PART I
THE SYNTHESIS AND CHARACTERIZATION OF SOME DIHYDROBIS(PYRAZOL-1-YL)BORATE COMPLEXES OF NIOBIUM(IV)

PART II
ESR STUDIES OF SOME SULFUR DONOR COMPLEXES OF NIOBIUM(IV)

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ABSTRACT

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Eight-coordinate $Nb[H_2B(Pz)_2]_4$ was isolated from the reaction of potassium dihydrobis(pyrazol-1-yl)borate ($K[H_2B(Pz)_2]$) with niobium tetrahalides. The infrared spectrum indicates that $H_2B(Pz)_2^-$ is bidentate. This is supported by the nmr spectrum of the analogous zirconium complex. The electronic spectrum exhibits one d-d transition and one strong band at 340 nm. This intense band in the ultraviolet region is due to ligand charge transfer. This assignment was confirmed by observing an identical band at 340 nm in the analogous zirconium complex. The esr spectra support a D_{2d} dodecahedral configuration for the complex with the parameters $\langle g \rangle = 1.955$, $g_{||} = 1.903$, $g_{\perp} = 1.982$ and $\langle a \rangle = 0.0148\ cm^{-1}$.

Complexes of the type $NbX_2[H_2B(Pz)_2]_2$ (X = Cl, Br and I) were obtained from the reaction of the niobium tetrahalides with two moles of $K[H_2B(Pz)_2]$. The infrared spectra indicate that $H_2B(Pz)_2^-$ is bidentate in all three complexes.

This is supported by the nmr spectra of isomorphous $ZrCl_2[H_2B(Pz)_2]_2$. Electronic spectra exhibited one d-d band in the chloride complex and two d-d bands in the bromide and iodide complexes. In addition, a band at 340 nm was observed in each case. This band in the ultraviolet region is due to ligand charge transfer. The assignment of this band was confirmed by observing an identical band in isomorphous $ZrCl_2[H_2B(Pz)_2]_2$. The nmr spectrum of isomorphous $ZrCl_2[H_2B(Pz)_2]_2$ suggests a trans geometry. This assignment is also supported by the far infrared and electronic spectra. The esr spectra proved that all the complexes are monomeric by exhibiting ten lines at ambient temperature. The esr spectral parameters show that $g_\perp$ is greater than $g_{||}$ in all cases. By using the molecular orbital theory developed for octahedral complexes, metal-ligand bonding parameters were obtained which indicate strong mixing of metal and ligand orbitals.

The infrared spectra, obtained by allowing one mole of $K[H_2B(Pz)_2]$ to react with one mole of NbX_4, indicate that $H_2B(Pz)_2^-$ is acting as a bidentate donor. Electronic spectra exhibited one d-d vibration and one ligand charge transfer band at 340 nm. The esr solution spectra indicate the presence of a monomer by exhibiting ten lines at ambient temperature. The esr spectra $g_\perp$ values were observed to be greater than the $g_{||}$ values in all cases.

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The esr spectra of $NbX_4(dth)_2$ (X = Cl, Br and I; dth = 2,5-dithiahexane) were investigated to determine the structures of these complexes in toluene or excess dth solution. This investigation confirmed a trigonal dodecahedral structure, which had been proposed based on the electronic spectra, with the parameters <g> = 1.954 and 1.973, $g_{||}$ = 1.917 and 1.960, $g_{\perp}$ = 1.972 and 1.974, and <a> = 0.0131 and 0.0124 cm^{-1} for $NbCl_4(dth)_2$ and $NbBr_4(dth)_2$ respectively. Metal-ligand bonding parameters, obtained from the molecular orbital theory developed for D_{2d} complexes, indicate strongly mixed metal and ligand orbitals in these complexes.

$[NbCl_2(dmtp)_2]_2$ results from the reaction of niobium tetrachloride with two moles of Nadmtp (dmtp = dimethyldithiophosphate). When $[NbCl_2(dmtp)_2]_2$ is diluted into a solution of the analogous zirconium complex, a powder esr spectrum which is indicative of an exchange coupled dimer is obtained. The esr parameters are $g_{||}$ = 2.092 and $A_{||}$ = 0.0110 cm^{-1}. The zero field splitting is 0.07325 cm^{-1} which corresponds to a niobium-niobium separation of 3.38 Å.

Examination of $Nb(dtc)_4$ diluted into the corresponding diamagnetic zirconium(IV) matrix by esr methods gives spectra which are anisotropic with two overlapping sets of ten lines. The esr spectra support the presence of a trigonal dodecahedral geometry with the parameters <g> = 1.948, $g_{||}$ = 1.902, $g_{\perp}$ = 1.971 and <a> = 0.0110 cm^{-1}.

PART I

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To The Family

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INTRODUCTION

The niobium tetrahalides of fluorine, chlorine, bromine, and iodine have each been prepared by several methods.[1-3] The preparation used in our laboratory involves the thermal gradient method.[4,5] The niobium(IV) halides are diamagnetic polymers whose basic unit can be represented as Nb_2X_8. They are dark solids and will thermally disproportionate to form the corresponding trihalides and pentahalides.[4-9]

Many niobium(IV) halide adducts and complexes have been formed from the niobium tetrahalides or as a result of the reduction of the pentahalides. The magnetic properties of these complexes have proven most interesting. The expected spin-only magnetic moment of a d^1 transition element is 1.73 B. M. Although this value is found in some of the complexes, many show lower values. Some are diamagnetic and this behavior has been attributed to Nb-Nb interactions in the polymeric compounds.[5,10,11]

The coordination number of niobium(IV) is usually six but as expected for relatively larger early second row transition elements, complexes with higher coordination numbers exist. There is even evidence[12] for nine-coordinate $Nb(acac)_4$ dioxane. Eight-coordinate complexes[12-18] are more common and have been prepared, studied and shown to be paramagnetic with magnetic moments ranging from 1.6 to 1.9 B. M.

The formation of direct Nb-Nb bonds in these complexes is hindered by the fact that the niobium is coordinatively saturated.

Lower coordination numbers are also known for niobium-(IV).[19,20]

The six-coordinate complexes, NbX_4L_2, could have D_{4h} or C_{2v} symmetry and both exist. Fowles, et al. have assigned the geometry of a series of niobium(IV) compounds, mainly with nitrogen donor ligands,[21] while Hamilton and McCarley[19] have worked with sulfur donor ligands. They have shown that sulfur donor ligands form complexes in which the coordination number of niobium(IV) varies from a low of five to at least eight. More recent studies with 1,1-dithiols, for example, dialkyldithiophosphates[18] and dialkyldithiocarbamates[13,22,23] reveal for the first time complexes of niobium(IV) in which a significant metal-metal interaction has a substantial impact on observable magnetic behavior.

REVIEW OF PREVIOUS WORK

This section shall consist of (1) a discussion of known complexes of niobium(IV) and (2) a consideration of some poly(pyrazol-1-yl) borate complexes formed by transition metals in the +2 and +4 oxidation states. There have been several reviews on the chemistry of niobium halides and their complexes.[3,24,25] A recent review[26] by Trofimenko considers the coordination chemistry of the poly(pyrazol-1-yl) borate ligands. In this review therefore primarily those aspects are discussed which are relevant to later discussions of results.

Complexes of Niobium(IV)

A. Eight-Coordinate Addition Complexes

Clark and coworkers[15] prepared eight-coordinate complexes with the bidentate ligand o-phenylenebis(dimethyldiarsine) (or diarsine). These complexes were prepared by heating NbX_4, NbX_5 or $NbOX_3$ with diarsine in a sealed evacuated tube. The $NbX_4 \cdot 2$ diarsine complexes are isomorphous with the dodecahedral titanium(IV), zirconium(IV), and hafnium(IV) halide diarsine complexes.[27] 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[16] obtained eight-coordinate complexes using 4-methyldiarsine and 4-ethyldiarsine as ligands. These compounds were assumed to be dodecahedral based on the similarity of the visible spectra to those of the diarsine complexes. Solutions of $NbCl_4(Etdiars)_2$ exhibit maxima at ν = 9.75 kK, ξ_{max} = 10; ν = 12.8 kK, ξ_{max} = 26; and ν = 17.5 kK, ξ_{max} = 6. The spectrum of $NbBr_4(Etdiars)_2$ exhibits maxima at 12.72 and 15.92 kK 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, as expected for a single d electron in a non-degenerate ground state. The high moment of the iodide complex was attributed to a large temperature independent paramagnetic contribution.

Hamilton and McCarley[14] obtained eight-coordinate complexes with composition $NbX_4(dth)_2$ using the sulfur donor ligand 1,2-bis(methylthio)ethane (more commonly referred to as 2,5-dithiahexane or dth). The adducts are all paramagnetic. 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 $NbX_4(Diars)_2$.[15] The magnetic

moments for the chloride, bromide and iodide complexes were reported to be 1.60, 1.61 and 1.28 B. M. respectively. Esr spectra were observed only for the solid (powders) complexes. The spectrum of the solid chloride complex consists of a broad asymmetric band with $\langle g \rangle = 1.92$, $g_{\perp} = 1.98$ 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 and Hamilton[28] who obtained solution esr spectra and found $g_{\perp} > g_{||}$ in the case of the chloride and bromide. In the case of the iodide the esr spectra were inconclusive. It has been demonstrated that $g_{\perp} > g_{||}$ for a dodecahedral complex and that $g_{||} > g_{\perp}$ for a square antiprismatic complex.[29-31] All of the complexes were assumed to be dodecahedral since $g_{\perp} > g_{||}$.

B. Eight-Coordinate Substitution Complexes

A number of eight-coordinate substitution complexes have been produced using beta-diketonates. Deutscher and Kepert[12,32] prepared niobium(IV) complexes of acetylacetone (Acac), benzoyltrifluoroacetone (Bta), thenoyltrifluoroacetone (Tta) and dibenzoylmethane (Dbm). Complexes with the ligands 8-hydroxyquinoline (OX) and tropolone (T) were also prepared. The complexes were prepared by allowing the appropriate niobium tetrahalide to react with the free ligand in an acetonitrile-triethylamine solution. The infrared spectra proved the ligands to be bidentate and equivalent in all

cases. The diffuse reflectance and solution spectra do not indicate any d-d transitions. The ambient temperature magnetic moments range from 1.43 to 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 $Zr(acac)_4$;[33] $Nb(Tta)_4$ is not isomorphous with square antiprismatic $Zr(Tta)_4$;[34] and $Nb(Dbm)_4$ is not isomorphous with the square antiprismatic $Th(Dbm)_4$.[35] The esr spectra of $Nb(acac)_4$ and $Nb(Dbm)_4$ show $g_\perp > g_{||}$. 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[36] prepared the tetrakisdipivaloylmethane (Dpm) complex of niobium(IV) by reaction of niobium tetrachloride with the free ligand in acetonitrile. The visible spectrum exhibits only two d-d transitions at 14.2 kK, $\xi_{max} = 280$ and at 15.3 kK, $\xi_{max} = 636$. Ten lines are observed in the esr spectrum with $\langle g \rangle = 1.95$ 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. The structure of $Nb(Dpm)_4$ was proposed to be a D_4 square antiprism on the basis of $g_{||} > g_\perp$ and the observation of only two d-d transitions. This was later confirmed by X-ray structural analysis[37] and represents the first reported case of a square antiprismatic niobium(IV) complex.

A number of workers have prepared eight-coordinate niobium(IV) complexes with diethyldithiocarbamates (Detc).[13,22,23] The ir spectrum indicates the ligand is bidentate. A band observed at 360 cm^{-1} is assigned as a metal-sulfur stretching mode. The visible spectrum exhibits one d-d band at 363 mμ with ξ_{max} = 48. The magnetic moment is 1.57 B. M. indicating a single unpaired electron. No esr was reported.

Kirksey[38] isolated from the reaction of ammonium piperdinyldithiocarbamate (NH_4pipdtc) with niobium tetrahalides the eight-coordinate $Nb(pipdtc)_4$ complex. The infrared spectrum indicates that $piptc^-$ 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 $\langle a \rangle$ = 0.0195 cm^{-1}, where $g_{\perp} > g_{||}$.

McGinnis and Hamilton[18] isolated eight-coordinate $Nb(Detp)_4$ from the reaction of sodium diethyldithiophosphate (NaDetp) with niobium tetrahalides. The infrared spectrum indicates that $Detp^-$ is bidentate. The electronic spectrum exhibits three d-d transitions and supports a D_{2d} dodecahedral configuration for the complex. The esr spectra values of $\langle g \rangle$ = 1.952, $g_{||}$ = 1.895, $g_{\perp}$ = 1.982 and $\langle a \rangle$ = 0.014 cm^{-1} confirm this geometry with $g_{\perp} > g_{||}$.

Griffith and coworkers[17,39] isolated the stable $K_4[Nb(CN)_8]$, $2H_2O$ salt by the reduction of methanolic solution of niobium pentachloride at a mercury pool cathode followed by reaction with concentrated aqueous potassium cyanide. The salt is paramagnetic with a magnetic moment of 1.69 B. M. at 293K. The esr spectra of the salt indicate a change in configuration from D_{2d} in the solid state to D_{4d} in solution. The vibrational and electronic spectra support this structural change.

C. Six and Lower Coordinate Complexes of Niobium(IV).

In addition to the large number of mononuclear, paramagnetic, eight-coordinate niobium(IV) complexes, a number of mononuclear, paramagnetic, six-coordinate niobium(IV) and dimeric niobium(IV) compounds have been prepared. The magnetic behavior of the mononuclear six-coordinate complexes is very similar to the magnetic behavior of the eight-coordinate complexes but the dimeric complexes all have small magnetic susceptibilities indicating retention of the metal-metal bond.

Safonov and Khorschunov[40-41] prepared the binary systems $NbCl_4$-MCl (M = Na, K, Rb and Cs) by the direct reaction of niobium(IV) chloride with the alkali metal halides and found evidence for the congruently melting compounds M_2NbCl_6. Morozov and Lipatova[42] prepared the ammonium, rubidium, and cesium hexachloroniobate(IV) by mixing together concentrated hydrochloric acid solutions containing

niobium tetrachloride and the salt MCl (M = NH_4^+, Rb^+ and Cs^+).

Walton and coworkers[21] prepared the hexahalo salts $[(C_2H_5)_4N]_2NbX_6$ by treating the appropriate acetonitrile complex $NbX_4 \cdot 2CH_3CN$ with tetraethyl ammonium halides using chloroform-acetonitrile as solvent. The octahedral species NbX_6^{-2} is used as a "model" for comparison of related measurements on coordination complexes of the types $NbX_2 \cdot 2L$ and $MX_4 \cdot B$, where M = Nb or Ta; X = Cl or Br; L = acetonitrile, tetrahydrofuran, tetrahydropyran, or 1,4-dioxane; and B = 2,2'-bipyridyl or 1,10-phenanthroline.

Knox and Brown[43] obtained the complex anions $Nb(NCS)_6^-$, $Nb(NCS)_6^{-2}$, and $Ta(NCS)_6^-$, respectively when potassium thiocyanate was allowed to react with $NbCl_5$, $NbCl_4$, and $TaCl_5$ in acetonitrile. Infrared data indicate that the thiocyanate groups are nitrogen bonded in all cases. A detailed study of the conductance of these compounds in acetonitrile showed that dissociation takes place at low concentrations.

Reductions of $NbCl_5$ in concentrated hydrochloric acid solutions by using mercury electrode were reported by Cozzi and Vivarelli.[44] At 13N HCl, the solutions were red-orange. As the HCl concentration was lowered, the solutions turned blue.

The niobium(IV) species in the blue solutions gave absorption maxima at 14.3 kK and the species present was believed to be $NbOCl_4^{-2}$. The red-orange species exhibited a band at 20.8 kK.

Wentworth and Brubaker[45] prepared complexes of the formula $Nb(OR)Cl_5^{-2}$ by the electrolytic reduction of $NbCl_5$ in HCl-saturated alcohols. The compounds exhibited spin-only paramagnetism for the d^1 ion. The molar magnetic susceptibilities exhibited Curie-Weiss dependence upon reciprocal temperature in all cases. Rasmussen, Kuska, and Brubaker[46] obtained esr spectra of the methoxo complex at ambient temperature and 77 K. From the spectra it was found that $g_{||} = 1.965$, $g_{\perp} = 1.809$, $A_{||} = 248$ gauss and $A_{\perp} = 144$ gauss. A molecular orbital treatment was consistent with covalent chlorine-niobium sigma bonds and appreciable π-bonding by the chlorine atoms. The molecule was assigned C_{4v} symmetry.

Wentworth and Brubaker[47] found that treatment of the above reduced alcoholic solutions with pyridine produced a diamagnetic species $NbCl(OCH_2CH_3)_3Py$. On the basis of the nonlability of the chlorine atoms, the molecular weight data and the low susceptibility, the complex was formulated to be dimeric with bridging chlorine atoms and a direct metal-metal bond. When the dimer was treated with sodium ethoxide, $Nb(OCH_2CH_3)_4$ was obtained. This compound is also diamagnetic with a corrected susceptibility of -100×10^{-6} c.g.s. units. Direct metal-metal bonds were proposed to account for the observed magnetic behavior.

Djordjevic and Katovic[48] isolated paramagnetic $Nb_2Cl_5(OCH_2CH_3)_3(bipy)_2$ (bipy = 2,2'-bipyridine) from an ethanol solution containing $NbCl_4$ and bipyridine. Properties of the compound suggested its formulation as an ionic derivative containing the ions $(Nb(OCH_2CH_3)_2(bipy)_2^{+2}$ and $(NbCl_5(OCH_2CH_3))^{2-}$.

McCarley and coworkers[49] prepared $NbX_4(py)_2$ (X = Cl and Br; py = pyridine) by reactions of NbX_5 with excess pyridine. McCarley and Torp[5] obtained the same species as well as $NbI_4(py)_2$ from reactions of NbX_4 with pyridine at ambient temperature. Visible spectra of pyridine solution exhibited bands with maxima at 20.6 kK for the chloride and 20.7 and 13.9 kK for the bromide. With larger extinction coefficients than expected for "d-d" transitions, the bands were attributed to either pyridine-to-metal or metal-to-pyridine charge transfer.

Brown and Newton[50] studied the reactions $NbCl_4$ and NbX_4 (X = Cl, Br and I) with triethylamine and N,N,N',N'-tetramethylethylenediamine respectively. 1:1 adducts were isolated which were diamagnetic in the case of the triethylamine. This indicated that the metal-metal bond of the tetrahalide had been retained. The diamine gave products of the formula $MX_4 \cdot B$. The visible spectra of the bidentate complexes were interpreted by using a tetragonally distorted octahedral model.

Bradley and Thomas[51] isolated $Nb(NR_2)_4$ (R = CH_3, CH_3CH_2, $CH_3(CH_2)_2$ and $CH_3(CH_2)_3$) from the direct reaction of $LiNR_2$ and $NbCl_5$. The oxidation state of niobium in these compounds was determined by treatment of their H_2SO_4-ethanol solutions with excess $FeCl_3$ followed by titration of the $FeCl_2$ formed with standard ceric sulfate solution.

Machin and Sullivan[22] reported substitution reactions of the tetrahalides with potassium cyanate, thiocyanate, cyanide and borohydride and sodium diethyldithiocarbamate (Na dtc). $Nb(NCS)_3Cl$ was obtained from the reaction of niobium tetrachloride with potassium thiocyanate. The magnetic susceptibility is extremely small on the order of 40×10^{-6} c.g.s. units and independent of field strength. This value is very close to $NbCl_4$ indicating similar structures. The diffuse reflectance spectrum exhibits an asymmetric band at about 18,000 cm^{-1} from the reaction of niobium tetrachloride with potassium cyanate $Nb(CNO)_3Cl$ was obtained. The magnetic susceptibility for this compound is also low, χ_{Nb} being of the order of 90×10^{-6} c.g.s. units. Four bands were observed, at 9,000; 15,000; 22,000; and 30,000 cm^{-1} in the diffuse reflectance spectrum. The origin of the bands is not clear. When potassium cyanide was allowed to react with niobium tetrachloride in the acetonitrile solution, a compound which supports the formulation $NbCl_3(CN)(CH_3CN)_2$ was obtained. The magnetic susceptibility is only 50×10^{-6} c.g.s., which is very low for a formulated six-coordinate monomer. The diffuse

reflectance spectrum shows only one band at 22,000 cm^{-1}. The reaction between $NbCl_4$ and a two-fold molar excess of KBH_4 in acetonitrile solution produced $(CH_3CN)_2NbCl_2(BH_4)_2$. This compound is also diamagnetic with a χ_{Nb} of only 40 x 10^{-6} c.g.s. units. When less than four moles of sodium diethyldithiocarbamate are allowed to react with niobium tetrabromide, $Nb_2(Detc)_5Br_3$ is obtained. This complex is a weak 1:1 electrolyte in nitromethane and $[Nb_2(Detc)_5Br_2]Br$ is proposed. The magnetic susceptibility is markedly field dependent. The diffuse reflectance spectrum shows bands at 23,500 cm^{-1} and 19,500 cm^{-1} with a shoulder at 16,000 cm^{-1}.

Fowles, Tidmarsh and Walton[52] obtained $NbCl_4 \cdot S(CH_3)_2$ by the direct reaction of $NbCl_4$ and dimethylsulfide. The complex was reported to be antiferromagnetic with a magnetic moment of 0.44 B.M. at ambient temperature. The electronic spectrum exhibited two bands 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 $TiCl_3 \cdot 2SC_4H_8$.[53] The reactions of tetrahydrothiophene (tht) with $NbCl_4$ and $NbBr_4$ were also investigated. This ligand formed diadducts with both $NbCl_4$ and $NbBr_4$. However, two different forms of the bromide complex were obtained. The far infrared spectra of the chloride and α-bromide species were similar. 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 in both $NbCl_4(tht)_2$ and α-$NbBr_4(tht)_2$. In the β-bromide complex only one strong band at 227 cm^{-1} was observed. The $NbCl_4(tht)_2$ and α-$NbBr_4(tht)_2$ were assigned a cis configuration and the β-$NbBr_4(tht)_2$ was assigned a trans configuration. Although most bis-adducts of niobium tetrahalides have been assigned as cis structures, there has been a trans structure reported for DMF complexes.[54] Bereman[55] proposed a trans structure for certain pyridine adducts on the basis of esr data.

Hamilton and McCarley[19] also investigated some monodentate alkyl sulfides including $S(CH_3)_2$. From the reaction of dimethylsulfide with $NbCl_4$ and $NbBr_4$ complexes of two types $NbX_4[S(CH_3)_2]$ and $NbX_4[S(CH_3)_2]_2$ were obtained in benzene. Under a dynamic vacuum the diadduct recovered from the original reaction mixture loses one mole of dimethylsulfide over a period of twelve hours yielding the monoadduct. 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,[52] the same molecular structure was proposed.

McGinnis[56] prepared complexes of the general formula $Nb_2X_4(dmtp)_4$ (X = Cl, Br and I; dmtp = dimethyldithiophosphate) 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 magnetic moment of 2.32 B.M. at ambient temperature. 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 first reported niobium(IV) electron-exchange coupled species.

Kirksey[38] prepared complexes of varying stoichiometries when two moles of ammonium piperdinyldithiocarbamate (NH_4pipdtc) were allowed to react with the tetrahalides. In each complex the $pipdtc^-$ was bidentate as determined from infrared spectra. Two bands were assigned as d-d transition in the visible spectrum. Esr spectra of these species were unresolved single peaks at both ambient and 77°K temperatures. However, when the chloro compound was diluted into a solution of the disubstituted zirconium complex a powder esr spectrum was obtained which was indicative of an exchange-coupled dimer. The esr parameters are $g_{||} = 1.7873$ and $A_{||} = 0.00642$ cm^{-1}. The zero field splitting is 0.05778 cm^{-1} which corresponds to a niobium-niobium separation of 3.30 Å.

D. Poly(pyrazol-1-yl)borate Complexes of Group 2 and d-Transition Elements.

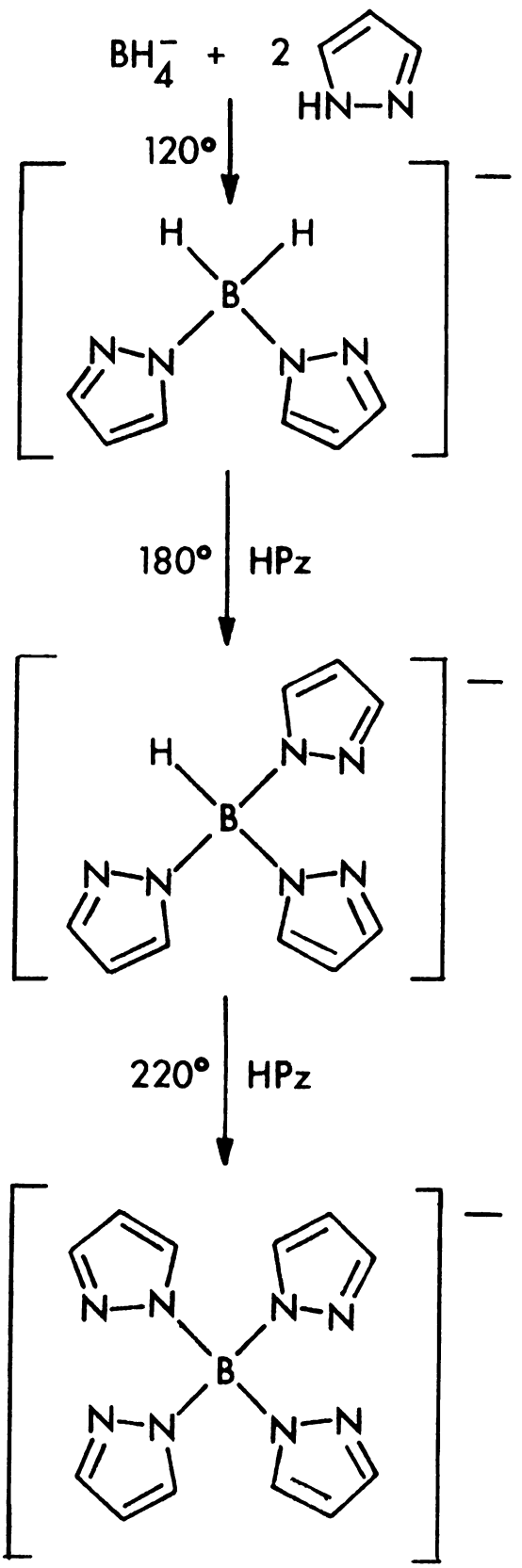
Since Trofimenko[57] first reported the poly-(pyrazol-1-yl)borate ligand a wide variety of Group 2 and

d-transition-element complexes have been described.[58] The poly(pyrazol-1-yl)borates, anions of the general structure $[H_nB(Pz)_{4-n}]^-$, where pz = 1-pyrazol-1-yl and n = 0, 1 and 2, have established themselves as a remarkably versatile class of ligands as summarized in a 1971 review.[59] By appropriate control of substituents they can be made to function as bidentate ligands, analogous to β-diketonates, as tridentate ligands of C_{3v} symmetry analogous to the cyclopentadienide anions and even as tetradentate (bis-bidentate) ligands in binuclear complexes.[60]

The poly(pyrazol-1-yl) borate ligands are readily available by the reaction of an alkali metal borohydride with pyrazole, the extent of substitution depending on the reaction temperature[61] as shown in Scheme 1. These salts are remarkable in that, on acidification, they yield isolable and stable free acids (unlike any other BR_4^- species) which may be converted via neutralization with NR_4OH to quaternary ammonium salts, unavailable by the direct route.

Ligands containing C substituents are prepared by using an appropriately substituted pyrazole in the above scheme, while B-substituted ligands are obtained by starting with a $[BR_nH_{4-n}]^-$ species instead of BH_4^-.

