DIMETHYLDITHIOPHOSPHATE COMPLEXES
OF
NIOBIUM(IV) TETRAHALIDES

Dissertation for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY
ROGER NOLAN McGINNIS
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ABSTRACT

DIMETHYLDITHIOPHOSPHATE COMPLEXES OF NIOBIUM(IV) TETRAHALIDES

By

Roger Nolan McGinnis

Eight-coordinate $Nb(Dmtp)_4$ was isolated from the reaction of sodium dimethyldithiophosphate (NaDmtp) with niobium tetrahalides.The infrared spectrum indicates that $Dmtp^-$ is bidentate. The electronic spectrum exhibits three d-d transitions and supports a D_{2d} dodecahedral configuration for the complex. The esr spectra confirm this geometry with the parameters $\langle g \rangle = 1.9494$, $g_{||} = 1.8971$, $g_{\perp} = 1.9756$, and $\langle a \rangle = 0.01354$ cm^{-1}. Using the molecular orbital theory developed for D_{2d} complexes, metal-ligand bonding parameters were obtained which indicate strong mixing of metal and ligand orbitals.

Complexes of the type $Nb_2(Dmtp)_4X_4$ (X = Cl,Br,I) were obtained from the reaction of the niobium tetrahalides with two moles of NaDmtp. The infrared spectra indicate that $Dmtp^-$ is bidentate in all three complexes. Three d-d transitions were observed in the electronic spectra. In addition, a band due to a double excitation was observed at 390 nm. indicating a metal-metal interaction. The complexes were proposed to be halogen bridged dimers with D_{2h} symmetry (C_{2v} about each niobium atom). The magnetic moments decrease in the order I > Br > Cl. The bromide and chloride complexes are diamagnetic while the iodide complex exhibits antiferromagnetism with a singlet-triplet separation of -140 cm^{-1} and a room temperature magnetic moment of 2.32 Bohr Magnetons. Additional confirmation of an electron exchange-coupled dimer was obtained by the observation of the triplet state esr spectrum of $Nb_2(Dmtp)_4I_4$ with both the $\Delta M_s = \pm 1$ and the $\Delta M_s = \pm 2$ transitions present. The esr parameters are $g_{||} = 2.0663$, $g_{\perp} = 1.9361$, $A_{||} = 0.00681\ \mathrm{cm}^{-1}$, and $A_{\perp} = 0.00345\ \mathrm{cm}^{-1}$. The zero field splitting is $0.06318\ \mathrm{cm}^{-1}$ which corresponds to a niobium-niobium separation of 3.53 Å. This complex represents the first reported case of electron exchange-coupling in niobium(IV).

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OF
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A DISSERTATION

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To Eva

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I. Introduction

The niobium tetrahalides are polymeric, diamagnetic solids whose basic unit can be represented as Nb_2X_8. The tetrahalides consist of an infinite chain of distorted octahedra sharing opposite edges and containing alternating metal-metal bonds.[1-3]

The niobium tetrahalides react with donor ligands to form paramagnetic six and eight coordinate complexes in which the metal-metal bond is cleaved. In some cases the metal-metal bond is retained giving diamagnetic or very weakly paramagnetic six-coordinate adducts. In addition to adduct formation, substitution of halogens can occur to give complexes of the type $NbX_{4-n}L_n$ (n=1-4) with either retention or cleavage of the metal-metal bond. Six and eight are the predominate coordination numbers of niobium(IV) although a number of complexes are seven-coordinate if one considers the metal-metal bond. The six-coordinate complexes are octahedral. The eight coordinate complexes are dodecahedral except for the dipivaloylmethane complex which is square antiprismatic.[4]

Metal-metal bonding is common for niobium(IV) due to the relatively expanded d orbitals which allow overlap to occur and the presence of an unpaired d electron. The fact that metal-metal bonding does occur accounts for the prominence of six-coordinate diamagnetic compounds.

The choice of ligands also influences the stereochemistry of niobium(IV). Small donor atoms decrease the steric repulsions and tend to favor the higher coordination numbers. In addition, a metal to ligand pi bonding capability favors a high coordination number. These two requirements appear to be mutually exclusive. For instance, the eight-coordinate complexes $Nb[S_2CN(C_2H_5)_2]_4$ and $NbX_4(diarsine)_2$ have been prepared but the corresponding oxygen and nitrogen complexes do not form. Nitrogen, halogen and phosphorus donors have been found to give only six coordinate addition compounds while with arsenic donors only eight-coordinate addition complexes have been obtained. Oxygen and sulfur donor ligands are more versatile, both forming six coordinate addition and substitution complexes. In addition, oxygen donors form eight-coordinate substitution complexes while sulfur donors form both eight-coordinate addition and substitution complexes.

II. Review of Previous Work

A. Eight Coordinate Niobium(IV) Complexes

Several comprehensive reviews have been published concerning the chemistry of niobium(IV).[5-7] This review will be primarily concerned with the eight-coordinate, paramagnetic niobium(IV) complexes; dimeric, diamagnetic niobium(IV) complexes; and other binuclear d^1 systems.

Clark and coworkers[8] obtained eight-coordinate complexes with the bidentate ligand o-phenylenebis(dimethylarsine)(or diarsine). Complexes of the type $NbX_4 \cdot 2$diarsine were prepared by heating NbX_4, NbX_5, or $NbOX_3$ with diarsine in a sealed evacuated tube. The complexes are isomorphous with the dodecahedral titanium(IV), zirconium(IV), and hafnium(IV) halide diarsine complexes.[9] The diffuse reflectance spectra exhibit four d-d transitions as expected for dodecahedral complexes. The magnetic moment of 1.69 Bohr Magnetons, calculated from the esr spectrum of the chloride complex, is consistent with a single d electron in an orbitally non-degenerate ground state.

Deutscher and Kepert prepared additional eight-coordinate complexes using 4-methyldiarsine and 4-ethyldiarsine.[10] These compounds exhibit visible spectra similar to those of the diarsine complexes and were assumed to be dodecahedral. The spectrum of $NbCl_4(Etdiars)_2$ exhibits maxima at $\nu = 9.75$ kK, $\varepsilon_{max} = 10$; $\nu = 12.8$ kK, $\varepsilon_{max} = 26$; and $\nu = 17.5$ kK, $\varepsilon_{max} = 6$. Solutions of $NbBr_4(Etdiars)_2$ exhibit maxima at 12.72 and 15.92kK and the iodide complex gives maxima at 10.1 and 12.7 kK. The effective magnetic moments are 1.63, 1.67 and 1.80 B.M. for the chloride, bromide, and iodide complexes, respectively, and are not unexpected for a single d electron in a nondegenerate ground state. The high moment of the iodide complex was attributed to a large temperature independent paramagnetic contribution.

A number of eight-coordinate substitution complexes have been prepared with beta-diketonates. Deutscher and Kepert have prepared niobium(IV) complexes of acetylacetone (Acac), benzoyltrifluoroacetone (Bta), thenoyltrifluoroacetone (Tta), and dibenzoylmethane (Dbm).[11, 12] In addition, complexes of 8-hydroxyquinoline (Ox) and tropolone (T) were prepared. The complexes were prepared by reaction of the appropriate niobium tetrahalide with the free ligand in an acetonitrile-triethylamine solution. In all cases the infrared spectra indicate that the ligands are bidentate and equivalent. The d-d transitions were not observed in the diffuse reflectance or solution spectra. The room temperature magnetic moments vary from 1.43 - 1.66 B.M. except for NbT_4 which has a magnetic moment of 0.74 B.M. Powder X-ray patterns indicate $Nb(Acac)_4$ is not isomorphous with the square antiprismatic $Zr(Acac)_4$;[13] $Nb(Tta)_4$ is not isomorphous with square antiprismatic $Zr(Tta)_4$;[14] and $Nb(Dbm)_4$ is not isomorphous with the square antiprismatic $Th(Dbm)_4$.[15] The esr spectra of $Nb(Acac)_4$ and $Nb(Dbm)_4$ consist of a broad asymmetric signal with the general shape expected for $g_\perp > g_{||}$. The values of $g_\perp$ are 1.95 and 1.98 for $Nb(Acac)_4$ and $Nb(Dbm)_4$, respectively. It has been demonstrated that $g_\perp > g_{||}$ for a dodecahedral complex and that the reverse is true for a square antiprismatic complex.[16-18] All of the niobium complexes were assumed to be dodecahedral since $g_\perp > g_{||}$ and they are not isomorphous with known square antiprismatic complexes.

Podolsky prepared the tetrakisdipivaloylmethane (Dpm) complex of niobium(IV) by reaction of niobium tetrachloride with the free ligand in acetonitrile.[19] Only two d-d transitions are observed in the visible spectrum at 14.2 kK., ϵ_{max} = 280 and at 15.3 kK, ϵ_{max} = 636. The esr spectrum exhibits ten lines with $<g>$ = 1.95 and a hyperfine splitting of 110 gauss. The anisotropic constants are found to be: $g_\perp$ = 1.928, $g_{||}$ = 1.997, $A_\perp$ = 141 gauss, and $A_{||}$ = 53 gauss. On the basis of observing only two d-d transitions and $g_{||} > g_\perp$, the structure of $Nb(Dpm)_4$ was proposed to be a D_4 square antiprism. This was later confirmed by X-ray structural analysis[4] and represents the first reported case of a square antiprismatic niobium(IV) complex.

Bidentate sulfur donor ligands have also been found to form eight coordinate niobium(VI) complexes. A number of workers have prepared the diethyldithiocarbamates (Detc).[20-22] The ir spectrum indicates the ligand is bidentate. A band observed at 360 cm^{-1} was assigned as a metal-sulfur stretching mode. One d-d band is observed in the visible spectrum at 363 mμ with ϵ_{max} = 48. The magnetic moment is 1.57 B.M. indicating a single unpaired electron. No esr data have been reported.

Hamilton and McCarley prepared eight-coordinate sulfur donor complexes with 1,2-dimethylthioethane(Dth).[23] The compounds are paramagnetic adducts with composition $NbX_4(Dth)_2$. The far infrared spectra indicate that the ligand is bidentate and metal-halogen and metal-sulfur stretching frequencies were assigned. The solid state electronic spectra are similar to those reported by Clark for $NbX_4(Diars)_2$.[8] The magnetic moments for the chloride, bromide and iodide complexes were determined to be 1.60, 1.61 and 1.28 B.M. respectively. An esr spectrum was observed only for the solid chloride complex. The spectrum consists of a broad asymmetric band with $<g>$ = 1.92, $g_\perp$ = 1.98, and $g_{||}$ = 1.80. The complexes were proposed to be dodecahedral on the basis of the solid state electronic spectra and the esr spectrum of the chloride. This was later confirmed by Wilson[24] who obtained the solution esr spectrum and found $g_\perp > g_{||}$ as expected for a dodecahedral complex.

B. Dimeric Niobium(IV) Systems

In addition to the mononuclear, paramagnetic, niobium(IV) complexes, a number of dimeric niobium(IV) compounds have been prepared. These complexes all have small magnetic susceptibilities indicating retention of the metal-metal bond. If any halogen atoms are present, two of them usually bridge the metal atoms.

Wentworth and Brubaker have prepared two diamagnetic niobium(IV) ethoxide complexes.[25] The electronic spectrum of $[NbCl(OC_2H_5)_3Py]_2$ (Py=pyridine) exhibits a single peak at 365 mμ with nonreproducible extinction coefficients. The complex is diamagnetic with a corrected susceptibility of -1150×10^{-6} c.g.s. units. On the basis of the nonlability of the chlorine atoms, the molecular weight data, and the low susceptibility, the complex was assumed to be dimeric with bridging chlorine atoms and a direct metal-metal bond. When the dimer was treated with sodium ethoxide, $Nb(OC_2H_5)_4$ was obtained. This compound is diamagnetic with a corrected susceptibility of -100×10^{-6} c.g.s. units. A single band is observed in the electronic spectrum at 380 mμ.

Brown and Newton prepared $NbCl_4 \cdot N(C_2H_5)_3$ by refluxing a mixture of $NbCl_4$ and triethylamine.[26] This complex is diamagnetic and has a single broad peak in the visible spectrum at 380 mμ similar to those reported for $NbCl_4$, $NbBr_4$, and those reported by Wentworth and Brubaker. This band was attributed to a niobium-niobium bond.

Machin and Sullivan prepared a number of compounds which were thought to be dimeric.[22] From the reaction of niobium tetrachloride with potassium thiocyanate they obtained $Nb(NCS)_3Cl$. The magnetic susceptibility is 40×10^{-6} c.g.s. units indicating a structure similar to that of $NbCl_4$. A band is observed in the diffuse relectance spectrum at 18,000 cm^{-1}. When potassium cyanate was allowed to react with niobium tetrachloride, $Nb(CNO)_3Cl$ was obtained. The magnetic susceptibility for this compound is also low, χ_{Nb} being 90×10^{-6} c.g.s. units. Four bands were observed in the diffuse reflectance spectrum but assignments were not made. When less than four moles of sodium diethyldithiocarbamate react with niobium tetrabromide, $Nb_2(Detc)_5Br_3$ is obtained. This complex was a weak 1:1 electrolyte in nitromethane and was postulated as $[Nb_2(Detc)_5Br_2]Br$. The magnetic susceptibility is markedly field dependent. Peaks are observed in the diffuse reflectance spectrum at 23,500 cm^{-1} and 19,500 cm^{-1} with a shoulder at 16,000 cm^{-1}.

Fowles, Tidmarsh and Walton[27] prepared $NbCl_4 \cdot S(CH_3)_2$ by the direct reaction of $NbCl_4$ and dimethylsulfide. The complex was reported to be antiferromagnetic with a room temperature magnetic moment of 0.44 B.M. Two bands were observed in the electronic spectrum at 11.2 and 16.0 kK. and were assigned as d-d transitions. The magnetic moment and far infrared spectrum of $NbCl_4 \cdot S(CH_3)_2$ suggest that this species is structurally similar to the related d^1 antiferromagnetic titanium(III) derivatives $TiCl_3 \cdot 2S(CH_3)_2$ and $TiCl_3 \cdot 2SC_4H_8$.[28]

Hamilton and McCarley also investigated the reaction of dimethylsulfide with $NbCl_4$ and $NbBr_4$.[29] Complexes of the type $NbX_4[S(CH_3)_2]$ were obtained by allowing the appropriate niobium tetrahalide to react with dimethylsulfide in benzene. The monoadducts are weakly paramagnetic with room temperature magnetic moments of 0.36 and 0.50 B.M. for the chloride and bromide complexes, respectively. While no evidence was found for an antiferromagnetic interaction as proposed by Fowles and coworkers, the same structure that Fowles proposed was suggested.

