ESR STUDIES OF TRANSITION METAL IONS IN UNSTABLE OXIDATION STATES

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This is to certify that the

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ABSTRACT

ESR STUDIES OF TRANSITION METAL IONS IN UNSTABLE OXIDATION STATES

By

John Robert Shock

There are some transition metal ions which form diamagnetic transition metal complexes almost exclusively. In this work, several new paramagnetic species containing these ions in unstable oxidation states have been made either by high-energy irradiation at 77°K or from the melt of alkaline halides containing the diamagnetic transition metal ion. In both cases, the ESR spectra were studied between 77°K and 300°K to determine the structure and to characterize the bonding of the resulting paramagnetic species.

The γ irradiation of $K_2 \text{NbOF}_5 \cdot \text{H}_2 \text{O}$ at 77°K produced two ⁹³Nb- centered radicals; one of these is shown to be $[\text{NbOF}_5]^{3-}$ with a d^1 configuration and a d_{xy} ground state. The g, $A(^{93}\text{Nb})$, and $A(^{19}\text{F})$ tensors have been completely analyzed in the single crystal at 77°K. The g and metal A tensor for this ion and those found previously for the $[\text{VOF}_5]^{3-}$ ion by other investigators were used in a self-consistent charge calculation of molecular orbital coefficients. Also, molecular orbital coefficients were determined from the equatorial fluorine A tensors of these systems. The other Nb-containing ion formed at 77°K is a hole species, thought to be $[NbOF_5]^-$. Warming the sample to 190°K resulted in the decay of the $[NbOF_5]^{3^-}$ ion allowing the study of the spectra of the hole species. The analyses of single crystal and powder spectra at 190°K suggest that some $[NbOF_5]^-$ ions remain at 190°K but that the majority of the ions decay to the NbOF₄ ion which rotates freely in the matrix.

The γ irradiation of $K_3CO(CN)_6$ at 77°K produced two ⁵⁹Co-containing radicals. A complete single crystal ESR study of the g and $A(^{59}Co)$ tensors for one of these species indicates that it has not undergone appreciable reorientation in the lattice. The g tensor is consistent with a d^7 configuration and a d_g^2 ground state. Superhyperfine structure from two equivalent nitrogen nuclei and the absence of ¹³C satellite lines in ¹³C enriched samples suggest that the axial cyanide ligands have rotated to form nitrogen-to-metal bonds. Also, the $A(^{59}Co)$ tensor of this radical, thought to be $[CO(CN)_4(NC)_2]^{4-}$, was used to estimate the covalency in molecular orbital containing the odd electron. The other Co-containing radical formed at 77°K is considered to be a Co(II) radical pair but its ESR parameters could not be determined.



Lastly, the Rh(II) ion in several chloro-complexes was studied. The γ irradiation of $K_3RhCl_6 \cdot H_2O$ at 77°K produced a radical whose g values are consistent with a d^7 system with a d_g^2 ground state. This radical, thought to be $[RhCl_6]^{4-}$, also appears to form in the melt of AgCl containing RhCl₃. In this matrix, the chlorine superhyperfine structure from the two axial chlorines was fully analyzed in the single crystal and the results used to estimate covalency in the complex. Also, γ irradiation of $K_2[RhCl_5(H_2O)]$ at 77°K produced a radical with g values consistent with a d^7 configuration and the unpaired electron in the d_g^2 orbital. The g values and the chlorine hyperfine splitting from one chlorine suggest that the radical is $[RhCl_5(H_2O)]^{3-}$ or $[RhCl_5]^{3-}$.

ESR STUDIES OF TRANSITION METAL IONS

IN UNSTABLE OXIDATION STATES

Ву

John Robert Shock

A THESIS

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

DOCTOR OF PHILOSOPHY

Department of Chemistry

To My Parents

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CHAPTER I

INTRODUCTION

A. General

The initial use of ESR to study transition metal complexes was by solid state physicists. Their primary concern was to develop the theory and experimental techniques from which information about local crystal environment and relative energies of various solid state interactions could be ascertained. This work started with the first observation of ESR by Zavoisky¹ in 1944 and is continued presently. Progress has been reviewed by Bleaney and Stevens² in 1953, Bowers and Owens³ in 1955, Low⁴ in 1960, Pake⁵ in 1962, Slichter⁶ in 1963, Low and Offenbacher⁷ in 1965, Orton⁸ in 1968, and in the recent classic by Abragam and Bleaney⁹ in 1970. The experimental methods, including design and construction of spectrometers, are discussed in monographs by Wilmshurst¹⁰, Poole¹¹, and Alger¹².

In an ESR study of a transition metal complex, one monitors the interaction of unpaired electrons with their environment. In the classical work of Owen and Stevens¹³, the unpaired electron was found not only

to interact with the central metal atom but also with the ligands, *i.e.*, unpaired spin density was transferred to the ligands resulting in ligand hyperfine splittings. Thus, it appeared that the unpaired electron was not localized just in the metal atomic orbitals but in molecular orbitals which spanned the entire molecule. The application then of molecular orbital theory to ESR by Stevens¹⁴, Owen¹⁵ and McGarvey¹⁶ generated much interest among the transition metal chemists. Since the unpaired electron is normally involved in the bonding of the molecular system, the chemist could use ESR as a sensitive probe to measure bonding changes and test bonding theories. Reviews of such studies include those by McGarvey¹⁷, König¹⁸, Kokoszka and Gordon¹⁹, and Fujiwara²⁰. Another series of reviews by Kuska and Rogers 21-23 are more complete but cover only the first row of the transition metals. Lastly, a recent review by Goodman and Raynor²⁴ gives comprehensive coverage of the d^1 to d^9 ions for the entire transition metal series. In addition to these, current literature is reviewed in the Annual Reports of the Chemical Society²⁵, and in the Annual Review of Physical Chemistry²⁶, Analytical Chemistry²⁷, and Spectroscopic Properties of Inorganic and Organometallic Compounds²⁸.

The use of ESR to study bonding in transition metal complexes, however, is restricted by the

requirement (1) that the system has at least one unpaired electron, (2) resonance occurs over a small range of values so that the signal is not inhomogeneously broadened to the point that it is undetectable, and (3) that the environment be such that the relaxation times are neither too long nor too short. Because of these restrictions most of the earlier single crystal work involved doping stable paramagnetic complexes of the firstrow transition metals into diamagnetic host lattices. Only stable oxidation states could normally be used since the host crystals were usually grown from solution and magnetic dilation in a diamagnetic host lattice was necessary to prevent dipolar interactions and exchange coupling which would broaden the signal. First-row transition ions were mostly used since they have relaxation times in the appropriate range for the signal to be observed at room temperature or 77°K. Also, these ions were of more interest initially since more chemistry and physical characterization of the first-row complexes had been done as well as ESR results could be compared with extended Hückel calculations for these ions. More recently, studies have been made of some of the second- and thirdrow transtion metals and of complexes with less common crystal symmetries.

There are, however, numerous transition metal ions that form diamagnetic complexes almost exclusively.

In order to study the bonding of these ions by ESR, conditions must be created whereby a paramagnetic oxidation state can be stabilized. One method of achieving such valence states is to grow crystals from the melts of various halide salts doped with a diamagnetic ion. Often in such instances, the melt will oxidize or reduce the transition metal ion to a paramagnetic oxidation state. The resulting crystals therefore have these paramagnetic sites trapped within the lattice and surrounded by halide ions in cubic, octahedral, distorted octahedral, or tetrahedral arrangements. This method is somewhat limited since, for the most part, only metal-halogen bonding can be studied and only a few coordination geometries can be studied. A more versatile method for making transition metal complexes with unstable oxidation states is to irradiate single crystals of the diamagnetic compounds at low temperatures with a high energy source. Often paramagnetic species will form by capture of an electron, loss of an electron, or by rupture of a bond.

In the study of stable oxidation states, one usually knows the oxidation state and the ligand field geometry beforehand. Also, the electron configuration of the ground state and the ordering of low-level excited states is usually known from optical spectroscopy. In the case of unstable oxidation states, on the other hand, the valence state, ligand field geometry, and ground state

must be inferred from the ESR parameters. Therefore, since transition metal complexes in unstable oxidation states were studied in this thesis, the radicals had to be identified before their bonding could be studied. With this as a background, introductions to the individual projects will be given in the order they appear in the thesis.

B. $\frac{\gamma \text{ Irradiation of}}{K_2 \text{ NbOF}_5 \cdot H_2 \text{ O}}$

There has been considerable interest in the ESR study of the transition-metal oxyanion complexes of the type $[MOX_5]^{2-}$ where M = Cr, Mo, W and X = F, Cl, Br, I^{29-45} . The g, metal hyperfine, and ligand hyperfine tensors have been used to investigate covalency in these compounds. On the other hand, the series $[MOX_5]^{3-}$ where M = V, Nb, Ta, cannot be studied as easily by ESR since niobium does not form a stable paramagnetic oxypentabalide ion and tantalum does not form an oxypentabalide ion at all. The stable $[VOF_5]^{3-}$ complex has been the subject of previous ESR studies 46-48, so a study of the analogous [NbOF₅]³⁻ complex would be of interest. The γ irradiation of $K_2NbOF_5 \cdot H_2O$ at 77°K is shown in this investigation to produce the paramagnetic $[NbOF_5]^{3-}$ radical along with the hole species identified as probably [NbOF₅] and NbOF₄. There are very few accounts of ESR spectra of

paramagnetic niobium compounds. Chester⁴⁹ obtained ESR spectra of Nb⁴⁺ in TiO₂, Edwards *et al.*⁵⁰ observed Nb hyperfine sturcture in γ -irradiated CaMoO₄ containing Sm and Nb, and Rasmussen *et al.*⁵¹ studied [Nb(OMe)Cl₅]²⁻, all in the solid; Lardon and Gunthard⁵² observed the [NbCl₆]²⁻ ion, and Gainullin *et al.*⁵³ NbO(acac)₂, [NbOCl₄]²⁻, and [NbOF₄]², all in solution.

In the present work the ligand superhyperfine interaction tensor of the $[NbOF_5]^{3-}$ complex has been determined and used to evaluate covalency effects for comparison with those found for the $[VOF_5]^{3-}$ complex. A complete calculation of molecular orbital coefficients has also been made using g and metal hyperfine splitting values for both $[VOF_5]^{3-}$ and $[NbOF_5]^{3-}$. While in most previous calculations the charge on the central metal atom is assumed, an attempt has been made in this work to arrive at a charge which is self-consistent with the calculated molecular orbital coefficients. And finally, a critical examination has been made for the use of secondorder theory of the g and metal A tensors to derive molecular orbital coefficients.

C. γ Irradiation of K₃Co(CN)₆

There has been several studies, including a complete single crystal analysis, of the radical formed by

the irradiation of $K_3CO(CN)_6$ at room temperature⁵⁴⁻⁵⁷ but there has not been any detailed single crystal analysis of the radical formed by irradiating this compound at 77°K. Since, for the studies of the room temperature radical, there are considerable discrepancies in the qand A parameters reported in the literature, a review of this work is given and a possible explanation for these discrepancies is offered. It has been generally accepted that this room temperature radical is $[Co(II)(CN)_{5}]^{3-}$. However, the ¹³C results in this thesis shed some doubt on this assignment and suggest that the radical might be $[Co(II)(CN)_{\lambda}]^{2-}$. In the case of the low-temperature radical, the metal q and A tensors with their direction cosines are derived from the analysis of the single crystal spectra. Because of the nitrogen superhyperfine splitting from two equivalent nitrogens is observed⁵⁸ and ¹³C satellite lines are absent in enriched samples, the structure of the radical has been assigned as $[Co(II)(CN)_{4}(NC)_{2}]^{4-}$. Also a second radical, formed by an ionic migration within the lattice, appears at 7.7^{σ} K and is possibly a Co(II) radical pair.

Variable temperature studies show that the room temperature radical forms directly from the low temperature radical by rupture of Co-NC bonds. The g values in conjunction with first-order theory indicate that both the room temperature and low temperature radicals have the

unpaired electron in the metal d_z^2 orbital. Covalency in these radicals is characterized using first-order hyperfine interaction theory.

D. Chlororhodate (II) Complexes

There hardly has been any d^7 rhodium complexes reported in the literature. In the host lattice $2nWO_4$, 103 Rh splittings have been observed⁵⁹; Dessy *et al.* have observed a rhodium radical thought to be $[(\pi-C_5H_5)Rh$ $(\pi-C_2H_2)_2]^+$ where $(\pi-C_5H_5)$ and $(\pi-C_2H_2)$ are π bonded cyclopentadiene and acetylene, respectively, as well as a rhodium radical produced by the one-electron reduction of $[(\pi-C_5H_5)Rh S_2C_2(CF_3)_2]^{60}$; Billig *et al.*⁶¹ and Maki *et al.*⁶² have observed the ^{103}Rh coupling in $[Rh(MNT)_2]^{2-}$ where MNT = maleonitriledithiolate; and Keller and Wawersik made a study of $Rh(\pi-C_5H_5)_2^{63}$. Therefore, since there had been no studies of d^7 halorhodate (II) complexes, such an investigation was the objective of this project.

The γ irradiation of $K_3RhCl_6 \cdot H_2O$ at 77°K produced a radical identified from the powder ESR data as $[RhCl_6]^{4-}$. Also, $K_2[RhCl_5(H_2O)]$, γ irradiated at 77°K, produced a radical identified from the powder ESR data as possibly $[RhCl_5]^{3-}$ or $[RhCl_5(H_2O)]^{3-}$. The $[RhCl_6]^{4-}$ ion was also prepared in an AgCl matrix by crystallization from the melt of AgCl containing RhCl₃. For each radical, first-order g theory was used to determine that the odd electron is localized mainly in the d_g^2 orbital. Because the ¹⁰³Rh doublet splitting was less than the line width for all of the spectra, first-order metal hyperfine theory could not be used to determine covalency in these complexes. However, since the chlorine superhyperfine tensor for the $[RhCl_6]^{4-}$ ion in the AgCl lattice could be fully analyzed, first-order hyperfine theory was applied to derive an expression for these splittings which enabled the covalency to be estimated.

E. Other Systems

This section includes examples for which the ESR spectra were not fully analyzed either as a result of experimental difficulties or inherent shortcomings of the system. The results which are discussed include the first ruthenium hyperfine splitting observed for a halide complex, the $[RuCl_5(H_2O)]^{2-}$ ion; identification of the $[Fe(CN)_6]^{5-}$ radical in $K_4Fe(CN)_6$ γ -irradiated at 77°K; and identification of a radical thought to be $[Ni(CN)_4(NC)]^{2-}$ in $K_2Ni(CN)_4 \cdot H_2O$ γ -irradiated at 77°K. Also, suggestions for future work on these systems, as well as for other systems that were investigated but for which ESR spectra were not observed are included.

CHAPTER II

THEORY

A. Introduction

Since the electron is a spinning charged particle, it has a magnetic moment given by

$$\mu_e = -g_e \beta_e^S (\text{erg/gauss}), \qquad (2.1)$$

where β_e is the Bohr magneton $(0.92731 \times 10^{-20} \text{erg/gauss})$, S = 1/2 is the spin quantum number of the electron, and g_e is the Landé g factor (g value) which is dimensionless and has a value of 2.0023 for a free electron. In the absence of a magnetic field, the two spin state with $m_S = \pm 1/2$ are degenerate but in the presence of a magnetic field the degeneracy is removed and the difference in energy between the states is given by

$$\Delta E = hv = g_e \beta_e H, \qquad (2.2)$$

where g_e and β_e have been defined above, H is the magnetic field in gauss, h is Planck's constant (6.6252 $\times 10^{-27}$ erg·sec) and ν is the frequency (Hz) of the energy required for a transition between the two states. Therefore, from this equation it is apparent that if the

radiation frequency v is fixed; the field at which the transition between states will occur depends upon the g value.

The g values for transition metal complexes, however, usually deviate from 2.0023 as a result of spinorbit coupling mixing orbital angular momentum of excited states into the ground state. The excited states which can mix with the ground state depend on the geometry of the complex and the amount of mixing depends on the spinorbit coupling constant of the metal atom and the energy difference between the ground state and the admixed excited states. Thus, for transition metal complexes the gvalues, together with theoretical expressions for this parameter, can provide much information about the complex's geometry, ground state, and excited states.

In systems where the unpaired electron can interact with nuclei which have a magnetic moment, there is another effect which influences the field position of the resonances. This effect is called the hyperfine interaction and it arises from the fact that in such cases the unpaired electron feels an "apparent field" which is the sum total of the applied field and the field produced by the local nuclei. Since a nucleus with a magnetic moment of spin I has (2I+1) possible orientations relative to the applied field, for a large number of molecules the number of electrons sensing each nuclear vector will be

the same. Hence, experimentally one observes (21+1) lines centered about the position at which resonance would occur if the nuclei were absent. The distance between the hyperfine lines is called the hyperfine splitting constant A. Its magnitude is related to the magnitude of the nuclear magnetic moment and to the average distance between the unpaired electron and the nucleus. Obviously, the hyperfine constant can also give much information about bonding in a complex, and those complexes having both a central metal and ligands with nuclear magnetic moments give the most information.

With this as a general background, we will examine the more specific molecular orbital considerations and the g-, metal A-, and ligand A-tensor theories used to calculate bonding coefficients for the series $[VOF_5]^{3-}$ and $[NbOF_5]^{3-}$. Also, most of the theoretical considerations necessary to understand the discussions of the other transition metal ions will be covered. More detailed treatments are available in the reviews and monographs already mentioned. Also, texts by Baird and Bersohn⁶⁴, Assenheim⁶⁵, and Carrington and McLachlan⁶⁶ provide elementary introduction to the subject. For additional information regarding the bonding theories for transition metal complexes, the monographs by Ballhausen⁶⁷, Figgis⁶⁸, Watanabe⁶⁹, Cotton⁷⁰, and Ballhausen and Gray⁷¹ are excellent references.

B. Determination of the Principal g and A Values

In ESR the experimental results are interpreted in terms of a spin Hamiltonian. For the $[MOF_5]^{3-}$ ions studied here, the spin Hamiltonian for the interaction of the unpaired electron with the central metal nucleus is

$$\hat{\mathcal{H}}_{M} = g_{||}^{\beta} e^{H_{z}\hat{S}_{z}+g} \underline{\beta} e^{(H_{x}\hat{S}_{x}+H_{y}\hat{S}_{y})} + A_{||}^{\hat{I}_{z}\hat{S}_{z}+A} \underline{\beta} e^{(H_{x}\hat{S}_{x}+H_{y}\hat{S}_{y})}, \qquad (2.3)$$

where \hat{s} is the electron spin operator, \hat{I} is the nuclear **spin** operator, and the other terms have been defined pre-**viously**.

Schonland's method⁷² has been used in this thesis to determine the principal values $(g_{||}, g_{\perp}, A_{||}, A_{\perp})$ and direction cosines for the g and A tensors. This method requires that the single crystal be rotated about three orthogonal axes. It should be noted, however, that this is only a restriction of this particular method; Waller and Rogers have solved the equations for the general case of rotation about any three axes⁷³. Since the direction cosines obtained from such a method relate the principal tensor directions to three orthogonal rotation axes, it is most informative to choose crystallographic axes for the rotations. Finally, the tensors found experimentally are for the physical quantities g^2 and g^2A^{266} . Since both g^2 and g^2A^2 are second rank tensors, the procedure for determining principal values is the same in both cases and hence only the theoretical development of the g^2 tensor and the procedure for its diagonalization will be discussed here.