Scheme I



The reaction of the parent bidentate ligand $H_2B(Pz)_2^-$ with most first row transition metal ions in the 2+ state gives rise to monomeric chelates $[H_2B(Pz)_2]_2M$.[59,61] The isomorphous Ni and Cu chelates are square planar, while chelates of Mn, Fe, Co, and Zn are tetrahedral.[62] An X-ray structure determination of $[H_2B(Pz)_2]_2Co$ confirmed the above assignment.[63] These chelates are precipitated immediately when aqueous solutions of $KH_2B(Pz)_2$ and the appropriate metal ion are mixed. Similarly, the compounds $M[H_2B(Pz)_2]_2$ are precipitated when M is Pb^{2+} or Cd^{2+}, but not when M is Mg^{2+}, Ca^{2+}, Sr^{2+} or Ba^{2+}.[61] Ag^+, Pd^{2+} and Hg^{2+} ions are reduced to the free metals. Compounds $M[H_2B(Pz)_2]_2$ are extractable with organic solvents, particularly well with methylene chloride. They are stable to air and moisture and can be stored in the solid state for years without decomposition, with the exception of the unstable, air-sensitive $Mn[H_2B(Pz)_2]_2$ and $Fe[H_2B(Pz)_2]_2$ derivatives.[64]

Compounds of the structure $M[HB(Pz)_3]_2$ are precipitated immediately upon mixing solutions of an alkali hydrotris-(pyrazol-1-yl)borate and of a divalent transition metal ion. In addition, such compounds are also precipitated with Mg^{2+}, Pb^{2+}, Cd^{2+} and Pd^{2+} ions. The compound $AgHB(Pz)_3$ is obtained using Ag^+ ion. On heating the Ag and Pd compounds decompose readily with formation of the free metal. From more concentrated solutions the Mg^{2+} and Ca^{2+} ions are also precipitated by the $HB(Pz)_3^-$ ion.

The transition metal compounds of $M[HB(Pz)_3]_2$ are all solids with high-melting points and are sublimable in vacuo. They are sparingly soluble in polar solvents such as alcohols or acetone but are readily dissolved by halocarbons and aromatic hydrocarbons and may be conveniently recrystallized from them. The nmr spectra show only one kind of pyrazolyl group. The octahedral nature of these compounds is also supported by electronic spectra, magnetic data, and nmr studies of paramagnetic compounds.[62] X-ray crystal structure determination on $Co[HB(Pz)_3]_2$ confirmed the above structure.[65]

The $B(Pz)_4^-$ ligand can act in a bidentate, tridentate or tetradentate fashion. As a tridentate ligand compounds $M[B(Pz)_4]_2$[61] are formed which have the same octahedrally coordinated structure around the metal ion as $M[HB(Pz)_3]_2$ but in many other ways they are different. They are prepared by substitution and have the same colors as their $M[HB(Pz)_3]_2$ counterparts. They, too, are sublimable but are more thermally stable, less soluble in organic solvents and have higher melting points. In addition to divalent first-row transition metal ions, Cd^{2+}, Pd^{2+}, Hg^{2+} and Ag^+ are readily precipitated from aqueous solutions. In the alkaline earth group Mg^{2+} is precipitated readily, Ca^{2+} less readily, and Sr^{2+} and Ba^{2+} are precipitated from very concentrated solution. The nmr and infrared spectra have proved that one of the four pyrazolyl groups attached to boron is different from the other three.[63,66]

The $B(Pz)_4^-$ acts in tetradentate fashion when pairs of N termini are bridged by appropriate four-coordinate species. Trofimenko[60] obtained $[L_2Pd(Pz)_2B(Pz)_2PdL_2]^+$ (L = π-allyl) when $B(Pz)_4^-$ was allowed to react with two equivalents of π-allylpalladium chloride dimer. In this species the ligand acts in a bis-bidentate (tetradentate) fashion. The nmr spectrum of this cation is fluxional, limiting spectra being observed at 87 and -44°. At 87° all four pyrazolyl groups are spectroscopically equivalent, while at -44° two different types of pyrazolyl groups are present.

Cotton and coworkers[67] reported the spectroscopic studies on $[B(Pz)_4](C_5H_5)(CO)_2Mo$ which, together with preliminary results from a single crystal X-ray crystallographic study, show the $B(Pz)_4^-$ ligand to be bidentate. The six-membered metallocyclic ring can exist in two conformers in solution, and these interconvert, with an activation energy of the order of 10 kcal/mol, thus giving rise to extensive variations in the proton nmr spectrum as the temperature is varied.

Examples of complexes of these ligands with elements in oxidation state IV appear to be unknown except for some recently reported uranium(IV) complexes. Bagnall and coworkers[68] obtained $U[HB(Pz)_3]_4$, $U[H_2B(Pz)_2]_4$ tht, and $[UCl_2(HB(Pz)_3)_2]$ when uranium(IV) tetrachloride was allowed to react with stoichiometric quantities of the potassium salt of the appropriate anion in tht. These complexes are soluble in dichloromethane and dimethylsulphoxide (dmso). The tetrakis complexes are also soluble in acetone, benzene, dme and thf.

Steric effects play an important role in polypyrazolylborates. In bidentate chelates the $B(NN)_2M$ ring is puckered in the boat form.[59] This leads, in the case of C_5H_5-$CoR_f(Pz)_nBH_{4-n}$ (R_f = CF_3, C_2F_5, $CF_3CF_2CF_2$, and $(CF_3)_2CF$) to isolable geometric isomers.[69] It also brings boron substituents into interaction distance with the metal, including an example of an aliphatic three-center two electron C-H-M bond in $Et_2B(Pz)_2Mo(CO)_2$-π-$CH_2C\phi CH_3$ such bonding being even able to compete effectively with olefinic π-bonding.[70]

The tridentate $RB(Pz)_3^-$ ligands form a host of half-sandwich complexes resembling those derived from C_5H_5 but, generally, much more stable. This characteristic was exploited in preparing a stable copper carbonyl, $HB(Pz)_3CuCO$[71] and a variety of stable, five-coordinate Pt(II) complexes.[72] Of interest are also hybrid sandwiches exemplified by $[B(Pz)_4RuC_6H_6]PF_6$.[73] The examples cited above indicate the $R_nB(Pz)_{4-n}^-$ ion to be a most versatile ligand.

PURPOSE OF THIS WORK

While a number of eight-coordinate mononuclear, neutral complexes of niobium(IV) have been prepared by the complete substitution of the niobium tetrahalides with oxygen and sulfur donor bidentate ligands no such species has been reported with a nitrogen donor ligand. In order to prepare such a complex a uninegative bidentate ligand is needed. Therefore potassium dihydrobis(pyrazol-1-yl)borate ($K[H_2B(Pz)_2]$) was used. This ligand has been found to form a wide variety of d-transition-element complexes.[58,68] It was anticipated that by replacing all of the halogen atoms in NbX_4 an eight-coordinate complex could be prepared.

It also seemed of interest to investigate the replacement of only one or two of the halogen atoms in NbX_4. By replacing two halides either a six-coordinate monomer or a seven-coordinate dimer with bridging halogen atoms could be obtained. By replacing only one of the halogen atoms either a monomeric five-coordinate complex or a six-coordinate dimer would be expected.

The primary goal of this work then was to gain insight into the structure and magnetic behavior of disubstituted and fully substituted complexes formed by reaction of $K[H_2B(Pz)_2]$ with NbX_4 (X = Cl, Br, I).

In order to attempt to determine the structure and mode of bonding in the eight-coordinate adducts $NbX_4(dth)_2$[14,28] (X = Cl, Br and I; dth = 1,2-bis(methylthio)ethane, more commonly referred to as 2,5-dithiahexane), the esr spectra of the solids dissolved in toluene or excess ligand were investigated and -- in conjunction with the electronic spectral data -- the esr data are used to determine the applicability of an ionic model to the systems.

In an attempt to investigate further exchange coupling in niobium(IV) complexes, the dimethyldithiophosphate system[56] was reinvestigated. It was hoped that by diluting $NbCl_2(dmtp)_2$ into $ZrCl_2(dmtp)_2$ powder (dmtp = dimethyldithiophosphate) an exchange-coupled complex could be prepared from which more insight into the metal-metal bonding which characterizes much of the chemistry of niobium(IV) would be obtained. The dimethyldithiocarbamate analogue was also investigated in the corresponding zirconium(IV) powder.

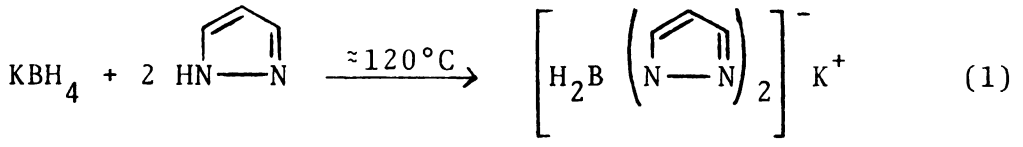
EXPERIMENTAL

All the compounds synthesized during this study were extremely sensitive to oxygen and moisture. It was, therefore, essential that all manipulations of these compounds be effected under a high vacuum or in a Vacuum Atmospheres Corporation nitrogen filled drybox containing less than 1 ppm water and oxygen.

Materials. Niobium pentachloride, zirconium tetrachloride and high purity (99.9%) niobium metal were purchased from Alfa Inorganics. Niobium pentabromide, niobium pentaiodide and the three niobium tetrahalides ($NbCl_4$, $NbBr_4$ and NbI_4) were prepared by using procedures previously described.[5,6]

Practical grade pyrazole (98%) obtained from Aldrich Chemical Company and potassium borohydride obtained from Pfaltz and Bauer, Inc. were used as received. Analytical grade methylene chloride was purchased from J. T. Baker Chemical Company and was dried by refluxing over calcium hydride. It was distilled under nitrogen atmosphere and stored over molecular sieves. 1,2-bis(methylthio)ethane purchased from Columbia Chemicals, was dried and deoxygenated. Toluene and hexane were standard reagent grade chemicals.

Potassium dihydrobis(pyrazol-1-yl)borate ($K[H_2B(Pz)_2]$) was prepared by previously described methods[61] via the reaction:



(1)

The salt was dried, analyzed by use of nmr and infrared spectra and stored in the drybox.

Analytical Determinations. 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 solutions were filtered and the filtrates analyzed for halogen ion by potentiometric titration with a standard silver nitrate solution. A Beckman expanded scale pH meter was used in conjunction with a silver indicator and a saturated calomel reference electrode. Niobium was not determined due to the presence of boron in the dihydrobis(pyrazol-1-yl)borate complexes. Final microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

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 m^{-1}). Freezing point depressions

were measured in the concentration range 0.01 to 0.1 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.

Conductance Measurements. Molar conductivities were measured with a Beckman Model RC-16B2 bridge. A Freas type conductivity cell with bright platinum electroles was used. The cell constant was determined to be 0.2275 cm^{-1} at 25°C by using a standard KCl solution.

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 V 4540 variable temperature controller. Samples were sealed in pyrex or quartz tubes under a nitrogen atmosphere. The magnetic field was calibrated by using strong pitch (g = 2.0028).

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

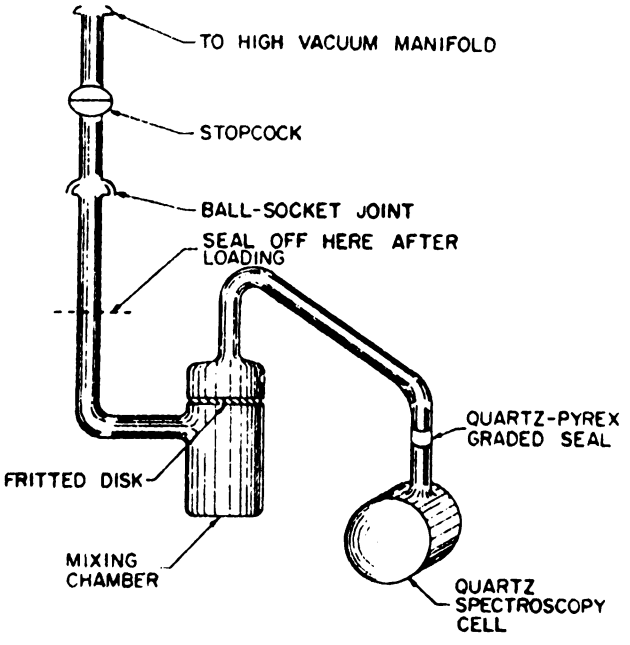
Electronic Spectra. Solution spectra were recorded by using a Cary Model 17 spectrophotometer. Cylindrical fused silica cells, 1.0 cm long and adapted for use at low pressure (Figure 1), were used. Saturated solutions were loaded in the drybox. The cell assembly was then evacuated to ca 10^{-5} torr.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

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 on Nujol mulls between cesium iodide plates. Mulls were prepared immediately before recording the spectra.

Far infrared spectra were obtaind by using a Block Engineering Company Model-FTS 16 (3900-20 cm^{-1}) far infrared Fourier-transform spectrophotometer. High density polyethylene was used for windows.

X-Ray Powder Diffraction Analysis. Powder diffraction patterns of the sample were routinely obtained with a Haegg Type Guinier forward-focussing camera (radius 80 mm) and Cu $K\alpha_1$ radiation, $\lambda\alpha_1$ = 1.54051 Å, t = 24 $\pm$ 1°C. The X-radiation source was a fine focus X-ray tube powered by a Picker 809 B generator. Sample preparation and Guinier techniques have been reported elsewhere.[74,75] The oxygen and moisture-sensitive materials were protected by a thin film of sodium-dried Nujol.

Figure 1



(Taken from Reference 5) Apparatus for Determination of Electronic Spectra

Syntheses. Tetrakis[dihydrobis(pyrazol-1-yl)borate]-niobium(IV): A 3.72 g sample of potassium dihydrobis-(pyrazol-1-yl)borate [$K(H_2B(Pz)_2$] was introduced into a round bottom flask containing a magnetic stirring bar and 1.2 g of $NbCl_4$, 3.0 g in the case of NbI_4 and 2.06 g in the case of $NbBr_4$. 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 mixture was stirred for 4-5 days at ambient temperature. A greenish-brown solution and a dark green precipitate were obtained. The precipitate was removed by filtration and the filtrate was evaporated to dryness in vacuo. The filtrate was extracted with methylene chloride, and a greenish-brown solid was recovered by removal of methylene chloride in vacuo.

> Anal. Calculated for $Nb[H_2B(Pz)_2]_4$: Nb, 13.65; C, 42.33; H, 4.75; N, 32.92; B, 6.35. Found: Nb, 14.24; C, 39.30; H, 4.54; N, 29.79; B, 5.36. Molecular weight: Calculated, 680.87. Found, 626 in benzene. M.P., 70°-75°C. Molar conductance in CH_2Cl_2: 0.48 ohm^{-1} $moles^{-1}$ cm^2.

Dichlorobis[dihydrobis(pyrazol-1-yl)borate]niobium(IV): A mixture of 1.20 g of $NbCl_4$ and 1.86 g of $K[H_2B(Pz)_2]$ 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 brown. The complex was recovered as described above.

Anal. Calculated for $NbCl_2[H_2B(Pz)_2]_2$: Nb, 20.30; C, 31.47; H, 3.53; N, 24.47; Cl, 15.48; B, 4.72. Found: Nb, 21.58; C, 30.82; H, 3.79; N, 23.72; Cl, 15.60; B, 4.51. M.P., 130-137°C. Molar conductance in CH_2Cl_2: 1.38 ohm^{-1} $moles^{-1}$ cm^2.

Dibromobis[dihydrobis(pyrazol-1-yl)borate]niobium(IV): The bromide complex was prepared in exactly the same manner as the chloride complex. A mixture of 2.06 g of $NbBr_4$ and 1.86 g of $K[H_2B(Pz)_2]$ was allowed to react. The resulting brown solution contained a greenish-brown solid.

Anal. Calculated for $NbBr_2[H_2B(Pz)_2]_2$: Nb, 16.99; C, 26.36; H, 2.96; N, 20.50; Br, 29.23; B, 3.95. Found: Nb, 17.62; C, 25.02; H, 3.33; N, 18.97; Br, 27.18; B, 3.30. M.P., 155-160°C. Molar conductance in CH_2Cl_2: 1.17 ohm^{-1} $moles^{-1}$ cm^2.

Diiodobis[dihydrobis(pyrazol-1-yl)borate]niobium(IV): The iodide complex was also prepared in the same manner as the chloride complex. Mixture of 3.0 g of NbI_4 and 1.86 g of $K[H_2B(Pz)_2]$ was allowed to react. The resulting solution and solid were a dark brown.

Anal. Calculated for $NbI_2[H_2B(Pz)_2]_2$: Nb, 14.50; C, 22.49; H, 2.52; N, 17.49; I, 39.61; B, 3.37. Found: Nb, 19.49; C, 26.76; H, 3.43; N, 19.22; I, 18.90; B, 3.80. M.P., 141-150°C. Molar conductance in CH_2Cl_2: 2.36 ohm^{-1} $moles^{-1}$ cm^2.

Trichlorodihydrobis(pyrazol-1-yl)borate niobium(IV): The trichloro complex was prepared in exactly the same manner as the dichloro complex. A mixture of 1.2 g of $NbCl_4$ and 0.93 g of $K[H_2B(Pz)_2]$ was allowed to react. The resulting solution was a yellowish-green containing a pink solid.

Molar conductance in CH_2Cl_2: 0.56 ohm^{-1} $moles^{-1}$ cm^2.
M.P., 250-255°C.

Tribromodihydrobis(pyrazol-1-yl)borate niobium(IV): This compound was prepared in a manner (2.06 g of $NbBr_4$ and 0.93 g of $K[H_2B(Pz)_2]$ analogous to the previous description. It appeared greenish in solution and was isolated as a dark green-brown solid.

Molar conductance in CH_2Cl_2: 2.4 ohm^{-1} $moles^{-1}$ cm^2.
M.P., 230-235°C.

Triiodo[dihydrobis(pyrazol-1-yl)borate niobium(IV): A dark brown solid was obtained by using the procedures (3.0 g of NbI_4 and 0.93 g of $K[H_2B(Pz)_2]$) applied for synthesis of the analogous chloride and bromide compounds.

Molar conductance in CH_2Cl_2: 4.2 ohm^{-1} $moles^{-1}$ cm^2.
M.P., 140-145°C.

Tetrakis[dihydrobis(pyrazol-1-yl)borate]zirconium(IV): This compound was prepared in a manner analogous to the previous description of the niobium(IV) compound. It was isolated as a cream-white solid.

Molar conductance in CH_2Cl_2: 3.3 ohm^{-1} $moles^{-1}$ cm^2.
M.P., 55-60°C.

Dichlorobis[dihydrobis(pyrazol-1-yl)borate]zirconium(IV): A pinkish-white solid was obtained by using the procedure applied for the synthesis of the analogous niobium(IV) chloride complex.

Molar conductance in CH_2Cl_2: 6.2 ohm^{-1} $moles^{-1}$ cm^2.
M.P., 210-216°C.

Tetrahalobis[1,2-bis(methylthio)ethane]niobium(IV): Compounds[14] of composition $NbX_4(dth)_2$ [x = Cl, Br, and I; dth = 1,2-bis(methylthio)ethane (more commonly referred to as 2,5-dithiahexane)] were obtained by direct reaction of NbX_4 with a solution of excess dithiahexane in ca. 50 ml of dry toluene. A 2-3 g quantity of NbX_4 was introduced into a 100 ml round bottom flask to which an excess (10 ml) of dithiahexane had been added. A magnetic stirring bar was introduced and the flask was evacuated to ca. 10^{-5} torr, toluene was distilled in and the flask was isolated from the vacuum system. This mixture was stirred continuously at ambient temperature for 4-5 days. During this period all the tetrahalide reacted.

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

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

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

Dichloro-μ-dichlorotetrakis(dimethyldithiophosphato)-diniobium(IV): A two to one molar ratio of sodium dimethyldithiophosphate: MCl_4 (M = Nb, Zr) was placed in a round bottom flask containing a magnetic stirring bar and 75 ml of

dry toluene. The mixture was stirred for 7-8 days in the drybox at ambient temperature. A clear colorless solution and violet precipitate were obtained. The precipitate was removed by filtration. The original mixture was prepared so that the $ZrCl_4$ to $NbCl_4$ ratio was ten to one.

Tetrakis(dimethyldithiophosphato)niobium(IV): The four to one molar ratio complexes were prepared in the same manner as above. A yellow solution and a violet precipitate were obtained. The precipitate was recovered by filtration. A pinkish-yellow solid was obtained from the filtrate by removal of toluene in vacuo.

Tetrakis(dimethyldithiocarbamato)niobium(IV): Essentially the same procedure was used here as has been described for the analogous dimethyldithiophosphate complex. The final product was a colorless solution containing a violet precipitate. The mixture was treated as described above.

Dichloro-μ-dichlorotetrakis(dimethyldithiocarbamato)-diniobium(IV): By using the same technique involved in the preparation of two to one (molar ratio) dimethyldithiophosphate complex the dimethyldithiocarbamate complex was isolated as a violet powder.

PART I

THE SYNTHESIS AND CHARACTERIZATION OF SOME DIHYDROBIS(PYRAZOL-1-YL)BORATE COMPLEXES OF NIOBIUM(IV)

RESULTS AND DISCUSSION

Preparation and Properties of Dihydrobis(pyrazol-1-yl)borate Complexes of Niobium(IV)

The reaction of the niobium(IV) halides with stoichiometric amounts of potassium dihydrobis(pyrazol-1-yl)borate in dichloromethane or toluene proceeds according to equation 2.

$$NbX_4 + 4K[H_2B(Pz)_2] \rightarrow Nb[H_2B(Pz)_2]_4 + 4KX \qquad (2)$$

The complex was isolated as a dark green powder which is quite soluble in ethanol dichloromethane and toluene. The complex is air and water sensitive as indicated by a color change from green to white. The complex melts over the range of 70-75°C without decomposition.

When two moles of potassium dihydrobis(pyrazol-1-yl)-borate are allowed to react with one mole of NbX_4 (X = Cl, Br, I) reaction occurs according to equation 3.

$$NbX_4 + 2K[H_2B(Pz)_2] \rightarrow NbX_2[H_2B(Pz)_2]_2 + 2KX \qquad (3)$$

Solid species were isolated as brown, greenish-brown and dark brown powders for the chloride, bromide, and iodide respectively. The complexes are air and/or water sensitive as indicated by color changes when exposed to the atmosphere or placed in water. The melting point ranges of 130-137°C, 155-160°C and 141-150°C are observed respectively for the

chloride, bromide and iodide. The complexes are only slightly soluble in toluene and dichloromethane. The $NbX_2[H_2B(Pz)_2]_2$ complexes interact with ethanol to produce a deep blue solution. The following equation is proposed based on spectral data to be subsequently discussed.

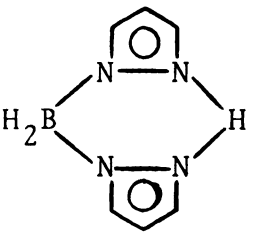
$$NbX_2[H_2B(Pz)_2]_2 \xrightarrow{CH_3CH_2OH} Nb(CH_2CH_2O)_2[H_2B(Pz)_2]_2 + 2HX \quad (4)$$

Spectral data also indicate that when either two or four moles of potassium dihydrobis(pyrazol-1-yl)borate are allowed to react with one mole of NbX_4 (X = Cl, Br, and I) in ethanol the same product is obtained in solution. In each case the solution was tan in color and all efforts to recover a solid product from the solution resulted in a red-brown thick oil or tar-like substance. The following equation is proposed for the production of the paramagnetic species.

$$NbX_4 + 2K[H_2B(Pz)_2] + 4CH_3CH_2OH \rightarrow$$
$$Nb(OCH_2CH_3)_4[H_2B(Pz)(Pz\text{-}H)]_2 + 2HX + 2KX \quad (5a)$$

Upon standing or when solvent is removed a diamagnetic species results, for which the following equation is proposed.

$$Nb(OC_2H_5)_4[H_2B(Pz)(Pz\text{-}H]_2 \rightarrow [Nb(OC_2H_5)_4]_n + 2$$



(5b)

Brubaker[47] reported the formation of similar complexes by electrolytically reducing NbX_5 in ethanol saturated HCl to which pyridine was later added. $Nb(OCH_2CH_3)_4$ was obtained by adding $NaOCH_2CH_3$ dissolved in ethanol to the reduction product $[NbCl(OCH_2CH_3)_3(C_5H_5N)]_2$ obtained from the above solution.

If only one mole of potassium dihydrobis(pyrazol-1-yl)-borate is present reaction occurs according to equation 6 in dichloromethane solutions.

$$NbX_4 + K[H_2B(Pz)_2] \rightarrow NbX_3[H_2B(Pz)_2] + KX \qquad (6)$$

The complexes are obtained as pinkish-brown, dark greenish-brown, dark brown powders for the chloride, bromide, and iodide respectively. These complexes are also air and moisture sensitive. The melting point ranges of 250-255°C, 230-235°C and 140-145°C are observed for the chloride, bromide, and iodide respectively. Like the $NbX_2[H_2B(Pz)_2]_2$ complexes, these complexes are only slightly soluble in toluene and dichloromethane. For all practical purposes, the chloride complex appears to be insoluble in ethanol but the bromide and iodide turn a dark greenish-brown and are quite soluble in ethanol.

In a manner analogous to the reaction of the niobium(IV) halides with stoichiometric amounts of potassium dihydro-bis(pyrazol-1-yl)borate in dichloromethane the zirconium(IV) complex is obtained according to equation 7.

$$ZrCl_4 + 4K[H_2B(Pz)_2] \rightarrow Zr[H_2B(Pz)_2]_4 + 4KCl \qquad (7)$$

The species was isolated as a cream-white powder with a high solubility in dichloromethane. The complex is air and water sensitive as indicated by a color change. The complex melts over the range of 55-60°C.

When only two moles of potassium dihydrobis(pyrazol-1-yl)borate are allowed to react with one mole of $ZrCl_4$ reaction occurs according to equation 8.

$$ZrCl_4 + 2K[H_2B(Pz)_2] \rightarrow ZrCl_2[H_2B(Pz)_2]_2 + 2KCl \qquad (8)$$

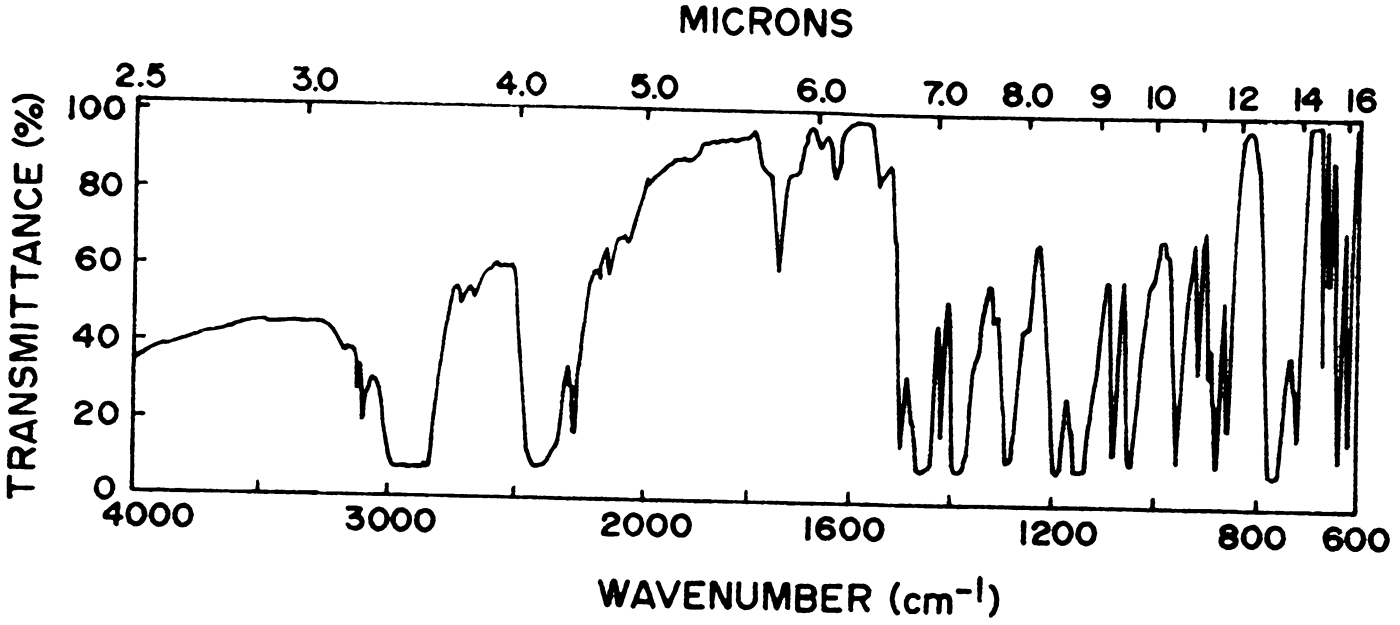
A pinkish-white solid was obtained, which is air and moisture sensitive as indicated by a color change when exposed to the atmosphere. This complex melts over the range 210-216°C and is only slightly soluble in dichloromethane.