C. Exchange-coupled Dimeric d^1 Complexes

While Fowles and coworkers found $NbCl_4 \cdot S(CH_3)_2$ to be antiferromagnetic, Hamilton and McCarley found that it was diamagnetic. There have been no other reports of exchange interactions in niobium(IV) pairs. However, a number of complexes containing other d^1 metal ions exhibiting electron exchange have been prepared.

Electron exchange interactions can be detected in two ways. An important indication of intramolecular exchange coupling in complexes which contain more than one transition metal ion is the characteristic deviation of the magnetic susceptibility of these compounds from the Curie-Weiss Law. When an isotropic interaction occurs between two paramagnetic metal ions, each with a single unpaired electron, the exchange interaction term $JS_1 \cdot S_2$ is required in the spin Hamiltonian. J is defined such that a negative value corresponds to an antiferromagnetic interaction in which the ground state is a singlet and the triplet state is J energy units above the ground state. The magnetic susceptibility of such a system, as first formulated by Bleaney and Bowers,[30] is in accordance with the relationship:

$$\chi_M = \frac{g^2 N \beta^2}{3kT} [1 + 1/3 \exp(J/kT)]^{-1} + N_\alpha \qquad (1)$$

where N_α is the temperature independent paramagnetism and the other constants have their normal meaning.

Another indication of exchange coupling in dimeric systems is the characteristic esr spectrum. The esr of a triplet state system consists of $2nI + 1$ lines with a hyperfine splitting $A/2$ where A is the normal splitting for the individual ions with a nuclear spin, I. In addition to the normal $\Delta M_S = \pm 1$ transitions, a "forbidden" $\Delta M_S = \pm 2$ half-field transition may be observed at g *ca.* 4 arising from the magnetic dipole-dipole interactions of the paramagnetic metal ions in a dimeric species. This half-field transition is usually only observed in the frozen solution spectrum and its presence is definitive evidence for an exchange coupled system.[31]

Most cases of exchange coupling have been reported for copper(II) dimers,which by the hole formalism can be treated as d^1 ions, and several reviews are available.[32,33] While there are fewer examples of exchange-coupled dimers among metals of the left side of the transition series a number of complexes have been prepared.

Martin and Winter investigated the magnetic behavior of $[Cp_2TiCl]_2$.[34] The complex is antiferromagnetic with a Neél temperature of 170°K indicating singlet and triplet states in thermal equilibrium. Assuming a titanium-titanium separation of *ca.* 3.5 Å, the singlet-triplet separation, J, was calculated to be $-387\ cm^{-1}$.

Coutts, Martin,and Wailes[35] investigated the magnetic susceptibilities of $[(Cp)_2TiX_2Ti(Cp)_2]$ (X=F,Cl,Br, and I). Characteristic singlet-triplet behavior was observed with the strength of the titanium-titanium interaction increasing in the order $F < Cl \simeq I < Br$. The values of the singlet-triplet separation, J, are -62, -159 to -186, -276, and -168 to -179 cm^{-1} for the F, Cl, Br, and I complexes, respectively.

Fowles, Lester, and Walton[28] prepared thioether complexes of the type $[TiX_3\cdot 2L]_2$ where X = Cl, Br, and I and L = dimethylsulfide or tetrahydrothiophene. For X = Cl the complexes are strongly antiferromagnetic with Neèl temperatures of *ca*. 320°K, while for X = Br or I Curie-Weiss behavior is exhibited. From the magnetic and far infrared data they concluded that the chloride complex is most likely a dimer with a direct metal-metal bond but they did not rule out the possibility of bridging chlorine atoms.

Smith, Lund, and Pilbrow[36] studied the esr spectra of a number of dimeric titanium(III) hydroxycarboxylic acids. Both the $\Delta M_s = \pm 1$ transition at g *ca*. 2 and the "forbidden" $\Delta M_s = \pm 2$ transition were observed giving definitive proof of exchange coupled dimers. Magnetic parameters were evaluated by computer simulation of the spectra. The metal-metal separation varies from 4.7 Å for the mandelic acid complex to 8.6 Å for the 8-hydroxyquinoline complex with most of the complexes having a separation of *ca*. 6.5 Å.

Carr, Boyd, and Smith[37] prepared the binuclear tetrakis(aminomethyl)-methane complex of titanium(III) chloride. The triplet state esr spectrum was observed with both the $\Delta M_s = 1$ and $\Delta M_s = 2$ transitions present. Computer generated spectra were compared with the experimental solution esr spectra and the titanium-titanium separation was found to be 5.6Å.

Only one exchange coupled molybdenum complex has been reported.[38] Huang and Haight prepared a binuclear molybdenum(V) oxoglutathione complex. They obtained a solution esr spectrum containing eleven lines using isotropically enriched ^{95}Mo, indicating electron exchange coupling in the dimeric complex. Under the imperfect assumption of axial symmetry the magnetic parameters were found to be $< g > = 1.962$, $g_{||} = 1.966$, $g_{\perp} = 1.960$, $< a > = 0.0029$ cm^{-1}, A = 0.0047 cm^{-1}, and B = 0.0020 cm^{-1}. The zero field splitting,D, is 0.0083 cm^{-1} which corresponds to a metal-metal separation of *ca.* 6.0 Å. The low field $\Delta M_s = \pm 2$ transition was not observed.

Carr, Boyd, and Smith[39] reinvestigated this system by computer simulation of the esr spectrum.They found that the symmetry is less than axial and the magnetic parameters which best fit the spectrum are $g_{||} = 1.97$, $g_{\perp} = 1.96$, R = 5.0 Å.

In marked contrast to the few complexes prepared with other early transition metals a large number of exchange coupled vanadyl complexes have been prepared.One of the earliest reports concerned the preparation of vanadyl complexes of tridentate Schiff bases. Ginsberg, Koubek, and Williams[40] investigated the magnetic susceptibilities of a series of 5-substituted N-(2-hydroxyphenyl)salicylideneimine complexes of VO^{2+}.The compounds are strongly antiferromagnetic with Neél temperatures ranging from 80 to 120°K.The singlet-triplet separation varies from -90 to -218 cm^{-1} with most of the complexes having J *ca.* 120 cm^{-1}. The results were interpreted to be due to a direct metal-metal interaction between unpaired spins of the d_{xy} orbitals of vanadium in contrast to the analogous copper complex where superexchange occurs through bridging oxygen atoms.

The most work on exchange coupled vanadyl compounds has been devoted to the study of anionic α- hydroxycarboxylates, particularly the tartrate complexes. Initially there was a great deal of controversy as to whether exchange coupling actually took place. Various authors offered differing explanations[41-45]. Tapscott and Belford[41] initially investigated the properties of vanadyl dl-tartrate in aqueous solutions. At pH greater than 7 they found a dimeric anionic complex was formed which contained two vanadyl ions bridged by two tetranegative tartrate groups. The solution esr spectrum exhibits fifteen lines indicative of exchange coupling with $< g > = 1.98$ and a hyperfine splitting of 40 gauss (about half the splitting of monomeric vanadyl d-tartrate). The magnetic moments are normal indicating the energy difference between the singlet and triplet states is small. The vanadium-vanadium distance was proposed to be *ca.* 4.0 Å as determined by molecular models and later confirmed by X-ray crystallography.

Dunhill and Smith[42] investigated both the vanadyl citrate and tartrate systems. They could not confirm the tartrate was dimeric from esr measurements since no hyperfine structure was observed in the low temperature spectrum and there was no linear variation of intensities. The vanadyl citrate complex is dimeric. The "forbidden" $\Delta M_S = \pm 2$ transition consisting of fifteen lines was observed at g *ca.* 4.05. The $g = 2$ portion of the spectrum was complicated and could not be unambiguously interpreted.

Dunhill and Symons[43] reinvestigated the vanadyl tartrate system because triplet state esr spectra like those reported earlier by Tapscott and Belford are normally not observed in solution. They observed the fifteen lines at g *ca.* 2 but in addition, they found a set of very weak high and low field satillite peaks which support the conclusion that a triplet state is involved.

Belford and coworkers[44] reinvestigated the tartrate system and a number of other α -hydroxycarboxylates. Contrary to Dunhill and Smith's results, the half-field, $\Delta M_s = \pm 2$, transitions were clearly visible giving definitive evidence for dimer formation. The zero field splitting was calculated to be *ca*. 0.033 cm^{-1}.

James and Luckhurst[45] by computer simulation of the esr spectrum, found that the tartrate complex is rigid in solution and the metal-metal separation is essentially the same as for the solid confirming Belford's work.

Recently, Smith and coworkers[46] investigated a series of other vanadyl α -hydroxycarboxylates by computer simulation of the esr spectra. With 1-hydroxycyclohexanecarboxylate they found a dimeric vanadyl complex was formed which gave a fifteen line esr spectrum with both the $g = 2$ and the $g = 4$ transitions present. The zero field splitting was calculated to be 0.055 cm^{-1} corresponding to a vanadyl separation of *ca*. 3.6 Å which is consistent with the analogous copper compound.

III. Purpose of This Work

In view of the number of electron exchange-coupled complexes which have been prepared with d^1 ions it is suprising that no such niobium(IV) complex has been reported. Exchange-coupled complexes of vanadium(IV) and titanium(III) have been prepared with bidentate oxygen donor ligands. Niobium(IV) reacts with most oxygen donor ligands to give paramagnetic complexes in which the metal-metal bond is completely cleaved. This reactivity of niobium(IV) to oxygen and water and its ability to abstract oxygen from donor solvents seriously limits the number of ligands which could be used to prepare dimeric electron exchange coupled complexes. Metal-metal bonding occurs much more often in niobium(IV) complexes with sulfur donor ligands. The complexes in which metal-metal bonding occurs have been prepared with neutral sulfur donor ligands and are diamagnetic. In an attempt to prepare exchange coupled niobium(IV) complexes a different type of sulfur donor ligand was used. The uninegative, bidentate ligand, sodium dimethyldithiophosphate (NaDmtp), has been found to form a large number of substitution complexes with other metals of varying size.[47] It was hoped that by replacing only the nonbridging halogen atoms in NbX_4 that an exchange-coupled complex could be prepared in order to gain insight into the metal-metal bonding which characterizes much of the chemistry of niobium(IV).

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.

A. Materials

High purity (99.9%) niobium metal and niobium pentachloride were purchased from Alpha Inorganics. Phosphorus pentasulfide was obtained from Matheson, Coleman, and Bell and was used as received. Analytical grade methanol was obtained from J.T. Baker Chemical Co. and was dried by refluxing over sodium methoxide. Analytical grade methylene chloride was purchased from J.T. Baker Chemical Co. and was dried by refluxing over calcium hydride. It was distilled under nitrogen atmosphere and stored over molecular sieves.

B. Preparation of Niobium Halides

Niobium pentabromide, niobium pentaiodide, and the three tetrahalides were prepared by using procedures previously described.[48,49]

C. Preparation of sodium dimethyldithiophosphate

An excess of dry methanol was allowed to react with phosphorus pentasulfide according to the equation:

$$P_2S_5 + 4CH_3OH \rightarrow 2HS_2P(OCH_3)_2 + H_2S \qquad (2)$$

The crude dimethydithiophosphoric acid was purified by distillation under a vacuum of 5 torr over a temperature range of 80 - 85°C and was obtained as a viscous, colorless liquid. The acid was dissolved in an equal volume of anhydrous ether and neutralized with excess anhydrous sodium carbonate. The sodium dimethyldithiophosphate(NaDmtp) was dissolved in anhydrous spectrograde acetone and the solution was filtered. The solvent was removed by pumping under dynamic vacuum at room temperature and the salt was stored in the drybox.

D. Analytical Determinations

Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Preliminary analyses were performed to determine halogen. Samples of the complexes were added to aqueous ammonia and heated until solution was complete. The samples were cooled and acidified with dilute nitric acid. The solution was filtered and the filtrate was analyzed for halogen ion by potentiometric titration with standard silver nitrate solution. A Beckman expanded scale pH meter was used in conjunction with a silver indicating and a saturated calomel reference electrode. Niobium was not determined due to the presence of phosphorus.

E. Molecular Weight Determinations

The molecular weight of the complexes was determined cryoscopically in dry benzene. Recrystallized benzil was used as the calibrating solute in the determination of the molal freezing point depression constant of benzene (5.38°C $\underline{m}^{-1}$). Freezing point depressions were measured in the concentration range 0.01 to 0.08 $\underline{m}$ with a Beckman differential thermometer graduated at 0.01° intervals. Temperature readings were estimated to ± 0.001° with the aid of a magnifying thermometer reader.

F. Conductance Measurements

Molar conductivities were measured with a Wayne-Kerr Model B221 universal bridge and a Freas type solution cell with bright platinum electrodes. The cell constant was determined to be 0.2175 cm^{-1} at 25°C by using a standard KCl solution. Both purified nitromethane and methylene chloride were used for molar conductance measurements.

G. Electron Spin Resonance Spectra

All esr spectra were obtained on solutions and powders 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. Low temperature spectra were obtained by use of a liquid nitrogen insert dewar or a Varian Model V4540 variable temperature controller. Samples were sealed in quartz tubes under a nitrogen atmosphere. The magnetic field was calibrated using strong pitch ($g=2.0028$).

H. Nuclear Magnetic Resonance Spectra

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

I. Electronic Spectra

Solution spectra were recorded using a Cary Model 17 spectrophotometer. Cylindrical fused silica cells, 1.0 cm long and adapted for use at low pressure (Figure 1), were used.[48] Saturated solutions were loaded in the dry box. 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 distilled through a medium porosity frit into the cell.

