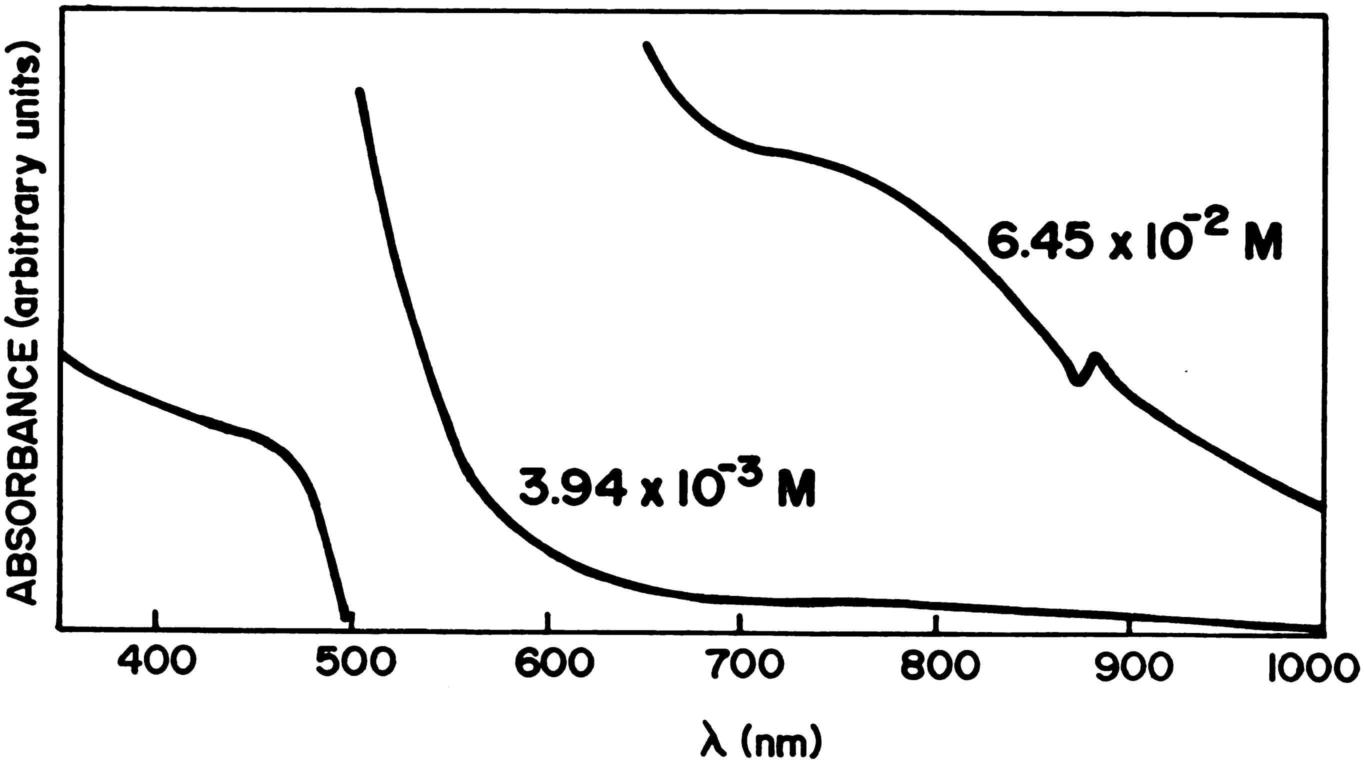


Figure 10. Electronic Spectra of Chloride Complex

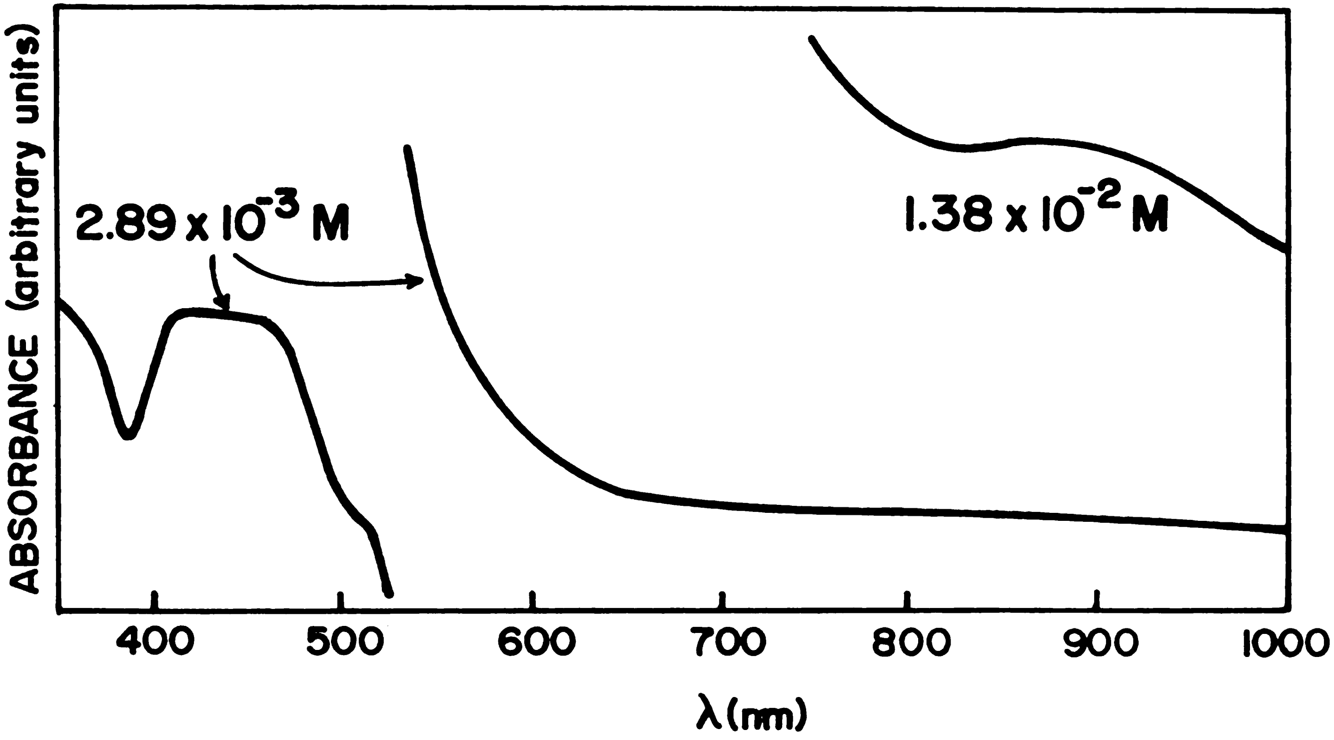


Figure 11. Electronic Spectra of Bromide Complex

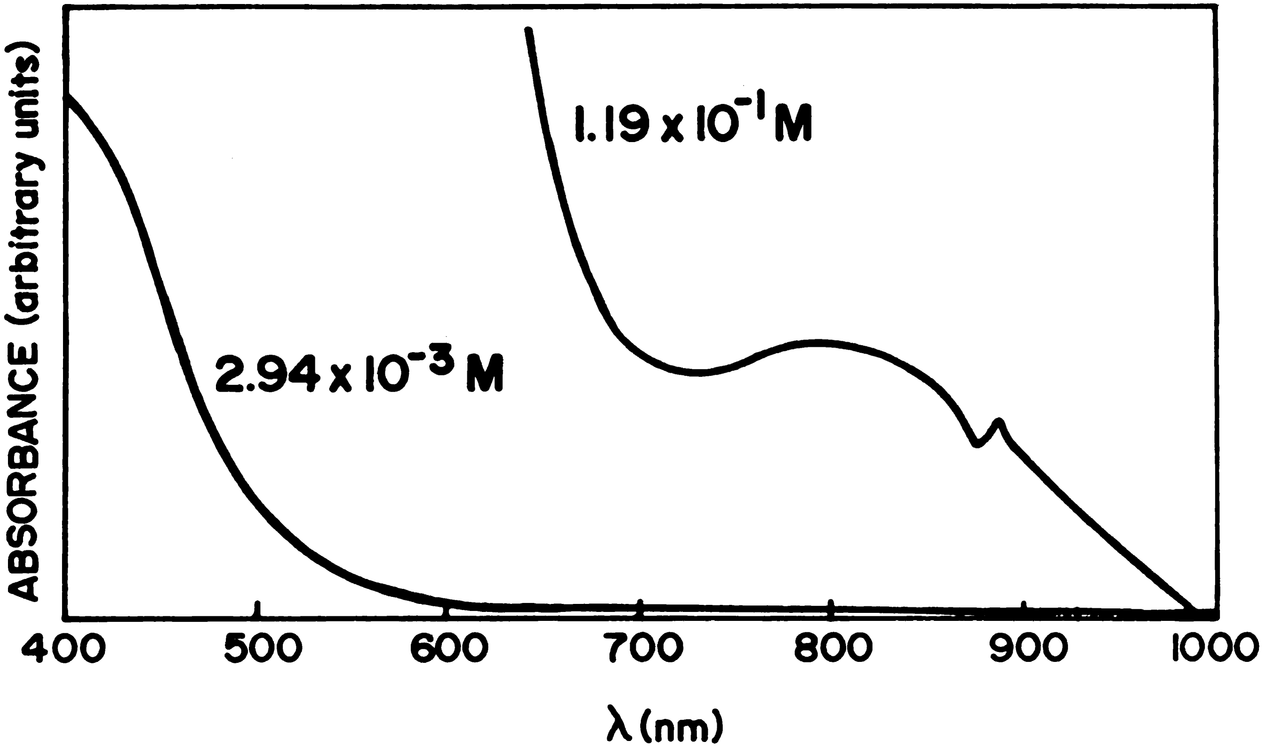


Figure 12. Electronic Spectra of Iodide Complex

Table 11

Electronic Spectral Data for Halogen Complexes

Cl	Br	I
11.3 (7.51)	11.4 (59)	11.3 (11.4)
13.5 (13.1)	13.4 (75)	12.4 (12.5)
22.4 (337)	19.7 (400)	21.3 (314)
24.4 (840)	22.8 (525)	24.8 (308)
	27.8 (520)	

Wave number maxima are in units x 10^3 cm^{-1}.
Extinction coefficients are in parentheses.

compound. All of the complexes exhibit bands corresponding to those found in the spectrum of Nb(pipdtc)$_4$. In addition, a band *ca.* 24.0 x 10^3 cm^{-1} is not present in Nb(pipdtc)$_4$.

The broad bands observed for these species prevent rigorous assignment of these transitions as being d-d transitions. Fowles[16] has reported that the acetonitrile adducts of the tetrahalides have halogen(π) → niobium(d) transitions throughout the visible region and as a result the d-d transitions may be masked. The yellowish-brown color of the solutions would also influence transitions in the visible region as has been reported for the complex Cu(dmdtc)$_2$.[56]