Vibrational Spectra

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

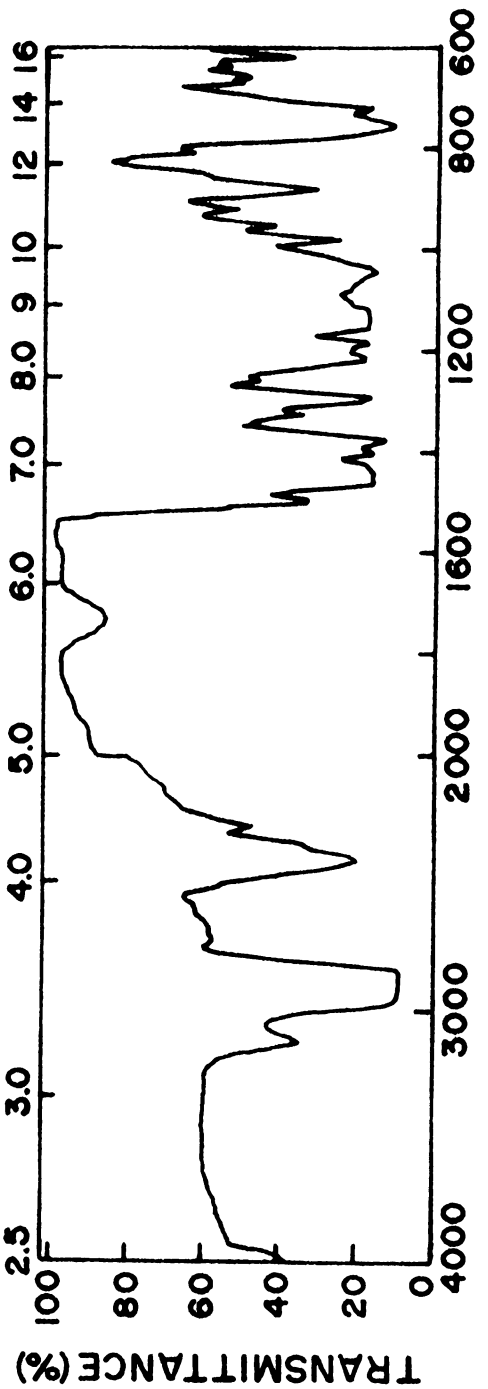
There has not been a detailed study of potassium dihydrobis(pyrazol-1-yl)borate in the infrared region. The spectra of the ligand, the completely substituted complex, and disubstituted chloride complex are presented in Figures 2, 3, and 4 respectively. The infrared spectra of the disubstituted chloride may serve as representative of the bromide and iodide spectra.

Figure 2



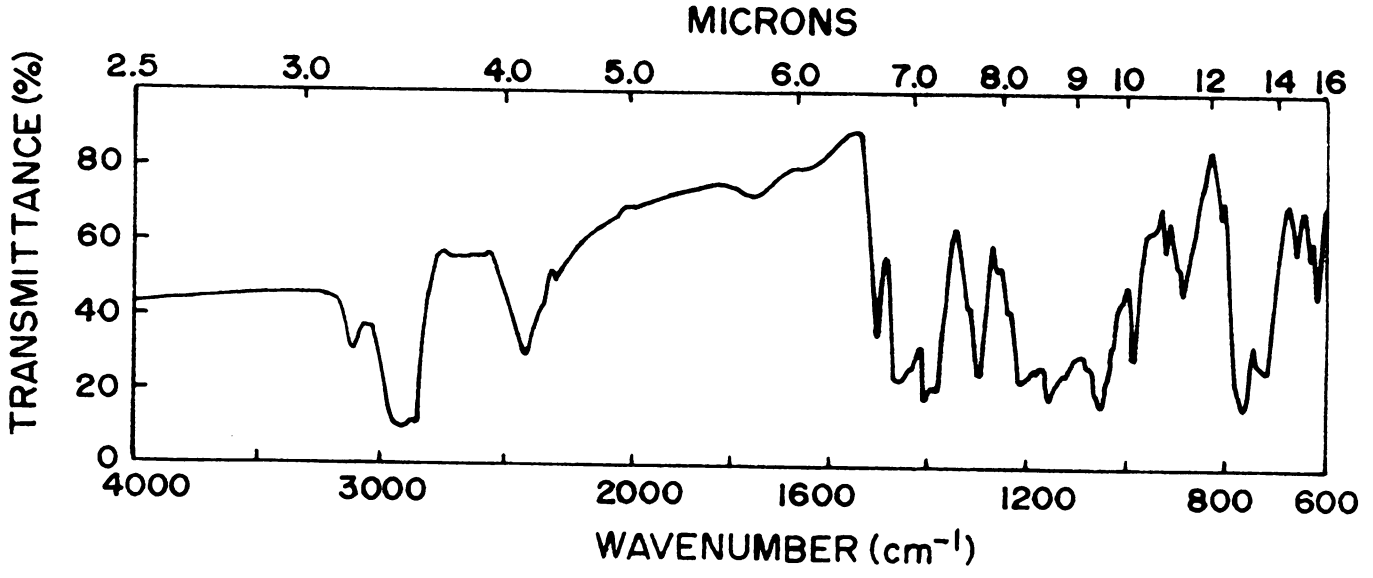
Infrared Spectrum of $K[H_2B(Pz)_2]$ (Nujol)

Figure 3



Infrared Spectrum of $Nb[H_2B(Pz)_2]_4$ (Nujol)

Figure 4



Infrared Spectrum of $NbCl_2[H_2B(Pz)_2]_2$ (Nujol)

In complexes containing the dihydrobis(pyrazol-1-yl)-borate anion several regions are of interest in the infrared. A strong BH_2 stretching multiplet is observed at 2230-2460 cm^{-1} and resembles that of pyrazabole. A strong band at 2900 cm^{-1} is due to δ(C-H) of Nujol and the multiplet at 3100 cm^{-1} is a combination of vibrations due to the δ(C-H) of the aromatic rings of the dihydrobis(pyrazol-1-yl)borate.

The infrared spectra of the analogous zirconium complexes were recorded. The infrared spectra of all the niobium and zirconium complexes are very similar. However, closer examination reveals that these compounds can be divided into two groups, the spectra within each group being virtually identical. To the first group belong the $M[H_2B(Pz)_2]_4$ complexes and to the second group complexes of the general formula $MX_2[H_2B(Pz)_2]_2$ (M = Nb; X = Cl, Br, and I: For M = Zr; X = Cl only). These are three regions of the spectrum where differences are apparent: (1) the band around 1300 is a doublet in $M[H_2B(Pz)_2]_4$ but a singlet in $MX_2[H_2B(Pz)_2]_2$, (2) the 1100-1250 cm^{-1} region is distinctly different in each group; (3) the band at 950 cm^{-1} in $M[H_2B(Pz)_2]_4$ is absent in $MX_2[H_2B(Pz)_2]_2$.

As the same ligand is involved in all these compounds, and the ionic radii of the metal ions are comparable, the observed spectral differences are ascribed to differences in molecular geometry, and the presence of halogen atoms in $MX_2[H_2B(Pz)_2]_2$.

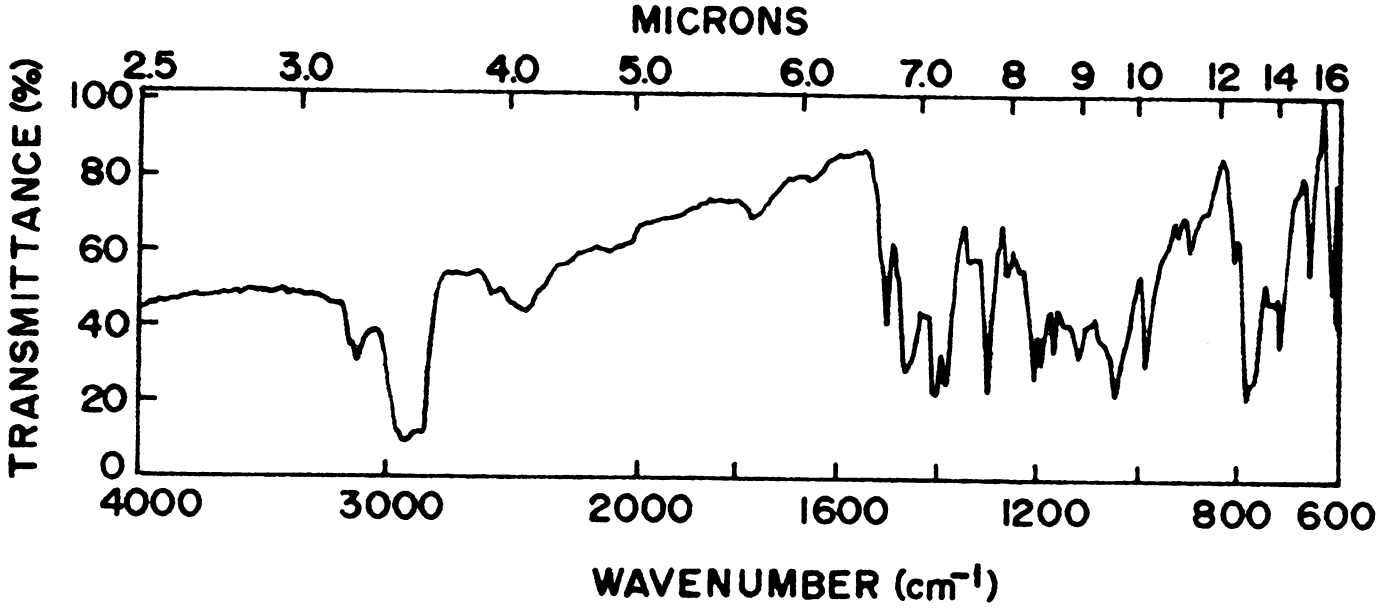
The infrared spectra of the niobium and zirconium complexes are also very similar to those observed for other metal dihydrobis(pyrazol-1-yl)borates.[61] Comparison of the multiplet at 2230-2460 cm^{-1} with other known chelated structures[61] indicate that the ligand is acting as a bidentate donor.

Infrared spectra were also recorded on the products obtained by the interaction of one mole of $K[H_2B(Pz)_2]$ with NbX_4 (X = Cl, Br, and I) in dichloromethane. The representative spectrum is presented in Figure 5. This spectrum is virtually identical to spectra obtained from the $NbX_2[H_2B(Pz)_2]_2$ complexes and identical for the chloride, bromide and iodide complexes. The region at 1100-1200 cm^{-1} is the only region which shows any difference in $NbX_3[H_2B(Pz)_2]$ and $NbX_2[H_2B(Pz)_2]_2$ complexes. Therefore, one can predict similar behavior of the ligand in these complexes.

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

The far infrared spectra for the potassium salt and the complexes were recorded. The data are presented in Table 1 and the spectra are shown in Figures 6 and 7 for the ligand and $M[H_2B(Pz)_2]_4$ complex respectively. Two bands at 331 and 270 cm^{-1} were present in the spectrum of the complex and are not present in the spectrum of the ligand. These bands have been assigned as ν(Nb-N) vibrations.

Figure 5



Infrared Spectrum of $NbBr_3[H_2B(Pz)_2]$ (Nujol)

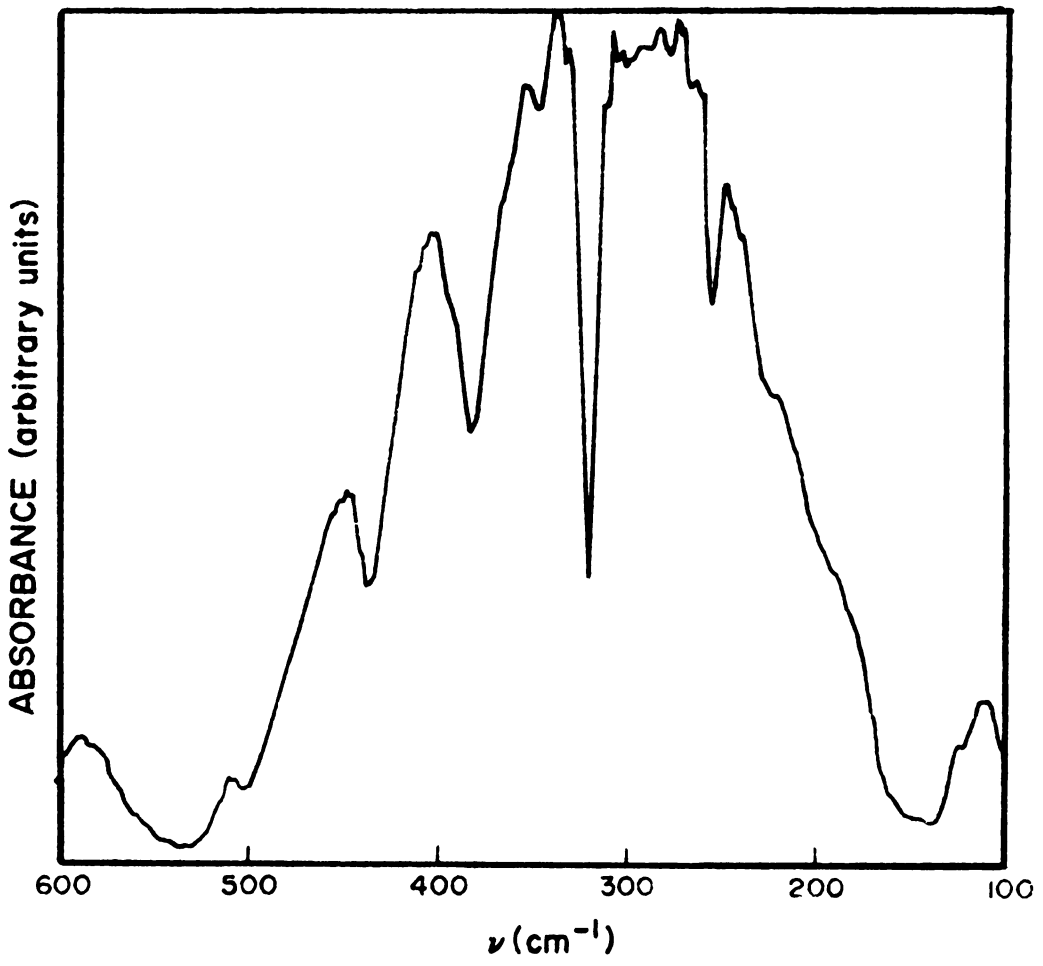
Table 1

Far Infrared Spectral Data for $K[H_2B(Pz)_2]$ and $Nb[H_2B(Pz)_2]_4$ (600-100 cm^{-1})

$K[H_2B(Pz)_2]$	$Nb[H_2B(Pz)_2]_4$
540 b	540 b
505 sh	505 sh
440 s	438 s
400 m	384 s
385 s	346 sh
348 m	ν(Nb-N) 331 m
335 sh	316 sh
324 s	305 s
304 m	294 m
292 w	283 sh
282 m	ν(Nb-N) 270 s
268 w	254 m
257 s	230 m
227 sh	217 sh
204 sh	206 m
143 b	195 w
125 sh	180 w
	175 w
	154 s
	141 m
	120 sh

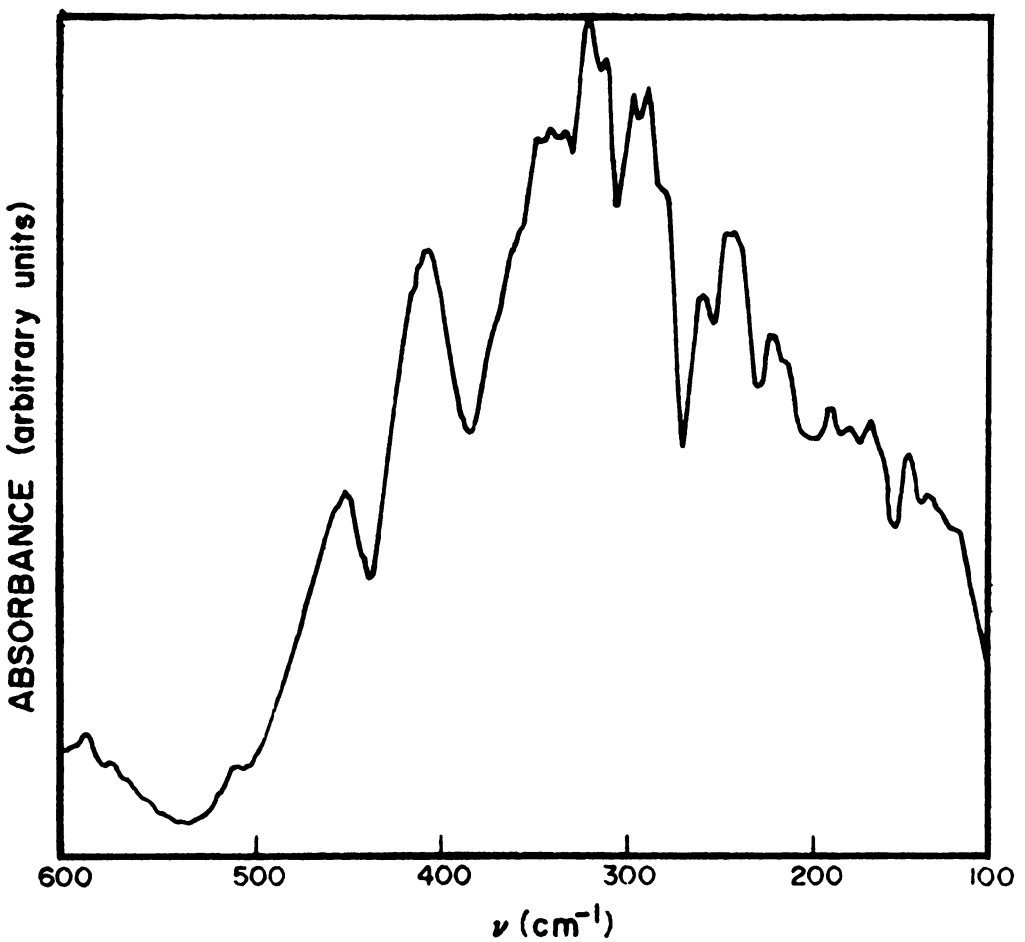
b = broad, s = strong, m = medium, w = weak and sh = shoulder.

Figure 6



Far Infrared Spectrum of $K[H_2B(Pz)_2]$ (Nujol)

Figure 7



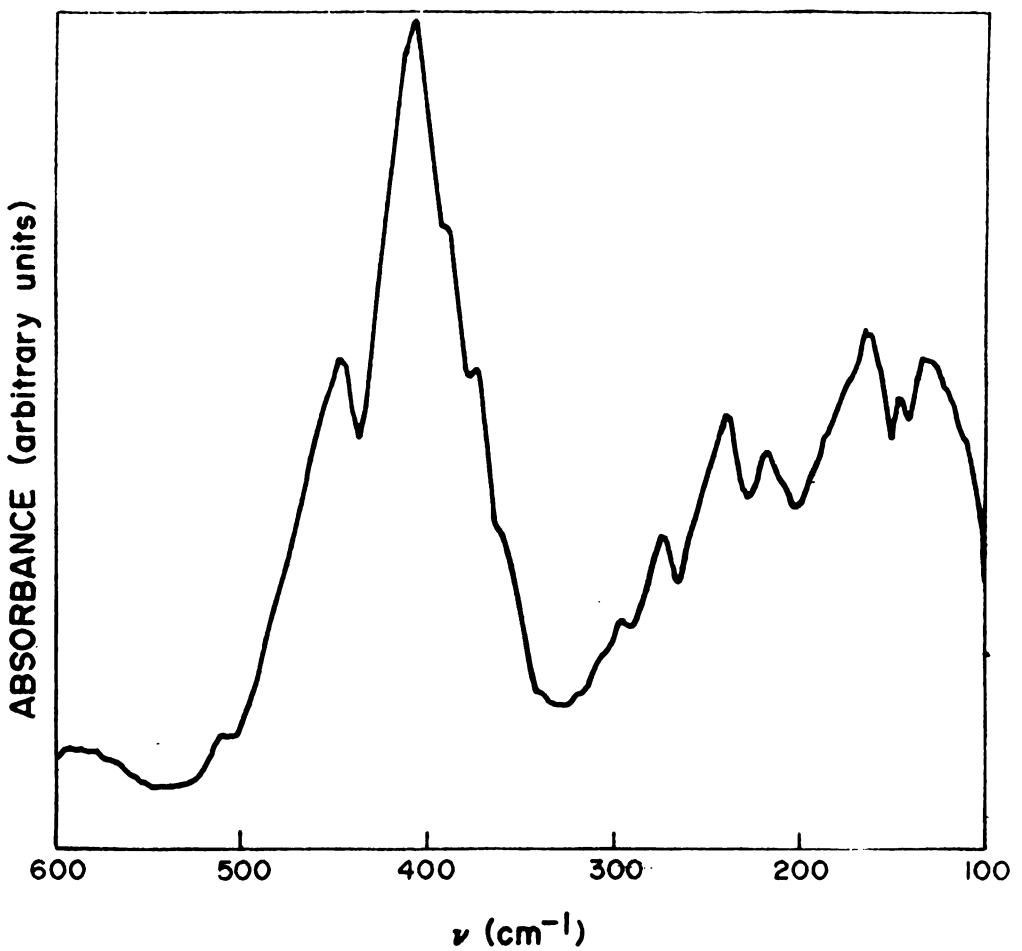
Far Infrared Spectrum of $Nb[H_2B(Pz)_2]_4$ (Nujol)

The far infrared spectra of $NbX_2[H_2B(Pz)_2]_2$ are shown in Figures 8, 9, and 10, and the data are presented in Table 2. The band at 263 is assigned as a ν(Nb-N) vibration in the disubstituted chloride. In the case of the disubstituted bromide complex, it was not possible to distinguish clearly a band which could be assigned as a ν(Nb-N) vibration. The band at 333 cm^{-1} is assigned as a ν(Nb-N) vibration in the iodide complex. The presence of only one ν(Nb-N) band suggests a trans stereochemistry. While this suggestion is only tentative, it is pertinent to point out that for a cis complex (approximating to C_{2v} symmetry) four ν(Nb-N) bands are allowed in the infrared ($2A_1 + B_1 + B_2$) whereas for a trans (D_{4h}) complex, only one ν(Nb-N) vibration is allowed (E_u).

Halogen sensitive bands are also found when the spectra of the complexes are compared. In $NbCl_2[H_2B(Pz)_2]_2$ the band at 328 cm^{-1} has been assigned as the ν(Nb-Cl) vibration because of the intensity, general shape and absence from the spectra of the tetrakis compound and ligand.

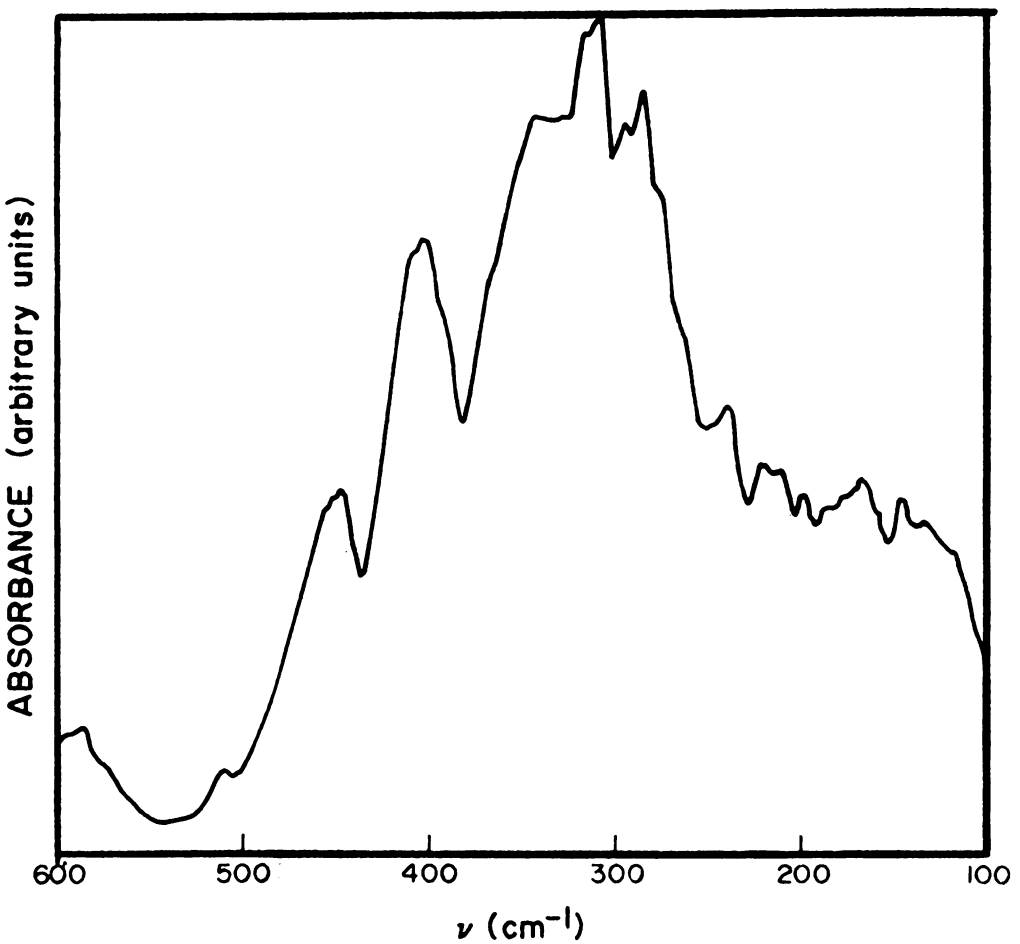
By using the ratio ν(Nb-Br)/ν(Nb-Cl) = 0.76, that was found for the monodentate thioether adducts of NbX_4,[19] one expects to find a ν(Nb-Br) mode at ca. 249 cm^{-1}. A broad intense band found at 253 cm^{-1} is assigned as the ν(Nb-Br) mode because of its absence in the chloride and iodide complexes. The ratio ν(Nb-I)/ν(Nb-Cl), calculated as 0.56 predicts a ν(Nb-I) mode ca. 184 cm^{-1}. A strong band is observed at 192 cm^{-1} and is assigned as ν(Nb-I).