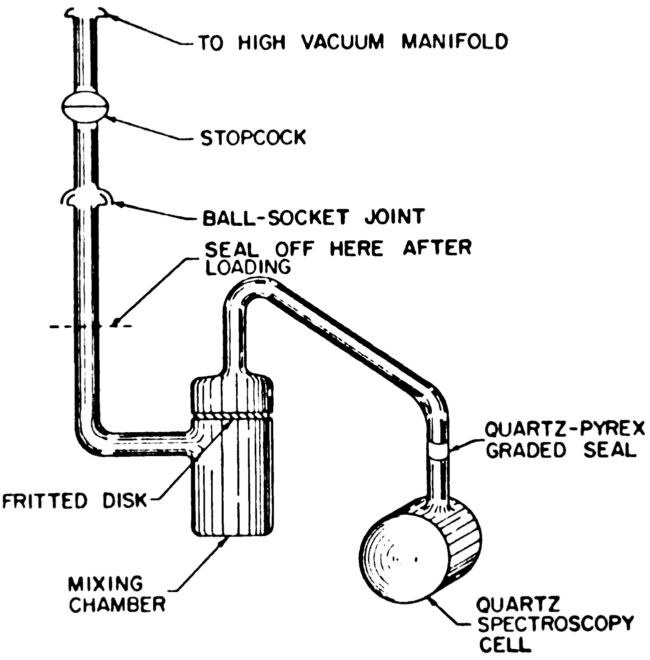


Figure 1. (Taken from Reference 48) Apparatus for determination of electronic spectra.

J. Vibrational 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 (3900-20cm^{-1}) far infrared Fourier-transform spectrophotometer. High density polyethylene was used for windows.

K. Magnetic Susceptibility Measurements

Magnetic susceptibility measurements were obtained using an Alpha electronic Faraday balance. An Alpha model 4600 magnet provided with variable gap, four-inch pole pieces and constant H·dH/dZ pole caps was used with an Alpha model 3002-1 current regulated power supply. Force measurements were obtained with an Alpha electrobalance to detect weight change between field-on and field-off conditions. The electrobalance, suspension wire, and sample container were protected from air currents and moisture condensation by a vacuum enclosure.

The sample temperature was maintained using an Alpha model 3013 temperature regulator which was calibrated with a platinum resistance thermometer. The sample container was machined from teflon rod to form a cylindrical bucket 10mm. in length and 7 mm. in diameter. A threaded cap on the bucket permitted a tight seal to prevent decomposition due to exposure to air. The samples were loaded into bucket in the drybox.

The compound $(NH4)_2Ni(SO_4)_2 \cdot 6H_2O$ was used as a magnetic susceptibility standard. Simmons[50] has indicated that nickel ammonium sulfate hexahydrate is one of the most satisfactory of several common standards. With this material consistently reproducible results were obtained. The temperature dependence of the magnetic susceptibility of this standard follows the relationship:

$$\chi_g = (3065/T + 0.5) \times 10^{-6} \text{ emu/g.} \qquad (3)$$

L. Syntheses

1. Tetrakis(dimethyldithiophosphato)niobium(IV)

A 3-5 g sample of NbX_4 (X=Cl, Br, I), excess NaDmtp, and a magnetic stirring bar were introduced into a round bottom flask. The flask was evacuated to *ca.* 10^{-5} torr and 50-80 ml of methylene chloride was vacuum distilled into the flask. The flask was isolated from the vacuum system and the mixture was stirred for 4-5 days at room temperature. A yellow solution and a yellow-brown precipitate were obtained. The precipitate was recovered by filtration, extracted with methlyene chloride, and filtered again to remove sodium halide. A yellow, crystalline solid was recovered from the filtrate by removal of methylene chloride *in vacuo*. This product was then washed with dry pentane and dried *in vacuo*.

Anal. Calcd. for $Nb(Dmtp)_4$: Nb, 12.9; C, 13.3; H, 3.35; S, 35.5. Found: Nb, 12.9; C, 13.2; H, 3.28; S, 35.1. Molecular weight in benzene: Calcd., 721; Found, 660. M.P., 128° C with decomp.

2. Dichloro-μ-dichlorotetrakis(dimethyldithiophosphato)diniobium(IV)

A mixture of 1.20 g. of $NbCl_4$ and 1.85 g. of NaDmtp were placed in a round bottom flask in the same manner as above and stirred for 7-8 days. The solution and solid obtained were both dark green-brown. The complex was recovered as described above.

Anal. Calcd. for $Nb_2Cl_4(Dmtp)_4$: Nb, 19.5; C, 10.0; H, 2.5; S, 26.8; Cl, 14.9. Found: Nb, 19.6; C, 10.2; H, 2.3; S, 22.6; Cl, 14.5. Molecular weight in benzene: Calcd., 956; Found: 935. Molar conductance in nitromethane: 45 ohm^{-1} cm^{-1} M^{-1}

3. Dibromo-μ-dibromotetrakis(dimethyldithiophosphato)diniobium(IV)

The bromide complex was prepared in exactly the same manner as the chloride complex. A mixture of 2.12 g of $NbBr_4$ and 1.85 g of NaDmtp was allowed to react. The resulting solution and solid were both a deep red-brown.

Anal. Calcd. for $Nb_2Br_4(Dmtp)_4$: Nb, 16.4; C, 8.4; H, 2.1; S, 22.6; Br, 28.2. Found: Nb, 16.3; C, 8.4; H, 2.1; S, 22.5; Br, 27.8. Molecular weight in benzene: Calcd., 1134; Found 1165. Molar conductance in nitromethane: 50 ohm^{-1} cm^{-1} M^{-1}

4. Diiodo-μ-diiodotetrakis(dimethyldithiophosphato)diniobium(IV)

The iodide complex was also prepared in the same manner as the chloride complex. A mixture of 3.08 g of NbI_4 and 1.85 g of NaDmtp was allowed to react. The resulting solution and solid were a deep red-brown color.

Anal. Calcd. for $Nb_2I_4(Dmtp)_4$: Nb, 14.1; C, 7.25; H, 1.81; S, 19.4; I, 38.4. Found: Nb, 14.5; C, 7.52; H, 1.88; S, 20.2; I, 38.6. Molecular weight in benzene: Calcd., 1322; Found, 1396. Molar conductance in nitromethane: 39.6 ohm^{-1} cm^{-2} M^{-1}.

V. Results and Discussion

A. Preparation and Properties of Complexes

The reaction of the niobium(IV) halides with excess sodium o,o-dimethyldithiophosphate in toluene or dichloromethane proceeds according to equation 4.

$$NbX_4 + 4NaDmtp \rightarrow Nb(Dmtp)_4 + 4NaX \qquad (4)$$

The complex was isolated as a light yellow powder which is quite soluble in benzene, toluene, and dichloromethane. The complex is air and water sensitive as indicated by a color change and the distinctive odor of the dithiohposphoric acid on exposure to such conditions. The complex melts with decomposition over the range of 123-128°C.

If only two moles of sodium dimethyldithiophosphate are present reaction occurs according to equation 5.

$$2NbX_4 + 4NaDmtp \rightarrow Nb_2X_4(Dmtp)_4 \qquad (5)$$

The complexes are obtained as deep red powders which are only slightly soluble in toluene and dichloromethane. These complexes are also air and moisture sensitive. They each react with additional sodium dimethyldithiophosphate to give $Nb(Dmtp)_4$ according to equation 6.

$$Nb_2X_4(Dmtp)_4 + 4NaDmtp \rightarrow 2Nb(Dmtp)_4 + 4NaX \qquad (6)$$

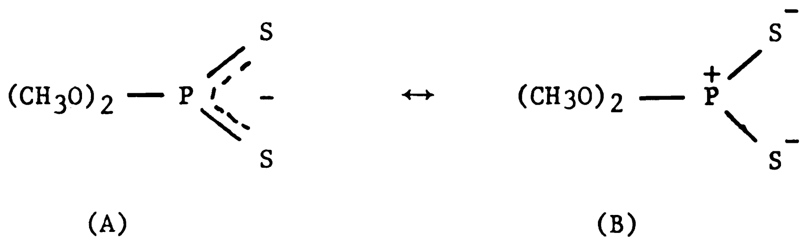
This also indicates that the oxidation state of niobium remains +4 throughout. While Machin and Sullivan[22] reported the diethyldithiocarbamate complex, $Nb_2(Detc)_5Br_3$, no evidence was found for a corresponding dithiophosphate compound.

B. Vibrational Spectra

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

Dimethyldithiophosphoric acid has been studied in the infrared region by McIvor, Grant, and Hubley[51] who assigned the vibrations by comparison of the spectrum with those of other substituted phosphates. The results from this study of NaDmtp are presented in Table 1. Assignments were made by comparing the infrared spectra of the free acid and the sodium salts of dimethyldithiophosphate and diethyldithiophosphate. Infrared spectral data of the complexes are presented in Tables 2 and 3.

In complexes containing Dmtp, bonds due to phosphorous-sulfur stretching modes are expected to be most sensitive to coordination via sulfur. Casey, MacKay, and Martin[52] suggested that Dmtp^{1-} may be depicted by the resonance forms in equation 7.



(7)

Two ν(P-S) modes are observed in NaDmtp at 560 and 740 cm^{-1}. On coordination both are shifted to higher energy to *ca.* 600 and 790 cm^{-1} which is expected as the bond order of the phosphorous-sulfur bond is increased, as shown in the resonance forms.

Table 1

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

	$\nu(cm^{-1})$		
Assignment	HDmtp		NaDmtp
	McIvor *et al*[51]	This work	
ν(C-H)	3070 m	2980 m(sh) 2935 s	2920 m
ν(S-H)	2500	2450 s(b)	
$\delta(CH_3)$	1460 m	1445 s	1430 m
$\nu(P-OCH_3)$			1203 m
$\nu(CH_3-O)$	1185 m	1175 s	1170 m
$\nu(P-OCH_3)$	1030 s(b)	1010 s(b)	1015 s(b)
CH_3 rock			630 m
ν(SP=S)	658 s(b)	650 s(b)	
unassigned bands		2830 m	3350 m(b)
		1830 w	1605 m(b)
		1310 w	1145 w
		945 m	1100 w
	815 m	850 m	655 w

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

Table 2

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

$\nu(cm^{-1})$

Assignment	This work
ν (P-OCH$_3$)	1198 m
ν (O-CH$_3$)	1165 s
ν (P-OCH$_3$)	1015 s(b)
ν (P-S)	788 m(b)
unassigned bands	1308 m 1253 s 1148 w(sh) 965 s(b) 885 w 680 w 650 w

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

Table 3

Infrared Spectral Data for $Nb_2(Dmtp)_4X_4$ (4000-600 cm^{-1})

	$\nu(cm^{-1})$		
Assignment	Cl	Br	I
$\nu(P-OCH_3)$	1200 w	1198 w	1198 w
$\nu(O-CH_3)$	1163 m	1163 m(b)	1163 m
$\nu(P-OCH_3)$	1012 m(b)	1015 m(b)	1008 s(vb)
$\nu(P-S)$	790 m(b)	788 m(b)	790 s(b)
CH_3 rock	632 w(sh)	630 w(sh)	635 m
unassigned bands	1310 m	1308 m	1308 m
	1255 s	1253 s	1253 s
	1150 w(sh)	1148 w(sh)	1150 w(sh)
	965 s(b)	960 s(vb)	965 m(sh)
	930 m(sh)		
	885 w	885 w(sh)	885 w(sh)
		840 w	
	765 w	765 w(sh)	
	680 w	680 w	680 w
	650 w		650 w

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

Far infrared spectra (600-50cm^{-1})

The far infrared spectra were recorded for the free acid and its sodium salt and are presented in Table 4. The far infrared spectral data for Nb(Dmtp)$_4$ are presented in Table 5. The niobium-sulfur bands were assigned by comparison of the spectra of the complex with that of NaDmtp and other dithiophosphate complexes.[53] Two strong, broad bands which are observed at 385 and 345 cm^{-1} but are not present in NaDmtp are assigned as ν(Nb-S) modes.

The far infrared spectra for Nb$_2$(Dmtp)$_4$X$_4$ complexes are presented in Table 6. The two strong, broad bands observed at *ca.* 350 and 390cm^{-1} are assigned as ν(Nb-S). These bands are in the range typically found for eight-coordinate sulfur donor complexes of niobium(IV), 320-270 cm^{-1}.[20-22, 53]

Halogen sensitive bands are also found when the spectra of the complexes are compared. In Nb$_2$(Dmtp)$_4$Cl$_4$ the band at 302 and its shoulders at 313 and 273 cm^{-1} have been assigned as ν(Nb-Cl) modes. This band is in the range (299-310 cm^{-1}) typically found for ν(Nb-Cl) in eight-coordinate niobium complexes.[23, 54] The shape of the band, its relative intensity, and its absence in NaDmtp and the other complexes support this assignment.

By using the ratio ν(Nb-Br)/ν(Nb-Cl) = 0.76 that was found for the monodentate thioether adducts of NbX$_4$[29], one expects to find a ν(Nb-Br) mode *ca.* 230 cm^{-1}. A band not present in NaDmtp, Nb(Dmtp)$_4$ nor in the chloride and iodide complexes is found at 235 cm^{-1} with a shoulder at 202 cm^{-1} and is assigned as ν(nb-Br). The ratio ν(Nb-I)/ν(Nb-Cl) calculated as 0.56[29] predicts a ν(Nb-I) mode *ca* 169cm^{-1}. A band is observed at 173 cm^{-1} with shoulders at 183 and 158 cm^{-1} and is assigned as ν(Nb-I).

Table 4

Far infrared Spectral Data for Dmtp$^-$ (600-50 cm^{-1})

Assignment	ν(cm^{-1})		
	HDmtp		NaDmtp
	McIvor *et al.*[51]	This work	
ν(P-S)			560 s
ν(P-SH)	525 s(b)	525 m	
	493 s(b)	490 m	
δ(P-O-CH$_3$)		423 m	428 m
unassigned bands		390 w	528 m
		365 w(sh)	508 w
		340 m	435 w
			395 w
			375 m
			367 m
			328 m
			315 w
			305 w
			295 w
			240 s(b)
			220 w
			200 w
			182 w
			172 w

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

Table 5

Far Infrared Spectral Data for $Nb(Dmtp)_4$ (600-50 cm^{-1})

Assignment	$\nu(cm^{-1})$
ν(P-S)	595 s
ν(Nb-S)	385 s, 345 s
unassigned bands	515 m 502 m 433 m 425 w 390 m(b) 375 w(sh) 360 m 295 w 273 s(b) 255 w 235 m 225 w 190 m 178 m 170 w

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

Table 6

Far Infrared Spectral Data of $Nb_2(Dmtp)_4X_4$ Complexes (600-50 cm^{-1})

$\nu(cm^{-1})$

Assignment	X = Cl	X = Br	X = I
ν(P-S)	600 s	600 s(b)	600 s(b)
ν(Nb-S)	390 s	388 s	387 s
	350 m	353 m	350 m
ν(Nb-X)	313 m(sh)		183 m(sh)
	302 s	235 s(vb)	173 s
	273 m(sh)	202 m(sh)	158 m(sh)
unassigned bands	512 m	512 m	520 m(sh)
	485 s(b)	470 m(b)	510 m
	465 w	435 w	490 m(sh)
	455 m	430 w	485 s
	440 m	405 w	468 m
	435 w	375 w	452 m
	425 w	365 m(b)	438 w
	412 w(sh)	345 m(sh)	420 w
	400 w	325 w	400 w(sh)
	370 w	310 m	372 m
	330 m(b)	300 s	362 m
	287 w(sh)	283 m	320 w
	255 m	278 w(sh)	295 m
	237 s(b)	255 m	280 w
	220 m	220 w(sh)	275 m
	208 w	205 w	265 w
	187 s	185 w	255 w
	177 m	170 m	243 s(b)
	168 w	140 w	225 w
	160 w		203 w
			183 w
			170 w

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

C. NMR Spectra of $Nb_2(Dmtp)_4X_4$ (X = Cl, Br)

The proton magnetic resonance data are presented in Table 7.