We begin by rewriting the spin Hamiltonian in **terms** of the crystal axes as

$$\mathcal{H} = \beta [H_1, H_2, H_3] \begin{bmatrix} g_{11} & g_{12} & g_{13} \\ g_{21} & g_{22} & g_{23} \\ g_{31} & g_{32} & g_{33} \end{bmatrix} \begin{bmatrix} S_1 \\ S_2 \\ S_3 \end{bmatrix}, \qquad (2.4)$$

since the rotation axes are generally not coincident with the principal g axes. The electron spin does not interact directly with the field H but instead its energy depends on the magnitude and direction of vector $\vec{H} \cdot \overline{g}$. Thus, since there are two spins $|\alpha\rangle$ and $|\beta\rangle$ quantized along the direction defined by $\vec{H} \cdot \overline{g}$, the separation between these spin states is given by

$$(\Delta E)^{2} = \beta^{2} (\vec{H} \cdot \vec{g}) (\vec{g} \cdot \vec{H}) = \beta^{2} \vec{H} \cdot \vec{g}^{2} \cdot \vec{H} . \qquad (2.5)$$

Hence, experimentally the quantity that is measured at a **Particular** field position is given by

$$(g^{2}) = [l_{1}l_{2}l_{3}] \begin{bmatrix} (g^{2})_{11} & (g^{2})_{12} & (g^{2})_{13} \\ (g^{2})_{21} & (g^{2})_{22} & (g^{2})_{23} \\ (g^{2})_{31} & (g^{2})_{32} & (g^{2})_{33} \end{bmatrix} \begin{bmatrix} l_{1} \\ l_{2} \\ l_{3} \end{bmatrix}, \quad (2.6)$$

where l_1 , l_2 , l_3 are the direction cosines of \vec{H} relative to the crystal axes. Before this (g^2) tensor can be evaluated, however, its components $\sum_{i=1}^{3} \sum_{j=1}^{3} (g^2)_{ij}$ must be determined.

The Schonland method provides a straight forward method of determining these tensor components using the general expression

$$(g^2) = \alpha + \beta \cos 2\theta + \gamma \sin 2\theta , \qquad (2.7)$$

where θ is a rotation angle and α , β , and γ are parameters which must be determined. If the maximum and minimum values of g during a rotation are denoted by g^{\pm} and occur at θ^{\pm} , respectively, the above parameters can be defined as

$$2\alpha = g_{+}^{2} + g_{-}^{2}$$

$$2\beta = (g_{+}^{2} - g_{-}^{2})\cos 2\theta_{+}$$

$$2\gamma = (g_{+}^{2} - g_{-}^{2})\sin 2\theta_{+} .$$

(2.8)

The $(g^2)_{ij}$ tensor elements can then be determined from these α , β , and γ parameters or, as was done in this study, from a two-parameter method. In this method the diagonal terms are defined as

$$(g^2)_{11} = \alpha_2 + \alpha_3 - \alpha_1 \tag{2.9}$$

and the off-diagonal terms are given by

$$(g^2)_{12} = \pm [(\Delta_3 + \alpha_1 - \alpha_2) (\Delta_3 - \alpha_1 + \alpha_2)]^{1/2},$$
 (2.10)

where

$$\Delta = 1/2 (g_{+}^2 - g_{-}^2) .$$

The other components are generated by a cyclic permutation of the axes 1, 2, 3 throughout the expressions.

Having determined the elements of the (g^2) tensor, it can now be diagonalized by one of several methods. The Jacobian method has been used here to give the diagonal matrix.

$$\begin{bmatrix} (g^2)_{11} & & \\ & (g^2)_{22} & \\ & & (g^2)_{33} \end{bmatrix}$$
. Since these principal

Values are the same as the squares of the principal values of the g tensor, the two tensors naturally have the same **Principal axes.** Also, because the g values are positive from theory, there is no ambiguity arising from the fact that experimentally we observe the (g^2) tensor. In the **case** of the (g^2A^2) tensor, on the other hand, the sign of A can be positive or negative.

C. Signs of Metal Hyperfine Splitting Constants

After determining the magnitude of the principal A values, one must choose between the possible combination of signs. In the case of an axially symmetric hyperfine tensor, $A_{||}$ and A_{\perp} can either be positive or negative giving four possible sign combinations. Since these hyperfine tensors can be expressed as $A_{||} = A_{iso} + 2Ap$ and $A_{\perp} =$ $A_{iso} - A_p$, one can determine the correct sign combination if the signs of the isotropic splitting A_{iso} , and the anisotropic splitting A_p are known. In this thesis the method of Fortman⁷⁴ has been used to determine these signs.

Fortman determined the sign predicted for an odd electron in different type of metal orbitals using a model system in which the nucleus and unpaired electron are considered to be point charges and simple magnetic dipoles. The results are summarized here for the case of a positive nuclear moment; opposite signs are predicted for a negative nuclear magnetic moment. If the electron is in the orbital along the unique axis of the molecule (by convention the Z axis), the anisotropic splitting component will be Positive. On the other hand, if the unpaired electron is in an orbital perpendicular to the axis of symmetry, the anisotropic splitting component A_p will be negative. The isotropic splitting A_{iso} is normally negative but, if the valence shell s contribution is large, it is possible to
have a positive splitting. The latter case is predicted for those ions whose geometry allows the valence shell *s* orbital to mix with the ground state orbital.

D. LCAO Molecular Orbital Theory of Transition Metal Complexes

As mentioned previously, in the molecular orbital picture of bonding the electrons occupy orbitals which span the entire molecule. Applying this theory to transition metal complexes, expressions for these orbitals are ob tained by forming linear combinations of the atomic orbitals in the following manner. The valence shell or**bitals** of the ligands are used as a basis for a representation of the point group of the molecule, and this representation is decomposed into its component irreducible representations. The ligand orbitals are then combined into linear combinations belonging to these irreducible representations, and the interactions between ligand and metal orbitals of the same symmetry are computed. The energies obtained are then used to determine the metal and Ligand group-orbital coefficients which are the true **molecular** orbitals of the complex.

Applying this method to the $[MOF_5]^{3-}$ ion, where M = V,Nb, we start by choosing a coordinate system for the atomic orbitals. The coordinate system shown in Figure 2.1, was chosen to be consistent with the one



Figure 2.1--Coordinate system for the atomic orbitals of the $[MOF_{r_i}]^{3-}$ ions.

which will be used later to analyze the g, metal A, and the ligand A tensors for these ions. The metal orbital Z axis is along the F-M-O bond direction and X and Y axes are along the F-M-F bond directions. Also, the oxygen and the axial fluorine have this coordinate system but the equatorial ligands have their x axis along the M-F bond, their z axis parallel with the F-M-O bond, and their Y axis chosen to form a right-handed coordinate system. Using this axis system, the ligand atomic orbitals are combined into linear combinations having the symmetry of the various irreducible representations of the C_{4v} point group. These linear combinations, along with the metal orbitals having the same transformation properties, are listed in Table 2.1.

In order to form molecular orbitals from these atomic orbitals, all the linear combinations of ligand orbitals having the same symmetry are next combined into group symmetry orbitals. For instance, the group symmetry for the b_{γ} molecular orbital is

$$\Phi_{L} = o_{1}(s^{1} - s^{2} + s^{3} - s^{4}) + c_{2}(p_{x}^{1} - p_{x}^{2} + p_{x}^{3} - p_{x}^{4}) .$$
(2.11)

This is then combined with a linear combinations of the metal orbitals which transform under the same representation to form the molecular orbital.

When the energy of such molecular orbitals is determined, two solutions are found. One has less energy than the noninteracting atomic orbitals and corresponds to a bonding molecular orbital of the form $\Psi^{D} = a |\Phi_{M}\rangle + b |\Phi_{L}\rangle$; the other solution has energy greater than the noninteracting atomic orbitals and corresponds to an antibonding molecular orbital of the form $\Psi^{m} = a |\Phi_{M}\rangle - d |\Phi_{L}\rangle$. These molecular orbitals have two properties which enable the coefficients of both the antibonding and bonding molecular orbitals to be determined if only one coefficient is known. First, each molecular orbital is normalized, *i.e.*, $\langle \psi^b | \psi^b \rangle = 1$ and secondly, they are orthogonal to one another, *i.e.*, $\langle \psi^b | \psi^* \rangle = 0$. Finally, if there are no ligand group symmetry orbitals to combine with a metal orbital of a particular symmetry, the metal orbital experiences no interaction with the ligand orbitals; its energy remains the same and is referred to as a nonbonding orbital.

In order to calculate energy level diagrams using these molecular orbitals, certain approximations must be Ballhausen and Gray have used the VSIE method made. of calculating coulomb integrals, and the Wolfsberg-Helmholz approximation for evaluating exchange integrals, to arrive at the molecular orbital energy level scheme shown in Figure 2.2 for $[VO(H_2O)_5]^{2+75}$. In this calculation, π -bonding with the equatorial ligands was neglected and this bonding, in the case of the fluoride complexes is important. However, since this effect does not alter the energy levels very much, the diagram will be helpful in subsequent discussion. The major difference, in the case of the fluoride ions where π bonding is important, is that the b_{γ} orbital containing the odd electron is an antibonding orbital instead of a nonbonding orbital as shown for $[VO(H_2O)_5]^{2+}$.

All of the molecular orbitals shown in the energy level diagram play an important note in the bonding of the complex. In ESR, however, we can only acquire VANADIUM ORBITALS



Figure 2.2--The molecular orbital energy level scheme for $[VO(H_2O)_5]^{2+}$.

OXYGEN

ORBITALS

Symmetry	Transition Metal Orbitals	Ligand Orbitals
A ₁	8	8 ⁵ 2 ⁵
	P _z	8
	d _z 2	s ¹ +s ² +s ³ +s ⁴
		$p_{z}^{1}+p_{z}^{2}+p_{z}^{3}+p_{z}^{4}$
		$p_x^1 + p_x^2 + p_x^3 + p_x^4$
A 2		$p_{y}^{1}+p_{y}^{2}+p_{y}^{3}+p_{y}^{4}$
^B 1	$d_{x}^{2} - y^{2}$	s ¹ -s ² +s ³ -s ⁴
	-	$p_{z}^{1} - p_{z}^{2} + p_{z}^{3} - p_{z}^{4}$
		$p_{x}^{1} - p_{x}^{2} + p_{x}^{3} - p_{x}^{4}$
^B 2	d_{xy}	$p_{y}^{1} - p_{y}^{2} + p_{y}^{3} - p_{y}^{4}$
Ε	(d_{xz}, d_{yz})	(p_x^o, p_y^o)
	(p _x ,p _y)	(p_{x}^{5}, p_{y}^{5})
		(s ¹ -s ³),(s ² -s ⁴)
		$(p_{a}^{1}-p_{a}^{3})(p_{a}^{2}-p_{a}^{4})$
		$(p_x^1 - p_x^3) (p_x^2 - p_x^4)$
		$(p_{y}^{1}-p_{y}^{3})(p_{y}^{2}-p_{y}^{4})$
		- <i>y</i> - <i>y</i> - <i>y</i> - <i>y</i>

Table 2.1. Classification of atomic orbitals into the irreducible representations of the C_{4v} point group.

information about the ground state and admixed excited states. How this information is acquired is, in part, the topic of the following section.

E. Molecular Orbital Theory of g and Metal A Parameters

DeArmond *et al.*³⁴, extending the basic theory of Abragam and Pryce⁷⁶, have related the ESR parameters $(g_{||}, g_{\perp}, A_{||} \text{ and } A_{\perp})$ of the spin Hamiltonian given by Equation (2.3) to bonding coefficients for the series $[MOF_5]^{2-}$ where M = Cr, Mo, W. The theoretical development of these expressions is included here since they will be used in this study of bonding in the analogous series $[MOF_5]^{3-}$ where M = V, Nb.

The general Hamiltonian for the $d^1 [MOF_5]^{3-}$ ions is given as a sum of terms listed in decreasing energy:

$$\hat{\mathcal{F}} = \sum_{i} \sum_{k} - \frac{\hbar^2}{2m} \nabla_i^2 - \frac{z_k e^2}{r_{ik}} + \sum_{i < j} \frac{e^2}{r_{ij}}$$
(a)

+
$$\lambda(\mathbf{r})\hat{\boldsymbol{z}}\cdot\hat{\boldsymbol{s}}$$
 (b)

+
$$\beta_e(\hat{l}+g_e\hat{S})\cdot\hat{H}$$
 (c)

$$+ g_e g_n \beta_e \beta_n \left[\frac{(\hat{l} - \hat{s}) \cdot \hat{l}}{r^3} + \frac{3(\hat{r} \cdot \hat{s})(\hat{r} \cdot \hat{l})}{r^5} \right]$$
(d)

$$+ \frac{\partial \pi}{\partial s} (\delta_{r=0}) (\hat{I} \cdot \hat{S})$$
 (e)

 $+ g_n \beta_n \hat{I} \cdot \hat{H}$, (f) (2.12)

where (a) expresses the total kinetic and potential energy of the elctrons, $\sim 10^5 \text{ cm}^{-1}$, (b) is the spin-orbit energy due to the coupling of the spin and orbital motions, $\sim 10^2$ - 10^3cm^{-1} , (c) describes the interaction of the magnetic field with the orbital and spin magnetic moments, ~1- 10^{-1} cm⁻¹, (d) is the dipolar hyperfine energy arising from the interaction of the nuclear moment with the orbital and spin magnetic moments $\sim 10^{-2} - 10^{-4} \text{ cm}^{-1}$, (e) is the Fermi contact interaction energy resulting from unpaired spin density at the nucleus, $\sim 10^{-2} - 10^{-4} \text{ cm}^{-1}$, and (f) is the nuclear Zeeman term which expresses the interaction of the nuclear magnetic moment with the external magnetic field $\sim 10^{-3} \text{ cm}^{-1}$. From these energies, it is apparent that the sum of the terms (b)-(f) is small relative to the first term and can be considered as a perturbation. Thus, using eigenfunctions of the Hamiltonian for the total electronic and kinetic energies, a perturbation treatment will be used to evaluate the perturbation Hamiltonian $\hat{\mathcal{H}}' = [(b) - (f)].$

In this treatment, the basis set will be the ground state and those excited states which will mix with the ground state through spin-orbit coupling. From the energy diagram for this type of ion, we recall that the ground state wave function is $|B_2\rangle = \beta_2 |d_{xy}\rangle - \beta'_2 |\Phi_{xy}\rangle$, and, under the C_{4v} point group, the $|B_1\rangle = \beta_1 |d_x^2 - y^2\rangle - \beta'_1 |\Phi_x^2 - y^2\rangle$ and $|E\rangle = \epsilon |d_{xz,yz}\rangle - \epsilon' |\Phi_{xz,yz}\rangle$ excited state

wave functions will mix. For convenience, the ground state will be denoted here by $|0\rangle$ and the excited states by $|n\rangle$. The first-order energy then is simply $\langle 0 | \hat{\mathcal{L}C'} | 0 \rangle$. In calculating this energy, the following assumptions are made: (1) all integrals involving $\lambda(r)$ between transition metal functions and ligands are neglected and (2) all integrals involving r^{-3} which contain ligand functions are neglected. Since $\langle 0 | \hat{l} | 0 \rangle = 0$, this calculation yields following first-order solution

$$E^{(1)} = g_{e}\beta_{e}\hat{H}\cdot\hat{S} + \beta_{2}^{2}P[\frac{4}{7}I_{z}S_{z} - \frac{2}{7}(\hat{I}_{x}\hat{S}_{x} + \hat{I}_{y}\hat{S}_{y}) + \kappa\hat{I}\cdot\hat{S}] . \qquad (2.13)$$

In correcting this solution to second order, only the $\langle 0 | (b) | n \rangle \langle n | (c) | 0 \rangle / (E_n - E_0), \langle 0 | (b) | n \rangle \langle n | (d) | 0 \rangle / (E_n - E_0), and <math>\langle 0 | (b) | n \rangle \langle n | (f) | 0 \rangle / (E_n - E_0)$ terms are considered, since $\hat{l} \cdot \hat{s}$ is much greater than the other terms and $\langle 0 | (n) | n \rangle^2 / (E_n - E_0)$ does not give terms in the spin Hamiltonian. This procedure yields:

$$E^{(2)} = \Lambda_{ij} \beta_{e}^{H}_{i}\hat{S}_{j} + (\Lambda_{ij}^{*} - 3\mu_{ij})\hat{S}_{i}\hat{I}_{j}^{*}, \qquad (2.14)$$

where

$$\begin{split} \Lambda_{ij} &= -2 \sum_{n \neq 0} \left\langle 0 \left| \lambda(r) \hat{l}_{i} \right| n \right\rangle \left\langle n \left| \hat{l}_{j} \right| 0 \right\rangle / E_{n} - E_{0} \right\rangle \\ \Lambda_{ij} &= -2 \sum_{n \neq 0} \left\langle 0 \left| \lambda(r) \hat{l}_{i} \right| n \right\rangle \left\langle n \left| \hat{l}_{j} / r^{3} \right| 0 \right\rangle / (E_{n} - E_{0}) \\ \mu_{ij} &= -i \varepsilon_{ikm} \sum_{n \neq 0} \left\langle 0 \left| \lambda(r) \hat{l}_{m} \right| n \right\rangle \left\langle n \left| r_{k} r_{j} / r^{5} \right| 0 \right\rangle / \\ \left(E_{n} - E_{0} \right) \end{split}$$
(2.15)

The suffixes i, j, etc. refer to the Cartesian coordinates X, Y, Z and $\varepsilon_{ikm} = \pm 1$ as ikm represents an even or an odd permutation of X, Y, Z and is zero if any pair of i, k, or m are the same.

The above matrix elements are evaluated to determine the second-order correction which is then combined with the first-order solution to obtain the following expression for the spin Hamiltonian parameters found in Equation (2.3).

$$g_{||} = 2.0023 = -\left[2\frac{(2\lambda_{M}\beta_{2}\beta_{1}-\lambda_{L}\beta_{2}\beta_{1})}{\Delta E(b_{2}+b_{1})}\right] \quad (2\beta_{2}\beta_{1}-2\beta_{1}\beta_{2}S_{b_{2}}) \\ - 2\beta_{2}\beta_{1}S_{b_{1}}-\beta_{1}\beta_{2}S_{2} \quad (2.16)$$

$$\left[2\lambda_{M}\beta_{2}\varepsilon\right]$$

$$g_{\perp} - 2.0023 = -\left[\frac{2\lambda_M \beta_2 \varepsilon}{\Delta E(b_2 \to e)}\right] \quad (\beta_2 \varepsilon - \beta_2 \varepsilon' S_e - \varepsilon \beta_2' S_b_2) \quad (2.17)$$

$$- \frac{A}{P} = \kappa \beta_{2}^{2} + \frac{4}{7} \beta_{2}^{2} + 2.0023 - g_{||} + \frac{3}{7} (2.0023 - g_{||}) + \left[\frac{6}{7} \frac{\lambda_{M} \beta_{2} \varepsilon}{\Delta E (b_{2} + e)} \right] (\beta_{2} \varepsilon' S_{e} + \varepsilon \beta_{2}^{2} S_{b_{2}}) + \left[2 \frac{(2\lambda_{M} \beta_{2} \beta_{1} - \lambda_{L} \beta_{2}^{2} \beta_{1}^{2})}{\Delta E (b_{2} + b_{1})} \right] (2\beta_{2} \beta_{1}^{2} S_{b_{1}} + 2\beta_{1} \beta_{2}^{2} S_{b_{2}} + \beta_{1}^{2} \beta_{2}^{2}), \qquad (2.18)$$

$$-\frac{A_{\perp}}{P} = \kappa \beta_{2}^{2} - \frac{2}{7} \beta_{2}^{2} + \frac{11}{14} (2.0023 - g_{\perp}) + \frac{11}{7} \left[\frac{\lambda_{M} \beta_{2} \varepsilon}{\Delta E(b_{2} + e)} \right] (\beta_{2} \varepsilon' S_{e} + \varepsilon \beta_{2}' S_{b_{2}}) . \qquad (2.19)$$

where $P = g_e g_n \beta_e \beta_n \langle 0 | r^{-3} | 0 \rangle$, $\Delta E_{(b_2-e)}$ and $\Delta E_{(b_2-b_1)}$ are the energy differences between the ground state and those excited states which will mix, $S_{b_1} = \langle d_{x^2-y^2} | \Phi_{x^2-y^2} \rangle$, $S_{b_2} = \langle d_{xy} | \Phi_{xy} \rangle$, $S_e = \langle d_{xz,yz} | \Phi_{xz,yz} \rangle$, and κ is the Fermi contact term. The *P* values can be determined from Hartree-Fock wave functions for the atoms and the ΔE values can be determined from optical spectra. The determination of *S* values and κ demand more detailed discussion.