Figure 8



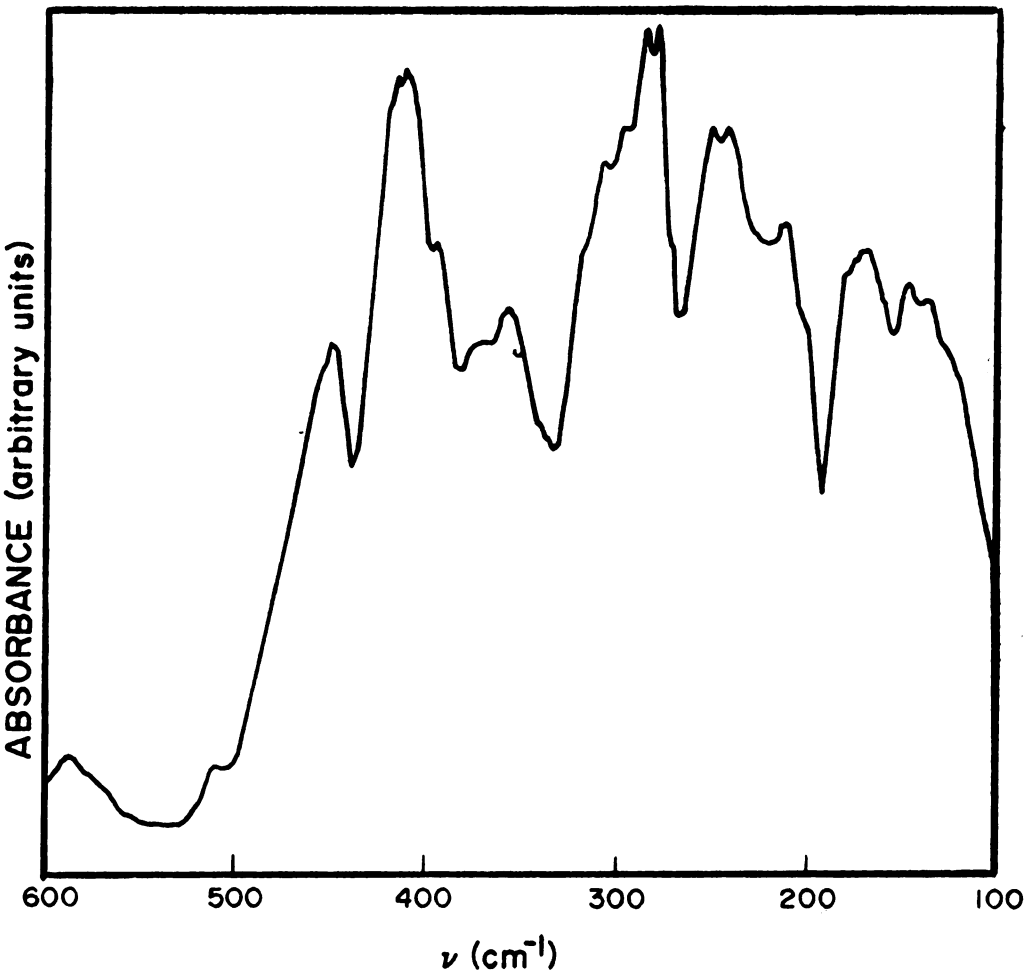
Far Infrared Spectrum of $NbCl_2[H_2B(Pz)_2]_2$ (Nujol)

Figure 9



Far Infrared Spectra of $NbBr_2[H_2B(Pz)_2]_2$ (Nujol)

Figure 10



Far Infrared Spectrum of $NbI_2[H_2B(Pz)_2]_2$ (Nujol)

Table 2

Far Infrared Spectral Data for $K[H_2B(Pz)_2]$ and $NbX_2[H_2B(Pz)_2]$ (600-100 cm^{-1})

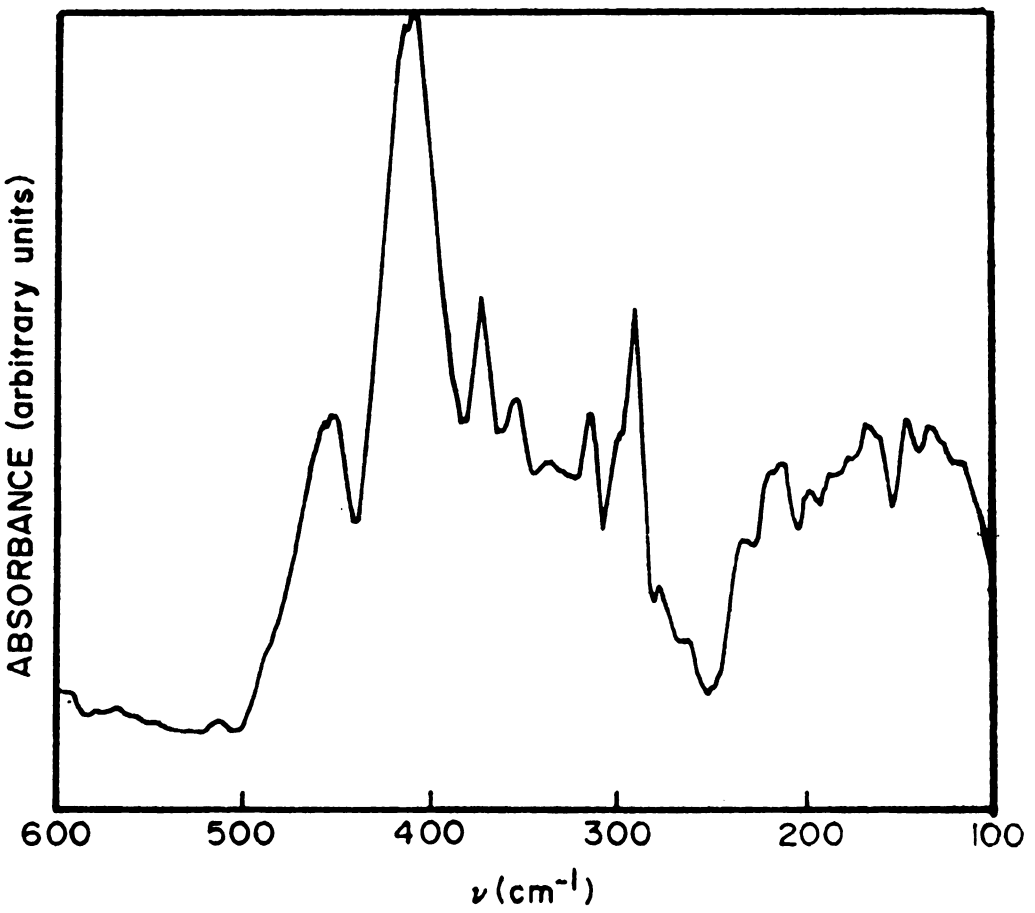
$K[H_2B(Pz)_2]$	X = Cl	X = Br	X = I
540 b	540 b	540 b	540 b
505 sh	505 sh	505 sh	505 sh
440 s	436 s	439 s	438 s
480 m	388 sh	384 s	395 sh
385 s	375 sh	335 m	383 m
348 m	358 sh	303 s	367 sh
335 sh	ν(Nb-Cl) 328 s,b	293 w	ν(Nb-N) 333 s
324 s	315 sh	277 sh	303 w
304 m	288 w	265 sh	293 sh
292 w	ν(Nb-N) 263 s	ν(Nb-Br) 253 s,b	268 s
282 m	227 m	230 m	222 m
268 w	200 m	205 w	ν(Nb-I) 192 s
257 s	150 m	194 w	155 m
227 sh	140 m	154 m	142 w
204 sh		140 w	
143 b			
125 sh			

b = broad, s = strong, m = medium, w = weak and
sh = shoulder.

Data for $Zr[H_2B(Pz)_2]_4$ and $ZrCl_2[H_2B(Pz)_2]_2$ are given in Table 3 and the spectra are shown in Figures 11 and 12. The metal-nitrogen vibrations are found at 252 and 362 cm^{-1} in $Zr[H_2B(Pz)_2]_4$. These bands were assigned as ν(Zr-N) bands because they are not present in $K[H_2B(Pz)_2]$. Bands at 255 and 325 cm^{-1} are assigned as ν(Zr-N) and ν(Zr-Cl) vibrations respectively for the $ZrCl_2[H_2B(Pz)_2]_2$. The far infrared indicates that bonding in niobium and zirconium complexes is very similar and possibly identical structures are present in each group of compounds. Actually the intensity and general shape of these spectra are virtually identical to those of the corresponding niobium complex with very little shift in some of the peaks.

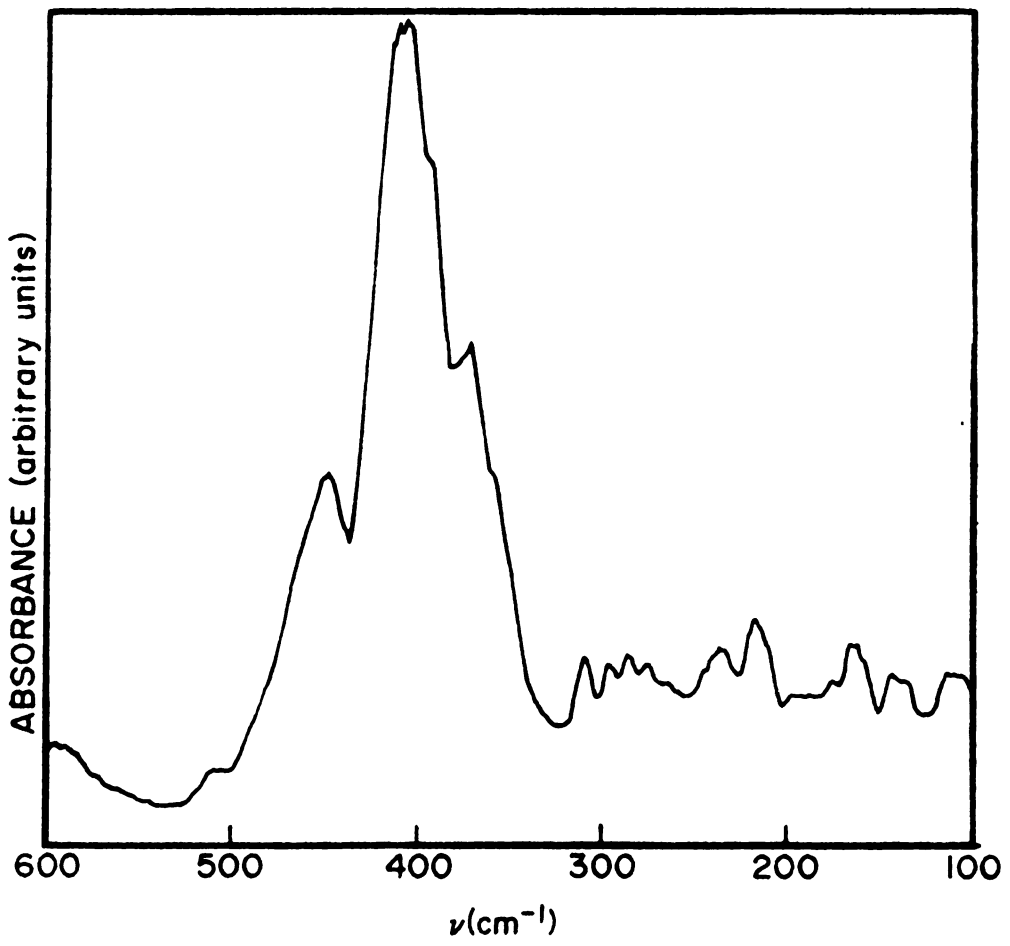
The products obtained by allowing one mole of potassium dihydrobis(pyrazol-1-yl)borate to react with one mole of NbX_4 (X = Cl, Br, and I) produced niobium-halogen stretching bands identical to those produced by $NbX_2[H_2B(Pz)_2]_2$. However, due to other changes in the spectra of the $NbX_3[H_2B(Pz)_2]$ complexes, it was not possible to assign the ν(Nb-N) vibration in the chloride complex, the bromide complex ν(Nb-N) band was clearly assigned at 362 cm^{-1} and the iodide complex ν(Nb-N) band was tentatively assigned at 330. Note in the $NbX_2[H_2B(Pz)_2]_2$ complexes the ν(Nb-N) assignments were made clearly for the chloride and iodide, and the bromide complex was unassigned. The spectra are presented in Figures 13, 14, and 15 and the parameters are given in Table 4.

Figure 11



Far Infrared Spectrum of $Zr[H_2B(Pz)_2]_4$ (Nujol)

Figure 12



Far Infrared Spectrum of $ZrCl_2[H_2B(Pz)_2]_2$ (Nujol)

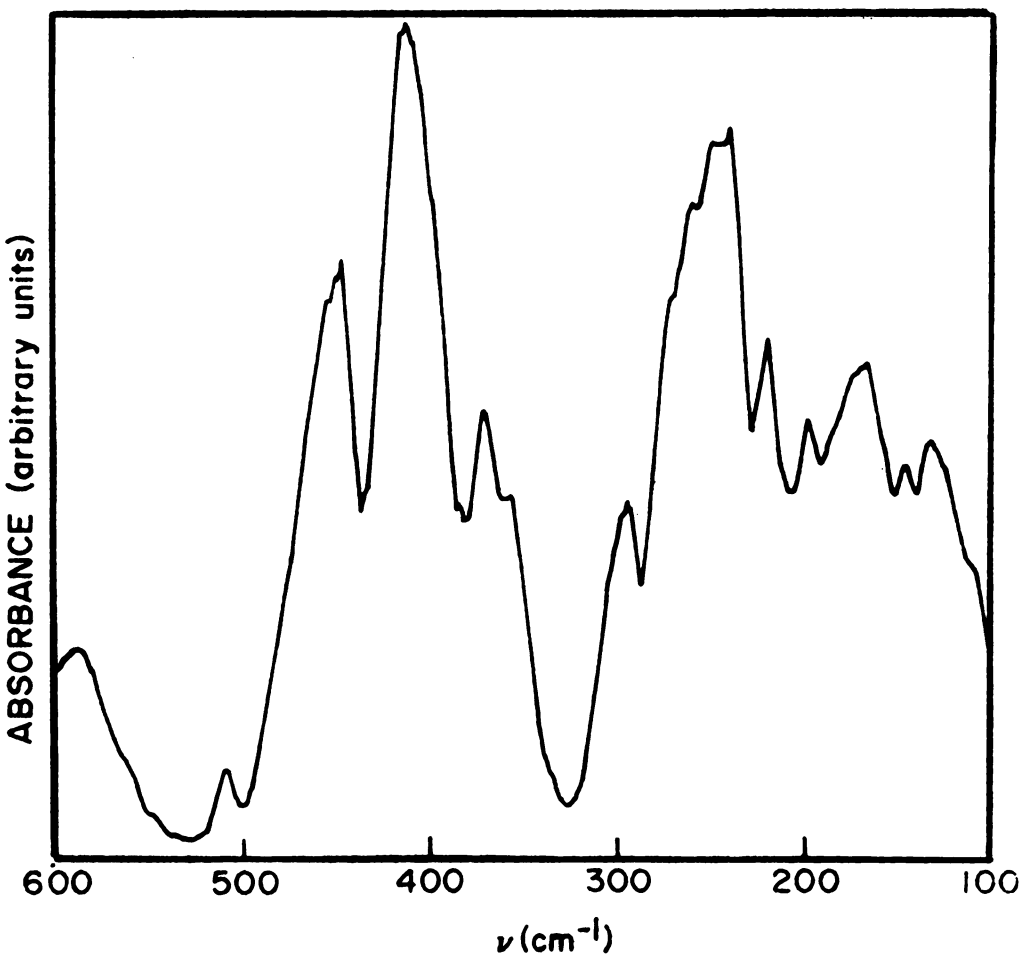
Table 3

Far Infrared Spectral Data for $K[H_2B(Pz)_2]$, $ZrCl_2[H_2B(Pz)_2]_2$ and $Zr[H_2B(Pz)_2]_4$ (600-100 cm^{-1})

$K[H_2B(Pz)_2]$	$ZrCl_2[H_2B(Pz)_2]_2$	$Zr[H_2B(Pz)_2]_4$
540 b	535 b	530 b
505 sh	506 sh	505 w
440 s	438 s	440 s
400 m	395 sh	383 s
385 s	383 m	ν(Zr-N) 362 m
348 m	365 sh	345 m
335 sh	ν(Zr-Cl) 325 s,b	323 w
324 s	305 m	307 s
304 m	293 w	280 w
292 w	282 w	268 sh
282 m	ν(Zr-N) 255 s,b	ν(Zr-N) 252 s,b
268 w	228 m	228 w
257 s	203 m	205 m
227 sh	174 w	192 w
204 sh	153 m	152 s
143 b	126 b	140 m
125 sh		

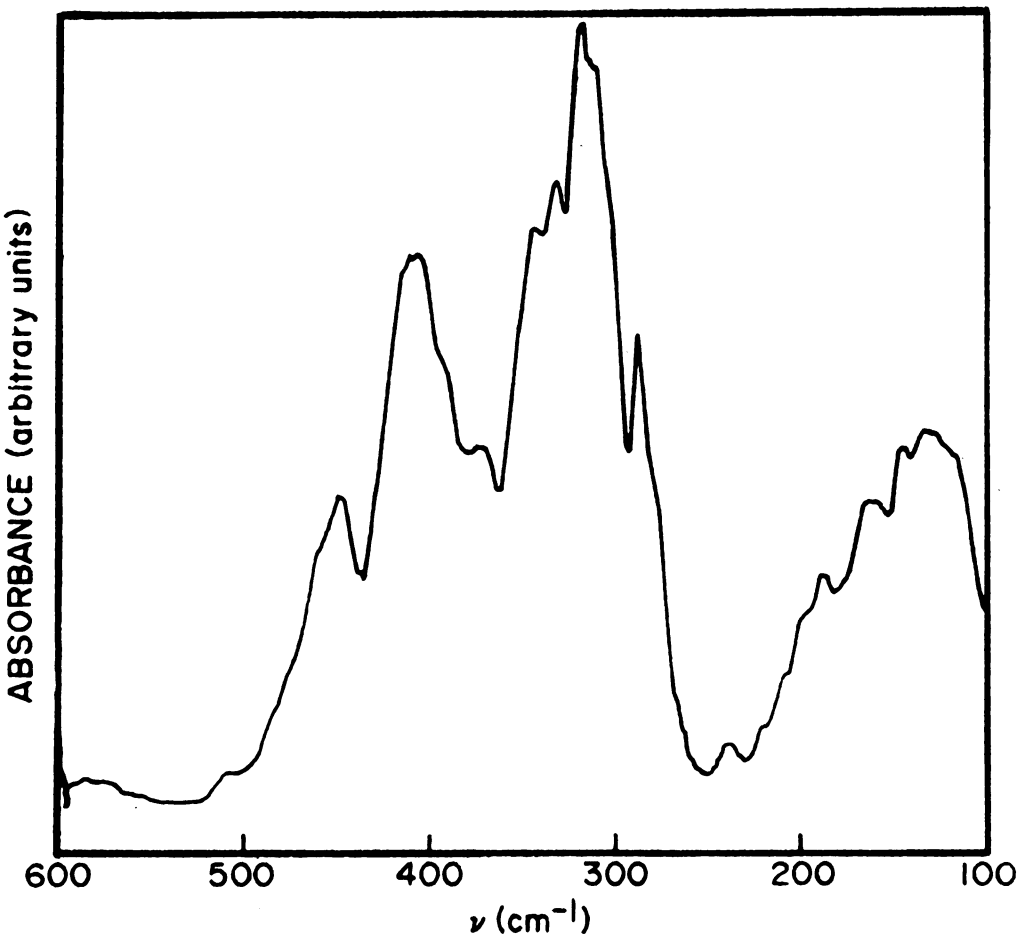
b = broad, s = strong, m = medium, w = weak and sh = shoulder.

Figure 13



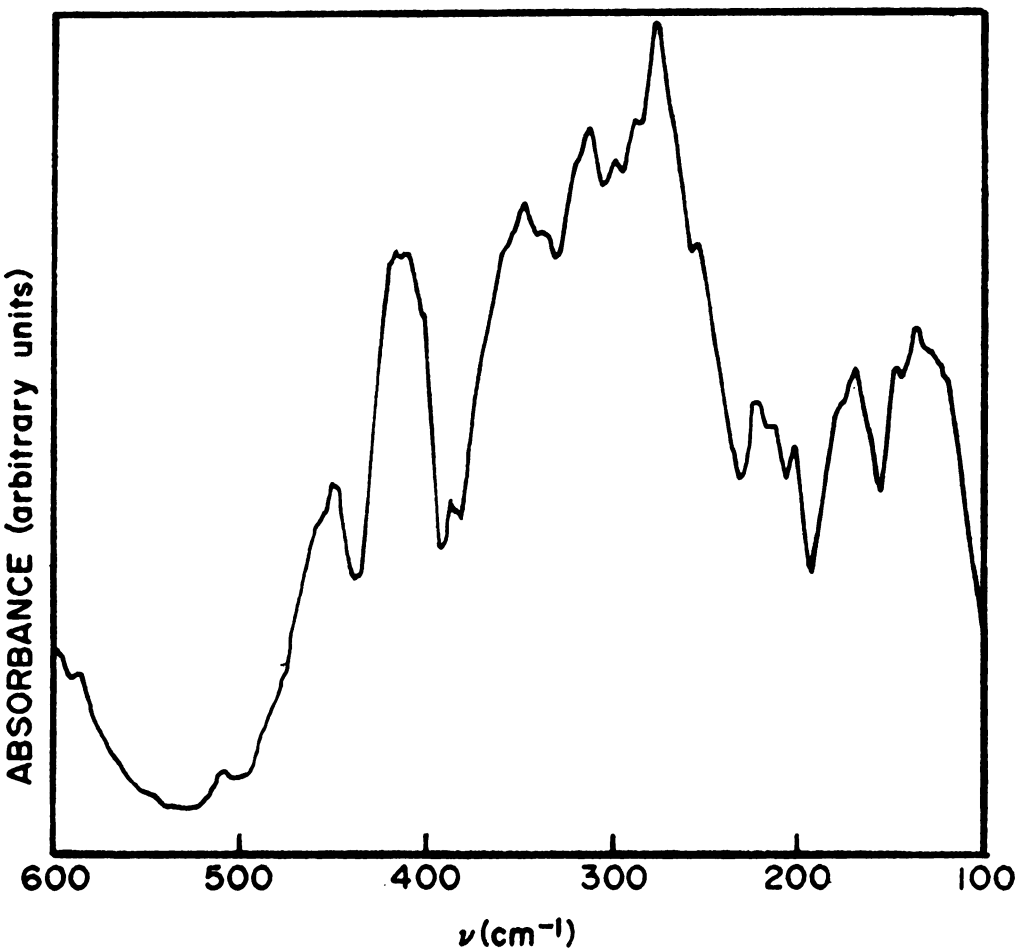
Far Infrared Spectrum of $NbCl_3[H_2B(Pz)_2]$ (Nujol)

Figure 14



Far Infrared Spectrum of $NbBr_3[H_2B(Pz)_2]$ (Nujol)

Figure 15



Far Infrared Spectrum of $NbI_3[H_2B(Pz)_2]$ (Nujol)

Table 4

Far Infrared Spectral Data for $K[H_2B(Pz)_2]$ and $NbX_3[H_2B(Pz)_2]$ (600-100 cm^{-1})

$K[H_2B(Pz)_2]$	$NbCl_3[H_2B(Pz)_2]$	$NbBr_3[H_2B(Pz)_2]$	$NbI_3[H_2B(Pz)_2]$
540 b	540 b	540 b	540 b
505 sh	503 m	505 sh	505 w
440 s	478 s	435 s	440 s
400 m	408 sh	380 w	393 s
385 s	383 s	ν(Nb-N) 362 s	382 s,sh
348 m	363 sh	338 sh	340 sh
335 sh	ν(Nb-Cl) 328 b,s	327 m	ν(Nb-N) 330 m
324 s	288 s	295 s	305 m
304 m	258 sh	ν(Nb-Br) 253 b,s	295 m
292 w	245 sh	232 m	285 sh
282 m	230 s	183 m	258 sh
268 w	210 s	155 m	230 s
257 s	192 m	142 m	205 m
227 sh	152 m		ν(Nb-I) 192 s
204 sh	140 m		155 s
143 b			145 w
125 sh			

b = broad, s = strong, m = medium, w = weak and sh = shoulder.

NMR Spectra of $Zr[H_2B(Pz)_2]_4$ and $ZrCl_2[H_2B(Pz)_2]_2$

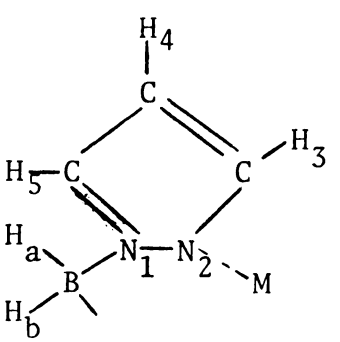
The ^1H nmr spectra of the tetrakis and bis complexes were recorded using $DCCl_3$ as solvent. The spectra of the diamagnetic chelates each consisted of two doublets and a triplet (made up of two overlapping doublets) in a 1:1:1 ratio, and an upfield singlet. The chemical shifts are shown in Table 5 relative to TMS.

Table 5

Proton Chemical Shifts (τ)

Assignments:	$Zr[H_2B(Pz)_2]_4$	$ZrCl_2[H_2B(Pz)_2]_2$
$B\text{-}H_a$	9.90	4.90
$B\text{-}H_b$	9.90	4.90
$C\text{-}H_3$	2.92*	4.00*
$C\text{-}H_4$	4.22	2.58
$C\text{-}H_5$	2.60*	3.92*

Measurements in $DCCl_3$ solution, relative to internal tetramethylsilane. *They could not be assigned unequivocally.



There are two possible conformations for the $B(N\text{-}N)_2Zr$ six-membered rings, one is the boat and the other is the chair. The boat[76] conformation allows, on the one hand, planarity of the nitrogen atoms and planarity for the rings. This results consequently in stabilization due to the delocalization of 6-π-electrons in each of the five-membered organic heterocyclic rings. In addition, a less angularly strained environment is obtained for the four-coordinate boron atoms. Such a structure places the hydrogen on boron in two unique environments. Such differently located hydrogen atoms should be clearly distinguishable by ^1H nmr. The fact that only one singlet is observed in these complexes implies that the two hydrogens on boron are equivalent. The equivalence of the two hydrogen atoms suggests that these complexes are stereochemically non-rigid in solution. Stereochemical nonrigidity has been proposed to account for similar behavior observed in many other transition metal complexes.[61,62,67] The fact that only one singlet is observed for the protons attached to the boron atom in the $ZrCl_2[H_2B(Pz)_2]_2$, is also direct evidence that the trans isomer is present in solution. A cis isomer would give a doublet (two singlets) for the two boron protons since these protons would be in two unique environments under all conditions of temperature. Solid state far infrared indicated previously that a trans isomer is present. Such an arrangement may also be used to explain the downfield shift of the protons attached to boron in the bis complex

as arising from protons interacting with the chloride. Trofimenko[77] has noted previously a downfield shift of half the methylene protons in the ^1H nmr spectra of the boron derivatives, $Ni(R_2B(Pz)_2]_2$ (R = Et, Bu), and postulated an interaction of these protons with the nickel atom to account for it.

The absence of a second set of aromatic protons in the ^1H nmr spectra indicates that the ligand is acting as a bidentate donor in both complexes. This is in agreement with the far infrared spectra.

X-Ray Powder Diffraction Analyses of $M[H_2B(Pz)_2]_4$ and $MX_2[H_2B(Pz)_2]_2$

Guinier powder patterns taken of the $MX_2[H_2B(Pz)_2]_2$ (M = Nb; X = Cl, Br, I) and (M = Zr; X = Cl) samples displayed considerable similarity for the zirconium(IV) chloride and the niobium(IV) chloride and bromide complexes but the pattern for the niobium(IV) iodide complex did not show any evidence of structure.

The $Zr[H_2B(Pz)_2]_4$ samples exhibited a powder pattern quite different from the above patterns and the $Nb[H_2B(Pz)_2]_4$, like the bis iodide complex, was devoid of structure. The fact that $NbX_2[H_2B(Pz)_2]_2$ (X = Cl, Br) proved to be isomorphous with $ZrCl_2[H_2B(Pz)_2]_2$ and that the ligand is acting bidentately in $ZrCl_2[H_2B(Pz)_2]_2$ supports the earlier conclusion, that $H_2B(Pz)^-$ is acting as a bidentate ligand in the niobium complexes. It also supports a proposed trans

configuration for the $NbX_2[H_2B(Pz)_2]_2$ complexes.

Electronic Spectra of $Nb[H_2B(Pz)_2]_4$

Visible and near infrared spectra of $Nb[H_2B(Pz)_2]_4$ were studied by using the technique described in the experimental section. These studies were carried out with dichloromethane solutions of the complexes. The spectra and wave number maxima of the $Nb[H_2B(Pz)_2]_4$ complex are given in Figure 16 and Table 6 respectively.