Table 7

Proton Magnetic Resonance Data

Compound	Chemical Shift (τ)	J_{POCH_3} (Hz)
$(CH_3O)_2PS_2Na$	6.40	14.8
$Nb_2(Dmtp)_4Cl_4$	6.40 6.21	15.0 15.0
$Nb_2(Dmtp)_4Br_4$	6.30 6.16	15.0 15.0

The spectra exhibit doublet structure from ^{31}P splitting of the methyl peak. Two different methyl resonances are observed, indicative of nonequivalent methyl groups. The chemical shifts and $POCH_3$ coupling constants are similar for the chloride and bromide complexes and are not greatly different from those of sodium dimethyldithiophosphate. This implies that transmission of metal d orbital effects *via* sulfur and phosphorus outer d orbitals is negligible[55] and that the orbital hybridization employed by phosphorus is essentially constant. No spectrum was observed for the iodide complex due to its paramagnetism, which will be discussed later.

D. Electronic Spectra

$Nb(Dmtp)_4$

Visible and near infrared spectra were studied by using the technique described in the experimental section. These studies were carried out with dichloromethane solutions of the complexes. The spectrum and and wavelength maxima are given in Figure 2 and Table 8 respectively for $Nb(Dmtp)_4$.

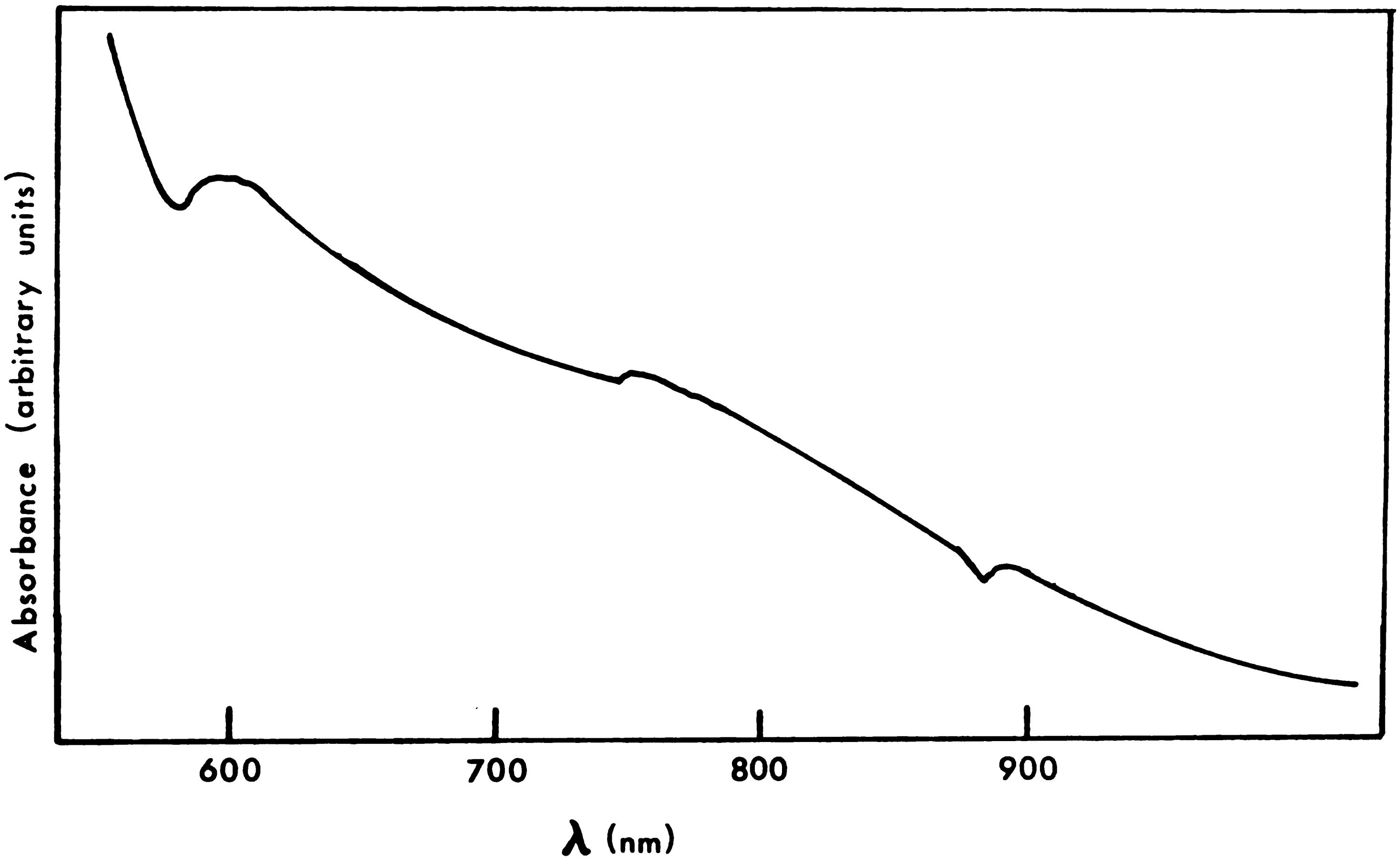


Figure 2. Electronic Spectrum of Nb(Dmtp)$_4$ in CH_2Cl_2 Solution.

Table 8

Electronic Spectral Data for Nb(Dmtp)$_4$ in CH_2Cl_2

λ (nm)	ε
890 sh (b)	0.96
765 sh (b)	1.92
610 sh (b)	2.18
260 (b)	

$c = 2.30 \times 10^{-2}$ M

The qualitative features of the spectrum include three weak broad bands at 890, 765 and 610 nm. In addition a strong broad band is observed at 260 nm. This intense band in the ultraviolet region is due to ligand charge transfer. This assignment was confirmed by observing an identical band at 260 nm for a dichloromethane solution of the isomorphous Zr(Dmtp)$_4$.

There are three possibilities for assigning the bands in the visible and near ir regions: The bands may be due to (1) d-d transitions, (2) metal to ligand charge transfer, and (3) ligand to metal charge transfer. In view of the low intensities of the bands at 890, 765 and 610 nm (ε = 0.96, 1.92 and 2.18 $M^{-1}cm^{-1}$ respectively) they can confidently be assigned as arising from d-d transitions. For an eight-coordinate transition metal complex two common symmetries are observed: the D_{2d} triangular dodecahedron and the D_{4d} square antiprism. Figure 3 shows the crystal field splitting diagrams for a D_{2d} dodecahedron and a D_{4d} square antiprism.[16, 55] In the case of D_{4d} symmetry, two d-d transitions are predicted while for D_{2d} symmetry three transitions are predicted. Since three bands were observed which are assigned as d-d transitions a D_{2d} dodecahedral symmetry is

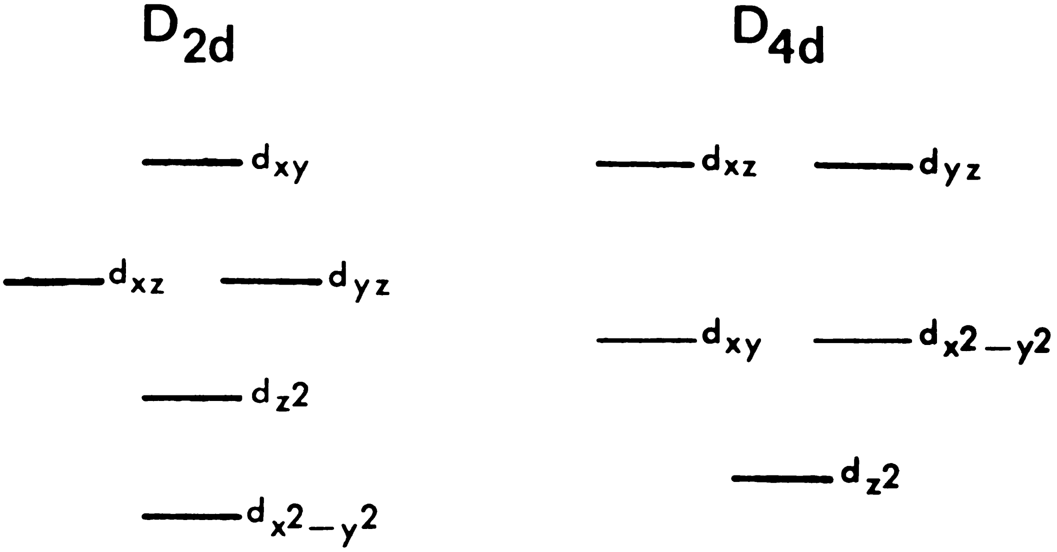


Figure 3. The crystal field splitting for D_{2d} and D_{4d} symmetries

suggested for Nb(Dmtp)$_4$. Further confirmation of this symmetry will be discussed when the esr data are presented.

Nb$_2$(Dmtp)$_4$X$_4$ complexes

The solution spectra and wavelength maxima are given in Figures 4,5, and 6 and Table 9 respectively for the Nb$_2$(Dmtp)$_4$X$_4$ complexes. The solution spectra consist of five bands for the chloride compound and six bands for the bromide and iodide compounds. All the observed bands are broad and there is a large uncertainty in their maxima. The ligand charge transfer band is observed in all three complexes *ca.* 38 kK. All the compounds exhibit peaks corresponding to those found in the spectrum of Nb(Dmtp)$_4$ with the exception of the chloride which lacks the band at 11.2 kK. In addition, all of the complexes have two peaks *ca.* 22.0 kK and 26.0-28.0 kK which are not present in the spectrum of Nb(Dmtp)$_4$.

Hansen and Ballhausen[57] observed bands at 14.0 and 27.0 kK in the electronic spectrum of dimeric copper acetate monohydrate. The band at 14.0 kK closely resembled the band observed at 14.0 kK in the spectrum of copper sulfate. A theoretical treatment of the spectra using a coupled chromophore model indicated the band at 27.0 kK, which is not present in the spectra of monomeric copper(II) complexes, arises from a double excitation. Their calculations predicted a number of such double excitations ranging in energy from 23.0 to 30.0 kK. Brown and Newton[26] attributed a band at 26.0 kK to a niobium-niobium bond in the spectrum of diamagnetic triethylamine adducts of NbCl$_4$ and NbBr$_4$. In light of Hansen's calculations this band can be assigned as a double excitation and while it is not evidence for a direct metal-metal bond, it does indicate a significant metal-metal interaction.

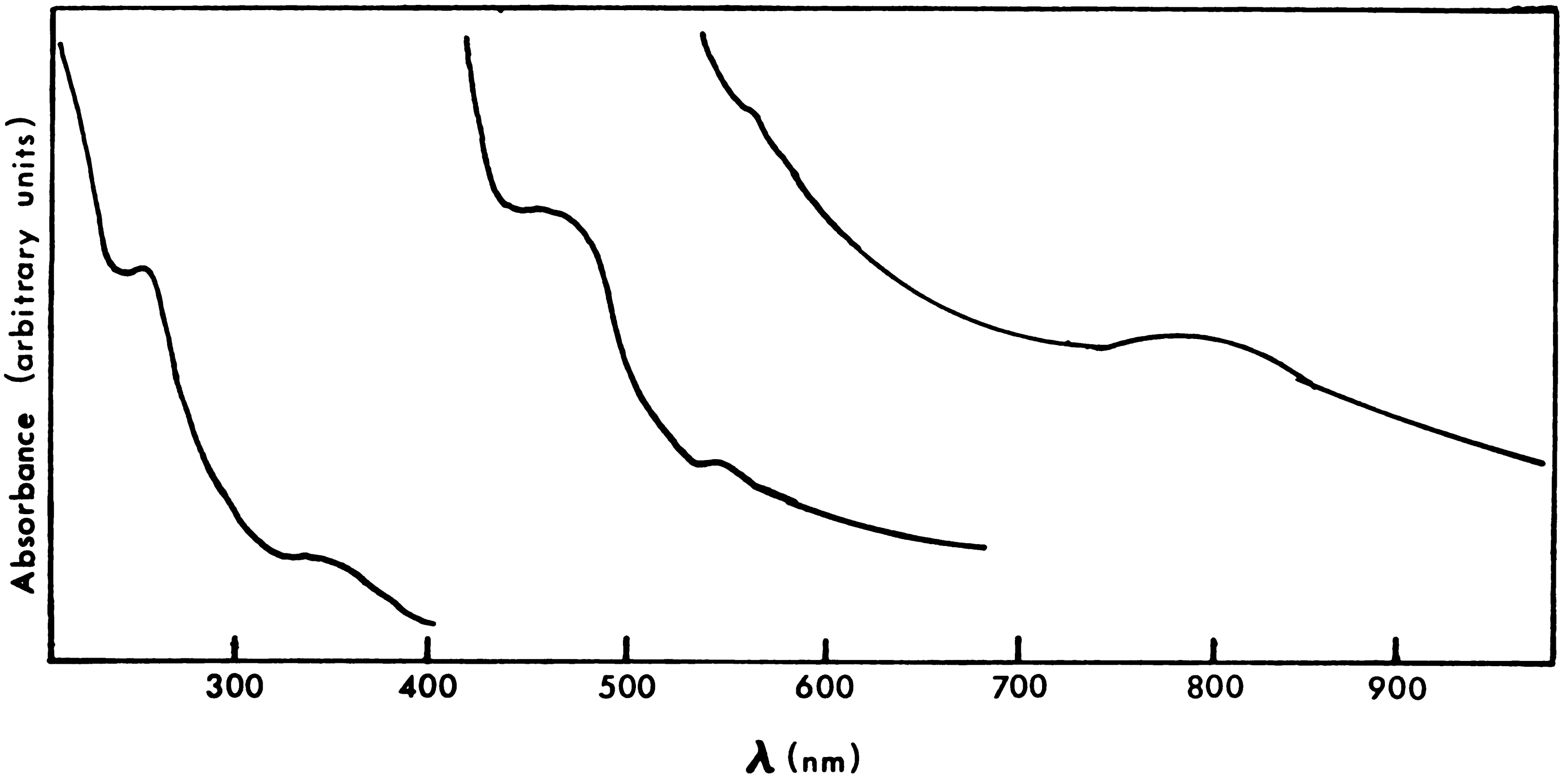


Figure 4. Electronic Spectrum of $Nb_2(Dmtp)_4Cl_4$ in CH_2Cl_2 Solution.