F. Evaluation of κ

In the case of d^1 complexes, where the unpaired electron is in a d_{xy} orbital, the value of κ is considered to be a measure of the polarization of the inner *s* electrons. This parameter can be evaluated by solving the first-order isotropic hyperfine expression²¹ for κ as follows:

$$\kappa = \frac{(\langle g \rangle - 2.0023)}{\beta_2^2} - \frac{\langle A \rangle}{\beta_2^2 P}, \qquad (2.20)$$

where

$$\langle A \rangle = (A_{||} + 2A_{\perp})/3$$

$$\langle g \rangle = (g_{||} + 2g_{\perp})/3$$

In order to evaluate κ using this expression, it is necessary to know the experimental isotropic $\langle g \rangle$ and $\langle A \rangle$ values and to assume values for P and β_2^2 . Since κ for a transition metal is considered constant for complexes with the same electronic configuration⁴⁵, the value of κ used for $[VOF_5]^{3-}$ is taken to be the same as that found for the solvated VO^{2+} ion in an aqueous solution of $VOSO_4$. For $[VO(H_2O)_5]^{2+}$ the Hartree-Fock radial function for V^{2+} was used to evaluate P and since the solvated VO^{2+} ion is considered nearly ionic, a value of 0.97 was assumed for β_2 . Using these parameters, a value of 0.85 was determined for κ .

Since solution spectra are not available for the NbO²⁺ species, a different approach was taken to evaluate κ for [NbOF₅]³⁻. The first-order expressions⁷⁷ for $\langle A \rangle$, $A_{||}$, and $A_{|}$ were solved for K and β_2^2 as shown below:

$$K = - \langle A \rangle + (\langle g \rangle - 2.0023) P \qquad (2.21)$$

$$\beta_2^2 = \frac{7}{2} \frac{(A_{\perp} + K)}{P} - \frac{11}{4} (g_{\parallel} - 2.0023) \qquad (2.22)$$

The K and β_2^2 values, determined for $[NbOF_5]^{2-}$ assuming a 2+ charge on niobium, were then used in the expression

$$\kappa = \frac{K}{\beta_2^2 P}$$
 to give $\kappa = 1.34$.

G. Evaluation of Group Overlap Integrals

There are several factors involved in determining accurate overlap integrals for transition metal complex ions. Good wave functions must be available for all of the atoms, bond distances must be known, and there should be some idea as to the charge distribution and orbital hybridization in the complex.

For the atomic wave functions of vanadium, oxygen, and fluorine, Burns functions have been used. From comparison with recent Hartree-Fock calculations, the Burns wave functions have been shown to provide accurate overlap intergrals for earlier numbers of the first-row transition metal⁷⁸. The Burns wave functions, much like the Slater functions, have the form

$$\psi(n,l,m) = Nr^{n-1}exp(\xi \cdot r/a_{o}), \qquad (2.23)$$

where N is the normalization constant, $\xi = \frac{Z-S}{n}$ is the orbital exponent, Z is the nuclear charge, S is the screening constant, and n is the principal quantum number.

The formulas for calculating the screening constant S are given in Table 2.2. In Table 2.3 are values of the orbital exponent ξ for the vanadium 4s, 4p, and 3d orbitals corresponding to charges +1 to +4. Shown in Table 2.4 are the ξ values of the oxygen and fluorine 2s and 2p orbitals for the appropriate charges.

The bond distances for $[VOF_5]^{3-}$ were determined by extrapolation from the bond distances found for $K_2NbOF_5^{79}$. It has been noted that the M-O bond distances in the $[MOL_5]^{n+}$ complexes are very nearly the same as those determined for the MO diatomic gas molecule. Evidence of this can be seen in

Type of electron	Contribution	to S of each s in the atom he nl electron	of the n' l'
for which S is	electron		(omitting
being calculated	t)
ns	0.9 (n-1) s	0.75(n-1)p	1.0 $(n-8)$ d 0.5 $(n-1)$ d
	0.4 ns	0.35 np	0.35 na
	0.1 (n+1) s	0.1 (n+1) p	0.1 (n+1) d
np	1.0 (n-1) s 0.5 ns 0.0 (n+1) s	0.9 (n-1) p 0.35 np 0.0 (n+1) p	1.0 (n-2) d 0.7 (n-1) d 0.35 nd 0.0 (n+1) d
nd	1.0 (n-1) 8	1.0 (n-1) p	0.9 (n-1) d
	0.75 ns	0.5 np	0.35 nd
	0.15 (n+1) s	0.05 (n+1) p	0.05 (n+1) d

Table 2.2. Contribution to S from each of the other n'l' electrons in the atom.a,b

^aThe sum of these contributions is used to calculate the screening constant (S) for the particular type of nlelectron under consideration [*i.e.*, for the 3*d* orbital in \mathbf{y}^{3+} (18², 28², 2p⁶, 38², 3p⁶, 3d²) one has $S = [2 \times 1.0 + 2 \times 1.0 + 6 \times 1.0 + 2 \times 0.75 + 6 \times .05 + 1 \times 0.35 = 14.85].$

^bFrom reference 78.

Table 2.3. Effect of charge on orbital exponent for vanadium.^a

Charge	48	4p	3d
+1	1.300	0.750	2.550
+3+4	1.550	1.050	2.716

^aCalculated from the Burns formulas.

Atom	Orbital	ξ
0 ^{+0.0}	2s 2p	2.200 1.975
0 ^{-1.0}	2s 2p	2.025 1.800
0-2.0	28 2p	1.850 1.625
F ^{+0.0}	2 s 2 p	2.525 2.300
F ^{-1.0}	2s 2p	2.350 2.125

Table 2.4. Orbital exponents for fluorine and for oxygen.

Table 2.5. Bond distances for the [NbOF₅]³⁻ and [VOF₅]³⁻ ions.^a

Species	M-O	^{M-F} eq	M-F _{ax}	References
vo	1.60			80
NbO	1.69			80
K2NbOF5	1.68	1.84	2.06	79
[VOF ₅] ³⁻	1.60	1.75	1.96	Extrapolated

^aAll bond distances are given in angstoms.

Table 2.5 for the NbO species. The bond distance for the VO diatomic gas molecule⁸⁰ has therefore been taken as the V-O bond length for $[VOF_5]^{3-}$. The $r_{(V-F)}_{ax}$ and $r_{(V-F)}_{eg}$ values for $[VOF_5]^{3-}$ have been estimated by multiplying the observed values for $r_{(Nb-F)}_{ax}$ and $r_{(Nb-F)}_{eg}$ by the observed ratio $r_{V-O/r_{Nb-O}}$ for the diatomic gas molecules (see Table 2.5).

With the above data as input, a computer program⁸¹ was used to calculate the necessary diatomic overlap integrals. These integrals are shown in Table 2.6, where a superscript o is used to designate oxygen orbitals, and the superscripts a and e are used to denote axial and equatorial fluorine orbitals, respectively.

Fortunately, these diatomic overlap integrals can be used to express the group overlap integral, $S = \int \Phi_M \Phi_L d\tau$, which is the total overlap between a metal atomic orbital and a linear combination of ligand orbitals. Φ_M is a normalized metal orbital and Φ_L is a normalized linear combination of ligand orbitals. The generalized expressions for the group overlap integrals necessary for the calculations of bonding parameters are as follows:

$$S_{b_{1}} = \left\langle d_{x^{2}-y^{2}} | \Phi_{x^{2}-y^{2}} \right\rangle$$

$$S_{b_{2}} = \left\langle d_{xy} | \Phi_{xy} \right\rangle$$

$$S_{e} = \left\langle d_{xz,yz} | \Phi_{xz,yz} \right\rangle, \qquad (2.24)$$

[VOF ₅] ³
for
integrals
overlap
Diatomic
2.6.
Table

)		
Charge of Vanadium	$\langle 3d_{xy} 2p_y^e \rangle$	$\langle 3d_x^2 - y^2 28^e \rangle$	$\langle 3d_x^2-y^2 2p_x^e\rangle$	$\langle 3d_{xs,ys} 2p_{x,y}^{o} angle$	$\langle sd_{xa,ya} 2p_{x,y}^a \rangle$
+1.0	0.082	0.131	0.163	0.157	0.047
+2.0	0.078	0.124	0.157	0.150	0.045
+3.0	0.069	0.110	0.145	0.135	0.039
+4.0	0.061	0.097	0.133	0.121	0.033

where

$$\Phi_{x^{2}-y^{2}} = c_{1}(s^{1}-s^{2}+s^{3}-s^{4}) + c_{2}(p_{x}^{1}-p_{x}^{2}+p_{x}^{3}-p_{x}^{4})$$

$$\Phi_{xy} = (p_{y}^{1}-p_{y}^{2}+p_{y}^{3}-p_{y}^{4})$$

$$\Phi_{xz,yz} = d_{1}(p_{x,y}^{0}) + d_{2}(p_{x,y}^{5}) + d_{3}(p_{z}^{1,2}-p_{z}^{3,4}) \quad (2.25)$$

The group overlap orbitals have been calculated both by considering just the dominant ligand p orbital overlap, and also by considering the entire ligand hybrid orbital overlap. In the former case, the c_1 , d_2 , and d_3 coefficients are taken as zero, giving the following group overlap integrals as expressed in terms of diatomic overlap integrals:

$$S_{b_{1}} = \sqrt{3} \left\langle 3d_{x^{2}-y^{2}} | 2p_{x}^{e} \right\rangle$$

$$S_{b_{2}} = 2 \left\langle 3d_{xy} | 2p_{y}^{e} \right\rangle$$

$$S_{e} = \left\langle 3d_{xz,yz} | 2p_{x,y}^{o} \right\rangle$$

$$(2.26)$$

In the latter case, the degree of hybridization used was that determined in Van Kemenade's⁴⁵ extended Hückel calculations for $[CrOF_5]^{2-}$.

Table 2.7. Orbital character ratios used for the hybrid group symmetry orbitals.

	$\Phi_x^2 - y^2$	Фе	
ratio	s /p	p°/p ⁵	p°/p ^e
[CrOF ₅] ²⁻	0.65	2.26	2.26

Using these orbital character ratios, shown in Table 2.7, to determine the ligand hybrid orbital coefficients, the group orbitals were normalized and integrated with their corresponding metal orbitals to give the following expressions for the overlap integrals:

$$S_{b_{1}} = 1.088 \left\langle 3d_{x^{2}-y^{2}} | 2s^{e} \right\rangle + 1.348 \left\langle 3d_{x^{2}-y^{2}} | 2p_{x}^{e} \right\rangle$$

$$(2.27)$$

$$S_{b_2} = 2 \left\langle 3d_{xy} | 2p_y^e \right\rangle$$
 (2.28)

$$S_{e} = 0.656 \left\langle 3d_{xz,yz} | 2p_{x,y}^{o} \right\rangle \\ + 0.436 \left\langle 3d_{xz,yz} | 2p_{x,y}^{a} \right\rangle \\ + 0.872 \left\langle 3d_{xy} | 2p_{y}^{e} \right\rangle$$
(2.29)

The group overlap integrals for $[NbOF_5]^{3-}$ were determined by extrapolation from those for $[VOF_5]^{3-}$ assuming that the ratio $s[VOF_5]^{3-}/s[NbOF_5]^{3-}$ for a given overlap integral such as s_e would be the same as found for $s[CrOF_5]^{2-}/s[MoOF_5]^{2-}$ in the extended Hückel calculations on Group VIb complexes⁴⁵. The overlap integrals for $[NbOF_5]^{3-}$ and for $[VOF_5]^{3-}$ calculated by considering only dominant ligand p overlap are shown in Table 4.5 and those values determined by considering ligand hybrid orbital overlap are shown in Table 4.6.

H. Determination of Bonding Coefficients from g and Metal A Expressions

For a particular assumed charge on the central metal atom, bonding coefficients were determined in the following manner. First, for a given set of parameters β_2 , β_1 and ϵ , the corresponding β'_2 , β'_1 and ϵ' coefficients were determined from the normalization condition. These coefficients were then substituted into Equation (2.16-2.19) to determine the theoretical values for $\Delta g'_1$, $\Delta g'_2$, A'_1 and A'_2 . Next, the total squared relative error between the experimental $\Delta g_{||}$, Δg_1 , $A_{||}$ and A_1 values and the above theoretical values was evaluated by use of the expression

$$\operatorname{Error} = \left[\left(\Delta g_{\parallel}^{\dagger} - \Delta g_{\parallel} \right) / \Delta g_{\parallel} \right]^{2} + \left[\left(\Delta g_{\perp}^{\dagger} - \Delta g_{\perp} \right) / \Delta g_{\perp} \right]^{2} \\ \left[\left(A_{\parallel}^{\dagger} - A_{\parallel} \right) / A_{\parallel} \right]^{2} + \left[\left(A_{\perp}^{\dagger} - A_{\perp} \right) / A_{\perp} \right]^{2} . \quad (2.30)$$

Finally, a best-fit solution was determined by a minimization program which systematically searched the space spanned by β_1 , β_2 and ϵ until the smallest value of "Error" was found.

I. Calculation of Charge on the Central Metal Atom

In order to calculate a charge on the central metal atom, the corresponding bonding molecular orbital coefficients were determined from the above antibonding coefficients using the orthogonality relationship $\langle \psi^* | \psi^b \rangle = 0$ and the normalization relationship $\langle \psi^b | \psi^b \rangle$ = 1. With the bonding and antibonding coefficients so determined, it is now possibly to correct the +4 formal charge on the central metal for valence shell covalency.

The formal charge of +4 assumes that the electron density of the bonding molecular orbital is completely on the ligand and the antibonding electron density is completely on the metal. However, using $\psi^{b} = a(\Phi_{M})$ + $b(\Phi_{L})$ as a general expression for a bonding molecular orbital, a Mulliken population analysis⁸² shows that there is $Q_{b} = 2(b^{2}+abS)$ electron density on the ligands for each filled bonding orbital and, using $\psi^{*} = c(\Phi_{M}) - d(\Phi_{L})$ to represent the half-filled antibonding molecular orbital, a Mulliken population analysis shows this orbital contributes a charge of $Q_{a} = (c^{2}-cdS)$ to the central metal atom. Thus, the calculated charge is given by

$$Q = 4.0 - \sum_{i=1}^{n} Q_{bi} + Q_{a}$$
, (2.31)

where n is the number of filled bonding molecular orbitals.

J. Determination of Ligand Hyperfine Values

The interaction of an unpaired electron with ligand nuclei is interpreted in terms of a spin Hamiltonian. For the $[NbOF_5]^{3-}$ ion, this Hamiltonian is given by

$$\hat{\mathcal{F}C}_{\mathbf{L}} = A_{z}\hat{S}_{z} \sum_{n=1}^{4} \hat{I}_{zn} + [A_{x}(\hat{I}_{x1}+\hat{I}_{x3}) + A_{y}(\hat{I}_{x2}+\hat{I}_{x4})]\hat{S}_{x} + [A_{y}(\hat{I}_{y1}+\hat{I}_{y3}) + A_{x}(\hat{I}_{y2}+\hat{I}_{y4})]\hat{S}_{y}. \qquad (2.32)$$

Since the unpaired electron in this case, as in most other cases, interacts with several ligand nuclei, the resulting hyperfine lines are difficult to follow in a rotation, especially when they are superimposed on metal hyperfine lines. Therefore, in this case one cannot use a diagonalization technique to determine the principal values. However, from theory we know that the principal values of the ligand hyperfine tensor lie along the ligand bonding directions, *i.e.*, for $[NbOF_5]^{3-}$, along the ligand p_{σ} , $p_{\pi y}$, and $p_{\pi z}$ directions. Thus, using the direction cosines determined from the g and metal A diagonalization, and available crystal structure information, the crystal can be oriented in the magnetic field such that the principal value are measured directly.

K. Determination of the Sign of the Principal Ligand A Values

The ligand hyperfine tensor is composed of an isotropic part and an anisotropic part. Since the trace of the anisotropic part sums to zero, in solution only the isotropic part is observed. Thus, from solution spectra one can usually establish the relative signs of the principal values using the relationship $A_{iso} = 1/3 [A_x + A_y + A_z]$. Although in the study of ions in unstable oxidation states solution spectra are not available, results for analogous compounds in stable oxidation states can be used to determine the relative signs.

Even if the relative signs are known, one must still determine the correct combination of signs. This is done by analyzing the possible combination of signs for the ligand hyperfine tensor in terms of its various component tensors. The component tensors are given here taking y and z to denote the ligand π bond directions and x to denote the σ bond direction.

$$\begin{bmatrix} A_{x} \\ A_{y} \\ A_{z} \end{bmatrix} = \begin{bmatrix} A_{iso} \\ A_{iso} \\ A_{iso} \end{bmatrix} + \begin{bmatrix} 2A_{d} \\ -A_{d} \\ -A_{d} \end{bmatrix} + \begin{bmatrix} 2A_{\sigma} \\ -A_{\sigma} \\ -A_{\sigma} \end{bmatrix} + \begin{bmatrix} -A_{\pi y} \\ 2A_{\pi y} \\ -A_{\pi y} \end{bmatrix} + \begin{bmatrix} -A_{\pi y}$$

Assuming that the ligand nucleus has a positive magnetic moment, the expected relative magnitudes and signs of these components are given for the different bonding cases (noting of course that in each case the component

would have opposite sign if the nuclear moment were negative). For the case where the unpaired electron is in a metal d orbital which has a π overlap with the ligand orbitals, the A_{iso} and A_{aniso} due to direct π delocalization will be positive and large relative to the negative A_{iso} and A_{aniso} arising from spin-polarization of the σ orbitals. For the case where the electron is in a metal d orbital which has a σ overlap with the ligand orbitals, A_{iso} and A_{aniso} , due to the direct σ delocalization, will be positive and large relative to the negative A_{iso} and A_{aniso} , due to the direct σ delocalization, will be positive and large relative to the negative A_{iso} and A_{aniso} arising from spin-polarization of the π orbitals. In both cases A_d is positive and its magnitude can be calculated from the expression $A_d = g_e \beta_e g_n \beta_n / r^3$ (ergs).

L. Determination of Bonding Coefficients from Ligand Hyperfine Splittings

Since ligand hyperfine splittings provide the best demonstration of covalency in transition metal complexes, one should be able to relate this parameter to molecular orbital bonding coefficients for these compounds. Two approaches to this problem were taken in this thesis work. For th $[VOF_5]^{3-}$ and $[NbOF_5]^{3-}$ series, certain assumptions about spin-polarization (or configuration interaction, depending on how one wants to look at this) enabled the anisotropic part of the ligand hyperfine tensor to be decomposed into axially symmetric tensors. The one tensor with its unique axis along the ligand $p_{\pi y}$ direction was considered to arise from direct delocalization of the unpaired electron in the metal d_{xy} orbital into the ligand $p_{\pi y}$ orbital. Relating a Mulliken population analysis for this molecular orbital to the total experimental spin density transferred to the ligand $p_{\pi y}$ orbitals, enabled the bonding coefficients to be determined.