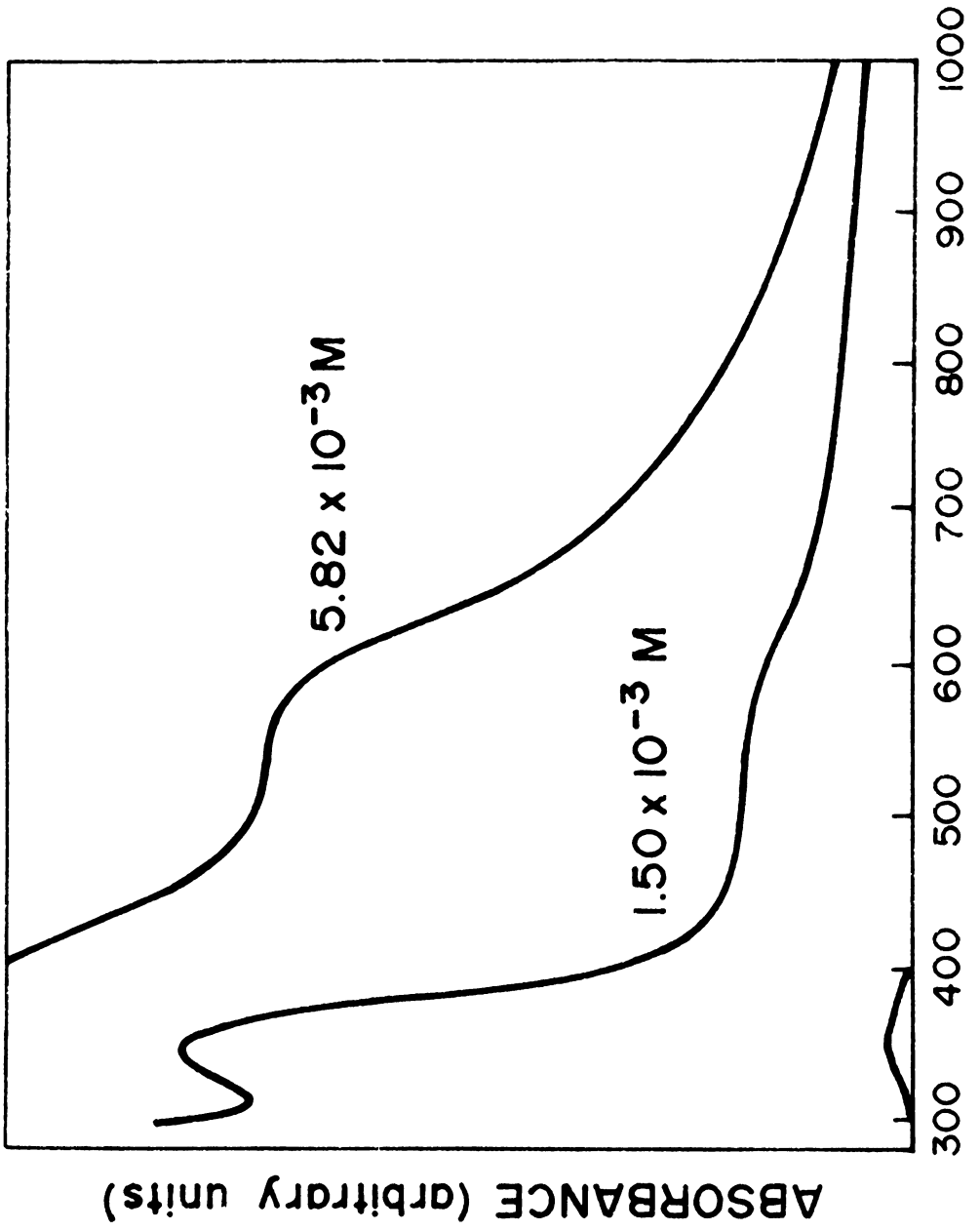
Table 6

Electronic Spectral Data of $Nb[H_2B(Pz)_2]_4$ in CH_2Cl_2

λ(nm)	$\bar{\nu}(cm^{-1}) \times 10^3$	$\varepsilon(cm^{-1}\ M^{-1})$
540	18.52	126.00
340	29.41	538.67

The qualitative features of the spectra include one weak broad band at 540 nm. In addition a strong band is observed at 340 nm. There are three possibilities for assigning these bands. 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 band at 540 nm (ε = 126.00) it can be assigned confidently as arising from a d-d transition. The extinction coefficient is in the range that other authors have assigned as d-d transitions.[24] The intense band in the

Figure 16



Electronic Spectra of $Nb[H_2B(Pz)_2]_4$ in CH_2Cl_2

ultraviolet region is due to ligand charge transfer. This assignment was confirmed by observing an identical band at ≈340 nm for a dichloromethane solution of the analogous zirconium complex.

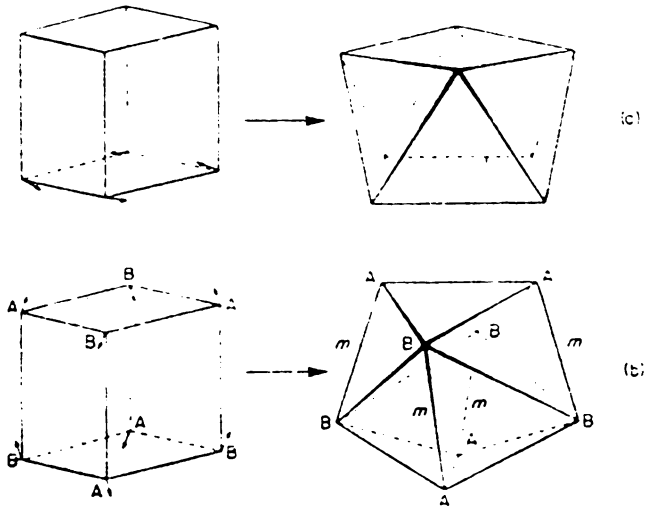
Two common symmetries are observed for eight-coordinate transition metal complexes: the D_{2d} triangular dodecahedron and the D_{4d} square antiprism. These structures are formed by distorting the cube. Figures 17 and 18 show the most common structures and the crystal field splitting diagrams for a D_{2d} dodecahedron and a D_{4d} square antiprism[29,78] respectively. In the case of D_{4d} symmetry, two d-d transitions are predicted while for D_{2d} symmetry three transitions are expected. Since only one band was observed which is assigned as a d-d transition no structure assignment can be made on the basis of the spectrum.

Electronic Spectra of $NbX_2[H_2B(Pz)_2]_2$

The solution spectra and wave number maxima of $NbX_2[H_2B(Pz)_2]_2$ (X = Cl, Br, and I) complexes are given in Figures 19, 20 and 21 and Table 7 respectively. The dichloromethane solution spectra consist of two bands for the chloride species, and three bands each for the bromide and iodide complexes. The ligand charge transfer band is observed in all three complexes ca., 340 nm. This assignment was again confirmed by observing an identical band at about 340 nm in the dichloromethane solution spectra of the isomorphous

Figure 17

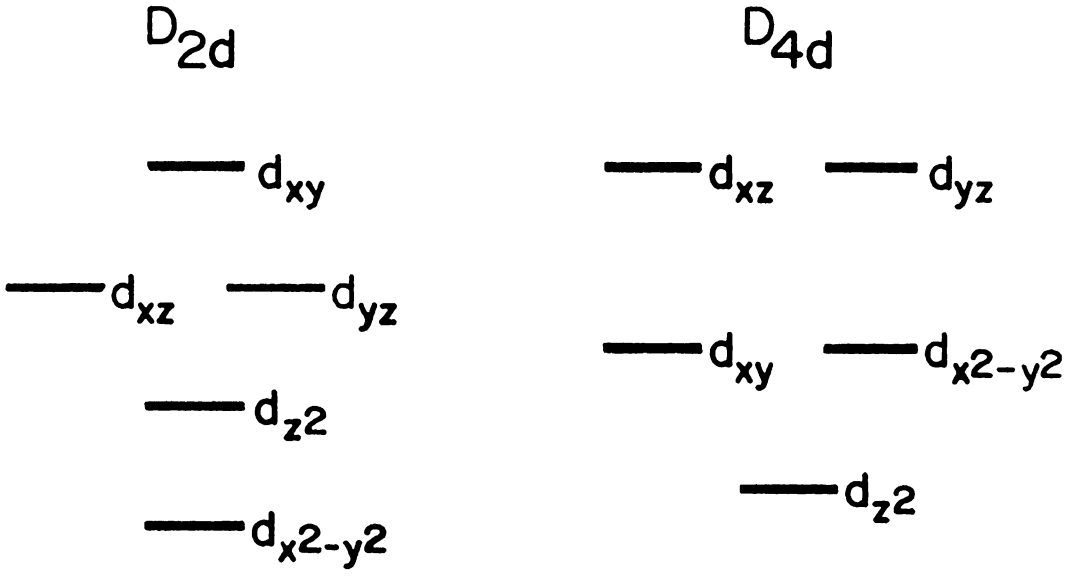
For coordination number 8, the most common structures may be viewed as distortion of a cube.



The two most important ways of distorting the cube: (a) to produce a square antiprism; (b) to produce a dodecahedron.

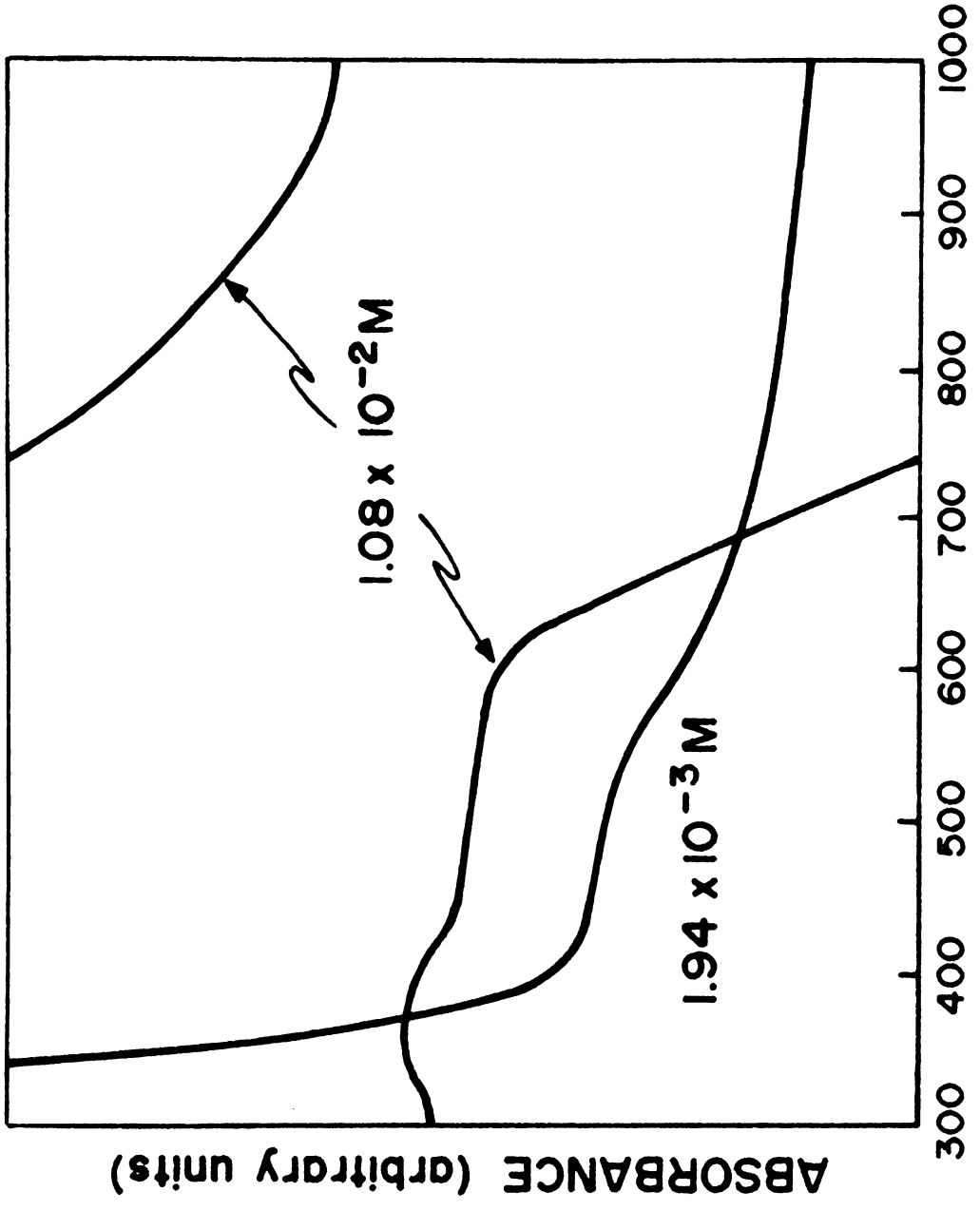
Distortion of a Cube

Figure 18



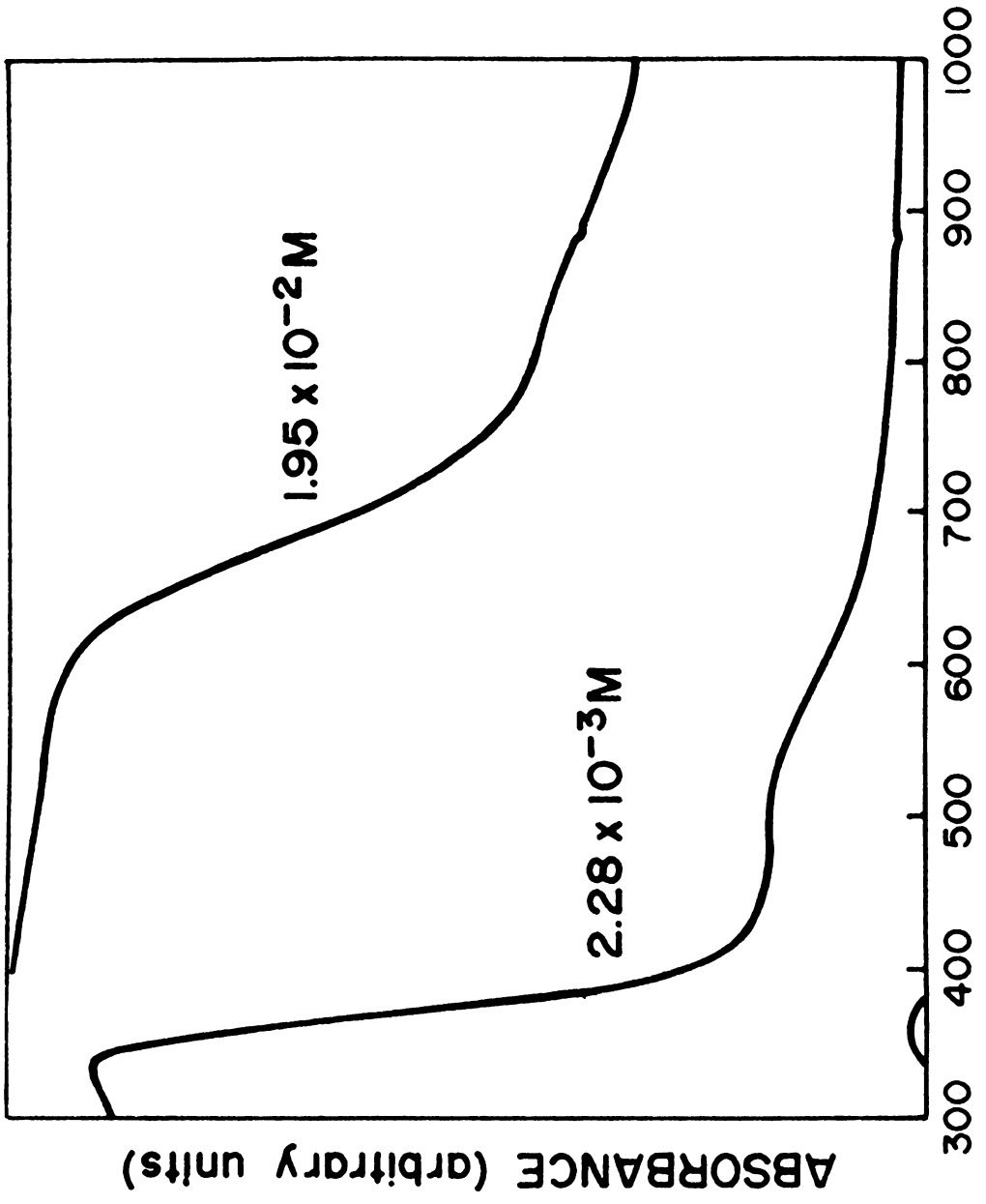
The crystal field splitting for D_{2d} and D_{4d} symmetries

Figure 19



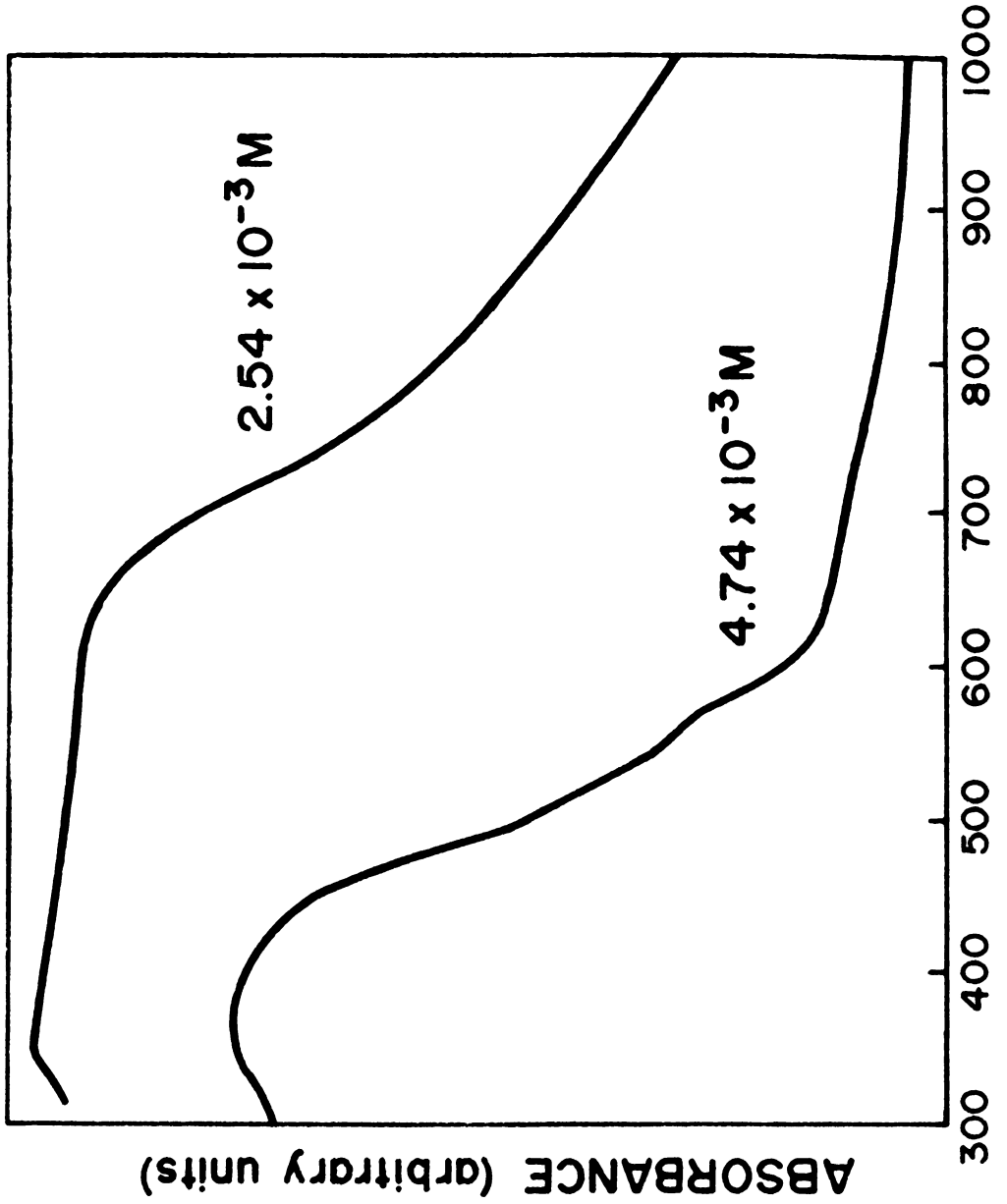
Electronic Spectra of $NbCl_2[H_2B(Pz)_2]_2$ in CH_2Cl_2

Figure 20



Electronic Spectra of $NbBr_2[H_2B(Pz)_2]_2$ in CH_2Cl_2

Figure 21



Electronic Spectra of $NbI_2[H_2B(Pz)_2]_2$ in CH_2Cl_2

Table 7

Electronic Spectral Data of $NbX_2[H_2B(Pz)_2]_2$ in CH_2Cl_2

Complex	λ(nm)	$\nu(cm^{-1}) \times 10^3$	$\varepsilon(cm^{-1}\ M^{-1})$
X = Cl	480	20.83	180.93
	340	28.41	380.61
X = Br	800	12.50	17.54
	500	20.00	75.00
	340	28.41	399.56
X = I	700	14.29	23.21
	560	17.86	61.81
	360	27.78	163.92

$ZrCl_2[H_2B(Pz)_2]_2$. This band also corresponds to the charge transfer band found in the spectrum of $Nb[H_2B(Pz)_2]_4$. In addition, a band at 480 nm is present in the chloride complex. Bands are located at 800 nm and 500 nm, and 700 nm and 500 nm in the bromide and iodide respectively. On the basis of the observed extinction coefficients of these bands they are assigned as due to d-d transitions.

The spectra of the trans-$NbX_2[H_2B(Pz)_2]_2$ complexes can be discussed relative to crystal field theory.[19] It has been shown, at least qualitatively, that the spectra of trans-MX_2B_2 molecular complexes can be discussed as tetragonally (D_{4h}) perturbed complexes.[79] The effect of a tetragonal component in the ligand field upon terms arising in O_h cause the $^2T_{2g}$ level to resolve into $^2B_{2g}$ and ^2E_g levels and the excited ^2E_g level to $^2B_{1g}$ and $^2A_{1g}$. Hence one would expect three transitions from the splitting of the d-manifold. Treating these trans complexes as D_{4h} symmetry the expected transitions will be from the ground $^2B_{2g}$ level to the excited ^2E_g, $^2A_{1g}$ and $^2B_{1g}$ levels. In no case are three bands observed. The absence of some of the d-d transitions are well-known[80,81] in related systems. Fowles[80] et al. have 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. Hence it is conceivable that a similar situation exists in these systems.

Electronic Spectra of "$NbX_3[H_2B(Pz)_2]$"

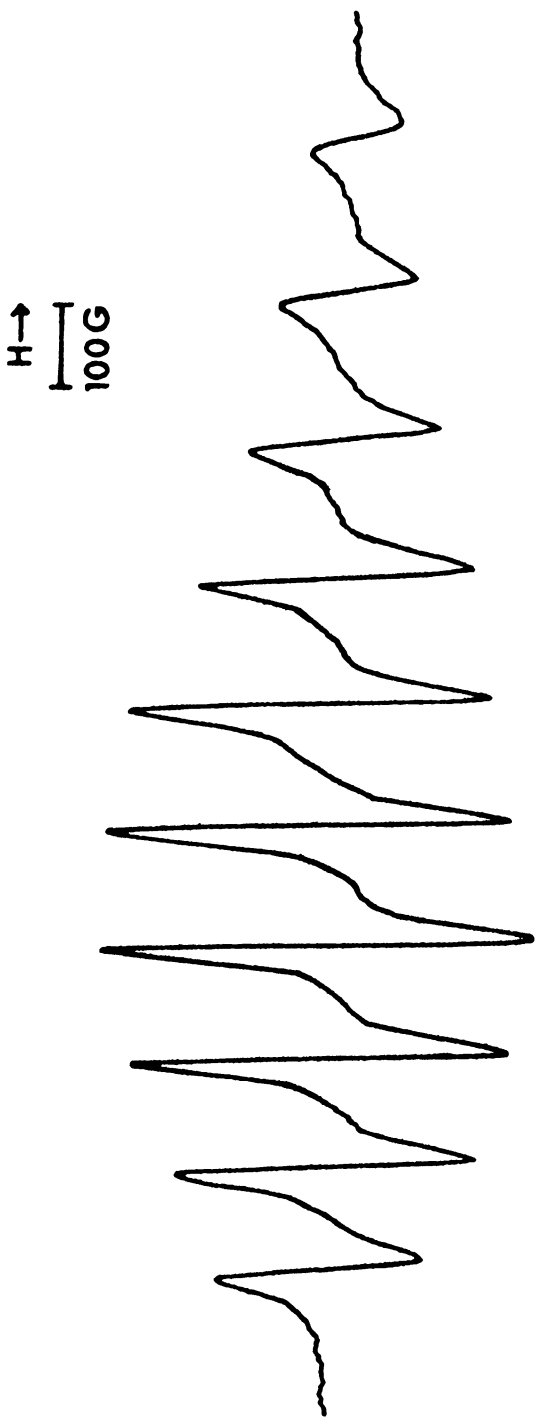
The visible and near infrared spectra of the species, obtained by allowing a one to one molar ratio of $K[H_2B(Pz)_2]$:NbX_4 (X = Cl, Br, and I) to react in dichloromethane, consisted of two bands in each case. A band observed at 340 nm was assigned as a ligand to metal charge transfer vibration as in the bis and tetrakis niobium complexes. The band ranging from 470 nm for the chloride complex to 570 nm for the iodide complex was assigned as a d-d transition. The extinction coefficient of each complex was in the range which other authors have assigned as d-d transitions.[24] Neither trigonal bipyramidal nor square pyramidal geometry can account for the spectra. At least two transitions are expected for both trigonal bipyramidal and square pyramidal complexes. As proposed in the $NbX_2[H_2B(Pz)_2]_2$ systems the d-d transitions could be masked by halogen(π)-niobium(d) transitions in these species.

These results are by no means conclusive, but they are indicative of the fact that a species is present which is different from both $Nb[H_2B(Pz)_2]_4$ and $NbX_2[H_2B(Pz)_2]_2$.