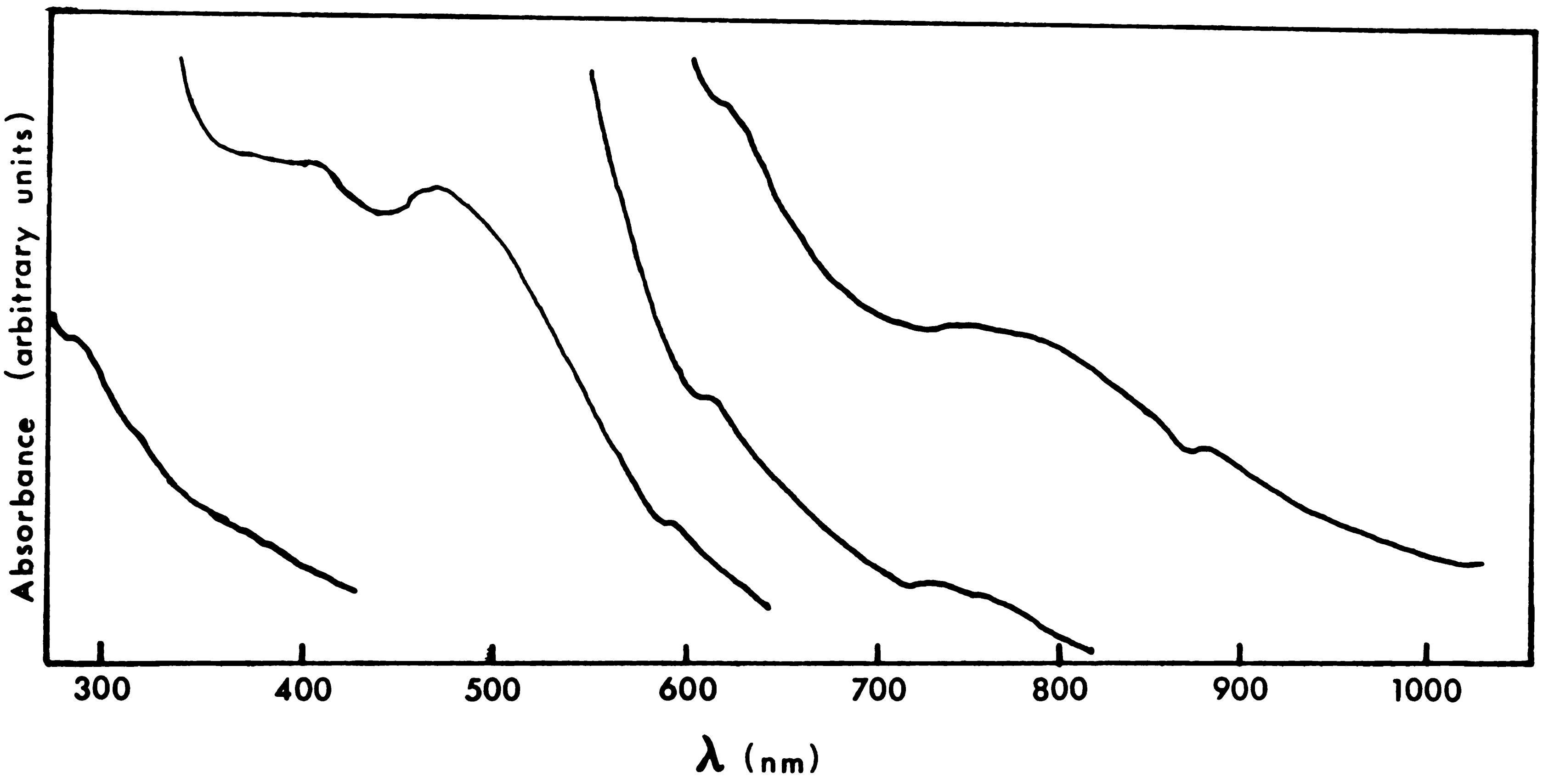


Figure 5. Electronic Spectrum of $Nb_2(Dmtp)_4Br_4$ in CH_2Cl_2 Solution.

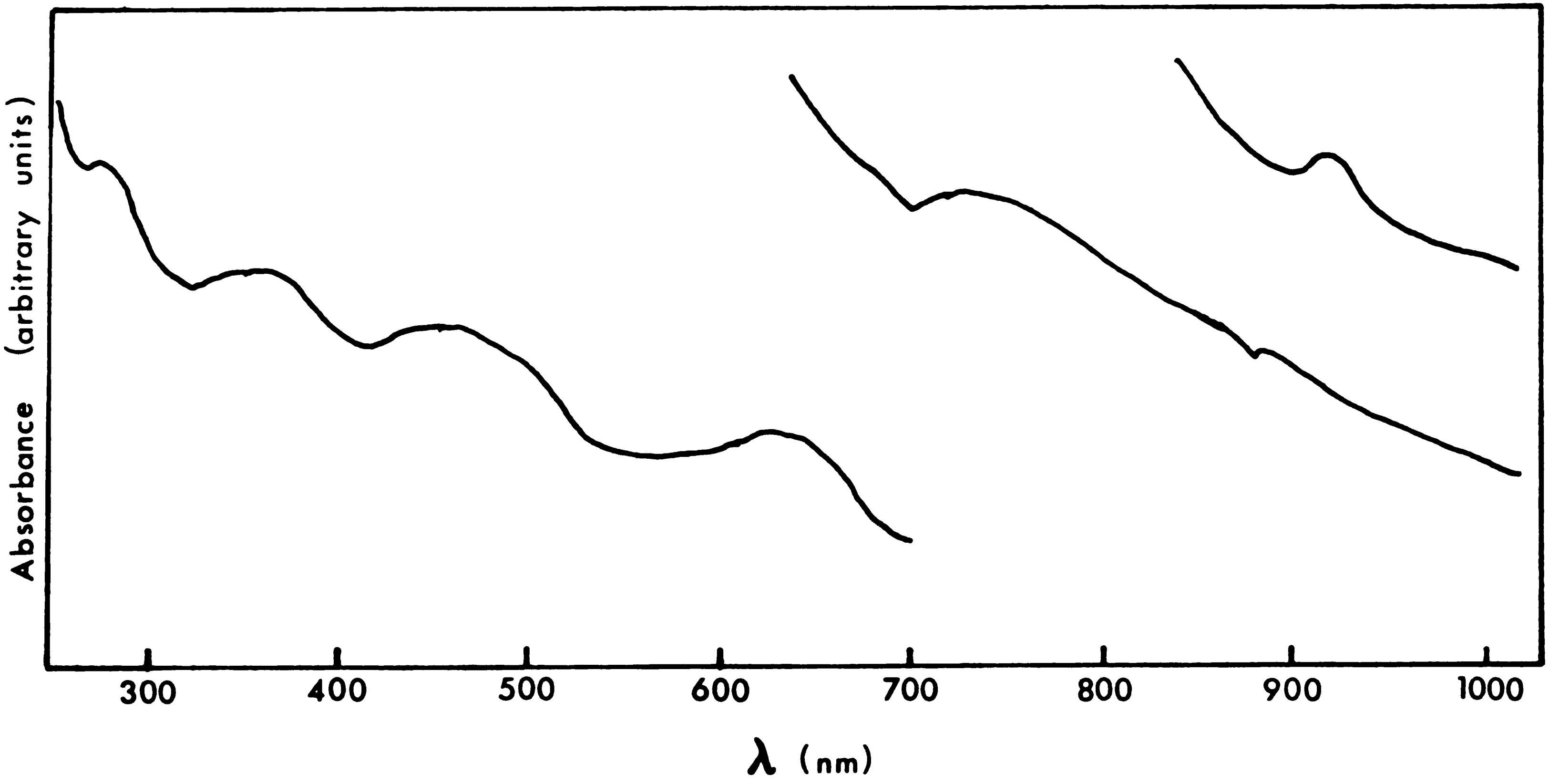


Figure 6. Electronic Spectrum of $Nb_2(Dmtp)_4I_4$ in CH_2Cl_2 Solution.

Table 9

Electronic Spectral Data of $Nb_2(Dmtp)_4X_4$ Complexes in CH_2Cl_2

Complex	λ(nm)	ε(cm^{-1} M^{-1})
X = Cl	750	3.25
	555	7.48
	460	25.7
	355	62.3
	260	713.0
X = Br	895	4.05
	770	9.18
	610	22.5
	455	70.3
	390	76.2
	270	733.0
X = I	890	4.90
	740	8.23
	595	19.6
	450	54.7
	380	65.2
	260	721.0

For a compound in which electron coupling occurs and the ground state splitting is small enough that both the singlet and triplet ground levels are populated at room temperature, the observed room temperature spectrum will contain both singlet-singlet and triplet-triplet transitions. These transitions are not expected to occur at equal energies[57] and therefore, the observed spectra are broad. In addition, Fowles and coworkers[58] found that in the acetonitrile adducts of the niobium tetrahalides halogen(π) → niobium(d) transitions occur throughout the visible region and as a result, the d-d transitions can be partially masked.

The band observed from 26,000-28,000 cm^{-1} can now confidently be assigned as due to a doubly excited transition. The bands at 11,000; 13,000; and 16,000 cm^{-1} are most likely due to d-d transitions on the basis of extinction coefficients and their presence in the spectrum of $Nb(Dmtp)_4$. The assignment of the peak at 22,000 cm^{-1} is unclear.It is unlikely that it arises from a d-d transition due to its intensity. However, it could arise from either a doubly excited transition or halogen(π) → niobium(d) charge transfer.

The dimeric $Nb_2(Dmtp)_4X_4$ posseses so many nonequivalent ligands that an exact structural determination based on chemical and physical properties alone is virtually impossible. However, if a number of assumptions are made a good approximation of the structure is possible.

The relative nonlability of the bridging halides in NbX_4[25] suggests that the dimeric complexes contain bridging halogen atoms rather than bridging dithiophosphate ligands or a direct metal-metal bonded complex. The infrared spectrum bears out this assumption. Secondly, the fact that the dimeric complexes react slowly with additional NaDmtp to form the paramagnetic $Nb(Dmtp)_4$ indicates that both metal atoms are in the +4 oxidation state rather than a Nb^{3+} - Nb^{5+} pair.With these two assumptions the number of possible isomers is reduced to four.Of these four possible isomers only one, the D_{2h} isomer, will give three d-d transitions in its electronic spectrum. The crystal field splitting diagram for D_{2h} symmetry is presented in Figure 7.

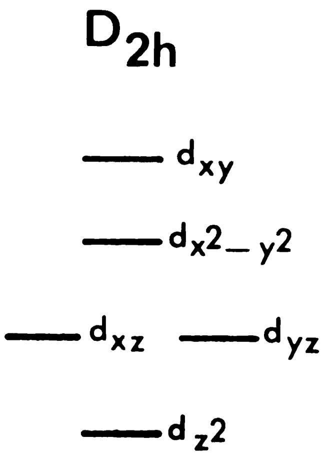


Figure 7. The crystal field splitting diagram for D_{2h} symmetry

Considering the atoms bonded directly to niobium the most likely structure has D_{2h} point symmetry (C_{2v} about each niobium atom) and is shown in Figure 8. The niobium atoms in this structure are seven-coordinate (excluding the metal-metal bond). While the dithiophosphate ligands are chemically equivalent, the methyl groups on each dithiophosphate are not.

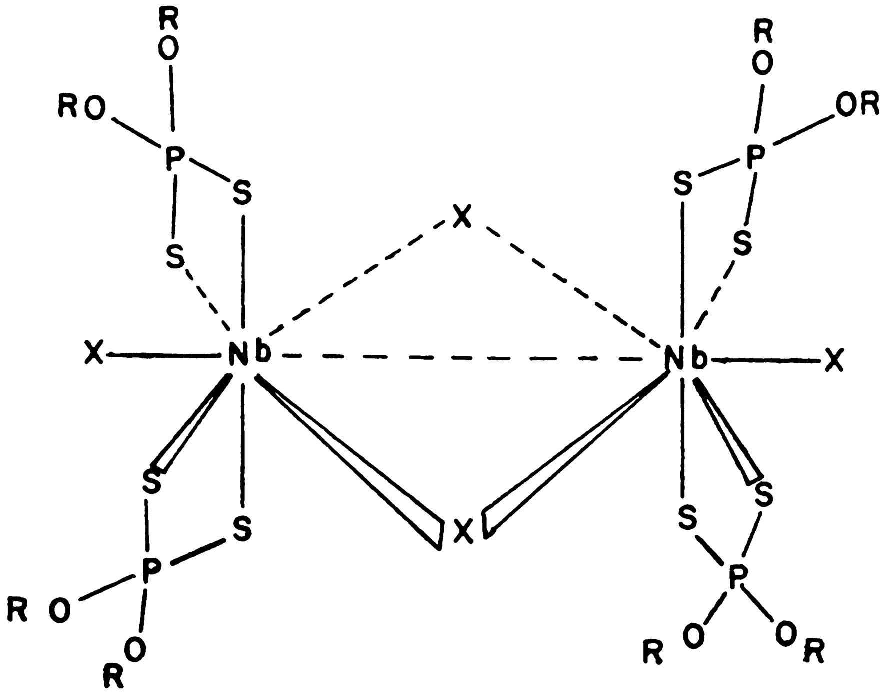


Figure 8. Proposed Structure for $Nb_2(Dmtp)_4X_4$

E. Electron Spin Resonance Spectra

Nb(Dmtp)$_4$

Esr studies were performed as described in the Experimental section.The spectra are presented in Figures 9, 10, and 11. Since the hyperfine splittings are on the order of 150 gauss the high field approximation cannot be rigorously 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[59]:

$$h\nu = g\beta H_o \qquad (8)$$

for isotropic g
$$H_o = H_m + \langle a\rangle m_I + \frac{\langle a\rangle^2}{2H_o}\left[\, I(I+1) - m_I^2 \,\right] \qquad (9)$$

for $g_{||}$
$$H_o = H_m + A_{||} m_I + \frac{A_{\perp}^2}{2H_o}\left[\, I(I+1) - m_I^2 \,\right] \qquad (10)$$

for $g_{\perp}$
$$H_o = H_m + A_{\perp} m_I + \frac{(A_{||}^2 + A_{\perp}^2)}{4H_o}\left[\, I(I+1) - m_I^2 \,\right] \qquad (11)$$

where H_m is the magnetic field position of the esr line due to the component m_I of the nuclear spin I, ν is the klystron frequency, and $\langle a\rangle$, $A_{||}$, and $A_{\perp}$ are the hyperfine splitting constants. The calculations are necessarily reiterative and were carried out by 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