If the structure for the chloro species is assumed to be pseudo D_{4h} symmetry, one would expect three transitions from the splitting of the d-manifold. The extinction coefficients for the bands at 11.3 and 13.5 x 10^3 cm^{-1} permit the assignment of these bands as d-d transitions. It is not unreasonable to assign the other band at 22.4 x 10^3 cm^{-1} as a d-d transition although the extinction coefficient is somewhat high. Other workers[5] have reported d-d transitions over the range of 15,000 cm^{-1} to 23,000 cm^{-1}. Hence it is conceivable that a similar situation exists in this system. The iodide species would fall into the series as expected. The bromo-compound poses problems in that the bands appear to be out of order. The stoichiometry of this compound which contains four bromide atoms may account for this anomaly.

Nuclear Magnetic Resonance Spectra

Solutions of these species for nmr study were prepared by concentrating the original filtrates from the reaction mixtures by removal of the solvent *in vacuo*. These viscous solutions were then diluted in the nmr tubes by the addition of solvent. The only resonance observed over the range of the instrument was the solvent peak which showed a shift of 5 ppm upfield from TMS. Paramagnetic complexes typically shift solvent peaks corresponding to the amount of interaction between the solvent and the paramagnetic center. The small shift observed here is indicative of little interaction between the solvent and the complex and the low paramagnetic character of the complexes.

Electron Spin Resonance Spectra

The filtrates from the reactions and the solid species dissolved into benzene gave esr spectra which consisted of a single unresolved broad peak at ambient temperature. At 77°K, this peak was lowered in intensity. A representative spectrum is presented in Figure 13.

Thus far, infrared, far infrared, and electronic spectra have supported the formation of species in which: (a) the ligand is bidentate; (b) the halogens are still attached to the metal; and (c) the chloride and iodide compounds are similar in structure. One can not rule out the presence in solution of a monomeric six coordinate species which has as contaminants other organic species in the outer coordination sphere of the metal ion.