Electron Spin Resonance Spectra of $Nb[H_2B(Pz)_2]_4$

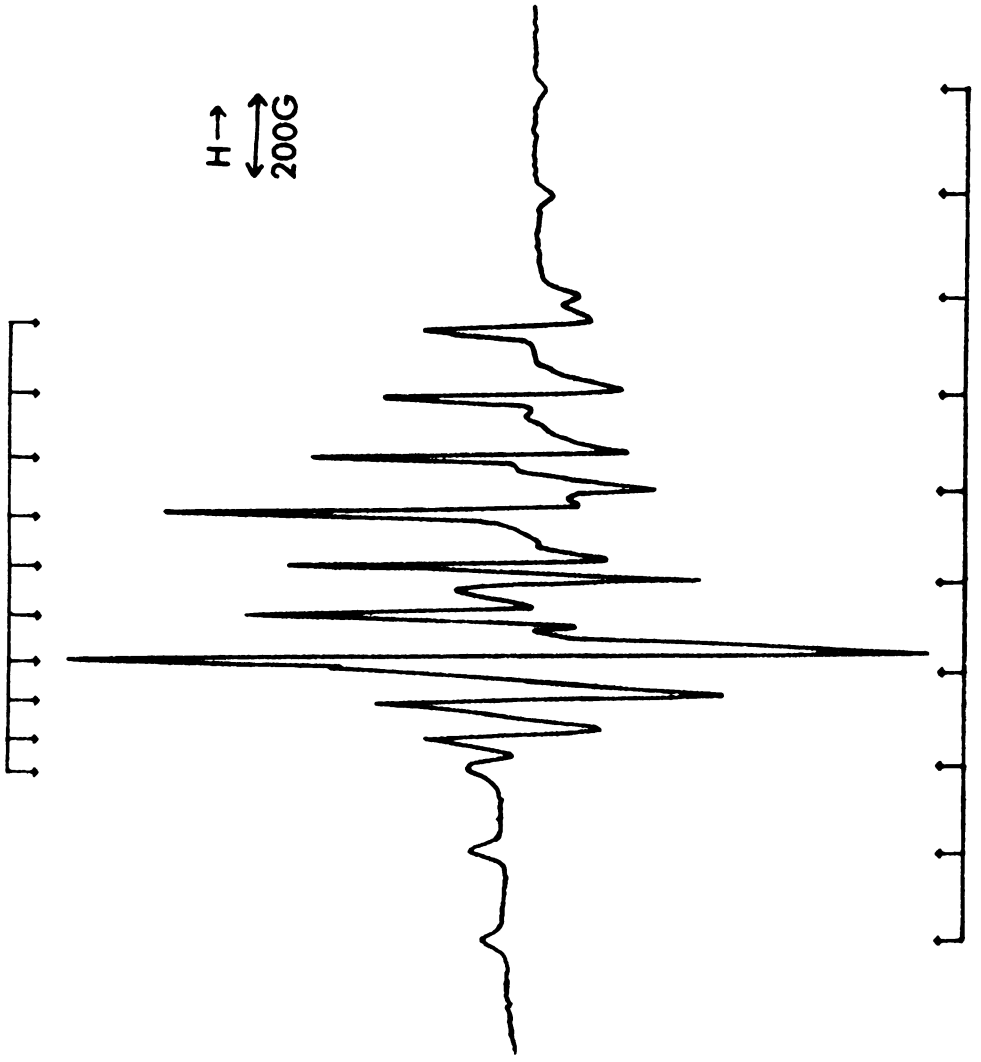
Esr studies were performed on $Nb[H_2B(Pz)_2]_4$ as described in the Experimental section. The spectra are presented in Figures 22, 23 and 24. Since the hyperfine splittings are on the order of 160 gauss the high field approximation cannot

Figure 22



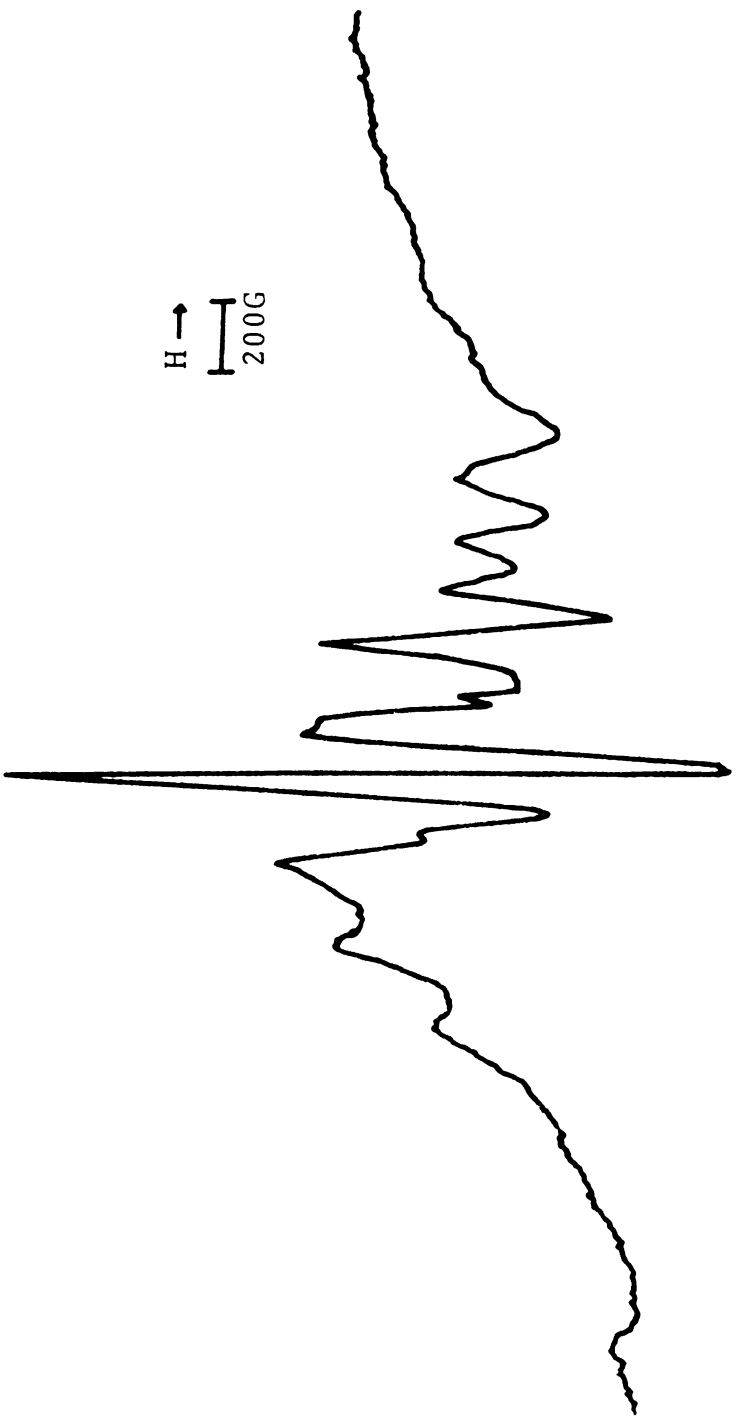
Esr Spectrum of $Nb[H_2B(Pz)_2]_4$ in Toluene at Ambient Temperature

Figure 23



Esr Spectrum of $Nb[H_2B(Pz)_2]_4$ in Toluene at 77 K

Figure 24



Esr Spectrum of Solid $Nb|H_2B(Pz)_2|_4$ at Ambient Temperature

be rigorously applied and second order corrections should be employed. The perturbation of the Zeeman transition resulting from the hyperfine interactions was corrected by means of the following equations:[82]

$$h\nu = gBH_o \tag{9}$$

$$\text{for isotropic g:} \quad H_m' = H_m + \langle a \rangle m_I + \frac{\langle a \rangle^2}{2H_m} [I(I+1) - m_I^2] \tag{10}$$

$$\text{for } g_{||}: \quad H_m' = H_m + A_{||} m_I + \frac{A_{\perp}^2}{2H_m} [I(I+1) - m_I^2] \tag{11}$$

$$\text{for } g_{\perp}: \quad H_m' = H_m + A_{\perp} m_I + \left(\frac{A_{||}^2 + A_{\perp}^2}{4H_m}\right) [I(I+1) - m_I^2] \tag{12}$$

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 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 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:

$$A\ (cm^{-1}) = g \times 4.6686 \times 10^{-5}\ A\ (\text{gauss}) \tag{13}$$

The experimental esr parameters are listed in Table 8 with the corrections due to second order effects.

Table 8

Esr Spectral Parameters of $Nb[H_2B(Pz)_2]_4$

		<g>	$g_{\|\|}$	$g_{\perp}$	*<a>	$*A_{\|\|}$	$*A_{\perp}$
Experimental	Solid	†2.012	1.892	2.072		227	113
Corrected		†1.955	1.903	1.982		254	93
Experimental	Soln.	2.012	1.892	2.072	153	227	113
Corrected		1.955	1.903	1.982	148	254	93

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

The esr spectral parameters were identical for the solid at both 298 and 77 K.

<> values were obtained from spectra recorded at 298 K and the $||$ and $\perp$ values were obtained from spectra recorded at 77 K.

†<g> is assumed to be the same in the solid as in the solution.

In dichloromethane or toluene glass at 77 K the esr spectrum may be described by the spin Hamiltonian with axial symmetry:[83]

$$H = g_{||}BH_zS_z + g_{\perp}(H_xS_x + H_yS_y) + A_{||}S_zI_z + A_{\perp}(S_xI_x + S_yI_y) \quad (14)$$

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:

$$H = \langle g \rangle BH \cdot S + \langle a \rangle I \cdot S \qquad (15)$$

Theoretical calculations of esr parameters for a D_{2d} dodecahedron and a D_{4d} square antiprism show that $g_{\perp} > g_{||}$ for a dodecahedron[29,30] and $g_{||} > g_{\perp}$ for a square antiprism.[29,31] For $Nb[H_2B(Pz)_2]_4$, $g_{\perp} = 1.982$ and $g_{||} = 1.903$ indicates dodecahedral symmetry. The $g_{||}$ and $g_{\perp}$ values for the solid powder esr spectra are the same as the above values indicating the stereochemistry remains the same in the solid and in solution. In comparison to other known eight coordinate complexes of Nb(IV) listed in Table 9, the data observed here fit well. Two complexes where $g_{||} > g_{\perp}$, $Nb(dpm)_4$[36,37] and $Nb(CN)_8^{4-}$ (soln)[17,39] 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. However, recent work[39] confirmed the belief that the $Nb(CN)_8^{4-}$ species actually change symmetry in solution. The esr spectrum of a magnetically dilute solid solution of $K_4[Nb(CN)_8] \cdot 2H_2O$ in isomorphous $K_4[Mo(CN)_8] \cdot 2H_2O$ shows $g_{\perp} > g_{||}$ in agreement with theoretical predictions.

Table 9

Esr Parameters for Eight-Coordinate Niobium(IV) Species

Compounds	<g>	$g_{\|\|}$	$g_{\perp}$	*<a>	$*A_{\|\|}$	$*A_{\perp}$
$NbCl_4(dth)_2$ [28]	1.9969	1.9314	2.0296	134.6	183.5	108.9
$Nb(dmtp)_4$ [56]	1.9791	1.8756	2.0308	136.9	216.9	92.0
$Nb(CN)_8^{-4}$ (solid) [17,39]	1.987	1.976	1.992	101	154	75
$Nb(pipdtc)_4$ [38]	1.9471	1.8969	1.9722	108	190	65
$Nb[H_2B(Pz)_2]_4$	1.955	1.903	1.982	148	254	93
†$Nb(dpm)_4$ [36,37]	1.9507	1.9967	1.9278	100.1	49.1	127.0
†$Nb(CN)_8^{-4}$ (soln) [17,39]	1.980	2.000	1.970	97	49	121

*In units of 10^{-4} cm^{-1}.

†Indicates square antiprism structures, all others are trigonal dodecahedron structures.

In most systems data from the esr studies can be used in conjunction with the electronic spectral assignments to determine the applicability of an ionic model to the system. It has been demonstrated that while the dodecahedral model has D_{2d} symmetry, it can be considered as arising from the distortion of a cube (see Figure 15). 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:[30]

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

where λ is the free ion coupling constant, $\Delta E_3 = ({}^2B_2 - {}^2B_1)$, and $\Delta E_2 = ({}^2E_3 - {}^2B_1)$. It was not possible to qualitatively assess the applicability of an ionic model in the case of $Nb[H_2B(Pz)_2]_4$ because only one d-d transition (ΔE) was observed in the electronic spectrum. The above equations will be used to assess a different system later in this study.

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:

$$\mu_{eff}(\text{B.M.}) = g\sqrt{S(S+1)} \tag{17}$$

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 10 lists calculated μ_{eff} values for the compounds listed in Table 9. From the table, the

Table 10

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

Compounds	μ_{eff}(B.M.)
$NbCl_4(dth)_2$[28]	1.73
$Nb(dmtp)_4$[56]	1.71
$Nb(dpm)_4$[36,37]	1.69
$Nb(CN)_8^{4-}$ (solid)[17,39]	1.72
$Nb(CN)_8^{4-}$ (soln)[17,39]	1.71
$Nb(pipdtc)_4$[38]	1.70
$Nb[H_2B(Pz)_2]_4$	1.69

ability of nitrogen-donor ligands to form fairly covalent species with Nb(IV) is illustrated.

Further confirmation of the bonding is obtained by using Equation 18 developed by McGarvey.[29]

$$A_{||} = P[-\kappa - 4/7 + (g_{||}-2.0023) + 3/7(g_{\perp}-2.0023)]$$

$$A_{\perp} = P[-\kappa + 2/7 + 11/14(g_{\perp}-2.0023)] \qquad (18)$$

where $P = g_e g_N \beta_e \beta \langle r^{-3} \rangle_{ave}$ and is defined as positive for ^{93}Nb which has a positive nuclear moment, $\langle r^{-3} \rangle_{ave}$ is the reciprocal cube of the average radical 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.

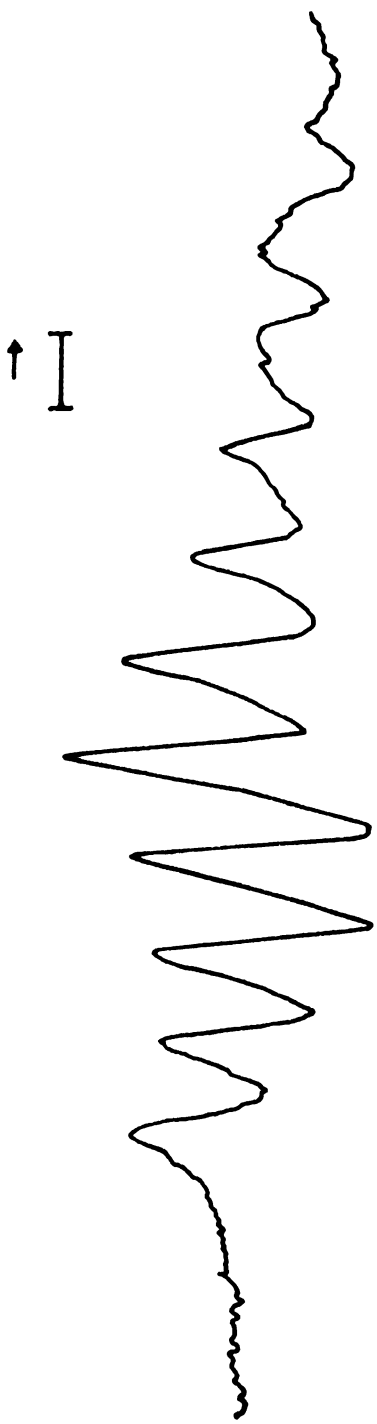
Agreement with experimental data is found for values of $\kappa = 0.818$ and $P = 169.6 \times 10^{-4}$ cm^{-1}. Comparing these values with those for a Nb^{4+} free ion, $\kappa = 1.0$ (pure d orbital) and $P = 192.0 \times 10^{-4}$ cm^{-1},[84] the smaller experimental value for P indicates that the unpaired electron is more delocalized, hence more covalent in bonding orbitals.

Electron Spin Resonance Spectra of $NbX_2[H_2B(Pz)_2]_2$ in Dichloromethene

Representative esr spectra of $NbX_2[H_2B(Pz)_2]_2$ (X = Cl, Br, and I) are presented in Figures 25, 26, 27 and 28. Since the hyperfine splittings are large, second order corrections were employed according to equations 9-12 to correct for the perturbation of the Zeeman transition resulting from the hyperfine interaction. The hyperfine components in gauss were converted to cm^{-1} by use of equation 13. The experimental esr parameters are listed in Table 11 with the corrections due to second order effects.

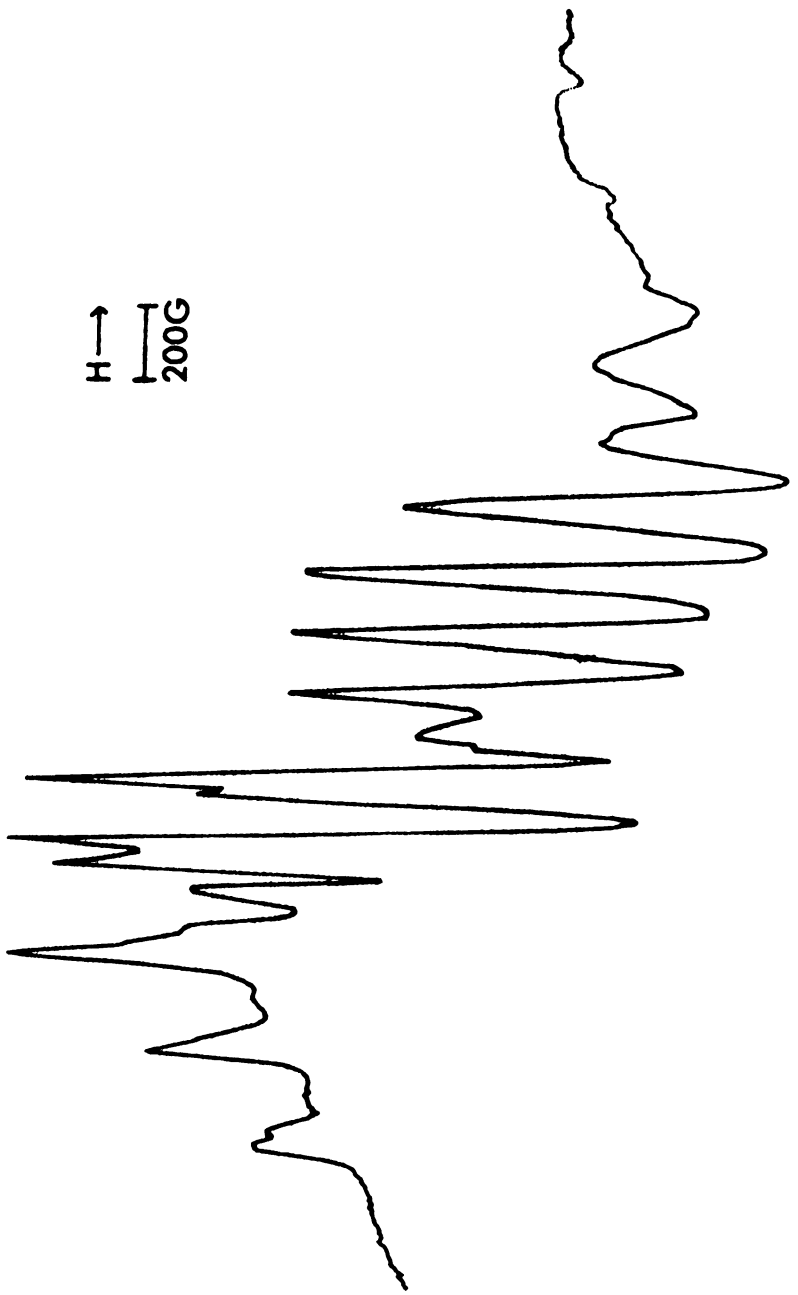
Examination of these data reveals the fact that in all cases $g_{||}$ is less than $g_{\perp}$. It is of interest to note that of those esr studies of octrahedral niobium(IV) complexes which have been reported most have $g_{||}$ greater than $g_{\perp}$. Exceptions to this appear to occur with transition metal complexes where the ligands bonded in both axial and equatorial sites have similar electron donating properties.[55,85]

Figure 25



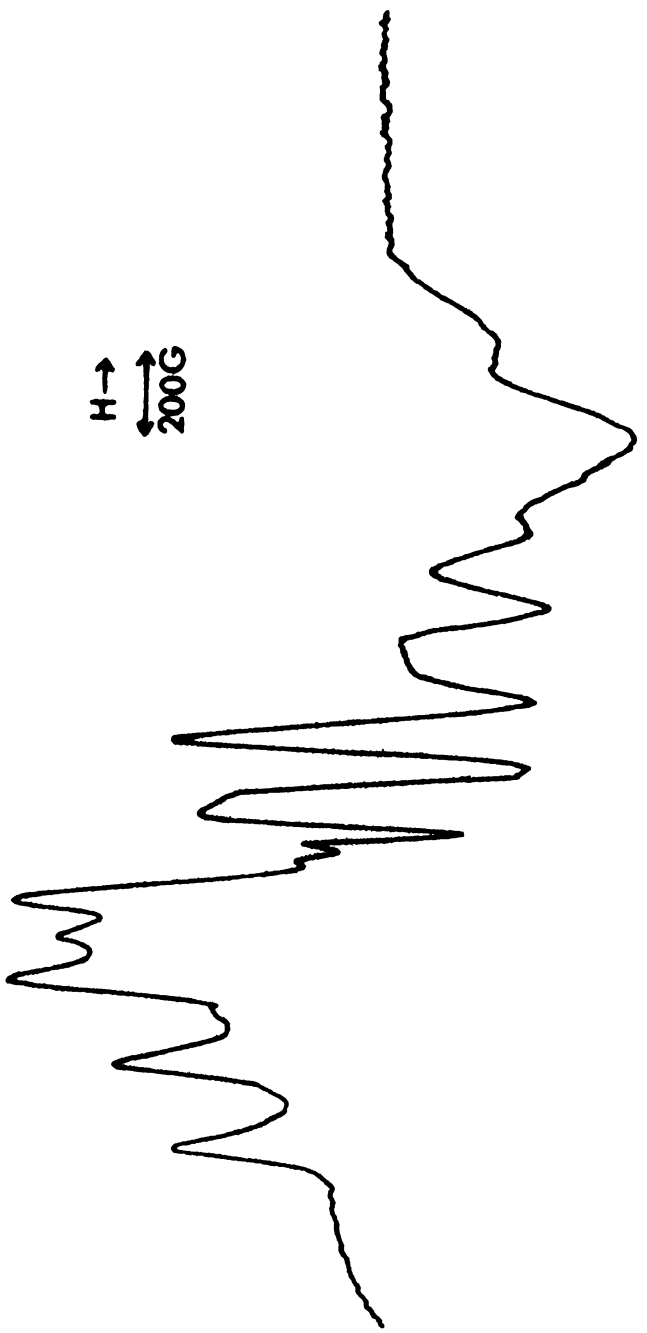
Esr Spectrum of $NbBr_2[H_2B(Pz)_2]_2$ in CH_2Cl_2 at Ambient Temperature

Figure 26



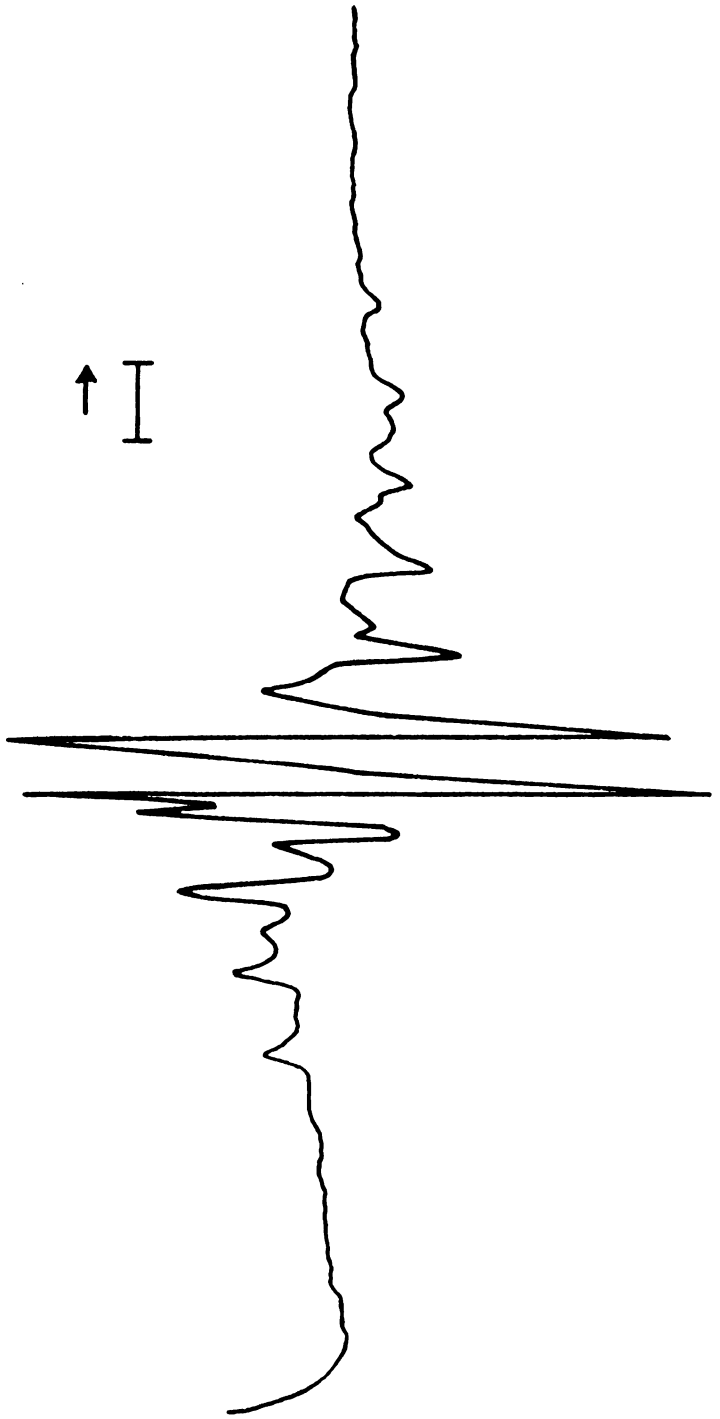
Esr Spectrum of $NbCl_2[H_2B(Pz)_2]_2$ in CH_2Cl_2 at 77 K

Figure 27



Esr Spectrum of $NbBr_2[H_2B(Pz)_2]_2$ in CH_2Cl_2 at 77 K

Figure 28



Esr Spectrum of $NbI_2[H_2B(Pz)_2]_2$ in CH_2Cl_2 at 77 K

Table 11

Solution Esr Spectral Parameters of NbX_2B_2 Complexes

Compounds	<g>	$g_{\|\|}$	$g_{\perp}$	*<a>	$*A_{\|\|}$	$*A_{\perp}$
$NbCl_2B_2$	1.965	1.763	2.066	151	224	108
$^{\dagger}NbCl_2B_2$	1.911	1.739	2.000	146	250	86
$NbBr_2B_2$	1.975	1.929	1.998	128	200	91
$^{\dagger}NbBr_2B_2$	1.936	1.909	1.950	125	217	78
NbI_2B_2	1.983	1.911	2.019	127	204	86
$^{\dagger}NbI_2B_2$	1.944	1.891	1.971	124	207	80

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

†Corrected values (due to second order effects).

B = $H_2B(Pz)_2^-$

<> values were obtained from spectra recorded at 298 K and the $||$ and $\perp$ values were obtained from spectra recorded at 77 K.

Data from the esr studies can now be used in conjunction with the electronic spectral assignments for $NbX_2[H_2B(Pz)_2]_2$ to determine the applicability of an ionic model to these systems. For a $d_{x^2-y^2}$ ground state, the gyromagnetic ratios are given by equation 16. Taking the spin-orbital coupling constant for Nb^{4+} as 748 cm^{-1} and ΔE_2 and ΔE_3 as 20.00×10^3 and 12.50×10^3 cm^{-1} respectively for $NbBr_2[H_2B(Pz)_2]_2$ and ΔE_2 and ΔE_3 as 14.29×10^3 and 17.86×10^3 respectively for $NbI_2[H_2B(Pz)_2]_2$, the calculated values of $g_{||}$ and $g_{\perp}$ are 1.52 and 1.93 respectively for $NbBr_2[H_2B(Pz)_2]_2$ and 1.58 and 1.92 respectively for $NbI_2[H_2B(Pz)_2]_2$. It was not possible to assess the chloride complex because only one d-d transition (ΔE) was observed in the electronic spectrum. These values are much lower than the experimental values and indicates the inadequacy of the ionic model.

It is possible to qualitatively assess the amount of covalent bonding via equation 19.[30]

$$g_{||} = 2.0023 - \frac{8\lambda\alpha^2\beta^2}{\Delta E_3} \qquad g_{\perp} = 2.0023 - \frac{2\lambda\alpha^2\gamma^2}{\Delta E_2} \tag{19}$$

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 $\alpha^2\gamma^2 = .699$ and $\alpha^2\beta^2 = .195$ for $NbBr_2[H_2B(Pz)_2]_2$, and $\alpha^2\gamma^2 = .374$ and $\alpha^2\beta^2 = .266$ for

$NbI_2[H_2B(Pz)_2]_2$. 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 $NbBr_2[H_2B(Pz)_2]_2$ and $NbI_2[H_2B(Pz)_2]_2$.

By using equation 18[29] agreement with experimental data is found for values of κ and P at 0.870 and 146.6 x 10^{-4} cm^{-1} respectively for $NbCl_2[H_2B(Pz)_2]_2$, 0.767 and 149.2 x 10^{-4} cm^{-1} respectively for $NbBr_2[H_2B(Pz)_2]_2$ and 0.864 and 132.7 x 10^{-4} cm^{-1} respectively for $NbI_2[H_2B(Pz)_2]_2$. In each case the P value is smaller than the P value for the Nb^{4+} free ion.[84] This indicates that the unpaired electron is more delocalized, hence more covalent in nature. The results are in good agreement with the conclusion made using the electronic spectral data in conjunction with esr spectral data.