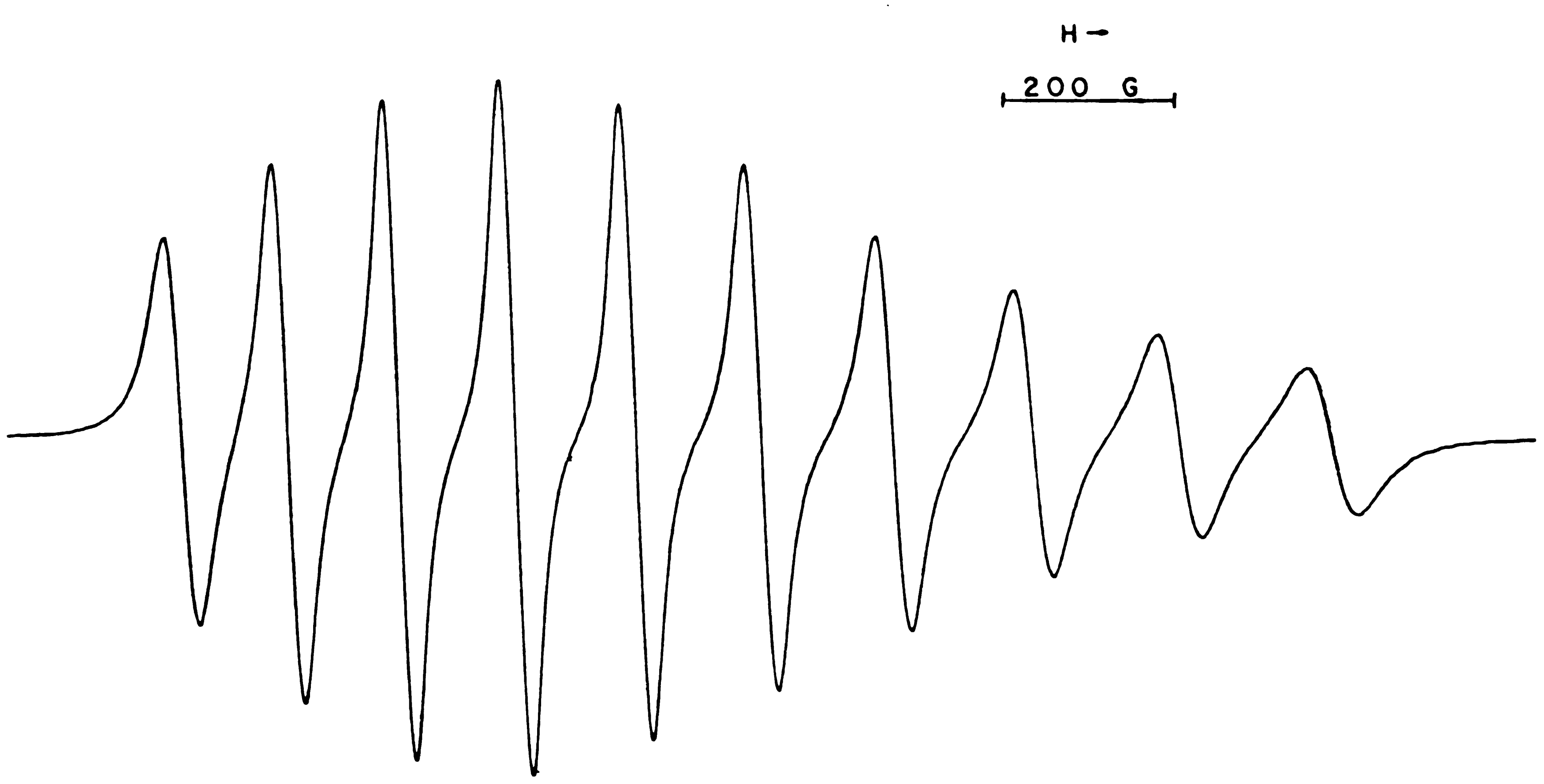


Figure 9. Esr Spectrum of Nb(Dmtp)$_4$ in CH_2Cl_2 at Ambient Temperature

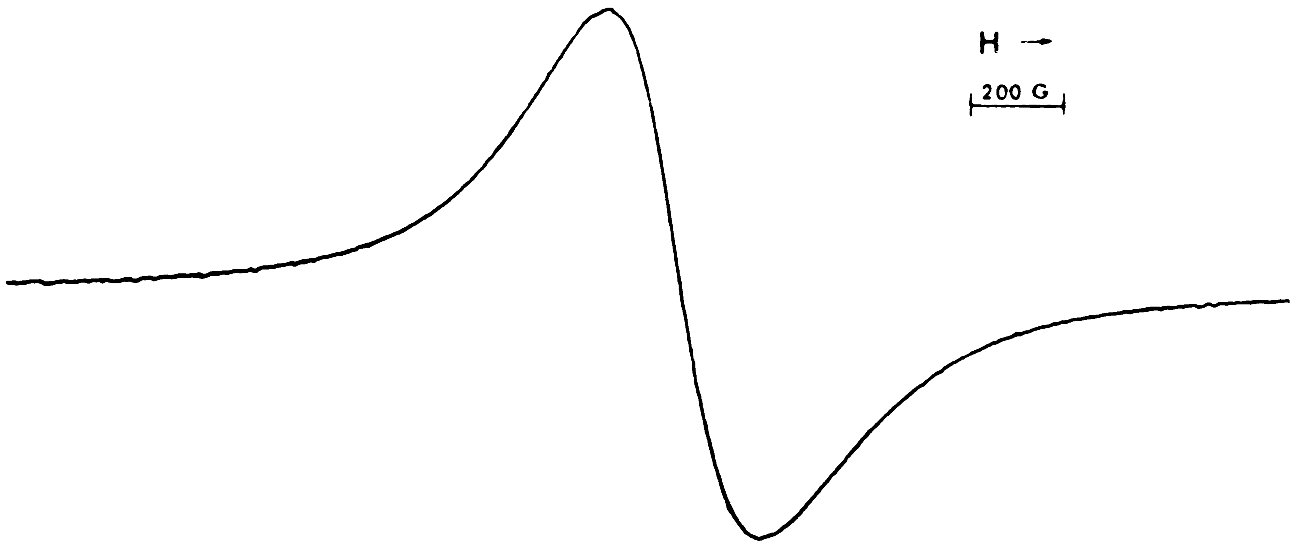


Figure 10. Esr Spectrum of Solid Nb(Dmtp)$_4$ at Ambient Temperature

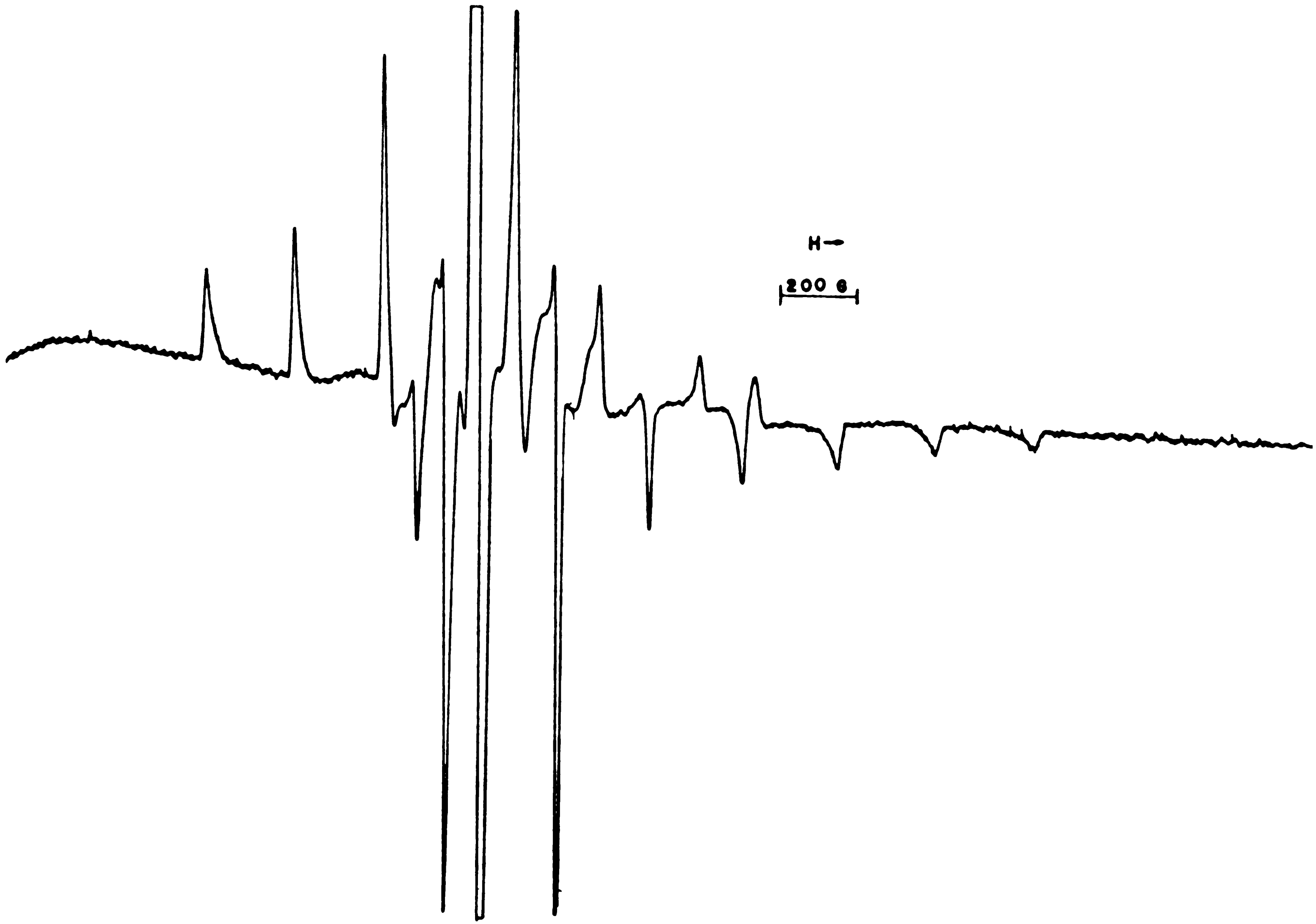


Figure 11. Esr Spectrum of Nb(Dmtp)$_4$ in CH_2Cl_2 at 77 °K

is related to the energy splitting in cm^{-1} between adjacent hyperfine levels as follows :

$$A(cm^{-1}) = g \times 4.6686 \times 10^{-5} \times A(gauss) \qquad (12)$$

The experimental esr parameters are listed in Table 10 with the corrections due to second order effects.

Table 10

Esr Spectral Parameters of $Nb(Dmtp)_4$

	$<g>$	$g_{\|\|}$	$g_{\perp}$	$<a>^*$	$A^*_{\|\|}$	$A^*_{\perp}$
solid (ambient temperature)	1.9780					
solution (experimental)	1.9791	1.8756	2.0308	136.9	216.9	92.0
(corrected)	1.9494	1.8971	1.9756	135.4		

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

In dichloromethane glass at 77°K the esr spectrum may be described by the spin Hamiltonian with axial symmetry[60]:

$$\mathcal{H} = g_{||}\beta H_z S_z + g_{\perp} (H_x S_x + H_y S_y) + A_{||} S_z I_z + A_{\perp}(S_x I_x + S_y I_y) \qquad (13)$$

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

$$\mathcal{H} = < g > \beta H \cdot S + < a > I \cdot S \qquad (14)$$

Theoretical calculations of esr parameters for a D_{2d} dodecahedron and a D_{4d} square antiprism show that $g_{\perp} > g_{||}$ for a dodecahedron[16,17] and

$g_{||} > g_{\perp}$ for a square antiprism[16,18]. For Nb(Dmtp)$_4$, $g_{\perp} = 1.9756$ and $g_{||} = 1.8971$ indicating dodecahedral symmetry in support of the electronic spectrum. The g values for the solid and solution esr spectra are essentially the same, 1.9780 and 1.9791 respectively, indicating the stereochemistry remains the same.

Data from the esr studies can now be used in conjunction with the electronic spectral assignments 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 Equation 15.[17]

$$g_{||} = 2.0023 - \frac{8\lambda}{\Delta E_3} \qquad g_{\perp} = 2.0023 - \frac{2\lambda}{\Delta E_2} \tag{15}$$

where λ is the free ion spin-orbit coupling constant , $\Delta E_3 = ({}^2B_2 - {}^2B_1)$, and $\Delta E_3 = ({}^2E_3 - {}^2B_1)$. Taking the spin-orbit coupling constant for Nb^{4+} as 748 cm^{-1}, the calculated values of $g_{||}$ and $g_{\perp}$ are 1.6374 and 1.8881 respectively. These values are much lower than the experimental quantities and this indicates the inadequecy of the ionic model. It is possible to qualitatively assess the amount of covalent bonding *via* Equation 16.[17]

$$g_{||} = 2.0023 - \frac{8\lambda\alpha^2\gamma^2}{E_3} \qquad g_{\perp} = 2.0023 - \frac{2\lambda\alpha^2\gamma^2}{E_2} \tag{16}$$

The parameters α^2, β^2, and γ^2 are associated with the 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 three parameters is 1.0(ionic bond) to 0.50(covalent bond). Agreement with the experimental g values is found for $\alpha^2\gamma^2 = 0.288$ and $\alpha^2\beta^2 = 0.234$. For pure covalent bonding in the ground and excited states $\alpha^2\gamma^2 = \alpha^2\beta^2 = 0.0625$. Thus, it appears that the niobium d orbitals are strongly mixed with ligand orbitals in the formation of $Nb(Dmtp)_4$.