The other method involves using the ground state molecular orbital to determine the expectation value for the dipolar interaction between the unpaired electron and the ligand nuclear magnetic moment. This method involves, for instance in the case of $[NbOF_5]^{3-}$, the following integrals:

$$\langle \mathbf{0} | \mathcal{H}_{\mathbf{L}} | \mathbf{0} \rangle = \beta_{2}^{2} \langle d_{xy} | \mathcal{H}_{\mathbf{L}} | d_{xz} \rangle$$

$$- 2\beta_{2}\beta_{2} \langle d_{xy} | \mathcal{H}_{\mathbf{L}} | \phi_{xy} \rangle$$

$$+ \beta_{2}^{2} \langle \phi_{xy} | \mathcal{H}_{\mathbf{L}} | \phi_{xy} \rangle.$$

$$(2.34)$$

However, when molecular orbital coefficients are actually determined we focus on the interaction with just one ligand, the expression used only involves the diatomic integrals:

$$A_{aniso}^{L} = \beta_{2}^{2} \left\langle d_{xy} | \mathcal{H}_{L} | d_{xy} \right\rangle$$

$$- \beta_{2} \beta_{2}^{*} \left\langle d_{xy} | \mathcal{H}_{L} | p_{\pi y} \right\rangle$$

$$+ \frac{\beta_{2}^{*}}{4} \left\langle p_{\pi y} | \mathcal{H}_{L} | p_{\pi y} \right\rangle. \qquad (2.35)$$

In applying this type of calculation to the chlorine hyperfine tensor in the radical $[RhCl_6]^{4-}$, we approximate the integral $\langle d_M | \mathcal{H}_L | d_M \rangle$ as A_d , ignore the second integral since good wave functions were not available, and use P_{Cl} for $\langle p_L | \mathcal{H}_L | p_L \rangle$. It should be noted that the molecular orbital coefficients calculated for $[RhCl_6]^{4-}$ in this manner are only very approximate, since Van Kemenade⁴⁵, applying the above method, found that not only did he have to evaluate all the integrals but also calculate second-order correction terms to achieve good agreement between experiment and theory.

CHAPTER III

EXPERIMENTAL

A. ESR Spectrometer Systems

The ESR measurements were carried out with 100 KHz field modulation using a Varian V-4502 X-band spectrometer, a Varian E-4 spectrometer, and a Varian 4503 Q-band spectrometer. Since the Varian V-4502 X-band spectrometer has provisions for measuring the frequency and field position very accurately, it was used for all quantitative measurements. And because of its operational stability and facility, the E-4 spectrometer was often used for initial qualitative work. The Q-band spectrometer, with a magnetic field range approximately four times that of the X-band spectrometer, was used to study systems which contained more than one species with different gvalues.

A rather complete description of the Varian V-4502 ESR system has been given by Kuska⁸³. A Varian Associates 12-inch electromagnet furnished the magnetic field. The field position was determined using a marginal-oscillator NMR probe with the oscillator frequency measured by a Monsanto counter - timer in conjunction with an Ameco

preamp. A calibrated TS-148/UP U.S. navy spectrum analyzer was used to measure the microwave frequencies. Spectra were recorded either on a Moseley 7000A x-y recorder or a Hewlett Packard 7005B x-y recorder.

B. Sample Preparation

1. $K_2NbOF_5 \cdot H_2O.$ -- This compound was purchased from Organic/Inorganic Chemical Corp., Sun Valley, Calif., and recrystallized from aqueous solution.

2. $K_3 CO(CN)_6$.--Cobalt cyanide was precipitated from a boiling solution of cobalt chloride by adding potassium cyanide. The cobalt cyanide was then added to a solution of potassium cyanide to obtain $K_4 CO(CN)_6$. By boiling the solution of potassium hexacyanocobaltate (II), the complex was oxidized to potassium hexacyanocobaltate (III)⁸⁴.

3. K_4 Fe(CN)₆·3H₂O.--Baker and Adamson potassium hexacyanoferrate (II) was recrystallized from water.

4. Na₃RhCl₆·12H₂O.--Sodium hexachlororhodate (III) was obtained by chlorination of a mixture of sodium chloride and rhodium (III) chloride at high temperatures. The sodium hexachlororhodate (III) dodecahydrate was then formed by crystallizing from a solution of this reaction mixture in the presence of excess sodium chloride⁸⁵. 5. K₃RhCl₆·H₂O.--The potassium hexachlororhodate (III) monohydrate was made directly by chlorinating a mixture of rhodium (III) chloride and potassium chloride at high temperatures and then crystallizing from a solution of the reaction mixture containing excess potassium chloride. The compound was also made indirectly by first converting the sodium hexachlororhodate (III) dodecahydrate to hexachlororhodic (III) acid and then adding potassium chloride in excess⁸⁵.

6. K₂[RhCl₅(H₂O)].--This compound was made by the recrystallization of potassium hexachlororhodate (III) monohydrate from water⁸⁶.

7. $\underline{\text{Na}_3\text{RuCl}_6 \cdot 12\text{H}_2\text{O}}_2$ -Ruthenium (III) chloride trihydrate and sodium chloride were added to a solution of ethanol and concentrated hydrochloric acid. This solution was taken to dryness. The product was crystallized from water⁸⁷.

8. $K_2[RuCl_5(H_2O)]$.--Ruthenium (III) chloride trihydrate was added to a boiling dilute solution of hydrcchloric acid and ethanol. After boiling for an appropriate period, potassium chloride was added and the solution taken to dryness⁸⁸.

9. K₃RuCl₆·H₂O.--This compound was made from a solution of potassium aquopentachlororuthenate (III) by cooling in ice water and passing hydrogen chloride gas through until the solution was saturated⁸⁷.

10. $(NH_4)_2[InCl_5(H_2O)]$.--Stoichiometric amounts of indium (III) chloride and ammonium chloride were dissolved in hydrochloric acid. Crystals were recovered by evaporating the solution⁸⁹.

11. $K_2 \operatorname{ReF}_6$.--There are two methods for preparing this compound in the literature^{90,91}. These preparations, however, give products with different physical appearances.

The method of Peacock⁹⁰ was first attempted. Ammonium hexaiodorhenate (IV) was made by evaporating a solution rhenium heptoxide and ammonium hydroxide with excess hydroiodic acid just to dryness⁹². The $(NH_4)_2$ ReI₆ was then fused with potassium hydrogen fluoride at 400°C. White crystals of K₂ReF₆ were recovered by recrystallization of the fusion product. The x-ray powder spectrum of this substance indicated that the product was mostly K₂ReO₄.

The method of Weise⁹¹ was tried next. Potassium hexabromorhenate (IV) was made by the reduction of potassium perrhenate with hypophosphorus acid in the presence of potassium bromide and hydrobromic acid⁹³. Using a nitrogen atmosphere, the $K_2 \text{ReBr}_6$ was then fused with anhydrous potassium hydrogen fluoride at 700°C. Pink crystals were recovered by recrystallization of the fusion product. The x-ray powder spectra of the pink substance indicated that this was pure $K_2 \text{ReF}_6^{91}$.

La Valle⁹⁴ also noted the discrepancies in the literature as to the color of the $K_2 \text{ReF}_6$ complex.

His infrared analysis indicated that the pink product was the pure compound.

12. $\underline{\text{Cs}_2\text{GeF}_6}$.--Germanium dioxide was dissolved in 20% HF solution and a solution of CsCl added. The volume of this mixture was reduced by heating. Cooling in an ice bath yielded clear crystals of $\text{Cs}_2\text{GeF}_6^{95}$.

13. $K_2 Ni(CN)_4 \cdot H_2 O$ and $Na_2 Ni(CN)_4 \cdot 3H_2 O$.--Nickel (II) cyanide was first made by adding a solution of KCN to an aqueous solution of $NiSO_4 \cdot 6H_2 O$. Next an appropriate amount of the Ni(CN)₂ was added to solutions of KCN or NaCN which were heated to obtain crystals of $K_2 Ni(CN)_4 \cdot H_2 O$ or $Na_2 Ni(CN)_4 \cdot 3H_2 O$, respectively⁹⁶.

14. Magnus' Green Salt $[Pt(NH_3)_4][PtCl_4]$.--The Magnus' green salt was prepared by mixing solutions of K_2PtCl_4 and $Pt(NH_3)_4Cl_2$ in a dilute solution of HCl.

C. Crystal Growing

1. <u>Crystals for Irradiation</u>.--Single crystals of $K_2NbOF_5 \cdot H_2O$, $K_3CO(CN)_6$, $K_4Fe(CN)_6 \cdot 3H_2O$, $K_2[RhCl_5H_2O)$], $K_2Ni(CN)_4 \cdot H_2O$, and $Na_2Ni(CN)_4 \cdot 3H_2O$ were obtained by slow evaporation of saturated aqueous solutions of the salts; crystals of $K_3RhCl_6 \cdot H_2O$ and $Na_3RhCl_6 \cdot 12H_2O$ were made by slow evaporation of saturated solutions of the salts with excess KCl and NaCl, respectively. All crystals obtained

by the evaporation technique were made in beakers coated with a thin film of Dow Corning high-vacuum silicone grease to prevent deposition of the salt onto the side of the beaker. Sheets of Parafilm (American Can Company) punched with small holes were stretched across the tops of the beakers to insure slow evaporation and to prevent dust from settling into the solutions. The solutions were kept in an isolated drawer to eliminate sudden thermal and vibrational disturbances.

A diffusion technique was employed to grow crystals of the Magnus' green salt. Saturated solutions of K_2PtCl_4 and $Pt(NH_3)_4Cl_2$ wer prepared in narrow-necked Erlenmeyer flasks. The flasks were placed in a large beaker which was carefully filled with 0.1M HCl and sealed with a sheet of Parafilm. The $[PtCl_4]^{2-}$ ions and $[Pt(NH_3)_4]^{2+}$ ions slowly diffused through the dilute hydrochloric acid medium to form crystals at the lip of the Erlenmeyer flasks.

2. Doped Crystals.

a. From Solution.--Crystals of NaCl doped with $[RuCl_6]^{3-}$ were obtained by evaporating a saturated solution of NaCl containing about 0.1% $Na_3RuCl_6 \cdot 12H_2O$. The yellow color of these crystals was a visible indication that the $[RuCl_6]^{3-}$ ions entered the NaCl lattice homogeneously. Attempts to dope the $[RuCl_6]^{3-}$ ion into the KCl lattice using 0.1% $K_3RuCl_6 \cdot H_2O$ in a saturated KCl solution did not appear as successful.

The very light color of these crystals could not be considered as positive evidence that the [RuCl₆]³⁻ ion had entered the lattice.

The $[RuCl_5(H_2O)]^{2-}$ ion was doped into the $(NH_4)_2InCl_5 \cdot H_2O$ lattice by evaporating a 1M HCl solution, saturated with $(NH_4)_2[InCl_5(H_2O)]$ and containing 0.1% $K_2[RuCl_5(H_2O)]$. The $[RuCl_5(H_2O)]^{2-}$ ion did not always enter the lattice homogeneously as was evidenced by areas of deeper red coloration.

Crystals of Cs_2GeF_6 doped with the $[ReF_6]^{2-}$ ion were grown by the slow evaporation of a 20% HF solution saturated with Cs_2GeF_6 and containing 0.1% K_2ReF_6 . The technique used to grow the doped crystals was the same as that described above for the crystals prepared for irradiation.

b. From the Melt.--These crystals were grown by zone melting. The furnace consisted of a 2cm tube 45cm long wrapped with asbestos tape with a nichrome wire heating element wound about the central portion. The ends of the furnace were made of Transite and the casing of aluminum. Vermiculite insulator was used to fill the area between the tube and the casing. A synchronous clock motor was geared to a spool of nichrome wire to lower the samples through the zone furnace at a rate of 2mm/min.

Crystals of AgCl containing various dopants were made in 6mm quartz tubes with cone tips. Rhodium was doped into this host lattice by placing homogeneous

mixtures of AgCl with 1% RhCl₃ into the tubes, evacuating, and passing the sealed tubes through the zone furnace set at 500°C. The cylindrical crystals obtained by this method were dark red. Also, mixtures of AgCl with 1% RuCl₃ were placed into the cone-tipped tubes, evacuated, and passed through the zone melter to give very dark, nearly black, cylindrical crystals.

The NaF samples were prepared in 1/4" i.d. graphite tubes with conical bottoms. The graphite tubes were placed in a larger quartz tube, evaculated, and heated with a hotair gun to insure dryness of the sample and container. The vapors from the molten NaF attacked the quartz tubing resulting in almost complete corrosion and decomposition. Placing about two atmospheres of helium in the tube before sealing alleviated the corrosion problem enough to obtain crystals. Both 1% RuCl₃ and RhCl₃ mixtures with NaF were used with the furnace set at 1000°C but only in the case of the RhCl₃ dopant was a single crystal obtained.

D. Identification of Crystallographic Axes

1. Irradiated Crystals.--The morphological descriptions in Groth⁹⁷ and other sources combined with the use of a polarizing microscope permitted optical identification of the crystallographic axes in almost all cases. One exception was the crystals of $K_2NbOF_5 \cdot H_2O$ which grew in thin sheets with the 001 plane as the only usable

morphological feature. The crystals were cut into rectangular slabs by cleaving parallel and perpendicular to the extinction axis in the 001 plane. The a and b axes were distinguished from one another by examining the ESR spectra of the irradiated crystals.

2. <u>Doped Crystals</u>.--The crystallographic axes of the doped crystals grown from solution could be easily identified from their morphology. On the other hand, by using cone-ended tubes, the cubic crystals grown from the melt could be assumed to have a crystallographic axis (assigned as the *c* axis) along the length of the crystal. Cylindrical slabs of these crystals were made by cleaving perpendicular to this axis. The other axes could be identified from the ESR spectra by rotating in the 001 plane.

E. γ -Irradiation Method

All samples (powders in vials, or tubes, crystals in vials, or pre-mounted on rods) were submerged in a Dewar of liquid nitrogen. The Dewar was placed in the center of the Michigan State University 60 Co γ -source and subjected to an effective dose of 1×10^6 rads/hr for a period of 3 to 4 hours.

F. Sample Handling of Irradiated Samples

1. <u>Single Crystals</u>.--Two methods were used for mounting the single crystals. One method consisted of

mounting the irradiated crystals between brass clips glued to the end of a quartz rod. This method involved mounting and aligning the sample under liquid nitrogen using forceps. A detailed description of this method, including figures, has been given by Watson⁹⁸. The other method consisted of gluing crystals to the flattened tip of a wire inserted into the end of a quartz tube. The entire sample holder with attached crystal was irradiated. The glue (Pliobond Cement, Goodyear Tire and Rubber Co.), when irradiated at 77°K gave only a broad line at g = 2.0026and the second-derivative signal was weak.

The "brass clip" and the "glue" methods each have different advantages. Since often the same crystal can be used for more than one rotation, the "brass clip" method is useful for systems where there are a limited number of single crystals available. Also, with this method there is no extraneous ESR signal from irradiated glue. One disadvantage of the method is that unless the crystals are large enough to be clamped firmly between the brass clips, the crystal alignment can change during a rotation due to vibrational disturbances caused by nitrogen gas bubbling from the tip of the ESR Dewar. Another disadvantage of this method is the difficulty involved in obtaining an accurate initial alignment of the crystal, since this must be done under liquid nitrogen.
The "glue" method, on the other hand, was found to be more advantageous and was used for all the systems except $K_3 Co(CN)_6$. This method allows thin crystals (as in the case of $K_2 NbOF_5 \cdot H_2 O$) to be mounted securely. Also, since the crystals are not mounted under liquid nitrogen, initial alignment can be made more accurately. The only disadvantages are that there is a weak second derivative signal from the glue and once a crystal is mounted it can rarely be removed intact to be used for another orientation.

Regardless of which method was used to mount the crystals, for studies at 77°K the crystal holder with the attached irradiated crystal was placed in a specially designed Dewar filled with liquid nitrogen. The quartz tip of the Dewar was made to fit inside the Varian V-4531 multipurpose cavity. Attached to the Dewar was a metal pointer which was used with a protractor scale to determine the angle of rotation. The rods were centered in the Dewar with a cylindrical foam insert at the top of the Dewar while the sample was adjusted vertically in the cavity until the signal was maximized. The initial alignment of the crystal in the Dewar was done visually with refinement using the oscilloscope mode of the ESR spectrometer.

For the variable temperature work, a Varian V-4540 variable temperature accessory was used. The sample rods were held in a goniometer attached to the ESR cavity.

2. <u>Powders</u>.--For powder studies at 77°K, the powder samples irradiated in vials were poured into the ESR Dewar filled with liquid nitrogen. After the sample settled into the tip of the Dewar, the vertical position of the Dewar in the cavity was adjusted to give a maximum signalto-noise ratio.

For variable temperature studies, the powders were irradiated in sealed quartz tubes. Since irradiated quartz gives an ESR signal, steps were taken to annihilate this signal from the tube. While keeping the end of the tube containing the sample submerged in liquid nitrogen, the other end was heated with a torch until white hot. The tube was then completely submerged in liquid nitrogen, inverted, and the sample transferred by tapping into the end which had been heated. Finally, the quartz tube was placed into the ESR cavity and the Varian V-4540 assembly used to vary the temperature.

G. Low Temperature Studies (below-77°K)

There were two methods used to achieve these temperatures. One method, which will be referred to as the flow method, consists of transferring helium gas from an externally located thirty-liter Dewar containing liquid helium to the cavity. Inserted into the cavity from below is an evacuated cold finger assembly to which the gaseous helium is transferred. The sample then is placed into

the cavity from above by centering it in the cold-finger jacket. The temperature is regulated by controlling the boil-off rate of the helium in the thirty-liter Dewar by adjusting the current going to a heating element located at the bottom of this Dewar. Temperatures in the range of 6°K can be approached with this system.

The other system which was used is called the Andonian Variable Temperature Cryogenic System (0-25/7M Series), Waltham, Mass. This consists of a three-liter Dewar with a spectrasil quartz cold finger extending from the bottom. The Dewar is positioned above so that the cold finger reaches into the center of the cavity. The sample, attached to a specially designed rod with a Lukolux tip, is lowered through the Dewar system until it reaches the proper position in the sample zone. Helium gas, which is admitted from the main helium reservoir to the sample zone through a throttle valve, flows around and in intimate contact with the sample and exits to the atmosphere. The throttle valve controls the flow rate of helium gas into the sample zone and consequently the rate of energy removed from it. This system can approach 4.2°K if the throttle valve is left wide-open long enough for liquid helium to reach the system.

H. Conversion Factors

The following conversion factors and equations were used for the analysis of spectra and are included for convenient reference:

$$H(gauss) = [2.348682 \times 10^{2}] [v_{p}(MHz)],$$
 (3.1)

$$g = \frac{[0.714489] [ve (MHz)]}{H_o (gauss)}$$
(3.2)

$$A(\text{ergs}) = A(\text{gauss})[9.274096 \times 10^{-21} \times g], \qquad (3.3)$$

$$A(cm^{-1}) = A(gauss) [4.668599 \times 10^{-5} \times g],$$
 (3.4)

$$A(MHz) = A(gauss) [1.399611 \times g].$$
 (3.5)

where H is the magnetic field position, v_p is the proton oscillator frequency, g is the electronic g factor, H_o is the field position at the center of the spectrum, v_e is the klystron frequency, and A is the measured hyperfine splitting.

CHAPTER IV

Y IRRADIATION OF K₂NbOF₅·H₂O

A. Introduction

At 77°K the ESR lines from a 93 Nb containing radical are observed for γ -irradiated polycrystalline K_2 NbOF₅·H₂O. The perpendicular features of the spectrum exhibit fluorine superhyperfine splittings and the parallel features spread over a 3000 gauss region. The g, $A({}^{93}$ Nb), and $A({}^{19}$ F) tensors for this radical obtained from a complete analysis of the single-crystal ESR spectra, show that it is [NbOF₅]³⁻ with a d^1 configuration and a d_{xu} ground state.