Because the nature of the species could not be determined well for any of the complexes except for the chloro-compound, this complex was diluted into a solution containing $ZrCl_2(pipdtc)_2$, and was handled in the manner described in the Experimental Section. A dark-brown powder was isolated. At ambient temperature, no esr signal was detected. On cooling the sample to 139°K, a spectrum, Figure 14, was observed that had twenty major lines.

The gross features of the spectrum suggest several possibilities for the stoichiometry of the complex. The intense lines in the middle of the spectrum are the type of lines found for monomeric Nb(IV) complexes. The other lines

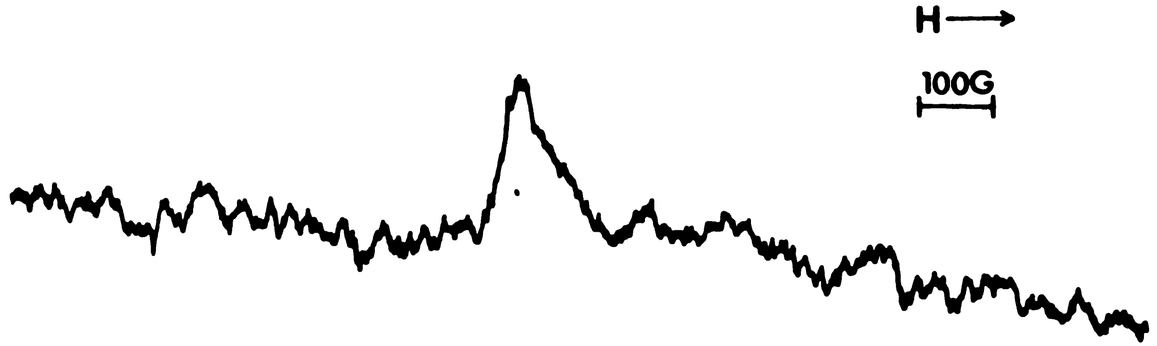


Figure 13. Esr Spectrum of Halogen Complexes at Ambient Temperature

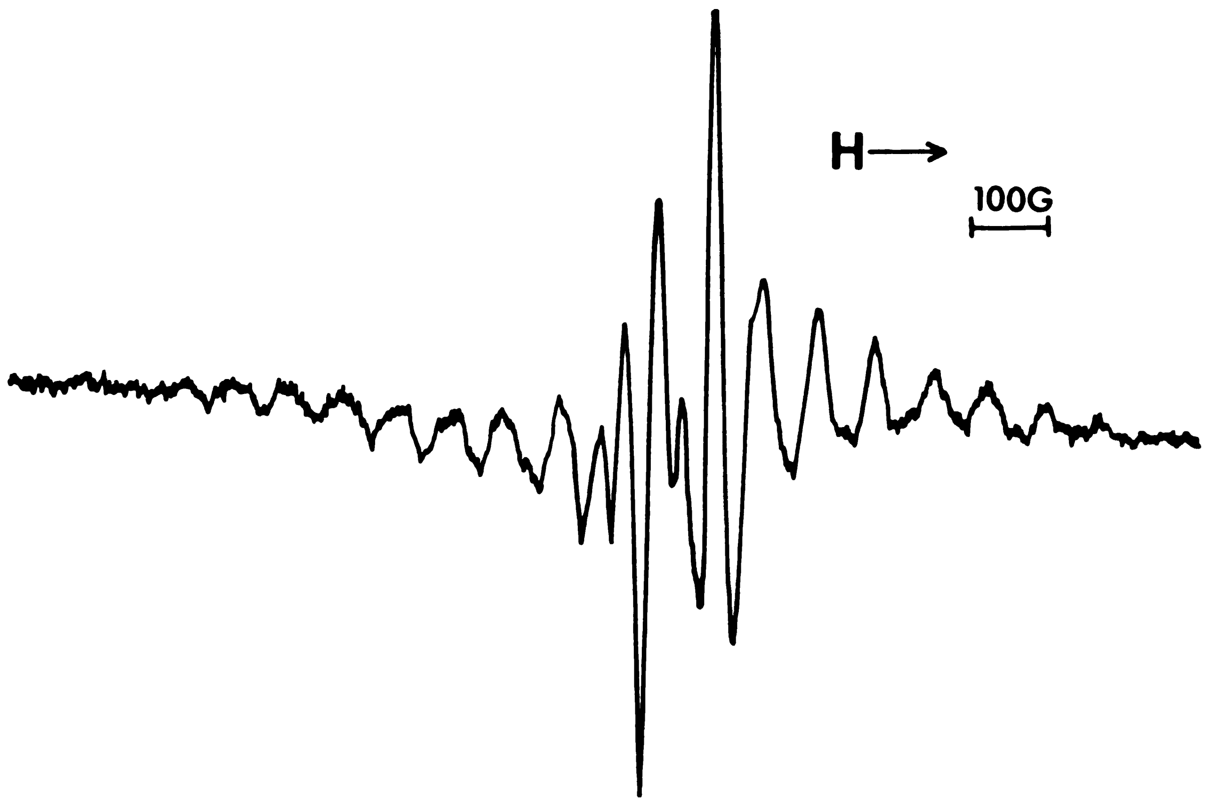


Figure 14. Esr Spectrum of the Chloride Complex Diluted into $ZrCl_2(pipdtc)_2$ at 139°K

are similar to the exchange-coupled dimer, Nb(dmtp)$_4$I$_4$, found by McGinnis.[8] From this information, the possible stoichiometries are: (a) [NbCl$_2$(pipdtc)$_2$]$_2$·[NbCl$_2$(pipdtc)$_2$] and (b) [NbCl$_2$(pipdtc)$_2$]·[ZrCl$_2$(pipdtc)$_2$]·[NbCl$_2$(pipdtc)$_2$].

A necessary condition for obtaining esr spectra due to dimers is that the paramagnetic ions are magnetically isolated from each other so as to keep experimental linewidths small.[57] The spectra of these systems consist of 2nI + 1 lines with a hyperfine splitting of A/2 where n is the number of atoms present with nuclear spin, I, and A is the normal hyperfine splitting for a single metal ion. In addition to the normal $\Delta M_s = \pm 1$ transitions, "forbidden" $\Delta M_s = \pm 2$ transitions arise when the magnetic field is off the symmetry axis of the molecule by the angle, θ. The intensity and resolution of these transitions are normally much less than for the $\Delta M_s = \pm 1$ transitions. This half field transition is normally only observed in the frozen solution spectrum and its presence is considered definitive evidence for an exchange-coupled system.[58] If dimer formation is incomplete, as is frequently the case, dimer $\Delta M_s = \pm 1$ spectra are often considerably obscured by residual monomeric spectra in the $g \approx 2$ region of the spectrum. This situation is often the case in powders containing small concentrations of the paramagnetic metal ions.[6]