Further confirmation of the bonding is obtained using Equation 17 developed by McGarvey.[16]

$$\begin{aligned} A_{\|} &= P[-\kappa + (g_{\|} - 2.0023) + 3/7\ (g_{\perp} - 2.0023)] \\ A_{\perp} &= P[-\kappa + 2/7 + 11/14\ (g_{\perp} - 2.0023)] \end{aligned} \tag{17}$$

where $P = g_e g_N \beta_e \beta < r^{-3} >_{ave}$ and is defined as positive for ^{93}Nb which has a positive nuclear moment, $< r^{-3} >_{ave}$ is the reciprocal cube of the average radial distance of the outer electrons from the nucleus, and κ is the isotropic contribution to the hyperfine constant due to polarization of the inner electron spin density by the unpaired d electron. Agreement with experimental data is found for values of $\kappa = 0.9665$ and $P = 131.1\ 10^{-4}cm^{-1}$. Comparing these values with those for a Nb^{4+} free ion, $\kappa = 1.0$(pure d orbital) and $P = 192\ 10^{-4}cm^{-1}$,[61] the smaller experimental value for P indicates that the unpaired electron is more delocalized, hence more covalent in bonding orbitals.

Since the molecular orbital calculations indicated mixing of metal and ligand orbitals, an attempt was made to observe superhyperfine structure arising from ^{31}P splitting in the esr spectrum. No phosphorous-niobium shf splitting is observed in the room temperature or frozen solution esr spectra.The powder esr spectrum of $Nb(Dmtp)_4$ diluted into an isomorphous $Zr(Dmtp)_4$ matrix shows extensive ^{31}P-^{93}Nb superhyperfine splitting giving additional evidence to support the delocalization of the lone electron.

$\underline{Nb_2(Dmtp)_4I_4}$

The esr spectra of $Nb_2(Dmtp)_4I_4$ are presented in Figures 12 and 13. The solid and frozen solution spectra are identical. The spectrum of a triplet-state system consists of 2nI + 1 lines with a hyperfine splitting of A/2 where n is the number of metal 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, a "forbidden" $\Delta M_s = \pm 2$, half-field transition may be observed at g *ca*. 4 arising from the magnetic dipole-dipole interactions of the paramagnetic metal ions in a dimeric species. The "forbidden" $\Delta M_s = \pm 2$ transitions arise when the magnetic field is off the symmetry axis of the molecule by an 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.[31] When two neighboring niobium(IV) ions interact, as occurs when dimeric complexes are formed, the Hamiltonian for the pair may be written:

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}_{int} \qquad (18)$$

where $\mathcal{H}_1$ and $\mathcal{H}_2$ are each of the form :

$$\mathcal{H}_{1,2} = g_{||} H_zS_z + g_{\perp} (H_xS_x + H_yS_y) + A_{||}S_zI_z + A_{\perp}(S_xI_x + S_yI_y) \qquad (19)$$

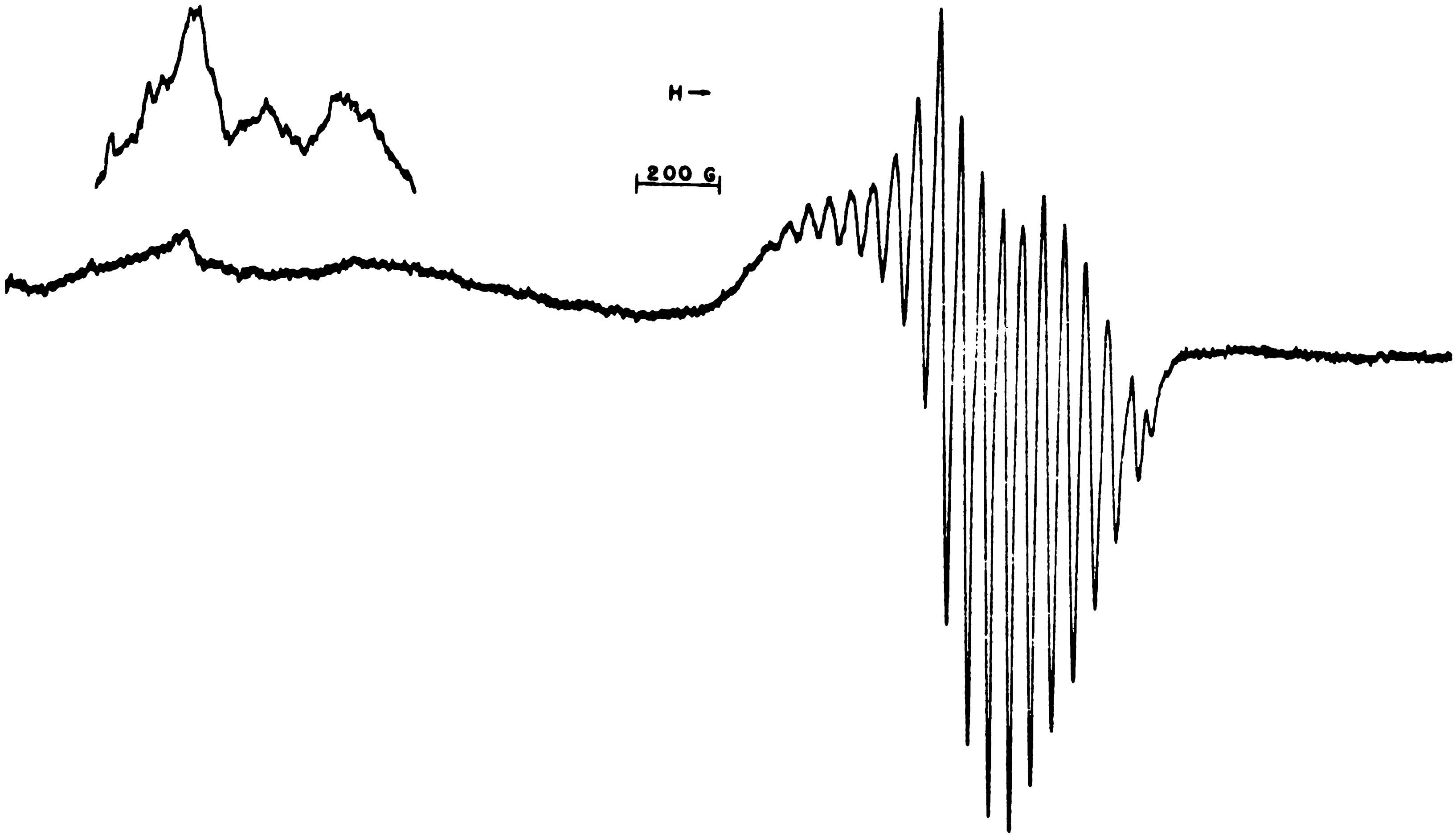


Figure 12. Esr Spectrum of $Nb_2(Dmtp)_4I_4$ in CH_2Cl_2 at Ambient Temperature

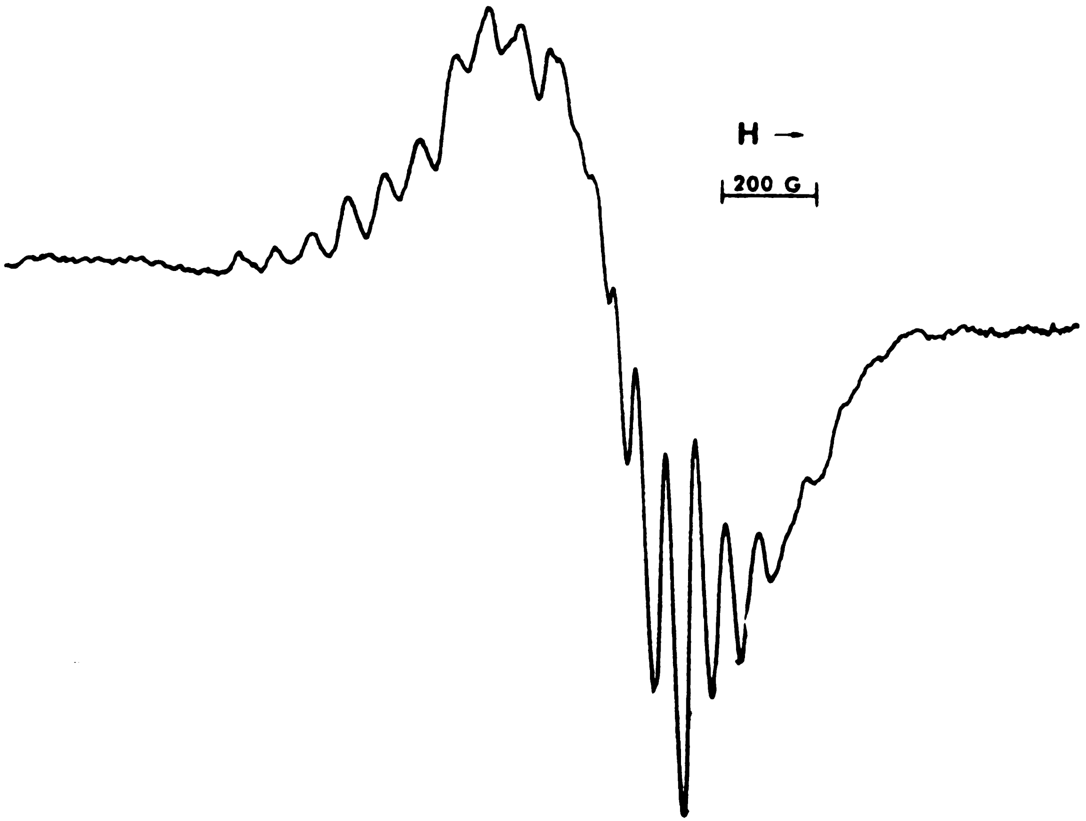


Figure 13. Esr Spectrum of $Nb_2(Dmtp)_4I_4$ in CH_2Cl_2 at 77°K

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

$$H_{int} = D[S_z^2 - 1/3\ S(S + 1)] + E(S_x^2 - S_y^2) - JS_1 \cdot S_2 \qquad (20)$$

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 the x and y symmetry axes are equivalent E = 0. Therefore, E can be considered a measure of the deviation from axial symmetry. Exchange between a pair of paramagnetic ions may be represented as a cosine coupling between the effective spins, S_1 and S_2. The exchange integral, J, represents the energy separation between the singlet and triplet states. When J is negative the ground state is a singlet and the complex is antiferromagnetic. The value of the singlet-triplet separation can be determined from both esr and magnetic susceptibility measurements. Since J can be determined more accurately by the latter method, it will be discussed with the magnetic susceptibility data.

Lacking single crystal esr data, the values of the zero field splitting constants have been determined in several ways including computer simulation of spectra[36,37,39,42,46]; use of Bleaney's equation[56] relating microwave frequency, $g_{||}$, $A_{||}$, $A_{\perp}$, and D[38,44]; and by making the approximation that the low and high field parallel lines are separated by 2D[38,44].

Assuming that the complex has axial magnetic symmetry, an approximate value for D can be obtained from the separation of the outermost pair of parallel lines in the frozen solution spectrum by :

$$H_{19} - H_1 \simeq 2D \tag{21}$$

The value of D was also determined through Bleany's equation[60] for the field direction along the symmetry axis :

$$\omega_o = g_{||}\beta H + 2D(M_s - 1/2) + A_{||}M_I + \frac{A_\perp^2}{\omega_o}[I(I + 1) - M_I^2 + (2M_s - 1)M_s] \tag{22}$$

where $I = 9$; $M_s = 1,0$; $M_I = \underline{+}9, \underline{+}8, \underline{+}7, \ldots 0$; and ω_o is the radiation frequency. The resultant esr parameters are presented in Table 11. The values obtained for the zero field splitting vary between 0.06328 cm^{-1} and 0.01876 cm^{-1} depending upon the method of calculation.

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 without exceedingly sophisticated computation. It is clear that accurate hyperfine and zero field splitting parameters cannot safely be extracted from these spectra without an analysis of considerable sophistication including a theoretical simulation of the frozen solution spectrum with general non-coincident axes for all of the magnetic interaction parameters. Nevertheless, the results of the esr studies on the copper[62] and vanadyl[44] 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

Table 11

Esr Parameters for $Nb_2(Dmtp)_4I_4$

$g_{\Delta M} = \pm 2$	4.1320
$< g >$	1.9795
$< a^* >$	45.3
$A^*_{\|\|}$	68.1
$A^*_{\perp}$	34.5
$g_{\|\|}$	2.0663
$g_{\perp}$	1.9361
D^*(Bleaney's equation)	187.6
$R(\theta = 0)$	4.76 Å
D^*(magnetic field approx.)	631.8
$R(\theta = 0)$	3.53 Å

* hyperfine splittings are given in units of $10^{-4} cm^{-1}$

interaction between two electron spins, it is expressed as[63] :

$$D = 3/4\ g^2\beta^2 < \frac{1 - 3\cos^2\theta}{r_{12}^3} >_{max} \qquad (23)$$

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 $1/<r_{12}^3> = 1/R^3$, R being the niobium-niobium distance, one obtains :

$$R_{calc}(\text{Å}) = \left[\frac{0.325g^2\ |1 - 3\cos^2\theta|}{D(cm^{-1})}\right]^{1/3} \qquad (24)$$

Taking $H_{||}$ to be along the Nb-Nb axis, *i.e.* $\theta = 0°$, one calculates a niobium-niobium distance of 3.53 - 4.76 Å. This can be compared with a Nb-Nb distance of 3.36 Å in α - NbI_4.

F. Magnetic Susceptibility Measurements

An important indication of electron exchange-coupling in complexes which contain more than one transition metal ion is the characteristic deviation of the magnetic susceptibility of these compounds from the Curie-Weiss law. When an isotropic interaction occurs between two paramagnetic metal ions, each with a single unpaired electron, the exchange interaction term, $JS_1 \cdot S_2$, is required in the spin Hamiltonian. J is defined such that a negative value corresponds to an antiferromagnetic interaction in which the ground state is a singlet and the triplet state is J energy units above the ground state. The susceptibility of $Nb_2(Dmtp)_4I_4$ passes through a maximum at 140°K and decreases rapidly as the temperature is lowered. Above 140°K the susceptibility decreases gradually but does not obey the Curie-Weiss law.