At 77°K strong lines in the g = 2.0023 region, arising from other radicals produced during irradiation, are also observed. The structure of these radicals could not be studied at 77°K since their spectra are obscured by the overlapping spectrum from the $[NbOF_5]^{3-}$ species. However, better spectra of these radicals were obtained by warming the γ -irradiated $K_2NbOF_5 \cdot H_2O$ powder sample from 77°K. On warming to 190°K, the signal from the $[NbOF_5]^{3-}$ radical slowly decays until it is completely gone; a sharp signal at 2.0014, presumably from trapped electrons, gradually increases in intensity to a maximum; a three

g-value pattern, shown to arise from the ozonide radical, also increases somewhat in intensity over this temperature range; and, lastly, a ten-line pattern, overlapping with the lines from the trapped electron and the ozonide radical, becomes better resolved. The ten-line pattern has been identified as a hole species, either $[NbOF_5]^-$ or possibly $NbOF_4$, with its unpaired electron density localized on the oxygen atom. This assignment is based on the small ^{93}Nb hyperfine splitting values for this radical and the gvalues being greater than the free-spin value. On warming the sample further, the line from the trapped electron decreases in intensity until it disappears at 220°K, the signal from the hole species decreases in intensity until it disappears at 250°K, and the ozonide radical very slowly decays but is still stable even at 550°K.

B. Results

1. Single Crystal at 77°K.--A detailed crystal structure for $K_2NbOF_5 \cdot H_2O$ has not been reported but crystallographic data⁹⁷ show the unit cell to be monoclinic with $\beta = 103°46'$. The crystals grow as thin, transparent plates with the 001 faces clearly developed; making the c^* axes easily identifiable. The *a* and *b* axes were found using a polarizing microscope in conjunction with ESR spectra of the γ -irradiated samples.

Isofrequency plots of the ⁹³Nb hyperfine lines for rotations about the three orthogonal a, b, and c^* axes indicate that the unit cell of $K_2NbOF_5 \cdot H_2O$ contains two magnetically distinct sites (Figures 4.1-4.3). Using Scholand's method⁷², principal values and direction cosines for the metal hyperfine tensors of these sites have been determined (Table 4.1). The direction cosines indicate that the two sites lie in the bc plane, tilted relative to one another. Although the angle between them can be determined by taking the dot product of the appropriate direction cosine vectors, a more precise determination was made from a rotation about the a^* axis.

Since the "apparent g" tensor does not vary appreciably and, as will be shown, does not appear to correspond to the true g tensor, the variation of A^2 instead of A^2g^2 was plotted for the rotation about the a^* axis. The A^2 plot for the ⁹³Nb hyperfine splittings did not, however, exhibit well defined maxima, making it necessary to use a least-squares curve fitting program to determine the precise angle at which the maxima occur. By curve fitting the ⁹³Nb hyperfine splitting data to the expression,

$$A^{2} \cong A^{2}g^{2} = \alpha + \beta \cos 2\theta + \gamma \sin 2\theta , \qquad (4.1)$$

values for a, b and γ were found for each site. These parameters were then used in the expression defining the

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Table 4.1.--ESR parameters^a for $[NbOF_{r}]^{3-}$.

Tensor Components	Dir	Direction Cosines ^b		
g = 1.870				
g_{\perp} = 1.914				
$A_{1}(9^{3}Nb) = 159.8$	0.976	0.000	-0.217	
	-0.018	±0.996	-0.082	
$A_{ }(^{3}Nb) = 302.1$	0.217	±0.084	0.973	
$A(^{19}F)_{eq} = 19.84$				
$A(^{19}F)_{eq} = 39.85$				
$A(^{19}F)_{eq} = 8.73$				

 $^a{}^{\rm The}$ parameters are corrected for higher-order effects and the hyperfine splittings are in $_{\rm CM}{}^{-1}$ \times 10^4 units.

^bRelative to the a, b, c^* crystallographic axes of $K_2NbOF_5 \cdot H_2O$.

angle at which the A^2 maximum occurs,

$$\theta^{\max} = [\tan^{-1}(\gamma/\beta)/2] , \qquad (4.2)$$

to determine the angle between the sites. The results show that the sites are tilted 6° on either side of the c axis giving an angle of 12° between them (Figure 4.4).

While most of the $[NbOF_5]^{3-}$ complexes are oriented with the Nb-O bond 6° from the *c* axis, some of the complexes are oriented with the oxygen at any of the four equatorial vertices of the original octehedral unit.



Figure 4.4--Second-derivative X-band ESR spectrum of γ -irradiated K₂NbOF₅·H₂O at 77°K; the magnetic field is in the *bc* plane, 6° from the *c* axis. The arrows indicate the ten Nb hyperfine lines from those ions with their F-Nb-O bond parallel to *H*.

In Figure 4.5 evidence of this distribution is shown in the spectrum taken with the magnetic field along the c axis. The spectrum shows both the strong absorption from the radicals oriented in the preferred direction, that are nearly parallel to the magnetic field, and the weak absorption from those radicals that have the orthogonal orientations. The estimated ratio for the number of radicals that have their Nb-O bond in the preferred orientation to those radicals having the perpendicular orentations is 13:1.

Efforts to diagonalize the g tensor using Schonland's method⁷² failed. Higher-order effects due to the large ⁹³Nb hyperfine tensor cause the "apparent g" values determined from the center of the spectra to deviate considerably from the true g values. The deviation from true gtensor behavior is evident in the plot of "apparent g" values for the b rotation (Figure 4.6), which exhibits two maxima 60° on either side of a minimum. The g and $A^{(93}Nb)$ tensors have therefore been determined by the method outlined below assuming that they are coaxial, as has been found for the other halooxymetallates.

To facilitate the analysis of the metal hyperfine and ligand hyperfine interactions, an appropriate coordinate system for the $[NbOF_5]^{3-}$ complex is defined (Figure 4.7). The metal hyperfine interaction is considered to originate at the niobium nucleus, so its Z axis is chosen along the



Figure 4.5--Second-derivative X-band ESR spectrum of γ -irradiated K₂NbOF₅·H₂O at 77°K with H//c. The intense 10-line pattern is from the two sets of magnetically equivalent ions with their F-Nb-O axes nearly parallel to H; the weak multiplets between the central six strong lines are from the radicals (about 8%) with their F-Nb-O axes nearly perpendicular to H.



Figure 4.6--A plot of the "apparent g" values for the [NbOF₅]³⁻ radical with the magnetic field in the a*c plane.



Figure 4.7--Coordinate system for the $[NbOF_5]^{3-}$ ion used for the ^{93}Nb hyperfine tensor, the g tensor, and the equatorial ^{19}F hyperfine tensors.

O-Nb-F bond with the X and Y axes along the F-Nb-F bond directions in the equatorial plane. The origin of the fluorine superhyperfine interaction tensor is the fluorine atom; hence each equatorial fluorine atom is assigned a coordinate system with the z axis parallel to the O-Nb-F bond, the x axis along the equatorial Nb-F-bond, and the y axis chosen to form a right-handed coordinate system.

If the nuclear quadrupole and nuclear Zeeman terms are neglected, the electronic Zeeman and metal hyperfine tensors obey the angular relationships

$$g = (g_Z^2 \cos^2\theta + g_X^2 \sin^2\theta \cos^2\phi + g_Y^2 \sin^2\theta \sin^2\phi)^{1/2}$$
(4.3)

and

$$gA = (A_{Z}^{2}g_{Z}^{2}\cos^{2}\theta + A_{X}^{2}g_{X}^{2}sin^{2}\theta\cos^{2}\phi + A_{Y}^{2}g_{Y}^{2}sin^{2}\theta\sin^{2}\phi)^{1/2}, \qquad (4.4)$$

where the spherical polar angles θ and ϕ relate the external magnetic field vector H to the Z and X axes, respectively. Thus, the spectrum obtained at $\theta = 0^{\circ}$ corresponds to g_Z , A_Z and the spectrum obtained at $\theta = 90^{\circ}$ and $\phi = 0^{\circ}$ corresponds to g_X , A_X . Since $[NbOF_5]^{3-}$ is axially symmetric, Equations (4.3, 4.4) may be simplified by letting $A_Z = A_{\parallel}$, $g_Z = g_{\parallel}$, $g_X = g_Y = g_{\perp}$, and $A_X = A_Y = A_{\parallel}$.

Since the ⁹³Nb hyperfine splitting values are quite large, it was decided to adjust the ESR parameters initially to second order. A least-squares fitting program was used to minimize the error for the magnetic field positions of the various m_I transitions as determined from the equations (see Appendix A):

$$hv = g_{||}^{\beta H(m_{I}) + A}_{||}^{m_{I} + \frac{A \perp^{2}}{2hv}} [I(I+1) - m_{I}^{2}] \quad (\text{for } \theta = 0^{\circ})$$
(4.5)

and

$$hv = g_{\perp}\beta H(m_{I}) + A_{\perp}m_{I} + \frac{(A \mid \mid^{2} + A_{\perp}^{2})}{4hv} [I(I+1) - m_{I}^{2}]$$
(for $\theta = 90^{\circ}$), (4.6)

where $(g = H_o/h_v)$, $H(m_I)$ is the resonance field corresponding to the nuclear quantum number m_I , v is the klystron frequency, and $A_{||}$ and A_{\perp} are the average parallel and perpendicular hyperfine splittings.

The $g_{||}$, g_{\perp} , $A_{||}$, and A_{\perp} values, corrected to second order by the above method, were then corrected for higher-order effects using the program MAGNSPEC 3^{99} . This program determines the spin Hamiltonian energy matrix, finds the diagonal values, and, finally, calculates the field positions of the various m_I transitions. The final adjusted parameters were selected as those giving the best fit between the calculated and experimental m_I resonance positions (see Table 4.2).

M _I	MAGNSPEC 3	Experiment	MAGNSPEC 3	Experiment
	Perpendicul	ar Lines	Parallel	Lines
9/2	2595 Gauss	2595	1957	1956
7/2	2680	2680	2265	2262
5/2	2794	2793	2582	2583
3/2	2933	2932	2908	2911
1/2	3095	3094	3245	3249
-1/2	3279	3278	3591	3594
-3/2	3484	3482	3947	3953
-5/2	3709	3710	4313	4319
-7/2	3953	3954	4688	4690
-9/2	4215	4215	5073	5072

Table 4.2.--Calculated line positions for ⁹³Nb hyperfine components.

In order to analyze the fluorine hyperfine splitting tensor, it is necessary to orient the crystal so that the magnetic field vector makes the appropriate angles with the $[NbOF_5]^{3-}$ complex. With the applied field parallel to the O-Nb-F bond (i.e., $\theta = 0^{\circ}$), the niobium parallel hyperfine lines are split into quintets of equal spacing with intensity ratios 1:4:6:4:1 (Figures 4.4 and 4.8(A)). These quintets arise from the four equivalent equatorial fluorines and their separation is designated as $A_g ({}^{19}F)_{eq}$. At the $\theta = 90^{\circ}$, $\phi = 0^{\circ}$ orientation the applied field is



Figure 4.8--Enlarged portions of the second-derivative spectra of γ -irradiated K₂NbOF₅·H₂O showing the superhyperfine splittings. (A) $\theta = 0^{\circ}$. The four equivalent equatorial fluorines give a quintet with intensity ratios 1:4:6:4:1. (B) $\theta = 90^{\circ}$, $\phi = 0^{\circ}$. The equatorial fluorines give a seven-line pattern with intensity ratios 1:2:3:4:3:2:1, since $A_x \cong (1/2)A_y$. (C) $\theta = 90^{\circ}$, $\phi = 45^{\circ}$. The four equivalent fluorines give 1:4:6:4:1 quintet. parallel to the A_{u} (¹⁹F) component of two equivalent equatorial fluorines and the $A_x({}^{19}F)_{eq}$ components of the other two equatorial fluorines. The spectrum recorded at this orientation shows the niobium hyperfine lines split into septets of equal spacing with intensity ratios 1:2:3:4:3:2:1 (Figure 4.8(B)) and is explained by assuming $A_x({}^{19}F)_{eq} \stackrel{\approx}{=} 1/2 A_y({}^{19}F)_{eq}$. This interpretation of the septet splitting was confirmed by measuring the superhyperfine splitting at another orientation of the magnetic field in the equatorial plane, namely $\theta = 90^{\circ}$ and $\phi = 45^{\circ}$. The four equatorial fluorines now become equivalent and give the expected five-line pattern shown in Figures 4.8(C) and 4.9, and the value $A(^{19}F)_{eq} = 35.88$ G found for this orientation agrees well with that determined from the expression $A = 1/2 [A_x ({}^{19}F)_{eq}^2 + A_y ({}^{19}F)_{eq}^2]^{1/2} = 35.34 \text{ G}$ using the septet splittings. The g, $A(^{93}Nb)$ and $A(^{19}F)_{eq}$ tensor values determined from the single crystal ESR analysis are compiled in Table 4.1.

2. <u>Powder at 77°K</u>.--The powder spectrum shown in Figure 4.10 exhibits clearly the parallel and perpendicular features. Ligand superhyperfine splittings of the parallel ⁹³Nb hyperfine lines are not resolved but the perpendicular ⁹³Nb hyperfine lines are split by the interaction with the equatorial fluorines. The intense lines in the middle of the spectrum arise from other radicals produce by γ irradiation.





The g and $A(^{93}Nb)$ values obtained from the powder spectrum facilitated the single-crystal analysis since it was then possible to know with certainty when the applied field was along the parallel or perpendicular directions. The powder spectrum also supplemented the single crystal spectra in providing the ⁹³Nb hyperfine line positions used to correct for higher-order effects.

3. Variable Temperature Study of Powder Spectra .--The first-derivative Q-band spectrum of polycrystalline $K_2NbOF_5 \cdot H_2O$, γ -irradiated at 77°K and warmed to 200°K, is shown in Figure 4.11(A). The ten-line pattern from a ⁹³Nb-containing radical partially overlaps at high field with the group of lines from the ozonide ion. On the other hand, in the X-band powder spectrum at 190°K (Figure 4.11(B)) the ten-line pattern is shown to completely overlap with the set of lines from ozonide. Also, on either side of the ten-line pattern, weak multiplets are seen at higher gain. To verify that the underlying structure in these spectra is from the ozonide ion, the samples were warmed until the signal from the ⁹³Nb-containing species disappeared. The underlying structure still remains at higher temperatures and gives the three g-value spectrum of the ozonide ion shown in Figure 4.11(C).



Figure 4.11--(A) The Q-band spectrum of polycrystalline $K_2NbOF_5 \cdot H_2O$, γ irradiated at 77°K and warmed to 200°K. The ten-line pattern is from a rotating niobium-containing hole species. (B) The same but at X-band and 190°K. The spectrum from the hole species overlaps with the spectrum from the ozonide ion and wing lines are seen at higher gain. (C) The same but warmed to 400°K. Only the ozonide ion remains and gives a three g-value pattern.

4. Single Crystal at 190°K.--Single crystals of $K_2NbOF_5 \cdot H_2O \gamma$ irradiated at 77°K were rotated at 190°K about their a, b, and c^* axes. The weak pattern in the wings of the spectra was difficult to resolve and could not be followed in the b and c^* rotations and only with marginal success in the *a* rotation. In this rotation, the greatest splitting of the outer set of lines occurs with the magnetic field along the b axis (see Figure 4.12). At this orientation, a considerable portion of the outer multiplets extends beyond the strong central ten-line pattern. It appears that these outer sets of multiplets arise from the weak interaction of an unpaired electron with a 93 Nb nucleus and a 19 F nucleus, giving two sets of ten lines. As the magnetic field is rotated away from the b axis toward the c^* axis, the weak outer multiplets move into the strong central ten-line pattern until the two patterns completely overlap. It is not possible therefore to determine the minimum of the fluorine split-Throughout this rotation, the line-widths and ting. resolution of the central ten-line pattern varied considerably but the outermost lines of the pattern did not move appreciably. This was also found for the b and c^* rotations, indicating that central ten-line pattern arises from the isotropic part of a ⁹³Nb hyperfine tensor.

The picture that emerges from this analysis is that the isotropic ten-line pattern arises from a rotating



Figure 4.12--The X-band spectrum of γ -irradiated $K_2NbOF_5 \cdot H_2O$ at 190°K with H//b; within the brackets are the weak wing lines.

niobium containing species. Since the niobium hyperfine splitting is small, the unpaired electron is considered to be localized mainly on the oxygen atom. The possible radicals that are consistent with these results are a rotating [NbOF₅] ion or a rotating NbOF₄ ion. Similarly, because of the small ⁹³Nb and ¹⁹F hyperfine splittings of the weak outer multiplets, these also appear to arise from a radical with the unpaired electron localized mainly on the oxygen atom. However, the radicals in this instance are stationary as evidenced by the anisotropic fluorine interaction seen in the *a* rotation. The only radical that is consistent with these results is the [NbOF₅] species. Also, assuming that this radical doesn't reorient within the site and therefore has the same orientation as the $[NbOF_5]^{3-}$ ion, the maximum fluorine splitting found along the b axis should correspond to the fluorine tensor component perpendicular to the F-Nb-O bond (*i.e.*, θ = 90°, $\phi = 45^{\circ}).$

There are two possible explanations for the spectrum at 190°K. First, the $[NbOF_5]^-$ species is formed through the ejection of an electron upon γ irradiation at 77°K and, on warming, slowly decays to the NbOF₄ species through the rupture of the weak axial Nb-F bond. At 190°K, then, most of the $[NbOF_5]^-$ ions have decayed to the NbOF₄ species. The NbOF₄ species, being somewhat contracted in size and without charge, would be expected to

have a lower barrier to rotation than the $[NbOF_5]$ species and rotates freely at 190°K. The other possibility is that, again, the [NbOF₅] species forms upon γ irradiation at 77°K but, as the sample is warmed, thermal energy alters the trapping site enough to allow rotation. However, in this case it is necessary that the isotropic part of the axial fluorine hyperfine tensor be negligible, since otherwise the rotating species would give an isotropic pattern with more than ten lines. The anisotropic pattern would be from those [NbOF₅] species which, as a result of thermal distribution, do not have enough energy to break the barrier to rotation. The fact that cooling back to 77°K does not seem to alter the distribution of the rotating and stationary species, seems to support the first explanation since the NbOF $_A$ would not be expected to change back to [NbOF₅] on cooling. However, the second explanation could still hold if the [NbOF₅] remained in the high-temperature site on recooling; such changes in radical environment on warming are often not reversible on cooling.

In Table 4.3 are shown the *A* and *g* values for the isotropic ⁹³Nb hyperfine value, and the *g* value for the anisotropic pattern with *H* parallel to *b* (all measured at 190°K); the *g* values for the ozonide ion measured at 400°K are also shown.

NbOF₄ (190°K) $\langle g \rangle = 2.02213$ A_{i80} (⁹³Nb) = -21.3 G [NbOF₅] (190°K) g = 2.0252 $H//b A (^{93}Nb) = -15.7 G$ $A(^{19}F) = 267 G$ $[NbO_4]^{2-}$ (195°K) [ref. 50] g_{||} = 2.0208 $A_{||} = -27.9$ G $A_{\parallel} = 27.0 \text{ G}$ $g_{\parallel} = 2.0250$ Ozonide $\gamma - K_2 \text{NbOF}_5 \cdot H_2 O$ (400K) $\gamma - KClO_3$ (77°K) [ref. 100] $g_{xx} = 2.0014$ 2.0025 $g_{yy} = 2.0388$ 2.0174 $g_{zz} = 1.9579$ 2.0013

Table 4.3.--The ESR parameters for the hole species and the ozonide ion.