When two neighboring niobium(IV) ions interact, as occurs when dimeric complexes are formed, the spin Hamiltonian for the pair may be written:

$$H = H_1 + H_2 + H_{int} \qquad (14)$$

where H_1 and H_2 are each of the form:

$$H_{1,2} = g_{||}H_zS_z + g_{\perp}(H_xS_x+H_yS_y) + A_{||}S_zI_z + A_{\perp}(S_xI_x+S_yI_y) \qquad (15)$$

H_{int}, representing the interaction energy between two ions, has the form:

$$H_{int} = D[S_z^2-1/3S(S+1)] + E(S_x^2-S_y^2) - JS/\cdot S_2 \qquad (16)$$

where $S = S_1 + S_2$ if the ions are in sites of the same symmetry and D and E are the zero field splitting parameters. In a complex which contains an even number of electrons the degeneracy of the ground state may be removed in accordance with the Jahn-Teller effect. For a system which exhibits axial symmetry, it has been found that D >> E and, in fact, if x and y symmetry axes are equivalent E = 0. Assuming that the complex has axial magnetic symmetry, an approximate value for D can be obtained from the separation of the outermost pair of lines in the low temperature powder spectrum by:

$$H_{19} - H_1 \approx 2D \qquad (17)$$

Since the D value provides a reasonable measurement of the intermetal distances which may give structural information for the paramagnetic species, the assumption of axial symmetry is made for this system so that D and the metal-metal distance can be obtained. Accurate hyperfine and zero-field splitting parameters cannot safely be extracted from the spectrum in the absence of single crystal esr analysis for all of the magnetic parameters. Esr studies of the copper[59] and vanadyl[60] tartrates suggest that the error in the derived esr parameters under the axial symmetry approximation is not very large. If D is attributed to the magnetic dipolar interaction between two electron spins, it is expressed as[61]