The close resemblence of this magnetic behaviour to that established for binuclear copper(II) acetate[64] and bis-π-cyclopentadienyltitanium(III) chloride[34] also suggests that isolated pairs of metal atoms interact to form a lower singlet state(S = 0, diamagnetic) and a slightly higher triplet state(S = 1, paramagnetic). As the temperature is lowered the singlet state becomes more populated at the expense of the triplet state and the susceptibility and magnetic moment decrease. The applicability of this hypothesis can be evaluated by comparing the experimental results with the $\chi_M(T)$ curve derived from Equation 25 which is appropriate for a singlet-triplet model[64]:

$$\chi_M = \frac{g^2 N \beta^2}{3kT} [\ 1 + 1/3 \exp(\ -J/kT)\ ]^{-1} + \chi_d + N_\alpha \qquad (25)$$

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

β = Bohr Magneton, 0.9273×10^{-20} erg/gauss

g = electron gyromagnetic ratio(from esr data)

k = Boltzman constant

T = absolute temperature, °K

χ_d = diamagnetic susceptibility, emu/mole

N_α = Van Vleck temperature independent paramagnetism, emu/mole

An estimate of the singlet-triplet separation can be obtained using the relationship[34]:

$$J \simeq -\ 1.247\ kT_N \qquad (26)$$

where T_N is the temperature of maximum susceptibility. In practice, one plots a family of curves and chooses a value of J which gives the best fit with the experimental data. At temperatures much greater than the Neèl temperature, one predicts exchange-coupled complexes to exhibit simple paramagnetism in accordance with the Curie-Weiss law. A plot of χ_M versus $1/(T + \theta)$ should yield a straight line with an intercept on the χ_M axis equal to the sum of the temperature independent paramagnetism and the diamagnetic susceptibility. Knowing the values of χ_d for specific atoms, ions, and molecules from tables[65], the value of N_α can be calculated. The diamagnetic core corrections are listed in Table 12.

Table 12

Diamagnetic Core Corrections

Ions	$_d$ (10^{-6} emu/mole)
Nb^{4+}	-14
Cl^-	-23.4
Br^-	-34.6
I^-	-50.6
$Dmtp^-$	-78.8

The compounds under investigation all decompose before Curie-Weiss behavior is observed.

The experimental susceptibility of $Nb_2(Dmtp)_4I_4$ is compared with the susceptibility calculated from Equation 25 in Figure 14. While the shapes of the calculated and experimental curves are qualitatively the same, their magnitudes differ. This is not totally unexpected since a

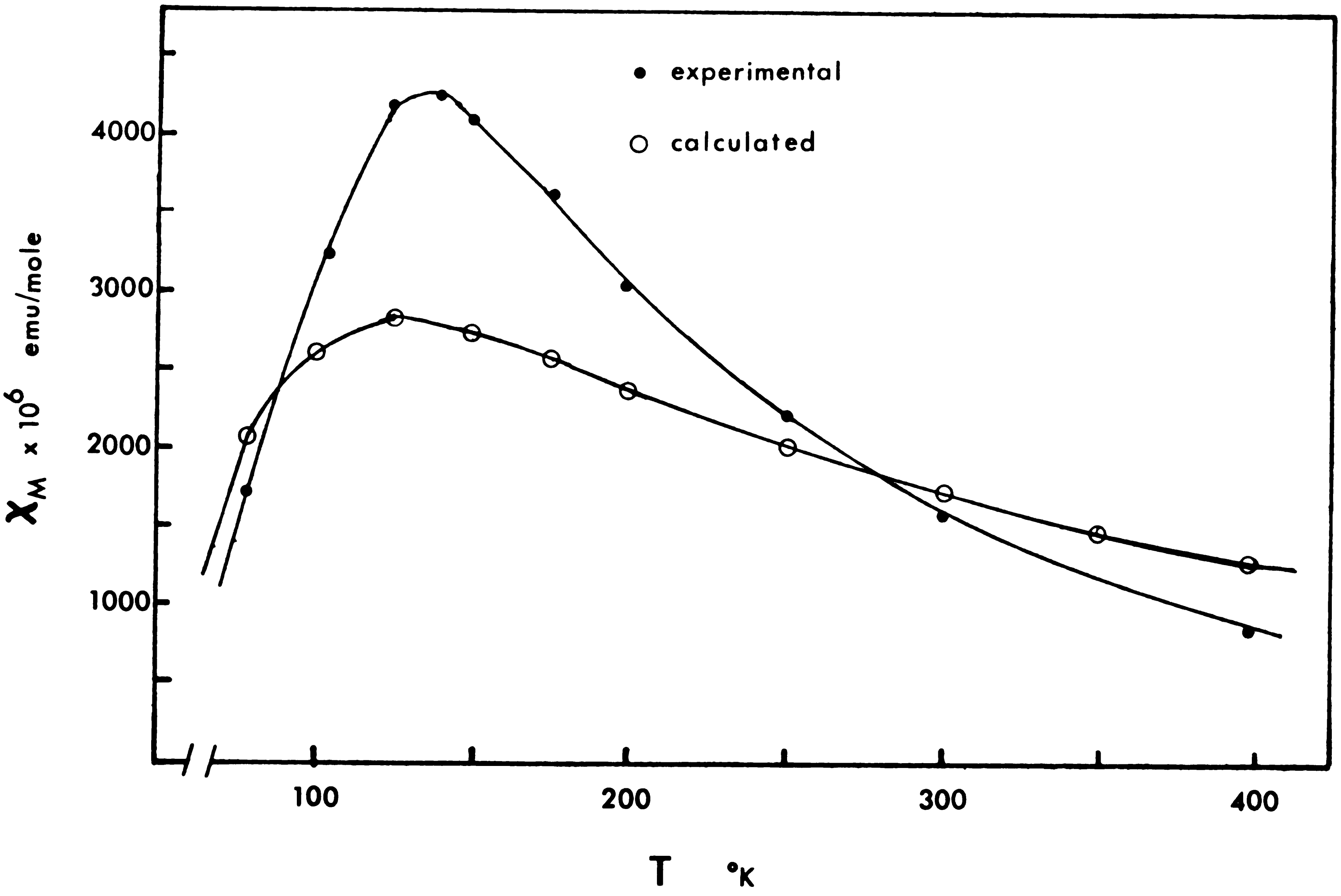


Figure 14. Experimental and calculated magnetic susceptibility of $Nb_2(Dmtp)_4I_4$

number of assumptions are implicit in Equation 25 which are not completely valid for this system. Assumptions which the esr data indicate may not be valid are (1) the ligand fields are strong enough to quench the orbital angular momentum and leave only the spin angular momentum free. This is unlikely in view of the large spin-orbit coupling constant for niobium(IV) and (2) the unpaired electrons are localized on metal atoms. In addition, other thermally accessible excited states may be available.

A magnetic moment which has been calculated from the slope of the Curie-Weiss plot has significance only if it has been established that θ arises from magnetic exchange. When the origin of θ is unknown or a complex does not obey the Curie-Weiss law, the common procedure is to calculate an effective magnetic moment at a specified temperature. The expression for the effective magnetic moment is given by Equation 27.

$$\mu_{eff} = 2.828\ [(\chi_M - \chi_d)T\ ]^{1/2} \tag{27}$$

Since values of μ_{eff} are given for the majority of paramagnetic compounds these will be reported here.The magnetic moment can also be calculated from the gyromagnetic ratio obtained from the esr studies. Equation 28 gives the relationship between the magnetic moment and the g factor for a specific total spin quantum number, S.

$$\mu = g[S(S + 1)]^{1/2} \tag{28}$$

Electron spin resonance measurements detect only temperature dependent paramagnetism whereas bulk susceptibility measurements detect the total magnetism of the material.

Both the chloride and bromide complexes are diamagnetic and their susceptibilities are essentially independent of temperature. This is consistent with the proposed structure of these compounds. In a halogen bridged complex the niobium atoms are much closer together with the smaller chloride or bromide bridges than in the case of iodine. Thus, since the metal atoms are closer together a stronger interaction of the unpaired electrons is expected for the case of chlorine and bromine causing the singlet-triplet separation to be much greater. These compounds might be expected to exhibit antiferromagnetic behavior at higher temperatures but they decompose before such behavior is observed. The susceptibility plots for the chloride and bromide complexes are presented in Figure 15 and the magnetic data for all the complexes are listed in Table 13. The magnetic susceptibilities increase in the order I > Br > Cl which is expected as the metal-metal separation decreases with smaller bridging ions.

Table 13

Magnetic Data for $Nb_2(Dmtp)_4X_4$ Complexes

compound	χ_M^*(300°K)	χ_d^*	$(\chi_M - \chi_d)^*$	μ_{eff}(300°K)
X = Cl	- 23.0	- 436.8	413.8	1.00
X = Br	- 19.0	- 481.6	462.6	1.05
X = I	1700	- 545.6	2245.6	2.32

* units are given in 10^{-6} emu/mole

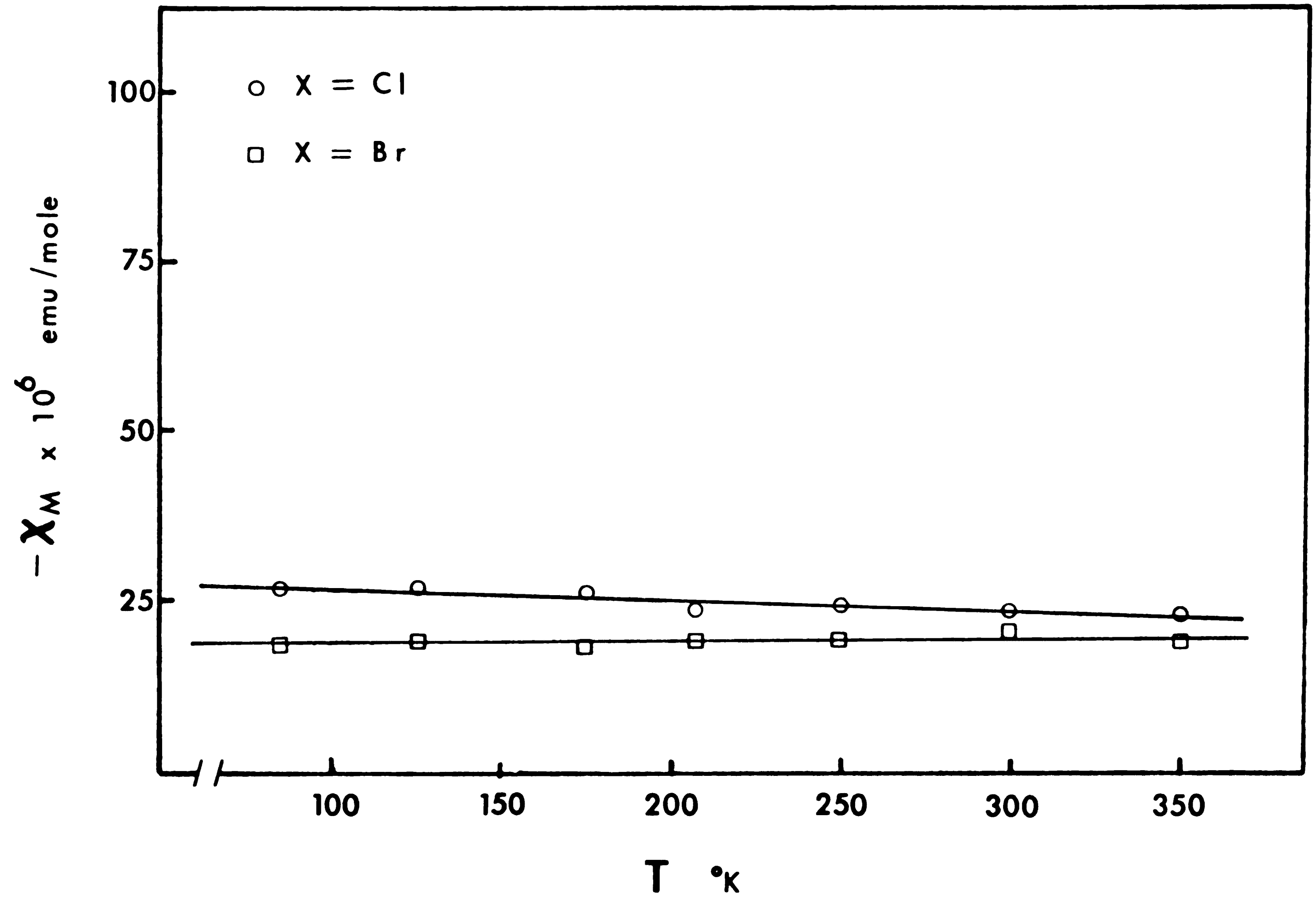


Figure 15. Magnetic susceptibility of $Nb_2(Dmtp)_4X_4$ (X = Cl,Br)

VI. Summary and Conclusions

Eight-coordinate $Nb(Dmtp)_4$ was isolated from the reaction of niobium tetrahalides with NaDmtp. The infrared spectrum indicates that $Dmtp^-$ acts as a bidentate ligand. The electronic spectrum exhibits three d-d transitions and supports a D_{2d} dodecahedral configuration for the complex. The esr spectra confirm this geometry with the parameters $< g > = 1.9494$, $g_{||} = 1.8971$, $g_{\perp} = 1.9756$, and $< a > = 0.01354$ cm^{-1}. Using the molecular orbital theory developed for D_{2d} complexes, metal-ligand bonding parameters were obtained which indicate strong mixing of metal and ligand orbitals.

Complexes of the type $Nb_2(Dmtp)_4X_4$ were obtained from the reaction of the niobium tetrahalides with two moles of NaDmtp. The infrared spectra indicate that $Dmtp^-$ is bidentate in all three complexes. Three d-d transitions are observed in the electronic spectra. In addition, a band due to a double excitation is observed at 390 nm indicating a metal-metal interaction. The complexes are proposed to be halogen bridged dimers with D_{2h} symmetry (C_{2v} about each niobium atom). The magnetic moments decrease in the order I > Br > Cl. The bromide and chloride complexes are diamagnetic while the iodide exhibits antiferromagnetism with a singlet-triplet separation of -140 cm^{-1} and a room temperature magnetic moment of 2.32 Bohr Magnetons.Additional confirmation of an electron exchange-coupled dimer was obtained by the observation of the triplet state esr spectrum of $Nb_2(Dmtp)_4I_4$ with both the $\Delta M_s = \pm 1$ and $\Delta M_s = \pm 2$ transitions present. The esr parameters are $g|| = 2.0663$, $g_{\perp} = 1.9361$, $A_{||} = 0.00681$ cm^{-1}, and $A_{\perp} = 0.00345$ cm^{-1}. The zero field splitting is 0.06318 cm^{-1} which corresponds to a niobium-niobium separation of 3.53 Å. This complex represents the first reported case of electron exchange-coupled niobium (IV).

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