C. Discussion

1. Molecular Orbital Coefficients for [NbOF]3and [VOF₅]³⁻.

a. Determined from g and Metal A Tensors.--Using an LCAO-MO method, Ballhausen and Gray⁷⁵ have described the electronic sturcture of the vanadyl ion (VO^{2+}) in the penta-aquo complex. They suggest that the most important feature of these ions is the presence of considerable oxygen-to-metal π bonding. The investigation of the electronic structures of VO(acac), and $[VO(NCS)_5]^{3-}$ by Fan¹⁰¹ indicates that the inclusion of both out-of-plane and inplane π bonding, as well as σ bonding to the equatorial ligands, is also important in describing their electronic structures. Quite similar to the electronic structures of these ions are those for the stable $[VOF_5]^{3-}$ ion, and for the $[NbOF_5]^{3-}$ ion formed by irradiation. In an attempt to further elucidate the bonding in these ions, MO coefficients have been determined using the secondorder expressions for the spin Hamiltonian parameters.

The $[MOF_5]^{3-}$ ion [M = V,Nb] has C_{4v} symmetry with the unpaired electron in a 2B_2 ground state. To derive spin Hamiltonian parameters, perturbation theory is applied using the perturbation Hamiltonian expression for the unpaired electron. The basis set chosen for the perturbation treatment consists of the ground B_2 state along with the lowest excited B_1 and E states arising from the promotion of the unpaired electron into the b_1 and e molecular orbitals. The LCAO-MO wave functions for these orbitals are

$$|B_{2}\rangle = \beta_{2} |d_{xy}\rangle - \beta_{2} |\Phi_{xy}\rangle,$$

$$|B_{1}\rangle = \beta_{1} |d_{x^{2}-y^{2}}\rangle - \beta_{1} |\Phi_{x^{2}-y^{2}}\rangle,$$

$$|E\rangle = \varepsilon |d_{xz}, d_{yz}\rangle - \varepsilon' |\Phi_{xz}, \Phi_{yz}\rangle,$$

$$(4.7)$$

where the ligand orbitals Φ are group orbitals of appropriate symmetry. Using second-order perturbation theory as described in the theoretical section, and the basic gand A tensor theory as developed by Abragam and Pryce⁷⁶, DeArmond, *et al.*³⁴ derived the expressions for the experimental spin Hamiltonian parameters shown in Equations (2.16-2.19).

Values for the group overlap integrals S_{b_1} , S_{b_2} and S_e , as well as for P and λ_M , all depend on the assumed charge on the transition metal ion; hence the calculated bonding coefficients are also sensitive to the assumed charge. In most previous work on pentahalooxymetallate systems a charge of +2 less than the formal charge on the transition metal ion was assumed in the calculation of bonding coefficients. In this work an attempt to arrive at a self-consistent charge was made by varying the assumed charge and, for each value so assumed, computing

a charge by obtaining the MO coefficients and carrying out a Mulliken population analysis. Using the β_1 , β_2 , and ε coefficients obtained from the normalization relationships, in conjunction with an iterative best-fit solution to Equations (2.16-2.19), the Mulliken population analysis was determined for the bonding b_2^b , b_1^b and e^b orbitals, and the anti-bonding b_{2} orbital (see program listed in Appendix B). Unfortunately, since this calculation does not account for population in the a_1 bonding orbitals, total consistency between the assumed and calculated charge could not be checked. Van Kemenade 45 did a similar variable-charge calculation on the series $[MOX_5]^{2-}$ where M = V, Mo, W and X = Cl, Br, F. From his extended Hückel calculations, he found a charge contribution of +0.5 to the population of the a_1 orbitals. It has been assumed that such a contribution should also hold here and therefore have selected as the "selfconsistent" charge that assumed charge which led to a calculated charge 0.5 greater.

The independent parameters needed to calculate the bonding coefficients of $[VOF_5]^{3-}$ and $[NbOF_5]^{3-}$ are listed in Table 4.4 and the charge dependent parameters are shown in Tables 4.5 and 4.6 for charges +1 to +4. The *A* and *g* values for $[VOF_5]^{3-}$ were measured by Manoharan and Rogers⁴⁸ for $(NH_4)_3 VOF_5$ doped into $(NH_4)_3 AlF_6$. Since V and Nb have positive nuclear moments, the vanadium

Parameter	[VOF ₅] ³⁻	[NbOF ₅] ³⁻
g I I	1.937	1.870
g	1.977	1.914
A^{\perp}_{\perp} (cm ⁻¹)	-0.01790	-0.0302
$A_{1}^{(cm^{-1})}$	-0.00641	-0.0160
$\lambda_{\mathbf{F}}^{\perp}(\mathbf{cm}^{-1})$	270	270
к	0.85	1.34
$\Delta E(b_2 \rightarrow e) (\text{cm}^{-1})$	14,100	15,000
$\Delta E(b_2 \rightarrow b_1) (\text{cm}^{-1})$	18,200	17,800

Table 4.4.--Parameters used in calculating bonding coefficients.

and niobium hyperfine parameters have been taken as negative. The spin-orbit coupling parameters λ_M for vanadium and niobium were taken from the tables of Griffith¹⁰² and λ_L from McClure¹⁰³. The electronic energies for the transitions $b_2 \rightarrow b_1$ and $b_2 \rightarrow e$ in the $[VOF_5]^{3-}$ complex have been assigned⁴⁸. These energies for $[NbOF_5]^{3-}$ were estimated by comparing the $[VOF_5]^{3-}$ values to those for $[CrOF_5]^{2-}$ and $[MoOF_5]^{2-104}$. The *P* values were calculated from the Hartree-Fock atomic orbital functions for the free ions^{105,106}. The calculation of the Fermi contact term and the overlap integrals involve more detailed consideraations, so their evaluation is included in Chapter II as Beparate sections.

Bonding coefficients for $[VOF_5]^{3-}$ and $[NbOF_5]^{3-}$ have been determined for assumed charges +1 to +4 on the transition metal ion and for the "self-consistent" charge. The calculations have been carried out both assuming only dominant ligand p overlap (Table 4.5), and also assuming overlap with hybrid ligand orbitals (Table 4.6). In each case the "self-consistent" charge is considered to provide the most reliable coefficients and is indicated by the superscript R. The β_2 coefficients indicate that there is a greater delocalization of the unpaired electron in the case of $[VOF_5]^{3-}$. These results do not agree with the conclusions from ligand spin densities, as will be shown in the following section. Van Kemenade's⁴⁵ variable-charge calculations for the series [MOF₅]²⁻, [M=Cr, Mo, W], gave similar results in that his molecular orbital coefficients indicate a greater delocalization for $[CrOF_5]^{2-}$ than for $[MoOF_5]^{2-}$, whereas the ligand spin densities indicate the reverse trend. Our calculation shows as was found in Van Kemenade's study, that as the assumed charge is increased the β_{2} coefficient decreases. In such studies the relative ordering of the spin delocalization indicated by the β_2 coefficient is therefore extremely sensitive to the charge assumed on the central metal atom, and this charge is a very difficult parameter to fix with any certainty. Also, the coefficients calculated for a particular charge

Table 4.	.5MO P C	coeffici werlap o	ents as a nly).a	function	of nuclear	charge	(considering	dominant	ligand
Assumed Charge (M)	$cm^{-1} $ ×1	.0- 4 ^b ^d M	s_{b_1}	$s_{b_{2}}$	cy ø	β	8 2	ω	Calc. Charge (M)
				5	/OF _E] ³⁻				
+1.00	108	136	.282	.164	.157	1.04	1.01	1.01	3.98
+2.00	128	167	.272	.156	.150	1.03	1.00	1.01	3.95
+3.00	150	209	.251	.138	.135	1.03	0.918	1.01	3.75
+4.00	172	248	.230	.122	.121	1.03	0.850	1.01	3.75
+3.20 ^R	154	217	.247	.135	.132	1.03	0.904	1.01	3.73
				[NF	00F5] ³⁻				
+1.00	110	490	.292	.167	.163	1.20	1.17	1.01	3.14
+2.00	148	560	.281	.159	.156	0.891	1.01	1.01	3.19
+3.00	170	670	.260	.141	.140	0.955	0.943	1.01	3.31
+4.00	192	750	.238	.124	.125	0.969	0.882	1.00	3.32
+2.85 ^R	167	652	.263	.144	.142	0.953	0.954	1.01	3.33
	a								

^aThe most reliable values of the central metal atom charge are believed to be the "self-consistent" values indicated by superscript R.

bunits of λ_M are cm⁻¹.

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Table 4.	.6M.O. with	coeffic hybrid	:ients as ligand or	a functio cbitals).a	n of nuc	lear charge:	(conside	ring over	lap
Assumed Charge (M)	$\operatorname{cm}^{-1^{P}_{\times 10}}$	4 4 8 8	s_{b_1}	$s_{b_{2}}$	ŝ	B 1	8 2	ω	Calc. Charge (M)
				[7	'OF]5 ³⁻				
+1.00	108	136	.362	.164	.195	1.07	1.01	1.02	3.95
+2.00	128	167	.346	.156	.186	1.24	1.01	1.02	3.27
+3.00	150	209	.315	.138	.166	1.05	.924	1.01	3.76
+4.00	172	248	.285	.122	.147	1.04	.856	1.01	3.65
+3.25 ^R	156	218	.309	.134	.161	1.05	.907	1.01	3.74
				OQN]	الارم 3- 13-				
+1.00	011	490	.374	.167	.202	1.04	1.16	1.02	3.56
+2.00	148	560	.359	.159	.193	.940	1.01	1.02	3.20
+3.00	170	670	.326	.141	.172	066.	.941	1.01	3.35
+4.00	192	750	.295	.124	.152	1.00	.880	1.01	3.34
+2.85 ^R	167	652	.331	.144	.176	.996	.952	1.02	3.36
	e								

^tThe most reliable values of the central metal atom charge are believed to be the "self-consistent" values indicated by superscript R.

bunits of λ_M are cm⁻¹.

are found to be sensitive to the particular overlap integrals and κ values used.

It may be noted that the g values of NbO²⁺ complexes follow trends previously found for complexes containing MOⁿ⁺ [M = V,Cr,MO], where it was found⁴³ that $g_{||} < g_{\perp}$ for most of these complexes but $g_{||} > g_{\perp}$ for $[CrOF_5]^{2-}$ and for $[MoOCl_5]^{2-}$. This reverse trend in the chloro complexes has been attributed⁴³ to the large spin-orbit coupling value of the chlorine ligand, which is shown in Equation (2.16) to influence $g_{||}$ through the $-\lambda_L \beta_2 \beta_1$ term. As for the NbO²⁺ complexes, both NbO(acac)₂ and $[NbOF_5]^{3-}$ have $g_{||} < g_{|}$ whereas $[NbOCl_4]^{2-}$ has $g_{||} > g_{|}$

b. Determined from Ligand Superhyperfine Interaction.--The most significant evidence of covalency in the $[NbOF_5]^{3-}$ complex is the presence of ligand superhyperfine interaction resulting from the transfer of unpaired electron spin to the ligands. The absolute magnitude of the ligand superhyperfine principal tensor components were determined from the single-crystal analysis. Since the $[NbOF_5]^{3-}$ complex is unstable in solution, the isotropic ligand superhyperfine value cannot be determined experimentally. However, the isotropic superhyperfine value can be determined by averaging the principal superhyperfine tensor components. But first the signs of the principal components must be determined. The experimental ligand $A({}^{19}\text{F})_{eq}$ values (in cm⁻¹ × 10⁻⁴) are shown in Table 4.1. For all pentahalooxymetallates where the ligand isotropic superhyperfine splitting $\langle a \rangle$ can be determined from the solution spectra, it has been found that $\langle a \rangle$ can only be equal to $(A_x + A_y + A_z)/3$ if $\langle a \rangle$ and A_y have the opposite sign to A_x and A_z . The absolute value is then determined by assuming that the dipolar part of A_y is positive, since the dominant contribution to the dipolar part comes from the ligand $2p_y$ orbital. The signs of experimental ligand superhyperfine tensor components have been assigned by this method and the tensor then decomposed into an isotropic component plus a dipolar tensor of zero trace:

$$\begin{bmatrix} A_{x} \\ A_{y} \\ A_{z} \end{bmatrix} = \begin{bmatrix} -19.84 \\ 39.85 \\ -8.73 \end{bmatrix} = \begin{bmatrix} 3.76 \\ 3.76 \\ 3.76 \end{bmatrix} + \begin{bmatrix} -23.6 \\ 36.1 \\ -12.5 \end{bmatrix}.$$
 (4.8)
Experimental Isotropic Dipolar

The dipolar tensor is not axially symmetric, as it would be if the unpaired density on fluorine were only in the $2p_y$ orbital; hence there must be some unpaired electron density also in the fluorine $2p_x$ or $2p_z$ orbital. The latter is probably negligible, since extended Hückel calculations show that out-of-plane π bonding with the equatorial fluorines is quite small⁴⁵. Therefore, we decompose the dipolar tensor further into two axially symmetric tensors with principal axes along x and y,

and maximum principal components $A_{px} = -7.4 \times 10^{-4} \text{ cm}^{-1}$, $A_{py} = +32.4 \times 10^{-4} \text{ cm}^{-1}$: $\begin{bmatrix} -23.6 \\ 36.1 \\ -12.5 \end{bmatrix} = \begin{bmatrix} -7.4 \\ 3.7 \\ 3.7 \end{bmatrix} + \begin{bmatrix} -16.2 \\ 32.4 \\ -16.2 \end{bmatrix}$ (4.9)

The experimental ¹⁹F superhyperfine interaction tensor for the equatorial fluorines of $[VOF_5]^{3-}$ has been analyzed in the same manner⁴⁸, and the spin densities in the equatorial fluorine 2s, $2p_x$, $2p_y$ and $2p_z$ orbitals for $[VOF_5]^{3-}$ and $[NbOF_5]^{3-}$ are shown in Table 4.7. These have been calculated using the appropriate values¹⁰⁷ for the isotropic contact term per 2s electron, $(A_o)_s =$ $(8/3) \pi g_e \beta_e g_n \beta_n |\psi(0)|^2$, where $\psi(0)$ is the value of the fluorine 2s wave function at the nucleus, and for the dipolar interaction per 2p electron. $(A_o)_p =$ $(4/5) g_e \beta_e g_n \beta_n < r^{-3}$, where $\langle r^{-3} \rangle$ is the average for the 2p wavefunction.

The strength of the in-plane π bonding between the d_{xy} orbital of vanadium (or niobium) and the ligand group orbital with b_2 symmetry can be related to the spin densities in the ligand p_y orbitals through a Mulliken population analysis⁸², $[(\beta_2')^2 - \beta_2 \beta_2' S_b_2]$, which gives the total spin density in the b_2 group symmetry orbital. Since the b_2 group orbital is the sum of the four equatorial p_y ligand orbitals, the Mulliken population analysis should give four times the spin density in the ligand $2p_y$

Orbital	f [%] [NbOF ₅] ³⁻	^f * 3-b [VOF ₅]
2,	0.025	0.027
2p _	0.77	0.342
2p,	3.34	2.92
2p ⁹ ₂	0.0	0.0

Table 4.7.--Calculated spin densities in the equatorial fluorine orbitals.^{a,b}

^aValues of $|\psi(0)|^2$ and $\langle r^{-3} \rangle_{2p}$ for these calculations were taken from Ref. 107.

^bSpin densities for [VOF₅]³⁻ are from Ref. 48.

orbital. By assuming an overlap value for s_{b_2} , the Mulliken population analysis and the normalization condition give two equations in two unknowns. Using the s_{b_2} values which were determined as most reliable in the metal hyperfine splitting calculations, this system of equations was then solved for β_2 and β'_2 . Using $s_{b_2} = 0.135$ for $[VOF_5]^{3-}$, $\beta_2 = 0.969$ and $\beta'_2 = 0.413$ were found, while using $s_{b_2} =$ 0.144 for $[NbOF_5]^{3-}$ led to the values $\beta_2 = 0.963$ and $\beta'_2 = 0.441$. These bonding coefficients, as well as the $2p_y$ spin densities, clearly indicate that the ordering of covalency for these complexes is $[NbOF_5]^{3-} > [VOF_5]^{3-}$.

The spin density in the fluorine 2p_y orbitals has been explained as arising directly from the delocalization of the unpaired electron in the b_2 molecular orbital. It is necessary to invoke a less direct mechanism to explain the spin density in the fluorine $2p_x$ and 2s orbitals. One possible explanation is configuration interaction, where an electron in the filled b_1^b bonding orbital is promoted to an empty b_1 antibonding orbital. This configuration is chosen since the $2p_x$ and 2s orbitals of the ¹⁹F equatorial ligands transform under the b_1 representation. Another possible explanation is that spin polarization¹⁰⁸ of the ligand 2s and $2p_x$ orbitals by the $2p_y$ spin density is important.

c. Conclusion.--We find the metal hyperfine splittings and g values for $[VOF_5]^{3-}$ and $[NbOF_5]^{3-}$ tend to be unreliable because of the sensitivity of the calculated coefficients to the charge on the central metal atom, a quantity which is difficult to evaluate with any certainty. The spin densities calculated from the ligand superhyperfine splittings appear to give a truer picture of the trends in covalency in these complexes, although precise data of this type are more difficult to obtain experimentally. Attempts to relate the ligand spin densities to bonding coefficients, however, also involve assumptions as to the charge on the central metal atom as well as to the degree of spin polarization or configuration interaction occurring in the complex. Thus, since ESR does not provide enough information to determine the charge distribution within the complex, or to predict quantitatively the extent of spin polarization or configuration interaction, it cannot be used alone as a tool to determine accurate bonding coefficients. However, if the charge distribution were to be measured by some other experimental means, the ESR parameters in conjunction with these data could possibly give accurate bonding coefficients. In spite of these shortcomings, the ESR parameters provide about the best means for evaluating the results of MO theory since, if the assumed bonding picture is accurate, the calculated bonding parameters for a particular complex should reproduce the experimental ESR data.

2. <u>The Hole Species</u>.--The molecular orbital energy level scheme has been calculated for $[MoOCl_5]^{2-}$ neglecting π bonding¹⁰⁹ and for $[MoOF_5]^{2-}$ including π bonding⁴⁵. Both schemes show the highest filled MO to be the e^b orbitals. By anology the highest filled orbitals in $[NbOF_5]^{2-}$ are also the e^b orbitals. If upon γ irradiation $K_2NbOF_5 \cdot H_2O$ an electron is removed from the $[NbOF_5]^{2-}$ ion, the resulting paramagnetic species, namely $[NbOF_5]^{-}$, would have an unpaired electron in the doubly degenerate e^b orbitals, giving a ${}^{2}E$ ground state.

The doubly degenerate e^b orbitals are composed of the niobium $d_{xz,yz}$ orbitals and $\Phi_{xz,yz}$, the appropriate hybrid ligand group symmetry orbitals. The $\Phi_{xz,yz}$ orbitals consist of the oxygen $p_{x,y}$ orbitals, the axial fluorine $p_{x,y}$ orbitals, and the equatorial fluorine $p_z^{1,2} - p_z^{3,4}$ orbitals, but they mostly have oxygen $p_{x,u}$ character. The MO coefficients for the e^b orbitals found from the self-consistent charge calculation of the ESR parameters for $[NbOF_5]^{3-}$ give a metal orbital coefficient of 0.0708 and a group symmetry orbital coefficient of 0.9851. Thus, for $[NbOF_5]$, the unpaired electron in the e^b orbital would spend most of its time on the oxygen atom, with some spin-density on the axial fluorine and even less on the equatorial fluorines and the niobium atom. Similarly, the NbOF, ion which also possibly forms, would have the unpaired electron in the e^b orbital, but in this case, there is no axial fluorine involved in the $\Phi_{xz,yz}$ orbital. Hence, the molecular orbital schemes for both ions are consistent with a radical having most of the spin density on the oxygen atom.