Electron Spin Resonance Spectra of $NbX_2[H_2B(Pz)_2]_2$ in Ethanol

Analyses of the esr spectra obtained from the deep blue solution produced by dissolving $NbX_2[H_2B(Pz)_2]_2$ (X = Cl, Br and I) in ethanol, give esr parameters quite different from the parameters obtained in dichloromethane. Identical spectra are obtained in all three cases. The esr spectra parameters are presented in Table 12.

Table 12

Esr Spectral Parameters of $NbCl_2[H_2B(Pz)_2]_2$
Dissolved in Ethanol

<g>	$g_{\|\|}$	$g_{\perp}$	*<a>	$*A_{\|\|}$	$*A_{\perp}$
1.907	1.859	1.931	156	262	93

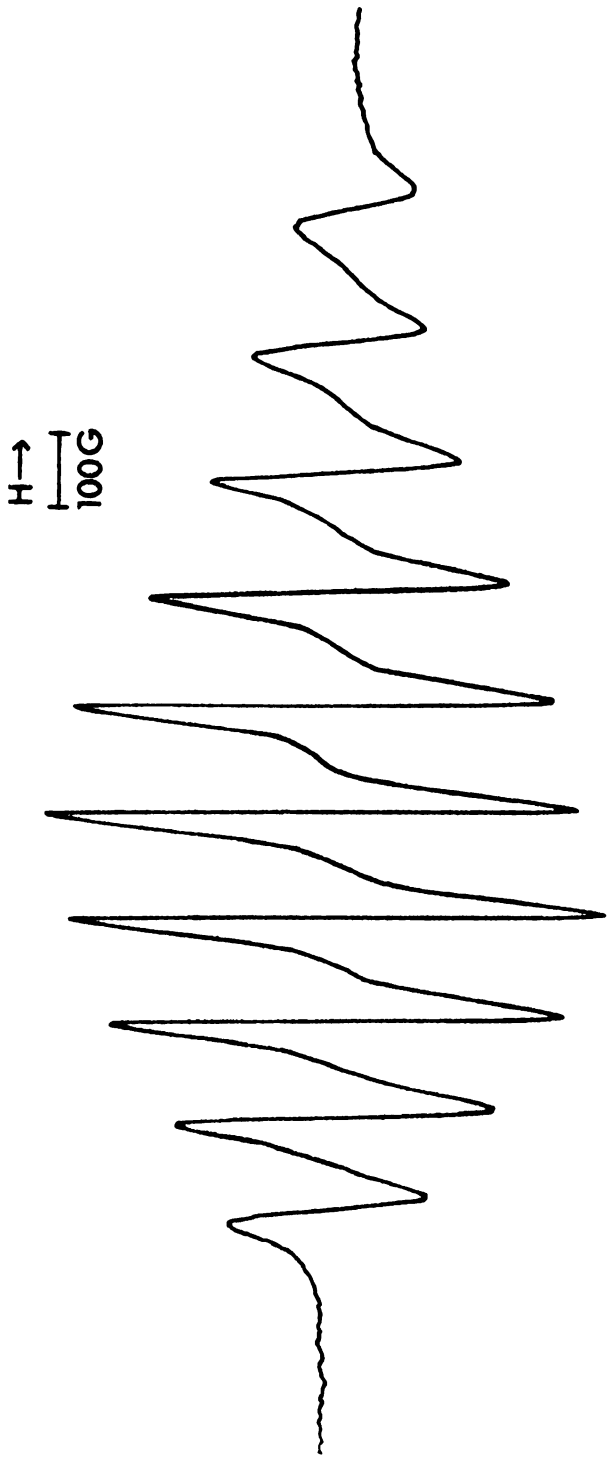
*Hyperfine splitting are given in units of 10^{-4} cm^{-1}.

<> values were obtained from spectra recorded at 298°K and the $\|\|$ and $\perp$ values were obtained from spectra obtained at 77°K.

It is apparent from the table that <g> and <a> are larger than the <g> and <a> for the corresponding complexes dissolved in dichloromethane. In contrast, when the tetrakis complex was dissolved in ethanol no change (relative to the esr results in CH_2Cl_2) was observed in <g> and <a>. It is then reasonable to suggest that some interaction between the ethanol and halogen atoms in $NbX_2[H_2B(Pz)_2]_2$ occurred. The fact that the same spectra is obtained from each of the three solutions, is evidence of a new common species as proposed in equation 4.

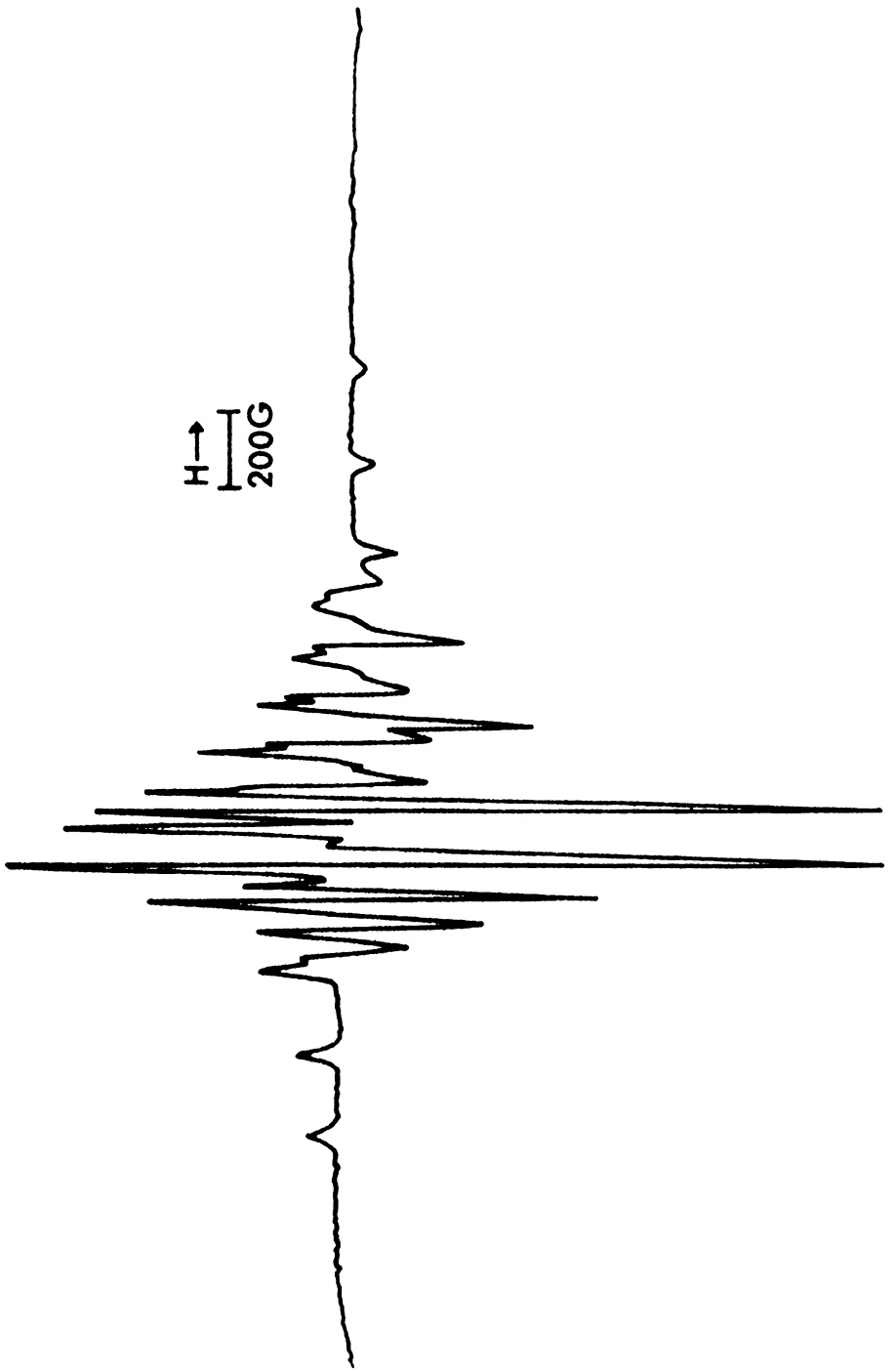
Efforts to prepare $Nb[H_2B(Pz)_2]_4$ and $NbX_2[H_2B(Pz)_2]_2$ complexes in ethanol result in the formation of the same species in solution. This species produces extremely clear esr solution spectra. The spectra are shown in Figures 29 and 30 and the esr parameters are listed in Table 13.

Figure 29



Esr Spectrum of $Nb(OCH_2CH_3)_4[H_2B(Pz)(Pz\text{-}H)]_2$ in CH_3CH_2OH at Ambient Temperature

Figure 30



Esr Spectrum of $Nb(OCH_2CH_3)_4[H_2B(Pz)(Pz\text{-}H)]_2$ in CH_3CH_2OH at 77 K

Table 13

Solution Esr Spectral Parameters of $Nb(OCH_2CH_3)_4[H_2B(Pz)(Pz\text{-}H)]_2$ in Ethanol

<g>	$g_{\|\|}$	$g_{\perp}$	*<a>	$*A_{\|\|}$	$*A_{\perp}$
1.938	1.870	1.972	133	218	88

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

<> values were obtained from spectra recorded at 298 K and the $\|\|$ and $\perp$ values were obtained from spectra recorded at 77 K.

It is clear from the table that these parameters are different from the parameters obtained by similar procedures carried out in toluene or dichloromethane using a two or four to one molar ratio of ligand to niobium tetrahalide. The fact that the solutions become diamagnetic upon standing, implies that the paramagnetic species is only an intermediate or is very unstable under these reaction conditions. Brubaker[47] has previously reported similar results with niobium(IV) chloride solutions in ethanol. Two diamagnetic compounds, $[NbCl(OCH_2CH_3)_3(C_5H_5N)]_2$ and $Nb(OCH_2CH_3)_4$, were obtained from the niobium(IV) chloride solutions. The former was prepared by the addition of pyridine to niobium(IV) chloride solutions in ethanol. The structure of the dimer is thought to involve chloride bridging on the basis of its chemical properties. $Nb(OCH_2CH_3)_4$ was prepared by the reaction of $NaOCH_2CH_3$ with $[NbCl(OCH_2CH_3)_3(C_5H_5N)]_2$. This compound is thought to be polymeric in nature. In view of

the above results, it is reasonable to propose the formation of diamagnetic $[Nb(OCH_2CH_3)_4]_n$ when attempting to prepare $NbX_2[H_2B(Pz)_2]_2$ and $Nb[H_2B(Pz)_2]_4$ in ethanol solutions. The paramagnetic intermediate is thought to be six-coordinate monomeric $Nb[OCH_2CH_3)_4[H_2B(Pz)(Pz\text{-}H)]_2$ which decompose to produce $[Nb(OCH_2CH_3)_4]_n$ as shown in equation 5b.

Electron Spin Resonance Spectra of "$NbX_3[H_2B(Pz)_2]$" in Dichloromethane

The esr spectra of the species, obtained by allowing a one to one molar ratio of $K[H_2B(Pz)]$:NbX_4 (X = Cl, Br and I) to react in CH_2Cl_2, were recorded as described earlier. Representative spectra are presented in Figures 31-34. Since the hyperfine splittings were large, the high field approximation could not be applied and second order corrections were employed by means of equations 9-12. The corrected esr parameters for the complexes are listed in Table 14.

Table 14

Solution (CH_2Cl_2) Esr Spectral Parameters of "$NbX_3[H_2B(Pz)_2]$" Complexes

Compounds	<g>	$g_{\|\|}$	$g_{\perp}$	*<a>	$*A_{\|\|}$	$*A_{\perp}$
$NbCl_3[H_2B(Pz)_2]$	1.940	1.700	2.060	122	234	52
$NbBr_3[H_2B(Pz)_2]$	1.943	1.860	1.984	121	220	68
$NbI_3[H_2B(Pz)_2]$	1.940	1.876	1.972	123	204	80

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

<> values were obtained from spectra recorded at 298 K and the $||$ and $\perp$ values were obtained from spectra recorded at 77 K.

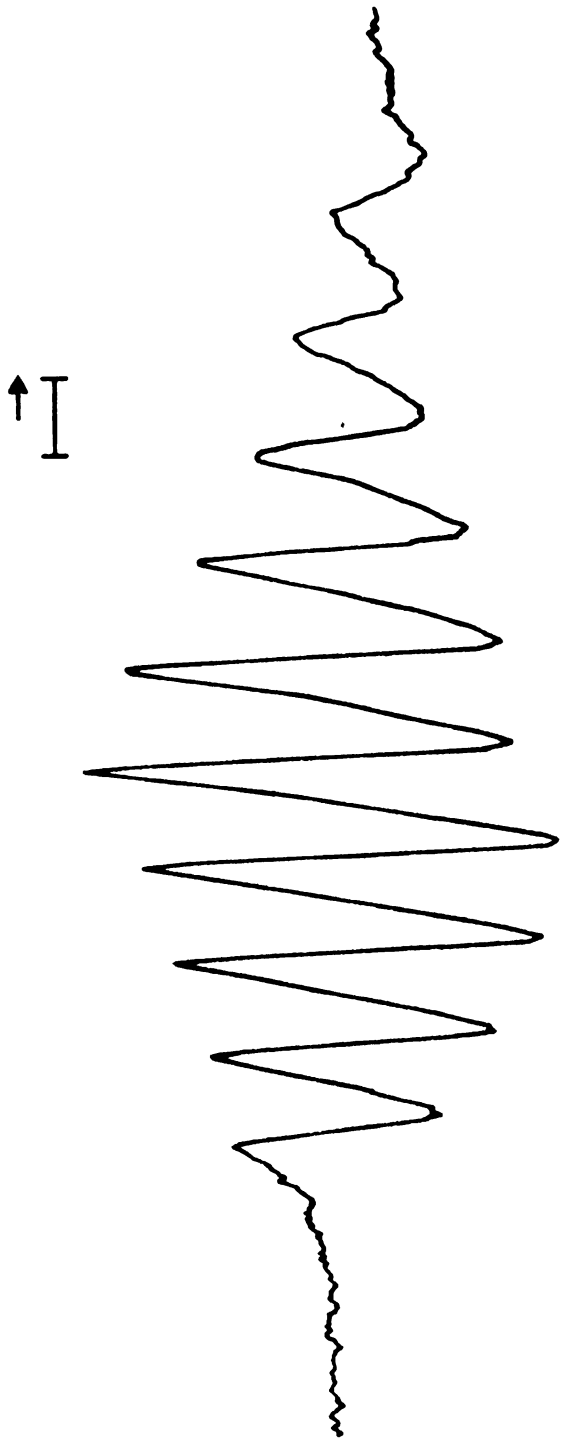
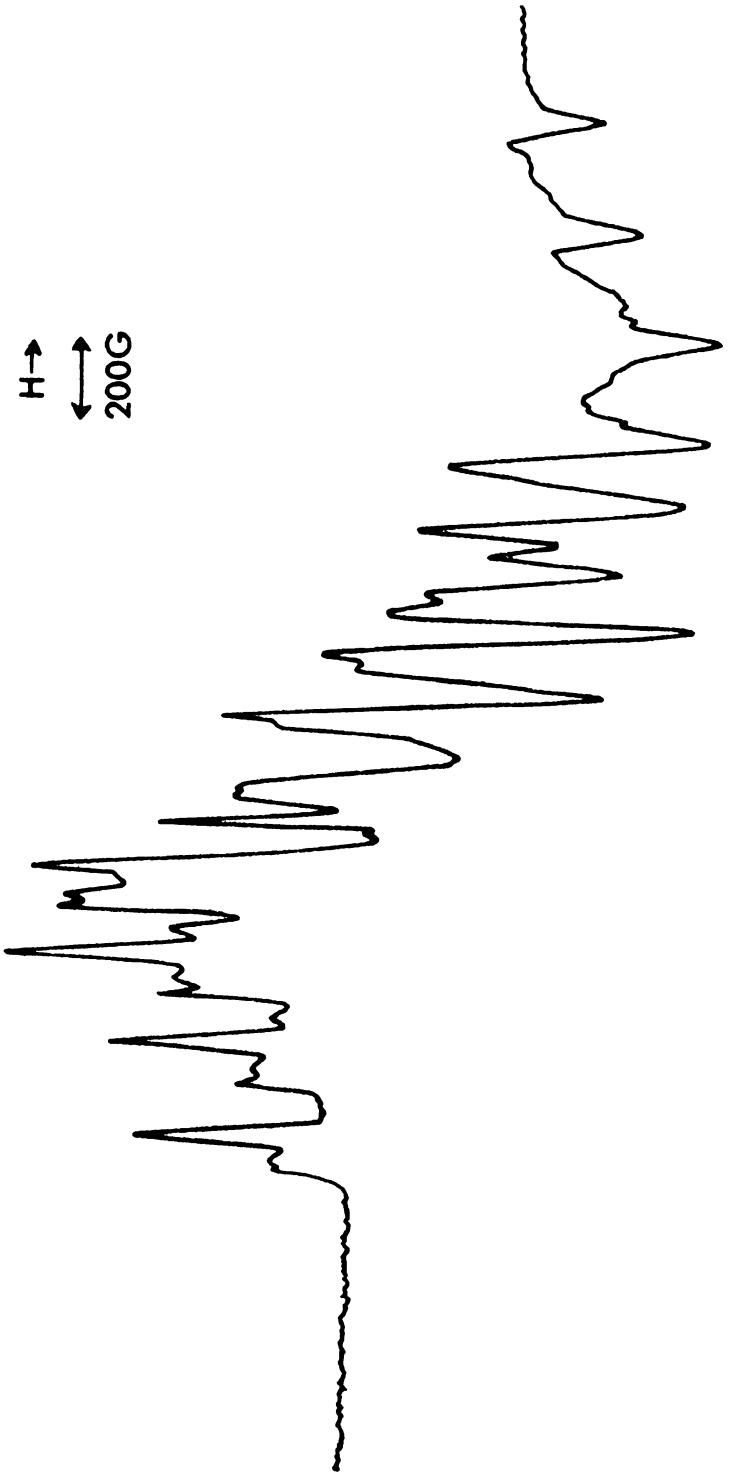


Figure 31

Esr Spectrum of $NbI_3[H_2B(Pz)_2]$ in CH_2Cl_2 at Ambient Temperature

Figure 32

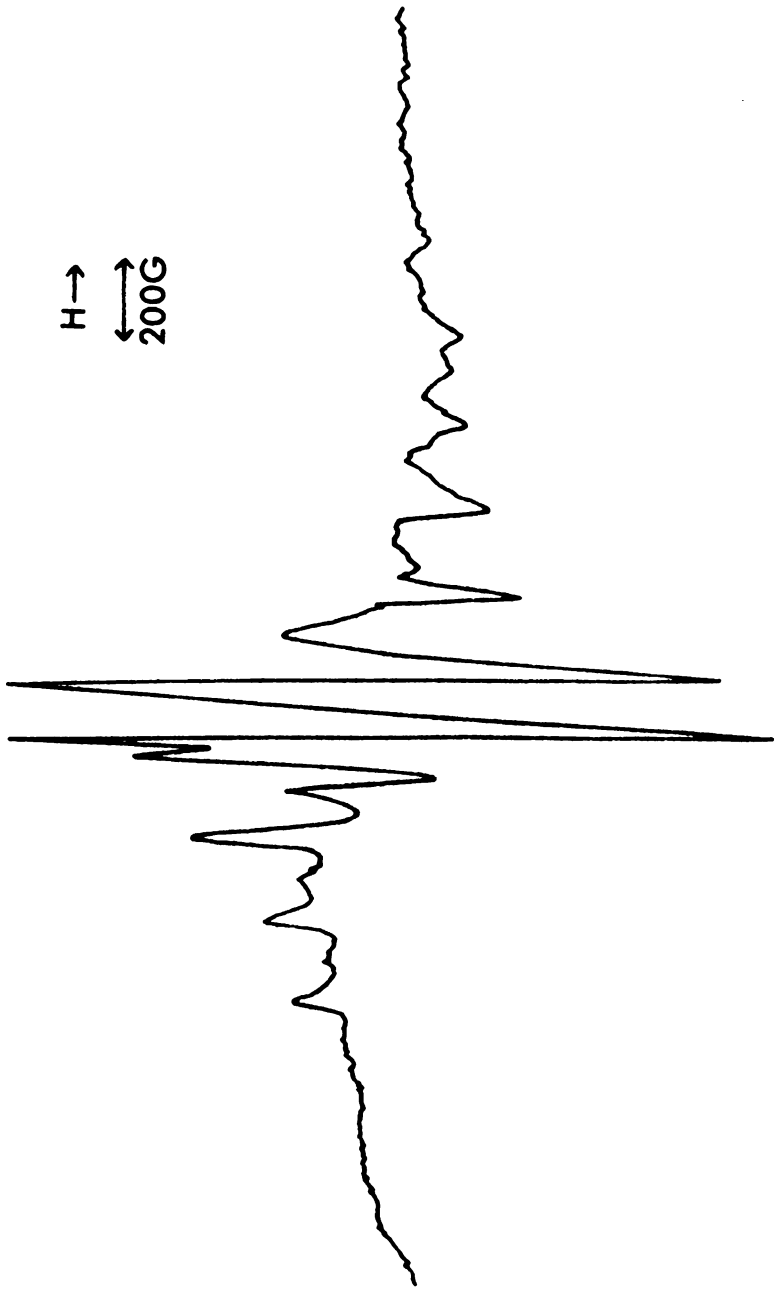


Esr Spectrum of $NbCl_3[H_2B(Pz)_2]$ in CH_2Cl_2 at 77 K

Figure 33

Esr Spectrum of $NbBr_3[H_2B(Pz)_2]$ in CH_2Cl_2 at 77 K

Figure 34



Esr Spectrum of $NbI_3[H_2B(Pz)_2]$ in CH_2Cl_2 at 77 K

For the series chloride, bromide and iodide, the <g> values are the same within experimental error. The significance of this observation is not clear.

The esr spectra are consistent with five-coordinate monomers, but in the absence of their molecular weights and analytical data one cannot preclude the presence of dimers or some other species. Efforts to prepare a pure species always resulted in the formation of $NbX_2[H_2B(Pz)_2]$ as a contaminant. This was apparent from the observation of a second set of lines or shoulders in the esr spectra.

PART II

ESR STUDIES OF SOME SULFUR DONOR COMPLEXES WITH NIOBIUM(IV)

RESULTS AND DISCUSSION

Preparation and Properties of 1,2-bis(methylthio)ethane Complexes of Niobium(IV)

The reaction of the niobium(IV) halides with excess 1,2-bis(methylthio)ethane (commonly referred to as 2,5-dithiahexane (dth)) proceeds according to equation 20.

$$NbX_4 + 2dth \rightarrow NbX_4(dth)_2 \qquad (20)$$

The complexes[14] were isolated as tan, green and brown solids for the chloride, bromide and iodide complex respectively. They are all air and water sensitive as indicated by a color change and the distinctive odor of carbon disulfide on exposure to the atmosphere.

Preparation and Properties of Dimethyldithiophosphate Complexes with Niobium(IV)

The reaction[56] of niobium(IV) chloride and zirconium(IV) chloride with a four to one molar ratio of Nadmtp:MX_4 (M = Nb, Zr; Nadmtp = sodium dimethyldithiophosphate) in toluene proceeds according to equation 21.

$$NbCl_4 + 10ZrCl_4 + 44Nadmtp \rightarrow Nb(dmtp)_4 + 10Zr(dmtp)_4 + 44NaCl \qquad (21)$$

The mixture was prepared so that the $ZrCl_4$ to $NbCl_4$ ratio was ten to one. A yellow solution containing a violet precipitate was obtained. The precipitate was recovered by filtration. A pinkish-yellow solid was obtained from the filtrate upon removal of the toluene.

The two to one molar of Nadmtp:MX_4 in toluene proceeds according to equation 22.

$$NbCl + 10ZrCl_4 + 22Nadmtp \rightarrow NbCl_2(dmtp)_2 + 10ZrCl_2(dmtp)_2 + 22NaCl \quad (22)$$

A violet precipitate was obtained by filtration leaving a colorless liquid. Removal of toluene <u>in vacuo</u> produced no recoverable solid. These complexes are air and water sensitive as indicated by a color change and the distinctive odor of dithiophosphoric acid.

Preparation and Properties of Dimethyldithiocarbamate Complexes with Niobium(IV)

Spectral data indicate, that when either a four to one or a two to one molar ratio of Nadtc:MX_4 (Nadtc = sodium dimethyldithiocarbamate) is used, the reaction proceeds according to equation 23 in toluene solutions.

$$NbCl_4 + 10ZrCl_4 + 44Nadtc \rightarrow Nb(dtc)_4 + 10Zr(dtc) + 44NaCl \quad (23)$$

The product was obtained as a violet powder from a colorless

liquid. These niobium(IV) complexes formed in the presence of the zirconium(IV) analog are also air and water sensitive as indicated by a color change and the distinctive odor of carbon disulfide.

Electron Spin Resonance Spectra of $NbX_4(dth)_2$

Esr studies were performed on $NbX_4(dth)_2$ (X = Cl, Br and I; dth = 2,5-dithiahexane) complexes as described in the Experimental section.

Representative spectra (X = Cl and Br) are presented in Figures 35, 36 and 37. In the case of the NbI_4 the esr spectra were inconclusive. After corrections for second order effects by means of equations 9-12, and conversions of hyperfine splitting from gauss to cm^{-1} by using equation 13. The corrected esr parameters are listed in Table 15.