$$D = 3/4g^2\beta^2 \left< \frac{1-3\cos^2\theta}{r_{12}^{\;3}} \right>_{max} \qquad (19)$$

where r_{12} is the interelectronic distance and θ is the angle between the r_{12} vector and the magnetic field direction. Assuming that θ equals the angle between the niobium-niobium axis and the magnetic field and $1/\left<r_{12}^{\;3}\right> = \frac{1}{R^3}$, R being the niobium-niobium distance, one obtains:

$$R_{calc}(\text{Å}) = \left[\frac{0.325g^2\,|1-3\cos^2\theta\,|}{D(\text{cm}^{-1})} \right]^{1/3} \qquad (20)$$

Taking $H_{||}$ to be along the Nb-Nb axis, and $\theta = 0°$, one obtains the esr parameters listed in Table 12.

Table 12

Esr Parameters for the Chloride Complex Diluted into $ZrCl_2(pipdtc)_2$

$g_{||} = 1.7873$
$A_{||}^{*} = 64.2$
$D^{*} = 577.8$
$R = 3.30$ Å

* in units of 10^{-4} cm^{-1}

The data for the chloro complex suggest that the species formed by the solid solution is an incomplete dimer. The $A_{||}$ value for the compound is similar to that reported by McGinnis for $Nb(dmtp)_4I_4$,[8] while $g_{||}$ is low compared to most Nb(IV) compounds. The fact that no resonance at $g \approx 4$ was observed down to 77°K does not exclude the formation of a dimeric species in the solid state. The effect of diluting a dimeric compound into a diamagnetic host allows for packing conditions to influence the nature of the complex in the solid as oppossed to the solution. $Nb_2(dmtp)_4Cl_4$ was reported to be diamagnetic based on magnetic susceptibility measurements by the Faraday method.[8] When a toluene solution of this compound was diluted into ten-fold concentration of $ZrCl_4(dmtp)_4$, a nineteen line esr spectrum was observed at both ambient and 77°K temperatures.[62] Hence, esr methods are superior to magnetic susceptibility methods in the determination of exchange-coupled species in which this interaction is not strong. The approximate Nb-Nb distance which was comparable to that found for α-NbI_4[2] but lengthened from the value of 3.06 Å for $NbCl_4$[3] illustrates the closeness of the metal atoms, which under dilute conditions can show electron exchange.

SUMMARY AND CONCLUSIONS

Eight coordinate Nb(pipdtc)$_4$ was isolated from the reaction of ammonium piperdinyldithiocarbamate (NH$_4$pipdtc) with niobium tetrahalides. The infrared spectrum indicates that pipdtc$^-$ is bidentate. The electronic spectrum exhibits four d-d transitions and supports a D_{2d} dodecahedral configuration for the complex. Esr spectra confirm this geometry with the parameters $\langle g \rangle = 1.9677$, $g_{||} = 1.9155$, $g_{\perp} = 1.9938$, and $\langle a \rangle = 0.0110$ cm^{-1}. By using molecular orbital theory developed for D_{2d} complexes, metal-ligand bonding parameters were obtained which indicate strong mixing of metal and ligand orbitals.

When two moles of NH$_4$pipdtc were allowed to react with the tetrahalides, complexes of varying stoichiometries were obtained. In each, the pipdtc$^-$ was bidentate as determined from infrared spectra. Far infrared spectra showed bands which could be assigned as ν(Nb-S) and ν(Nb-X) (X = Cl, Br, I). Two bands in the near infrared-visible region were assigned as d-d transitions. Esr spectra of these species were unresolved single peaks at both ambient and 77°K temperatures. The chloro compound when diluted into a solution of the disubstituted zirconium complex, gave a powder esr spectrum which was indicative of an exchange-coupled dimer. The esr parameters are $g_{||} = 1.7873$ and $A_{||} = 0.00642\ \text{cm}^{-1}$. The zero field splitting is $0.05778\ \text{cm}^{-1}$ which corresponds to a niobium-niobium separation of 3.30 Å.

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