With the niobium-containing species narrowed to $[NbOF_5]^-$ and possibly $NbOF_4$, certain predictions can be made regarding the observed ⁹³Nb isotropic hyperfine splittings. Since the unpaired electron is localized mainly on the $2p\pi$ orbitals of oxygen for both cases, the A_{iso} value would arise primarily from spin-polarization of the σ electron in the Nb-O bonds making the sign of

the coupling negative. This polarization mechanism results in unpaired spin-density in the 5s orbital and hence, an approximate 1.4% spin-density is determined for this orbital using the experimental A_{iso} (Nb) value along with the $A_{i,8,0}^{O}$ (Nb) value of 1550 gauss calculated for an electron in a 5s orbital¹¹⁰. Another possible mechanism contributing to the A_{iso} value is the spin-polarization of the inner filled s levels by unpaired electron density in the niobium $d_{xz,yz}$ orbitals. Using the e^b molecular orbital coefficients shown above and the appropriate overlap integrals, a Mulliken population analysis predicts an unpaired spin-density of about 1.65% in the niobium $4d_{xz,yz}$ orbitals. Judging then from the isotropic niobium hyperfine value of -235 gauss for $[NbOF_5]^{3-}$ where the unpaired electron is localized mainly in the d_{xu} orbital, the contribution from the inner filled s orbitals to A_{iso} should be small, about -3.9 gauss.

Using similar reasoning, predictions can be made about the anisotropic part of the 93 Nb hyperfine coupling. However, before this can be discussed, it is necessary to examine the electronic structure of these radicals more closely. The prediction that the unpaired electron should be in the e^b molecular orbital came from calculations which assumed C_{4v} symmetry in these ions. With an unpaired electron in the doubly degenerate e^b orbitals, however, the symmetry of the ion would lower to remove this orbital degeneracy. This distortion would be small and could arise inherently from the Jahn-Teller effect or from a lowering of the site symmetry by the neighboring ions. The equilibrium position of the distortion would give the lowest total lattice and electronic energies. Depending on the kind of influences involved, the unpaired electron could either be in a bonding ψ_{rr} molecular orbital for some of the ions in the crystal, and in an $\psi_{\mu z}$ orbital for the remaining ions, or in one of these types of molecular orbitals throughout the crystal. Unfortunately, since the anisotropic coupling could only be followed in the a axis rotation, it is not possible to determine which of these two cases occurs. However, at H//b the two sites are equivalent and the field lies along the θ = 90°, ϕ = 45° direction relative to the molecular axes, so the two cases would give identical results at this orientation. Hence, to expedite the discussion of the different sources of anisotropic coupling, the unpaired electron will be assumed to be in the bonding ψ_{xz} orbital. With this assumption then, the unpaired electron will spend most of its time in the p_{τ} orbital of the oxygen, giving rise to point-dipolar interaction with the Nb nucleus. Such an interaction for a Nb-0 bond length of 1.7 Å would give a dipolar tensor of (2.8 -1.4 -1.4) gauss with the maximum value directed along the Nb-0 bond. Also, polarization of the σ electrons

in the Nb-0 bond would result in a tensor with its unique axis along the same direction. Using the 1.4% spin density attributed to this mechanism in the discussion of the isotropic coupling, and an anisotropic coupling of -85 gauss calculated for an electron in a Nb 4d orbital¹¹⁰, the tensor resulting from polarization of the σ bond is estimated as $(-1.2 \ 0.6 \ 0.6)$ gauss. Lastly, the Mulliken population analysis shown above for the e^b orbital indicated a small spin-density in the $d_{xz, yz}$ orbitals and this would give rise to a dipolar tensor. Assuming this spin density to be the same for the bonding $\psi_{\pi\pi}$ orbital and using again the anisotropic value for an electron in a Nb 4d orbital, the estimated tensor for this interaction is (0.7 0.7 -1.4) gauss. The conclusion drawn from these estimated dipolar tensors is that the anisotropic coupling should be small and have at least one negative component.

Although tensor quantities calculated above for the Nb isotropic and anisotropic hyperfine coupling are only estimates, they are helpful in determining whether the isotropic ten-line pattern arises from a rotating NbOF₄ or $[NbOF_5]^-$ ion. In the above analysis, the isotropic coupling was shown to be negative, and the anisotropic coupling tensor was shown to be small and with at least one tensor component negative, this depending on the exact magnitude of the contributing dipolar tensors. Therefore, if the isotropic pattern arises from a rotating $[NbOF_5]^-$

ion, either the $A_{||}$ or A_{\perp} value for this ion should be greater than the A_{iso} value for the rotating species. However, rotation about the *a* axes shows that the $A_{||}$ and A_{\perp} value for [NbOF₅]⁻ are both less than the A_{iso} value for the rotating species. Thus, the isotropic ten-line pattern appears to arise from the rotating NbOF_A species.

The hyperfine splitting for the equatorial fluorine in [NbOF₅] found with H//b is 267 gauss. The magnetic field at this orientation lies along the θ = 90°, ϕ = 45° direction relative to the molecular axes. Thus, since the bonding ψ_{xz} orbital includes the fluorine p_x orbital, the fluorine splitting at this orientation can be expressed as $1/2[A_x({}^{19}F_{ax})^2 + 1/2A_x({}^{19}F_{ax})^2]^{1/2}$. This formulation assumes that there is no other contribution to the splitting and gives 477 gauss for A. Using 1084 gauss for an electron in a fluorine 2p orbital¹⁰⁷ and the A_r value found by the above manner, the axial fluorine p_x orbital is estimated to have a 44.0% spin-density. This spindensity is larger than expected, since only about 20% spindensity is estimated for this atom by extrapolating from the atomic orbital coefficients calculated for Φ_{xz} in $[MoOF_5]^{2-45}$. This discrepancy is most likely a result of spin polarization of the Nb-F $_{ax}$ σ bond and possibly other orbitals which overlap with F_{ax} , namely the ψ_{uz} orbital. Because of the incomplete experimental information for this axial fluorine tensor, it is difficult to

know with certainty which effect, if any, dominates the tensor. It should be noted that because of the large isotropic splitting ($A_{i80} = 17,200$ gauss) for an electron in the 2s orbital of fluorine¹⁰⁷, only a very small spin polarization of the Nb-F₂ σ bond is necessary to result in noticeable isotropic coupling. Spin polarization in this bond by an unpaired electron in a bonding Ψ_{xx} orbital is expected, especially since there is evidence that this bond is polarized in other pentahalooxymetallates even where the unpaired electron is in an antibonding ψ_{xu} orbital⁴³. Thus, according to this analysis, there most likely is an A_{iso} (F) component for the axial fluorine tensor and hence, the pattern arising from a rotating $[NbOF_5]$ ion would consist of more than ten lines. The conclusion therefore drawn from this analysis agrees with that from the ⁹³Nb hyperfine analysis, *i.e.*, the rotating species is $NbOF_4$ and the stationary species is [NbOF₅].

The g values are also consistent with the electronic structures proposed above for the $[NbOF_5]^-$ and $NbOF_4$ ions. As noted previously, there should be an electron deficiency in the e^b orbitals for these ions. However, the ions should undergo a distortion to remove the degeneracy of these orbitals. Thus, the orbital containing the unpaired electron (ψ_{xx} for discussion purposes), would be expected to mix through spin-orbit coupling with the nearly

degenerate filled ψ_{yz} orbital. Since the admixed ψ_{yz} orbital is filled, there should be a positive g shift from the free-spin value for these ions, as has been found. Because the ψ_{xz} orbital has mostly oxygen $2p\pi$ character, the g value should be similar in magnitude to those found for other oxyniobium complexes having an electron deficiency localized in the oxygen $2p\pi$ orbitals. This is found to be the case for just such an ion, $[NbO_4]^{2-}$, as shown by the reported g values in Table 4.3.

3. Ozonide Ion.--The ozonide ion has C_{2v} symmetry and 19 valence electrons. This according to the energy level scheme determined by Ballhausen and Gray⁷¹, would place the unpaired electron in a b_2 molecular orbital. Under the C_{2v} symmetry group, the resulting ${}^{2}B_2$ ground state will mix through spin-orbit coupling with various amounts of the ${}^{2}A_1$, ${}^{2}A_2$, and ${}^{2}B_1$ excited states along the different molecular axes. Thus, since there is no hyperfine coupling, the ESR spectrum of O_3^- should give a three g-value pattern, as has been found here. The g values shown in Table 4.3 vary more from 2.0023 than do the gvalues reported for ozonide in γ irradiated KClO₃¹⁰⁰, also shown in this table. This discrepancy arises from the different host lattices and temperatures used in the two measurements.

CHAPTER V

Y IRRADIATION OF K3CO(CN)6

A. Introduction

Single crystals and powders of $K_3Co(CN)_6$, γ irradiated and investigated with ESR at 77°K, give sets of lines belonging to two radicals. The most intense set of lines belongs to a ⁵⁹Co containing radical which exhibits ¹⁴N superhyperfine splittings from two equivalent nitrogens. A complete ESR study of the single crystal and of the powder have been made for this radical. The g, $A(^{59}Co)$, and $A(^{14}N)$ values have been used to identify the radical as a d^7 system in a weak, tetragonallyelongated field; the most probable structures are $[Co(II)CN]_{6}^{4-}$ or $[Co(II)(CN)_{4}(NC)_{2}]^{4-}$. Since this radical is only stable at low temperatures, it will be referred to as the low-temperature species. The other set of lines has considerably less intensity and, in the powder, shows a rather complex pattern centered at g =2.2760. When the powder sample is pressed into a pellet and irradiated, the low-field radical did not form. The high q value for this pattern coupled with the fact that it does not form in the irradiated pellet, suggests that

it may be a cobalt (II) radical pair. Since radical pairing involves some migration in the lattice, perhaps in the case of the pellet the crystal is broken into such small crystallites that they approach unit cell size, inhibiting the migration necessary for the radical to form. In any event, since the signal from this radical is weak and overlaps with the spectrum of the low-temperature species, it is not possible to follow the lines in the single crystal and thus obtain the g and A tensors necessary to further elucidate its structure. There is one additional feature in the spectra at 77°K. This is a peak around g = 2.0023, which seems more prominent in the case of the pellet, and has been identified as arising from an F center produced on γ irradiation.

When the γ irradiated powder samples are warmed from 77°K, the intensity of the low-temperature species signal decreases until it is gone at 133°K. At this temperature the low field pattern centered at g = 2.2760still remains and a triplet centered about the F center line has emerged. The triplet splitting is about 71.4 gauss and seems to be a result of an interaction of a neighboring nitrogen with the F center. At 193°K, the lines from the low-field pattern disappear; the intensity of the triplet has increased; its splitting has been reduced to 60.8 gauss; and the lines from another 59 Cocontaining radical have become more evident. At 253°K,

the resolution of the spectrum from the new ⁵⁹Co-containing radical improves and the triplet signal disappears, leaving the pattern from the F center at this field position. On warming to room temperature, only the ⁵⁹Co-containing radical remains along with the signal from the F center. Cooling back to 77°K did not reverse this process but did improve the resolution of the ⁵⁹Co-containing radical. Since this radical also forms upon irradiation at room temperature and is stable at this temperature, it will be referred to as the room-temperature species. The g values and $A({}^{59}Co)$ values found in the powder for this radical have been used to identify it as a d^7 system in a fairly strong tetragonally-elongated field with the structure of $[Co(II)(CN)_{E}]^{3^{-}}$ or possibly $[Co(II)(CN)_{A}]^{2^{-}}$.

Also, crystals made with 15.5% $K^{13}CN$ were γ irradiated and the spectra of the low-temperature and roomtemperature species studied.

B. Results

1. Single Crystal at $77^{\circ}K$.--Single crystals of $K_{3}Co(CN)_{6}$ about $4 \times 2 \times 2$ mm in dimension were selected for γ irradiation. Using the morphological data reported by Groth⁹⁷, the orthorhombic crystallographic axes a, b, and c could be identified. The 100 face was clearly developed, enabling easy identification of the a axis. Upon rotation of the crystal about the a axis under the

polarizing microscope, extinction occurred along the band c axes. The c axis could be distinguished from the b axis by identifying the edge formed by the intersection of the x and x' planes.

There is much confusion in the literature over the unit cell dimensions for $K_3CO(CN)_6^{111-114}$. This confusion has been resolved in an investigation by Kohn and Townes¹¹⁵, where they showed that $K_3Co(CN)_6$ exhibits polytypism (i.e., the existence of different well-defined stacking periodicities). They found four different structural types or polytypes, all having the same morphology. These are described by polytypic nomenclature as 1M (onelayer monoclinic), 20r (two-layer orthorhombic), 3M (threelayer monoclinic), and 7M (seven-layer monoclinic). The 1M polytype and the 20r polytype are the most common structures; their stacking relationships are shown in Figure 5.1. The 1M unit cell contains two molecules with cell dimensions a = 7.1 Å, b = 10.4 Å, c = 8.4 Å and $\beta =$ 107°20'. Within the unit cell the two nonequivalent octehedral sites transform into each other by reflection in the ac plane. Each of the two cyanide octahedral have a twofold symmetry axis directed along the c axis, while the fourfold symmetry axis perpendicular to the twofold axis makes an angle of about 27° with the b axis. From the neutron diffraction data of Curry and Runciman¹¹⁶, the direction cosines relating the $Co-C_1$, $Co-C_2$, and



Figure 5.1--The relationship of the 1M to the 20r cell as seen on the (010) plane.

 $Co-C_3$ bonds of one site to the orthorhombic crystallographic axes have been determined and are shown in Table 5.1.

Table 5.1.--Direction cosines of Co-C_i bonds in K₃Co(CN)₆ with respect to orthorhombic crystallographic axes.

Bonds	а	Ъ	С
co-c1	0.421	-0.906	±0.044
Co-C ₂	0.678	+0.237	±0.696
^{Co-C} 3	0.642	+0.325	±0.694

Single crystals, γ irradiated at 77°K, were rotated at this temperature about the orthorhombic *a*, *b*, and *c* axes and spectra recorded every 10°. As shown in the plots of the variation of ⁵⁹Co hyperfine lines with magnetic field orientation (Figures 5.2-5.4, the spectra consist of overlapping sets of eight lines except when the external field is parallel to one of the crystal axes. In this case, the two sets coalesce into a single set of eight lines. Each ⁵⁹Co hyperfine line is further split into multiplets. The multiplet in some orientations consists of a five-line pattern with intensity ratios 1:2:3:2:1 but in other orientations become six-line patterns with intensity ratios 1:3:5:5:3:1 and in a few orientations seven line patterns were found (Figures 5.5 and 5.6).















The quintet splitting has the appropriate intensity ratios to be attributed to an electron interacting equally with two ¹⁴N nuclei. The six- and seven-line multiplets could be explained by a slight g shift for nearly equivalent sites, probably due to a small error in alignment or a result of having a mixture of polytypes within the crystal¹¹⁷.

Using Schonland's method⁷² the g^2 and the $g^2 A^2$ tensors were diagonalized with the principal values and direction cosines shown in Table 5.2. The A tensor is orthorhombic with its principal values nearly along the bond directions of the octehedral site, and the q tensor, which is nearly axially symmetric, has its unique component parallel to one of the principal A components. With the perpendicular q tensor components nearly equal, the error in their direction cosines could be large. Thus, the direction cosine values associated with perpendicular qcomponents do not necessarily rule out the possibility that the A and q tensors are coaxial. These results imply that the radical formed by γ irradiation has not undergone appreciable reorientation in the lattice but the original octahedral unit has undergone appreciable distortion.

The experimental isofrequency plots, showing two sets of eight lines in all orientations except along the crystallographic axes, indicate that the crystals contains four magnetically distinct sites. This interpretation

Table 5.2.--The g, ⁵⁹Co hyperfine, and ¹⁴N hyperfine values with direction cosines for the low-temperature species in $K_3Co(CN)_6$.

	Powder analysis							
g_x	=	2.0913	A_{x}	= -70.07 G				
g_y	=	2.0904	A _y	= -60.60 G				
g _z	=	2.0080	A z	= 68.08 G	$^{14}N = 3.85 G$			
			Si	ngle crystal	$f^2 g^2$ diagonalization			
				a	Ь	C		
g_x	=	2.0927		0.560	-0.768	0.309		
g_y	-	2.0913		0.453	0.597	0.662		
g _z	=	2.0115		0.694	0.231	-0.682		
Single crystal $g^2 A^2$ diagonization								
				а	Ъ	C		
A_{x}	=	-70.05 G	;	0.438	-0.898	-0.043		
A _y	=	-60.35 G	;	0.638	0.278	0.718		
A z	=	68.17 G		0.632	0.342	-0.695		

is consistent with the orthorhombic polytype which contains four molecules per unit cell. Within the orthorhombic polytype are two monoclinic unit cells, each related to the other by a reflection in the *bc* plane and each containing two sites. The sites within each monoclinic unit are related by a reflection in the *ac* plane. The outcome of these geometric considerations is that each site is related to any of the others by changing one column of direction cosines.

This assumed geometric relationship for the four distinct sites, along with the experimental g values, Avalues, and direction cosines, were checked by computing the angular variation of the spectra. The appropriate spin Hamiltonian for this system, excluding the ¹⁴N superhyperfine interaction, is

$$\mathcal{H} = \beta \left(g_{xx}^{H} x^{S} x + g_{yy}^{H} y^{S} y^{+} g_{zz}^{H} z^{S} z \right)$$

$$+ A_{xx}^{I} x^{S} x^{+} A_{yy}^{I} y^{S} y^{+} A_{zz}^{I} z^{S} z$$

$$+ Q' \left[I_{z}^{2} - \frac{1}{3} I (I+1) \right] + Q'' (I_{x}^{2} - I_{y}^{2})$$

$$- g_{n} \beta_{n} (H_{x}^{I} x^{+} H_{y}^{I} y^{+} H_{z}^{I} z) . \qquad (5.1)$$

For systems described by this type of spin Hamiltonian, Tseng and Kikuchi¹¹⁸, using second-order perturbation theory have derived the equations for determining the resonance positions as a function of external field orientation. These equations, in conjunction with a plot routine, were employed to calculate isofrequency plots for the three rotations. The Q' and Q'' values were taken as zero and, since the g and A tensors are considered to be coaxial, the values found in the powder spectrum were used. With the A tensor clearly non-axial, the direction cosines found for the A diagonization were used for both the g and A tensors of one site. The direction cosines for each of the other three sites were obtained by changing the signs of one column of values. The computed isofrequency plots very nearly duplicated the experimental plots, with some measure of the fit indicated by the A and g values shown in Table 5.3 for various orientations of the magnetic field.

2. Powder and Pellet at 77°K.--The powder and pellet spectra are shown in Figures 5.7 and 5.8, respectively. Although these samples were irradiated at 77°K for the same period of time, in the case of the pellet only one radical appears to form whereas the powder spectrum shows two radicals. The pattern from this second radical extends at X-band frequencies from 2830 gauss up into the lower portion of the spectrum from the low-temperature species to about 2980 gauss with the pattern centered at q = 2.2760. Since this low-field pattern, presumably from a radical pair, doesn't appear in the case of the pellet, analysis of the spectrum from the low-temperature species is considerably facilitated. The powder spectrum, however, had the advantage of better resolution of the nitrogen superhyperfine splittings and thus aided the identification of the parallel features in the spectrum from the low-temperature species.

Table 5.3.--Comparison of experimental g and A values with calculated values for various orientations.