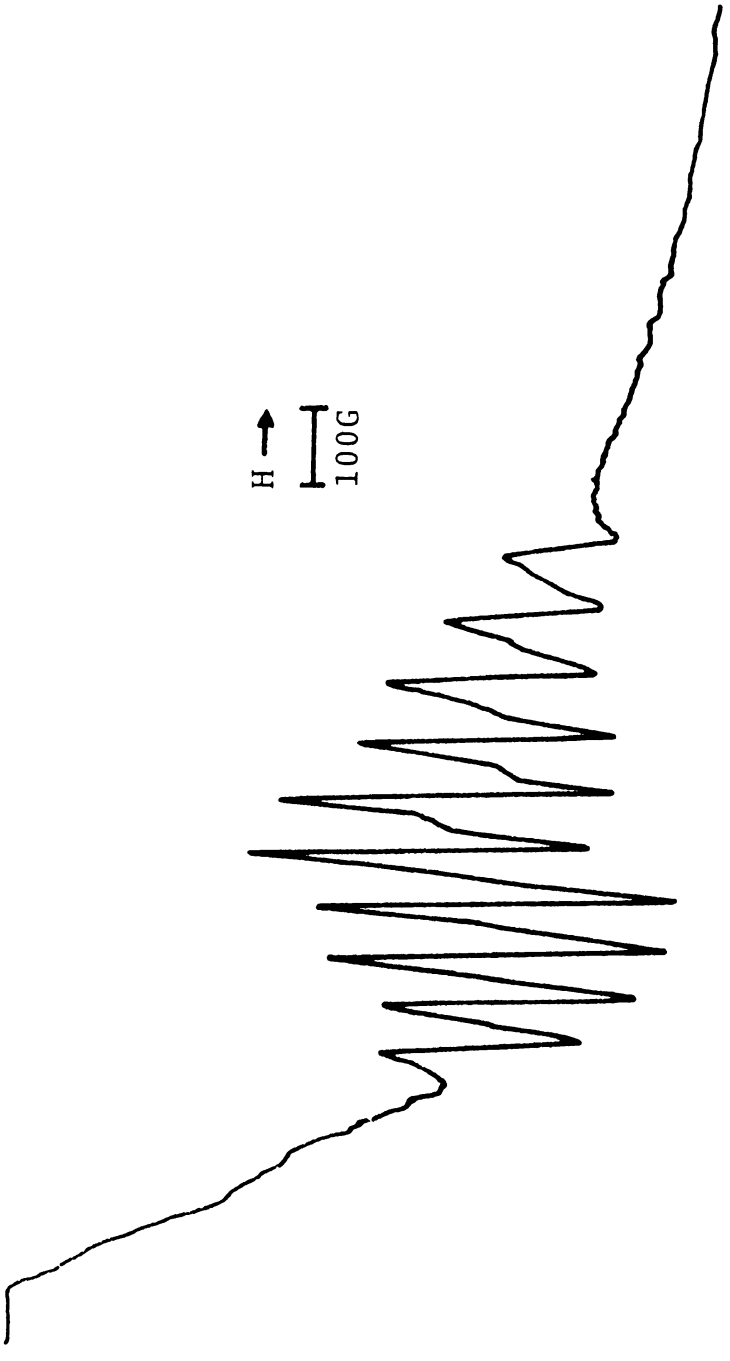
Table 15

Esr Spectral Parameters of Niobium(IV) Complexes

Compounds	<g>	$g_{\|\|}$	$g_{\perp}$	*<a>	$*A_{\|\|}$	$*A_{\perp}$
**$NbCl_4(dth)_2$	1.9947					
†$NbCl_4(dth)_2$	1.954	1.917	1.972	131	204	102
**$NbBr_4(dth)_2$	1.9970					
†$NbBr_4(dth)_2$	1.973	1.960	1.974	124	189	92

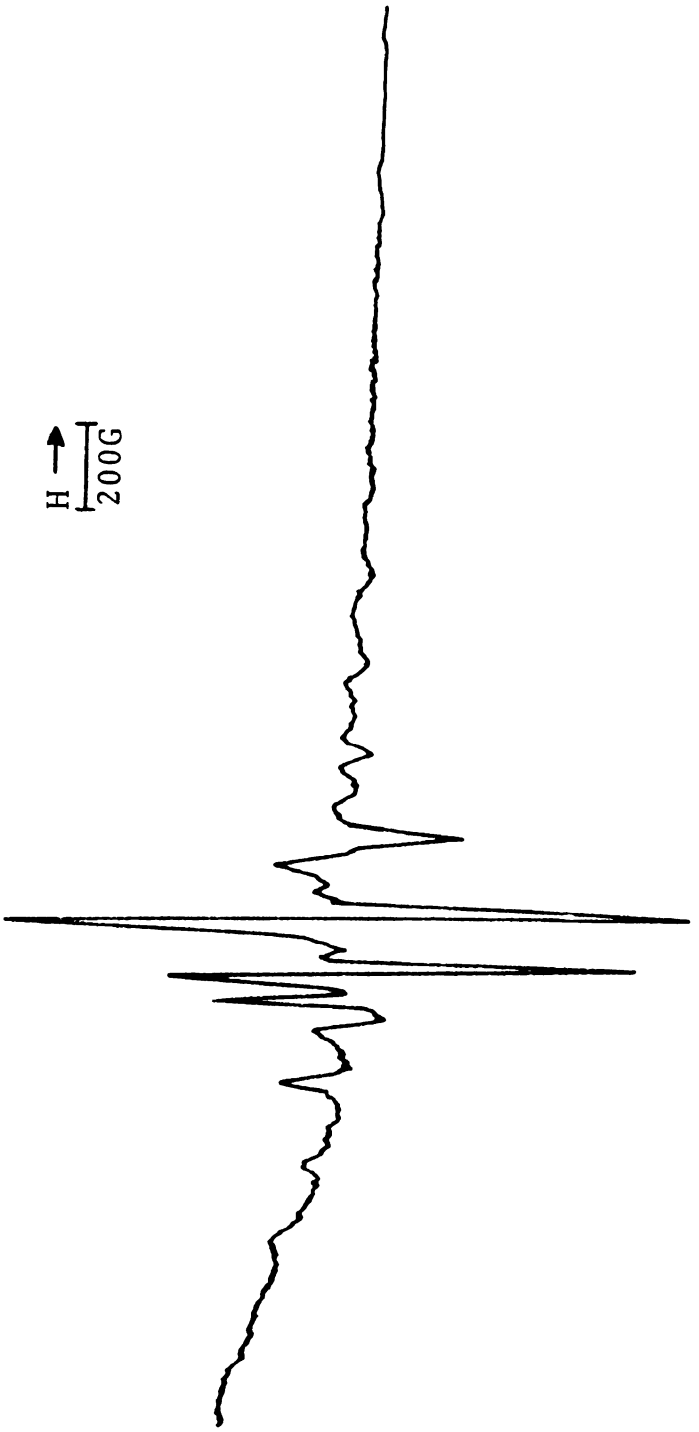
*hyperfine splittings are given in units of 10^{-4} cm^{-1}.
<> values were obtained from spectra recorded at 298 K and the || and $\perp$ values were obtained from spectra recorded at 77 K.
†spectra data obtained from excess 2,5-dithiahexane solutions.
**spectra data obtained from solids.

Figure 35



Esr Spectrum of $NbCl_4(dth)_2$ in Excess 2,5-dithiahexane at Ambient Temperature

Figure 36



Esr Spectrum of $NbCl_4(dth)_2$ in Excess 2,5-dithiahexane at 77 K

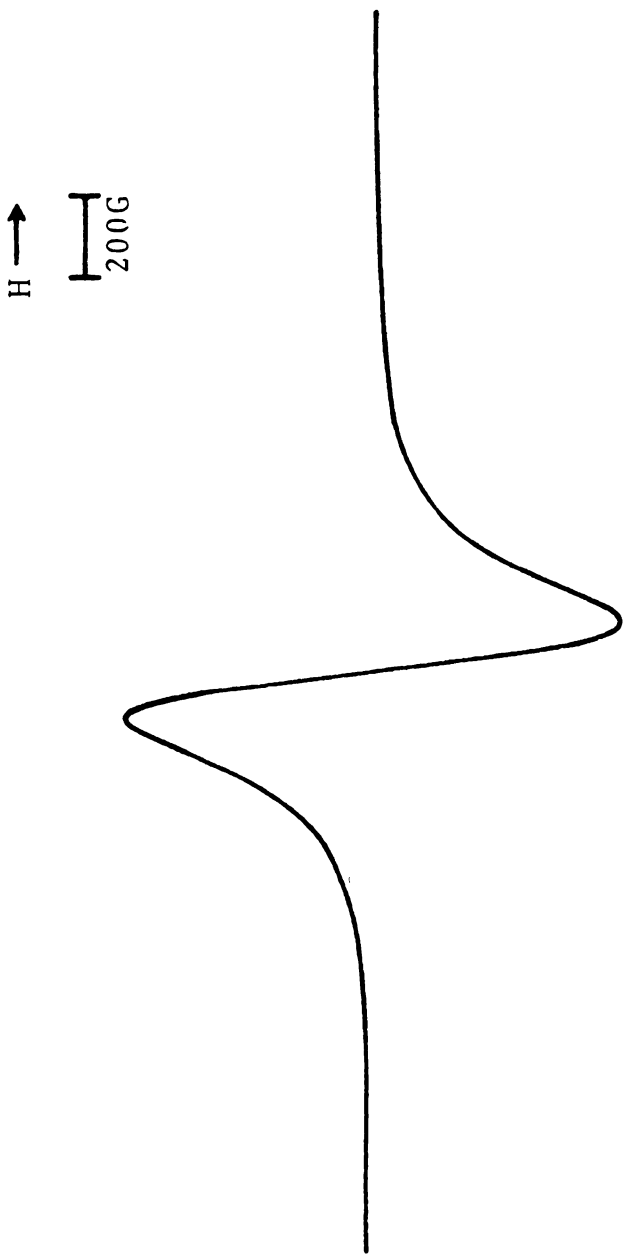


Figure 37

Esr Spectrum of Solid $NbCl_4(dth)_2$ at Ambient Temperature

It is apparent from the table that <g> soln ≈ <g> solid as expected if the same species is present in each phase. It is also apparent that $g_{\perp} > g_{||}$ which is as expected if the eight-coordinate complexes have the idealized triangular dodecahedral structure as has been proposed for other complexes.[29,30]

In the absence of electronic spectral data in solution, data from the esr studies were used in conjunction with the electronic spectral assignments[14] for the solid in order to determine the applicability of an ionic model to the present system.

By using equation 16 and taking the spin-orbit coupling constant for Nb^{4+} as 748 cm^{-1} and ΔE_2 and ΔE_3 as 17.3×10^3 and 13.8×10^3 cm^{-1} respectively for $NbCl(dth)_2$ and ΔE_2 and ΔE_3 as 16.9×10^3 and 13.7×10^3 cm^{-1} respectively for $NbBr_4(dth)_2$, the calculated values of $g_{||}$ and $g_{\perp}$ are 1.57 and 1.92 respectively for $NbCl_4(dth)_2$, and 1.57 and 1.91 respectively for $NbBr_4(dth)_2$. These values are much lower than the experimental quantities thus indicating the inadequacy of the ionic model. It is possible to qualitatively assess the amount of covalent bonding by use of equation 19.[30] Agreement with the experimental g values is found for $\alpha^2\gamma^2 = 0.368$ and $\alpha^2\beta^2 = 0.197$ for $NbCl_4(dth)_2$, and $\alpha^2\gamma^2 = 0.307$ and $\alpha^2\beta^2 = 0.098$ for $NbBr_4(dth)_2$. 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 $NbCl_4(dth)_2$ and $NbBr_4(dth)_2$.

Further confirmation of the bonding is obtained by using equation 18.[29] Agreement with experimental data is found for values of κ and P at 1.194 and 109.5 x 10^{-4} cm^{-1} respectively for $NbCl_4(dth)_2$ and 1.10 and 109.1 x 10^{-4} cm^{-1} respectively for $NbBr_4(dth)_2$. Comparing these values with those for a Nb^{4+} free ion, κ = 1.0 (pure d-orbital) and P = 192.0 x 10^{-4} cm^{-1},[84] the smaller experimental value for P indicates that the unpaired electron is more delocalized, hence appreciable covalent character. The results support the conclusion made using the electronic spectral data in conjunction with esr spectral data.

Electron Spin Resonance of $NbCl_2(dmtp)_2$

The powder esr spectrum of $NbCl_2(dmtp)_2$ diluted into an isomorphous $ZrCl_2(dmtp)_2$ is presented in Figure 38. The 19 line esr spectrum is very similar to the spectra obtained by McGinnis[56] for the exchange-coupled dimer, $[NbI_2(dmtp)_2]_2$. The proposed structure is shown in Figure 39.

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 linewidth small.[86] 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

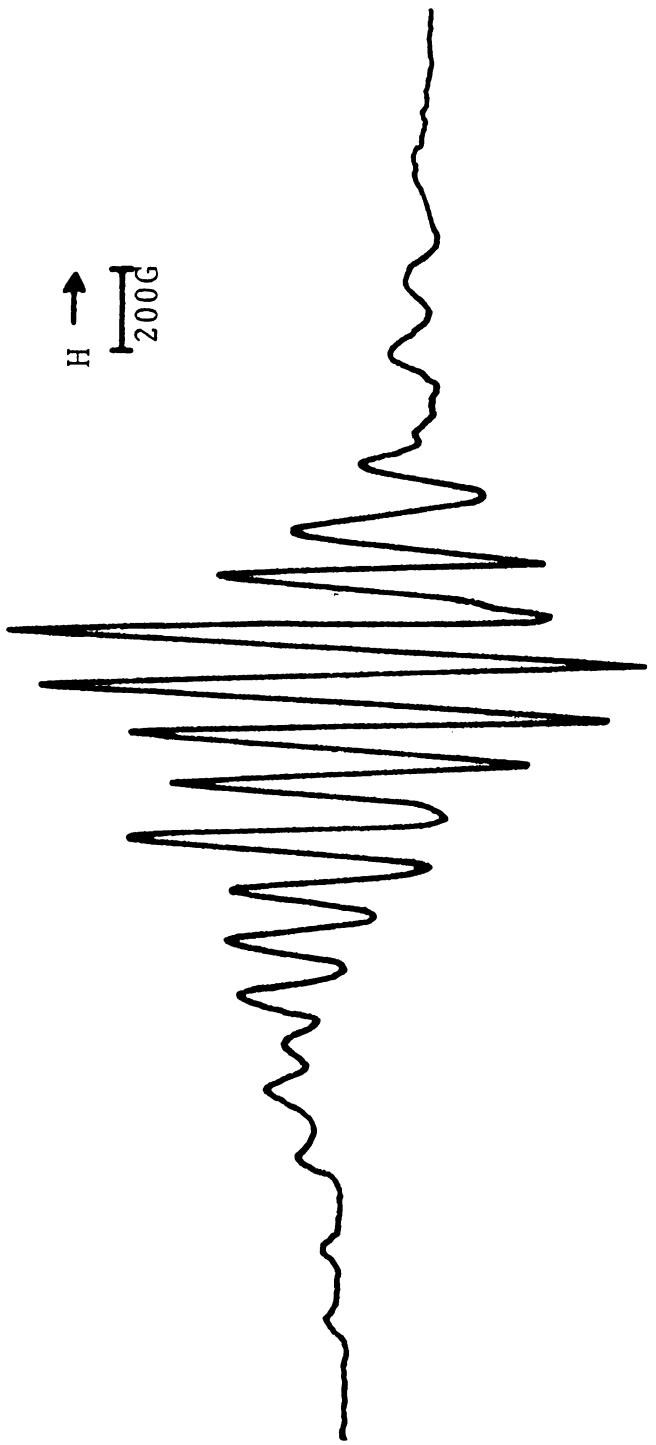


Figure 38

Esr Spectrum of $[NbCl_2(dmtp)_2]_2$ diluted into $ZrCl_2(dmtp)_2$ at 77 K

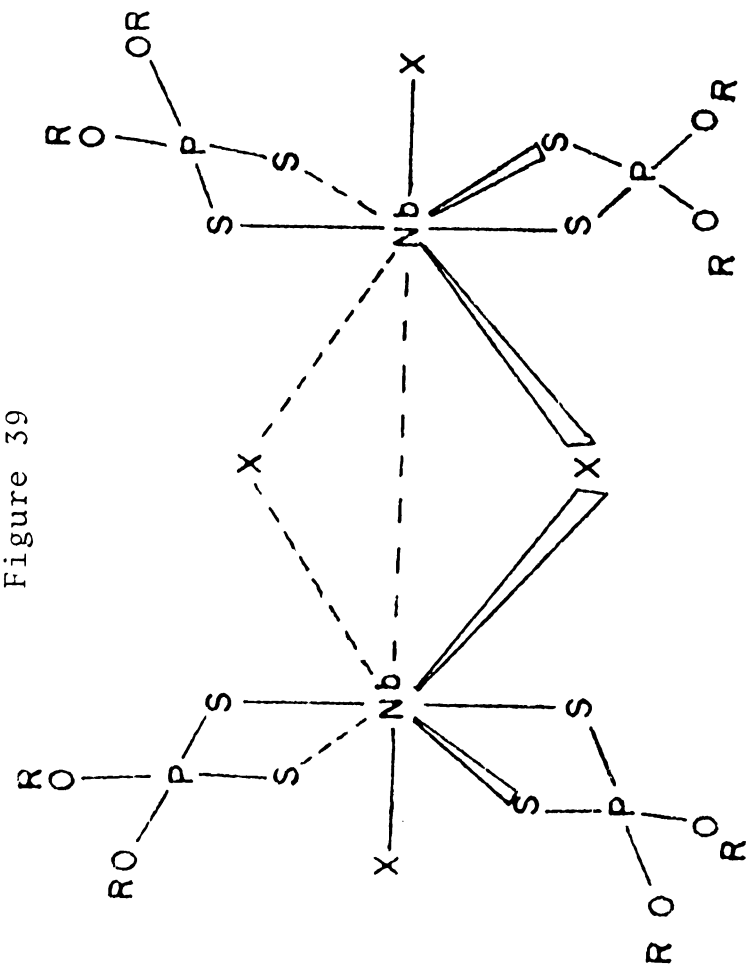


Figure 39

Proposed Structure for $Nb_2(Dmtp)_4X_4$

(Taken from Reference 56)

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.[87] 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 $g \simeq 2$ region of the spectrum. This situation is often the case in powders containing small concentrations of the paramagnetic metal ions.[88] The intensity of the $\Delta M_s = \pm 2$ transitions of niobium(IV)[56] are also much less than the $\Delta M_s = \pm 2$ for known cases of copper(II) complexes.[86,89,90]

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

$$H = H_1 + H_2 + H_{int} \tag{24}$$

where H_1 and H_2 are each of the form:

$$H_{1,2} = g_{||}H_zS_z + g_{\perp}(H_xS_x + H_yS_y) + A_{||}S_zI_z + A_{\perp}(S_xI_x + S_yI_y) \tag{25}$$

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

$$H_{int} = D[S_z^2 - 1/3S(S+1)] + E(S_x^2 - S_y^2) - JS_1 \cdot S_2 \quad (26)$$

where $S = S_1 + S_2$ if the ions are 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 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 outer-most pair of lines in the low temperature powder spectrum by:

$$H_{19} - H_1 \simeq 2D \quad (27)$$

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[91] and vanadyl[92] 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[93]

$$D = 3/4g^2\beta^2 \left\langle \frac{1-3\cos^2\theta}{r_{12}^3} \right\rangle_{max} \qquad (28)$$

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

$$R_{calc}(\text{Å}) = \left[\frac{0.325g^2|1-\cos^2\theta|}{D(cm^{-1})}\right]^{1/3} \qquad (29)$$

Taking $H_{||}$ to be along the Nb-Nb axis, and $\theta = 0°$, one obtains the esr parameters listed in Table 16.

Table 16

Esr Parameters for $NbCl_2(dmtp)_2$ Diluted into $ZrCl_2(dmtp)_2$

$g_{||}$	=	2.092
$*A_{||}$	=	109.9
*D	=	732.5
R	=	3.38 Å

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

$[NbCl_2(dmtp)_2]_2$ was reported to be diamagnetic based on magnetic susceptibility measurements by the Faraday method, as well as esr measurements in toluene or dichloromethane solution.[56] However, this data suggest that the species formed by the solid solution is an exchange-coupled dimer. The $g_{||}$ value for the compound is similar to that reported by McGinnis for $[NbI_2(dmtp)_2]_2$,[56] while $A_{||}$ is high compared to $A_{||}$ for $[NbI_2(dmtp)_2]_2$, it is in agreement with most niobium(IV) compounds. Hence, the effect of diluting a dimeric compound into a diamagnetic allows for packing conditions to influence the nature of the complex in the solid as opposed to the solution. The approximate Nb-Nb distance which was comparable to that found for α - NbI_4[8] (3.31 Å) and $[NbI_2(dmtp)_2]$ (3.53 Å) but lengthened from the value of 3.06 Å for $NbCl_4$[9] illustrates the closeness of the metal atoms, which under dilute conditions can show electron exchange.

Electron Spin Resonance of $Nb(dtc)_4$

Examination of $Nb(dtc)_4$ diluted into the corresponding diamagnetic zirconium(IV) matrix by esr methods gives a spectrum which is anisotropic with some overlapping of two sets of ten lines at both ambient and 77 K temperatures. Values for $g_{||}$, $g_{\perp}$, $A_{||}$ and $A_{\perp}$ were obtained directly from the low temperature spectrum. The values for <g> and <a> were obtained by using the relationships $<g> = 1/3(g_{||} + 2g_{\perp})$

and $\langle a \rangle = 1/3(A_{||} + 2A_{\perp})$. The esr spectrum is shown in Figure 40 and the esr parameters are summarized in Table 17.

Table 17

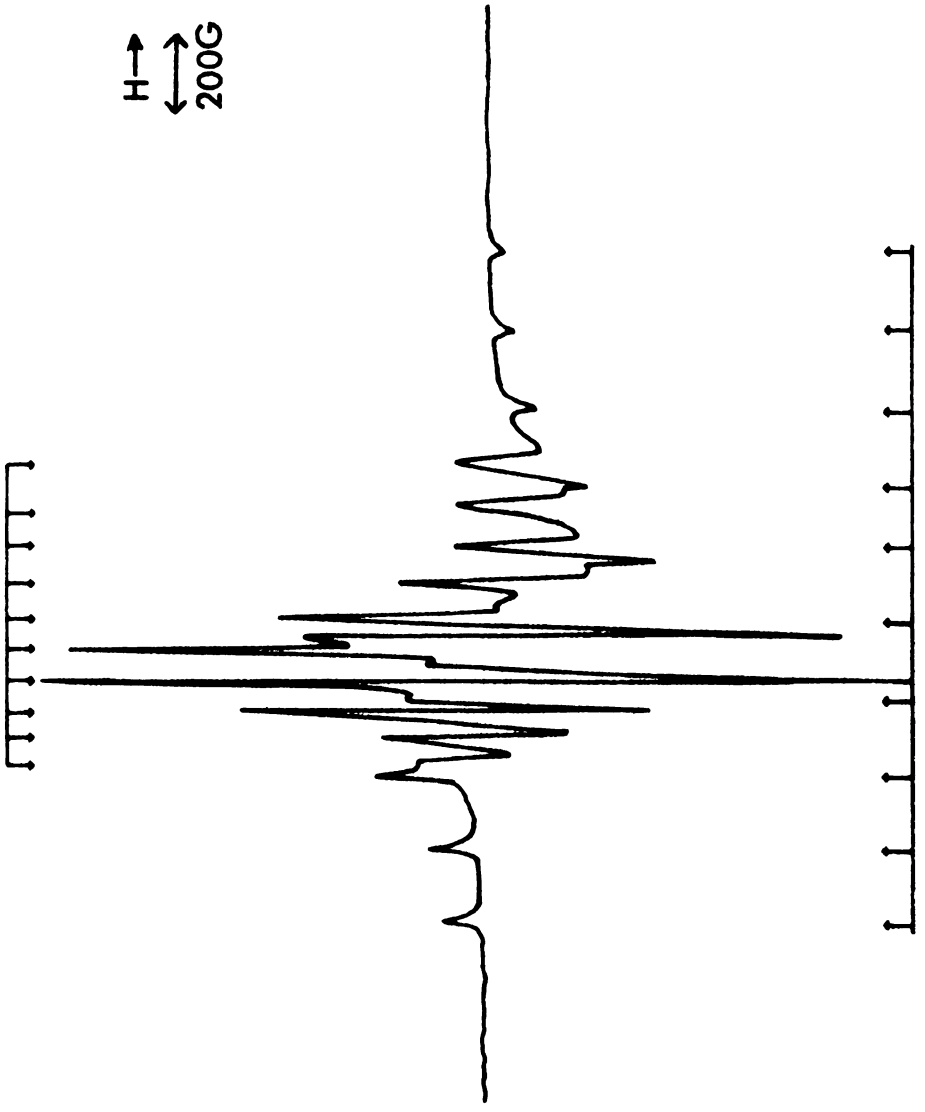
Esr Parameters for $Nb(dtc)_4$ Diluted into $Zr(dtc)_4$

$\langle g \rangle$	$g_{||}$	$g_{\perp}$	$*\langle a \rangle$	$*A_{||}$	$*A_{\perp}$
1.948	1.902	1.971	110.0	170.8	78.6

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

It is apparent from the table that $g_{\perp} > g_{||}$ indicating a triangular dodecahedral structure as were the cases with $Nb[H_2B(Pz)_2]_4$ and $NbX_4[dth)_2$ both included in this study. Esr studies[38] of piperdinyldithiocarbamate and a series of methyl-substituted piperdinyldithiocarbamates reveal that in each case $g_{||}$ is less than $g_{\perp}$.

Figure 40



Esr Spectrum of $Nb(dtc)_4$ Diluted into $Zr(dtc)_4$ at 77 K

SUMMARY AND CONCLUSIONS

Eight-coordinate $Nb[H_2B(Pz)_2]_4$ was isolated from the reaction of potassium dihydrobis(pyrazol-1-yl)borate ($K[H_2B(Pz)_2]$) with niobium tetrahalides. The infrared spectrum indicates that $H_2B(Pz)_2^-$ is bidentate. This is supported by the nmr spectrum of the analogous zirconium complex. The electronic spectrum exhibits one d-d transition and one strong band at 340 nm. This intense band in the ultraviolet region is due to ligand charge transfer. This assignment was confirmed by observing an identical band at 340 nm in the corresponding zirconium complex. The esr spectra support a D_{2d} trigonal dodecahedral configuration for the complex showing $g_{\perp}$ greater than $g_{||}$.

Complexes of the type $NbX_2[H_2B(Pz)_2]_2$ (X = Cl, Br and I) were obtained from the reaction of the niobium tetrahalides with two moles of $K[H_2B(Pz)_2]$. The infrared spectra indicate that $H_2B(Pz)_2^-$ is bidentate in all three complexes. This is supported by the nmr spectrum of isomorphous $ZrCl_2[H_2B(Pz)_2]_2$. The electronic spectra exhibited one d-d band in the chloride complex and two d-d bands in the bromide and iodide complexes. An intense band in the ultraviolet region due to ligand charge transfer was observed in each case. The esr spectra proved that all the complexes are monomeric by exhibiting ten lines at ambient temperature. By using the molecular orbital theory

developed for octahedral complexes, metal-ligand bonding parameters were obtained which indicate strong mixing of metal and ligand orbitals.

Complexes, obtained by allowing one mole of $K[H_2B(Pz)_2]$ to react with one mole of NbX_4, were proposed to be $NbX_3[H_2B(Pz)_2]$. In these complexes the infrared spectra indicate that $H_2B(Pz)_2^-$ is acting as a bidentate donor. Electronic spectra exhibited one d-d vibration and an intense band in the ultraviolet region due to ligand charge transfer. The esr solution spectra indicate the presence of a monomer by exhibiting ten lines at ambient temperature.

The adducts $NbX_4(dth)_2$ were prepared by using procedures previously described by Hamilton and McCarley[14] (X = Cl, Br and I; dth = 2,5-dithiohexane. The esr spectra of the solid dissolved in toluene or excess ligand were investigated to determine the structures of these complexes in solution. This investigation confirmed a trigonal dodecahedral structure, which had been proposed from observation of the electronic spectra, with the esr spectra $g_\perp$ values observed to be greater than $g_{||}$ values as expected for D_{2d} symmetry. By 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.

$[NbCl_2(dmtp)_2]_2$ results from the reaction of niobium tetrachloride with two moles of Nadmtp (dmtp = dimethyldithiophosphate). When $[NbCl_2(dmtp)_2]_2$ is diluted into a solution of the analogous zirconium complex, a powder esr spectrum which is indicative of an exchange coupled dimer is obtained. The esr spectra were very similar to spectra obtained by McGinnis[56] for $[NbI_2(dmtp)_2]_2$.

Examination of $Nb(dtc)_4$ diluted into the corresponding diamagnetic zirconium(IV) matrix by esr methods gives spectra which are anisotropic with two overlapping sets of ten lines. The $g_\perp$ value was observed to be greater than the $g_{||}$ value, which is indicative of D_{2d} dodecahedral configuration.

SUGGESTIONS FOR FURTHER WORK

While there is clearly evidence for the formation of an eight-coordinate complex in dichloromethane or toluene X-ray structure data will ultimately be required to confirm eight-coordination for niobium(IV) in $Nb[H_2B(Pz)_2]_4$ and would also provide a basic for esr study of single crystals.

The attempt to prepare $Nb[H_2B(Pz)_2]_4$ or $NbX_2[H_2B(Pz)_2]_2$ (X = Cl, Br and I) in ethanol resulted in the formation of a new common paramagnetic species which upon standing turned diamagnetic and polymeric in nature. This polymeric species should be investigated further. The nature of the deep blue paramagnetic complex produced by dissolving $NbX_2[H_2B(Pz)_2]_2$ into ethanol should be investigated by methods other than esr.

There is evidence for monomeric paramagnetic five-coordinate complexes of niobium(IV) in dichloromethane or toluene with $NbX_2[H_2B(Pz)_2]_2$ as a contaminant. These studies should be extended to other solvents where pure $NbX_3[H_2B(Pz)_2]$ may have an enhanced stability.

Extension of these studies to other metals should also be fruitful. Extension to third row transition elements (d^1 or d^2) will be fruitful where starting materials are available which are more reactive than the anhydrous halides themselves.

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