Orientation	Rotation abo Experimental	ut a axis . Computed	Rotation abou Experimental	t <i>b</i> axis Computed	Rotation abo Experimental	ut <i>e</i> axis Computed
g max	2.0918	2.0903	2.0919	2.0910	2.0924	2.0917
gmin	2.0450	2.0404	2.0159	2.0155	2.0492	2.0480
g//a			2.0522	2.0544	2.0518	2.0544
<i>d//b</i>	2.0853	2.0824			2.0830	2.0824
g//c	2.0490	2.0512	2.0501	2.0512		
Amax	69.50 G	69.80 G	68.41 G	68.04 G	70.04 G	69.86 G
Amin	63.86 G	63.57 G	61.13 G	61.56 G	64.50 G	64.42 G
A//a			65.39 G	65.57 G	65.60 G	65.57 G
A//b	68.80 G	69.22 G			69.58 G	69.22 G
A//c	64.22 G	64.14 G	64.23 G	64.14 G		









3. <u>Single Crystal and Powder at Room Temperature</u>.--In the single crystal the room temperature species gave two sets of eight lines which coalesced into one set when the field was along the crystallographic axes. A complete single-crystal analysis was not done, since Lin, McDowell, and Ward⁵⁴ had already completed this work. Spectra were, however, recorded along the crystallographic axes. The g and A values found at these orientations, in conjunction with principal g and A values found in the powder, were used to check direction cosines for this species (see Table 5.4) against those of McDowell, *et al.*⁵⁴

4. Analysis of Spectra of 13 C Enriched Samples--At this point in the analysis there are two possible radicals which could explain the spectra of the lowtemperature species and two different radicals which could explain the results for the room-temperature species. For the low-temperature species the g values indicate that the radical is a d^7 system with the unpaired electron in the d_2^2 orbital. The large nitrogen splitting along the $g_{||}$ direction of the radical indicates that considerable spin density has reached the nitrogen atoms of the two cyanide groups overlapping with this orbital. This could be either a result of spin-polarization through the C-N bond by spin density on the carbon atoms or a result of direct overlap of nitrogen orbitals with the d_2^2 metal orbital in

	_	J	0	
Powder	analysis			
g =	2.0037	g I	= 2.1545	
$A \downarrow \downarrow =$	89.70 G		= 26.62 G	
Single	crystal ^a	a	Ь	c
g =	2.010	0.65	0.27	0.71
g _⊥ =	2.170 2.167		\perp wrt above	
A =	83.5 G	0.62	0.29	0.73
^ =	26.9 G 25.2 G		\perp wrt above	

Table 5.4.--The g values and ⁵⁹Co hyperfine values with direction cosines for the room-temperature species in $K_3Co(CN)_6$.

^aThese values were obtained by McDowell *et al.*⁵⁴ for X-irradiated $K_3Co(CN)_6$.

the event that the cyanide groups turn around. The two possibilities for this radical therefore are $[Co(II)(CN)_6]^{4-}$ or $[Co(II)(CN)_4(NC)_2]^{4-}$.

The g values indicate that the room-temperature radical is also a d^7 system with the unpaired electron in a $d_g{}^2$ orbital but with a greater tetragonal distortion. Also, there is no nitrogen superhyperfine structure with this radical. Two possible radicals consistent with these results are $[Co(II)(CN)_5]^{3-}$ or $[Co(II)(CN)_4]^{2-}$. By using γ -irradiated crystals of K₃Co(CN)₆ made with 15.5% K¹³CN, one should be able to distinguish between these possibilities.

In the case of the low-temperature species, satellite splittings from the ¹³C nuclei should be evident for the $[Co(II)(CN)_6]^{4-}$ radical. Since the d_2^2 orbital in this instance directly overlaps with the carbons of two cyanide groups, the probability that the unpaired electron interacts with one ¹³C nucleus is 28.75% and that it interacts with two is 2.25%. The d_2 orbital is of the correct symmetry to overlap with the carbon s and p_{σ} orbitals, so the ¹³C splitting should be appreciable (i.e., much greater than the line width). To attempt to observe the ¹³C satellite lines, a γ -damaged crystal made with 15.5% K¹³CN was oriented at 77°K with the magnetic field in the ac plane 40° from the c axis. At this orientation one set of sites is nearly parallel to the $g_{\parallel \parallel}$ direction of the radical. If the radical is $[Co(II)(CN)_{6}]^{4-}$, there should be ¹³C satellite lines equally spaced on either side of the ⁵⁹Co lines with a peak height about 21% of the ⁵⁹Co peak heights. Inspection of the high field lines at this orientation did not reveal such lines. The conclusion then is that the lowtemperature radical must be $[Co(II)(CN)_4(NC)_2]^{4-}$.

In the case of the room-temperature species, ^{13}C satellite splittings should be evident for the $[Co(II)(CN)_5]^{3-}$ radical since here the d_z^2 orbital

overlaps with one cyanide group. The hyperfine splitting from the ¹³C nuclei should be appreciable, since again the d_a^2 orbital is of the correct symmetry to overlap with the carbon s and p_{σ} orbitals. For the [Co(II)(CN)_A]²⁻ radical, however, ¹³C satellite lines are not expected because the d_{σ}^2 orbital doesn't overlap with a cyanide group. To attempt to observe the ¹³C satellites, spectra were recorded with the magnetic field along the crystallographic c axis using enriched crystals γ irradiated at 77°K and warmed to room temperature. At this orientation all the sites become equivalent and the field is nearly along the $g_{||}$ direction of the radicals. There was no evidence of the ¹³C satellite lines at this orientation. Since the $[Co(II)(CN)_5]^{3-}$ radical would have peak heights only 9% of the ⁵⁹Co peak heights, the room-tempearture species has been tentatively identified as $[Co(II)CN_{A}]^{2-}$ until work with higher ¹³C concentration is completed.

C. Discussion

1. Low-Temperature Species.--The γ irradiation of $K_3Co(CN)_6$, a diamagnetic d^6 low-spin system, could result in the formation of paramagnetic radicals in several ways. The most probable mechanisms involve either the loss of an electron, the capture of an electron, or the rupture of metal-carbon bonds. Depending on which mechanism dominates, the resulting radical could either be a d^5 or d^7 low spin system.
One of the first steps in identifying the lowtemperature species is to establish which orbital the unpaired electron is in. This can be done by comparing the experimental g values with their theoretical expressions. The first-order expressions for $g_{||}$ and g_{\perp} determined for d^5 and d^7 systems⁵⁴ in all the most probable crystal field distortions are shown in Table 5.5 The only expression which describes the experimental g values adequately is that for a d^7 system in a crystal field with a weak tetragonal elongation (*i.e.*, with the electron in a d_g^2 orbital).

The presence of ¹⁴N superhyperfine splitting from two equivalent nitrogen nuclei also suggests that the electron is in a d_g^2 type orbital. These splittings could arise either from the d_g^2 orbital leaking enough spin density unto the carbon atom of the axial cyanide groups to result in appreciable spin polarization of the nitrogen sp σ bonds, or result from direct overlap of the d_g^2 orbital with two nitrogens, in the event that the axial cyanide groups turn around. The absence of ¹³C satellite lines in ¹³C enriched samples serves to support the latter possibility. A theoretical explanation for this phenomenon would be that after capturing an electron, the [Co(II)(CN)₆]⁴⁻ complex is unstable so the axial cyanides rotate to provide the necessary crystal field stabilization as shown in Figure 5.9.

Configuration	Orbital Containin Odd Electron	ng ^g	g⊥
d^7 , weak elongation		2	2[l+3\/A _l)]
d^7 , strong elongation	d_{xy}	$2[1-(4\lambda/\Delta_2)]$	$2[1+(\lambda/\Delta_3)]$
d^7 , weak flattening	dx^2-y^2	$2[1+(4\lambda/\Delta_2)]$	$2[1+(\lambda/\Delta_4)]$
d^7 , strong flattening	d _{x z} ,y z	very 2	large
d^{5} , weak elongation	d_{xy}	$2[1-(4\lambda/\Delta_2)]$	$2[1+(\lambda/\Delta_3)]$
d^5 , weak flattening	d _{xz,yz}	very 1	large
where $\Delta_1 = E_2 $	2 - E _{xz,yz}	$\Delta_2 = E_{x^2-y} $	$z^2 - E_{xy}$
$\Delta_3 = E_3$	cy - E _{xz,yz}	$\Delta_4 = E_x^2 - y $	2 - E _{xz,yz}

Table 5.5.--First order expressions for g values.*

*These expressions have been determined assuming a positive $\boldsymbol{\lambda}.$

With the structure of the low-temperature species established using first-order molecular orbital expressions for the g values, the discussion turns to the physical significance of the A tensor of the radical. The A_g component, that component coincident with $g_{||}$, is predicted to be positive by applying the method of Fortman⁷⁴. The other two components were taken as negative, since this was the combination of signs that gives the maximum spin density on the central metal atom. A measure of the



Figure 5.9--Schematic representation of the ligand-field stabilization acquired in going from the low-temperature species to the room-temperature species.

covalency was obtained by using the first-order expressions for $A_{||}$ and A_{\perp} as derived by McGarvey⁷⁷ for low-spin d^7 systems:

$$A_{\parallel} = -K + \frac{4}{7}\alpha^{2}P - \frac{1}{7}(g_{\perp} - 2.0023)P$$
 (5.2)

$$A_{\perp} = -K - \frac{2}{7}\alpha^2 P + \frac{15}{14}(g_{\perp} - 2.0023)P .$$
 (5.3)

Using $P = 0.0254 \text{cm}^{-1,77}$, the free-ion value for Co(II), the values of $\alpha^2 = 0.71$ and $K = 36.04 \ 10^{-4} \text{cm}^{-1}$ were found. The amount of delocalization indicated by the α^2 value is consistent with the type of σ bond found with a d_g^2 orbital. The small value for K is due to contribution from the 4s orbital to the contact term, this arising from the fact that the d_g^2 orbital is permitted to hybridize with the 4s orbital under the D_{4h} or C_{4v} point groups.

The ⁵⁹Co dipolar tensor for the low-temperature species is orthorhombic, revealing that the structure of the radical is somewhat distorted from axial symmetry. This distortion in γ -irradiated $K_3Co(CN)_6$ might be connected with the fact that it apparently experiences considerably different distortions in different host lattices and under different irradiation conditions (see Table 5.6). The effect of different lattices on the hyperfine values of the low-temperature species, shows this radical to be quite sensitive to the charge distribution of the Table 5.6.--ESR parameters for the room-temperature and low-temperature species in different matrices.

Radical ^a	Matrix	<i>β</i>	$\top_{\mathcal{B}}$	A (G	, A_ (G) A	i ₈₀ (G)	^ຄ ັອ	Reference
L.T.Species	γ-irrad.K ₃ Co(CN) ₆	2.0080	2.0913(x) 2.0904(y)	68.1	-70.1(x) -60.6(y)	-20.8	0.71	This work
L.T.Species	e-irrad.K ₃ Co(CN) ₆	2.0060	2.095	54.0	-70.0	-28.7	0.68	58
L.T.Species	e-irrad.[Co(CN) ₆] ³⁻ in KCl	2.0067	2.1006	70.3	-60.4	-16.8	0.71	119
R.T.Species	γ-irrad.K ₃ Co(CN) ₆	2.0037	2.1580	89.7	-26.6	12.2	0.73	This work
R.T.Species	γ-irrad.K ₃ Co(CN) ₆	2.0050	2.1680	0.06	-27.0	12.0	0.74	57
R.T.Species	e-irrad.K ₃ Co(CN) ₆	2.0040	2.162(x) 2.158(y)	88.5	-25.5(x) -27.7(y)	11.8	0.73	56
R.T.Species	X-irrad.K ₃ Co(CN) ₆	2.0100	2.170(x) 2.167(y)	83.5	-26.9(x) -25.2(y)	10.5	0.72	54
R.T.Species	e-irrad. Cs ₂ LiCo(CN) ₆	2.0070	2.1622	89.0	-25.0	13.0	0.73	119
R.T.Species	[Co(II)(CN) ₅] ³⁻ in ethylene glycol and water	2.0040	2.163(x) 2.160(y)	88.5	-28.0(x) -28.0(y)	10.8	0.73	56
R. T. Species	[Co(II)(CN) ₅] ³⁻ in methanol	2.0060	2.156	87.4	-28.6	10.1	0.73	55

^aL.T. stands for low temperature and R.T. stands for room temperature.

- The state of the

nearest-neighbor ions and possibly the next-nearestneighbor ions. The considerable sensitivity of the ESR parameters for the $[Co(II)(CN)_4(NC)_2]^{4-}$ radical to its ionic environment is most likely a result of having the negative end of the two axial cyanides directed outward.

The discrepancies between Danon's 58 hyperfine splitting values for electron irradiated $K_3Co(CN)_6$ and the values found in this investigation for γ -irradiated K₃Co(CN)₆ are more difficult to explain and most likely are related to the irradiation reaction mechanism. The fact that the $[Co(II)(CN)_{A}(NC)_{2}]^{4-}$ radical is formed by capturing an electron, coupled with the fact that F centers form during irradiation, strongly suggest that the reaction mechanism involves the formation of holes in the lattice. If the hole is close to the radical, its orientation relative to the radical would influence its structure. For instance, if the hole is stabilized close to the radical and to one side of the $g_{\parallel \parallel}$ direction, distortion from axial symmetry would occur. On the other hand, if the hole is stabilized along the $g_{||}$ direction or several ionic radii away, the hole would not distort the radical from axial symmetry. Whether or not the hole stabilizes close enough to the radical to distort the structure could be dependent on the type irradiation used, the temperature of the sample during irradiation, and even possibly the amount of irradiation.

One other possible influence which could explain the discrepancies between Danon's values and those found here is that we may be dealing with different polytypes. The effect of polytypism on the ESR parameters of substitutionally doped Cr^{3+} in the $K_3Co(CN)_6$ lattice has been noted by Townes, *et al.*¹¹⁷ They found that the sphere of influence for the Cr^{3+} sites extended beyond its nearest-neighbor ions resulting in slightly different *g* values for the *lM* and 20*r* polytypes. Although the differences were small for the Cr^{3+} case, they should be greater for irradiated $K_3Co(CN)_6$ since here there is the effect of the positive hole. Also, the -NC⁻ ligands should be more sensitive to the influence of the positive hole than the $-CN^-$ ligands, since the negative charge is largely on the carbon.

2. <u>Room-Temperature Species</u>.--The g values for this radical can be used to establish which orbital the unpaired electron is in. As shown in Table 5.5, only a d^7 system with the unpaired electron in a d_z^2 type orbital could explain the experimental g values.

One would expect the radical formed at room temperature to be considerably more stable than the radical formed at liquid nitrogen temperature. The $[E_{xz,yz}-E_z^2]$ values calculated from the first-order expression for g_{\perp} (Table 5.5) support this view. Using the spin-orbit

coupling value of 533 cm^{-1} found for the Co(II) free ion⁶⁶, calcutions of $[E_{(xz,yz)}-E_z^2]$ give $36,000 \text{ cm}^{-1}$ for the lowtemperature species and $20,500 \text{ cm}^{-1}$ for the room-temperature species. However, since the spin-orbit coupling value in complexes is usually 20\$-30\$ smaller than the free-ion value¹⁵, these $[E_{xz,yz}-E_z^2]$ quantities are probably too large. Perhaps a better expression of the increase in stabilization acquired in going from the low-temperature species to the room-temperature species is the 43\\$ change in energy of the d_z^2 orbital, this quantity being independent of the spin-orbit coupling value.

The considerable change in stability in going from the low-temperature to the room-temperature species indicates that the Co(II) ion must experience quite different ligand fields in the two radicals. Since the absence of any nitrogen superhyperfine splitting for the room-temperature species suggests that metal-nitrogen bonds are not present, the possible radicals which would provide greater ligand-field stabilization for the roomtemperature species are $[Co(II)(CN)_5]^{3-}$ or $[Co(II)(CN)_4]^{2-}$. Gray, et al. have studied this radical, and the $[Co(II)(CN)_5]^{3-}$ radical formed in ethylene glycol solution, with both optical and ESR spectrophotometry and concluded that the [Co(II)(CN)₅]³⁻ structure is correct⁵⁶. However, the absence of ¹³C satellite lines in 15% ¹³C enriched samples tends to contradict this conclusion.

The room-temperature species can be made either by γ irradiation of $K_3Co(CN)_6$ at room temperature or by decay of the low-temperature species upon warming. The decay mechanism appears to involve the loss of one or both of the axial cyanides. As the system is warmed up apparently the vibrational energy becomes too great for the weak isocyanide bonds resulting in their eventual rupture. The fact that the direction cosines for the $g_{||}$ components of both radicals are nearly the same also supports the supposition that both radicals occupy the same sites in the lattice with changes occurring along the axial bonds.

The ⁵⁹Co hyperfine splitting tensor can be used to shed additional light on the structure of the roomtemperature radical. However, before any physical significance can be attached to the tensor, signs must be ascribed to its principal components. The A_z component has been taken as positive using the analysis of Fortman⁷⁴. The A_x and A_y components have been taken as negative since, when the parallel and perpendicular components are of opposite sign, the spin localized on the metal is maximum; also, the trace of the components then gives an A_{iso} (⁵⁹Co) near that found in the solution spectra⁵⁶. Using these signs the experimental tensor was decomposed into a dipolar part and an isotropic part, and these used in the first-order expressions for $A_{||}$ and A_{\perp} given by Equations (5.2) and (5.3) to calculate the value $\alpha^2 = 0.73$.

This value indicates a fair degree of delocalization of the spin out of the d_2^2 orbital, resulting from either hybridization with the cobalt 4s orbital, spin density transferred to the ligand, or both. It should be noted that only the $[Co(II)(CN)_5]^{3-}$ radical offers the possibility of spin density transferring to the axial ligand.

In Table 5.6 are listed the other reported ESR parameters for this radical. There is general agreement in the A_{||} value except for the single crystal work of Lin, McDowell, and Ward⁵⁴, but there is very little consistency in the A_{\parallel} values. These discrepancies could be related to differences in analysis of the powder spectrum, since all the values were derived from powder spectra except those of McDowell, et al. When a computer calculated spectrum is fitted to the perpendicular portion of the powder spectrum, it has been shown that A_x and A_y have different values and that angular abnormalities give splittings which are too large for the low-field lines⁵⁶. Depending therefore on how the perpendicular features of the spectrum are interpreted, different numberical values of A_{\parallel} are obtained. Since both the single-crystal study and the computer fit of the powder spectrum of the roomtemperature species in irradiated K₃Co(CN)₆ show that the A tensor as being orthorhombic, this radical is considered to be distorted from axial symmetry. Such distortions are expected for the room-temperature species since depending

on its structure either one lobe or both lobes of the d_z^2 orbital is not bonded, making this radical very sensitive to its lattice environment. Again, either the effect of the neighboring ions or the hole produced by irradiation could provide the distorting influence.

CHAPTER VI

CHLORORHODATE (II) SYSTEMS

A. Introduction

Single crystals of $K_3RhCl_6 \cdot H_2O$ were γ irradiated at 77°K. ESR spectra of the crystals at this temperature showed chlorine superhyperfine structure but since the crystals were small, the signal was too weak to follow as the crystals were rotated in the magnetic field at X-band. The polycrystalline X-band spectrum of this sample at 77°K showed two g values, the rhodium hyperfine splitting to be within the line width, and poorly resolved chlorine structure superimposed on the high-field line. The radical formed appears to be the $[RhCl_6]^{4-}$ ion with its unpaired electron in the d_g^2 orbital interacting with the two axial chlorines.

Since the chlorine hyperfine structure could not be successfuly studied in the $K_3RhCl_6 \cdot H_2O$ matrix, attempts were made to make the radical in other host lattices. Single crystals of $Na_3RhCl_6 \cdot 12H_2O$ were made, but proved unsatisfactory since the crystals crumble upon radiation. Attempts to make the $[RhCl_6]^{4-}$ ion by γ irradiating single crystals of KCl and NaCl doped with $[RhCl_6]^{3-}$ also failed.

Finally, another approach was taken. Since molten AgCl is a good oxidizing and reducing medium, a 1% mixture of RhCl₃ in AgCl was passed through a zone melting furnace. The resulting crystals gave ESR parameters at 77°K which were consistent with a $[RhCl_6]^{4-}$ ion having its unpaired electron in the d_g 2 orbital and interacting equally with the two axial chlorine nuclei. A complete analysis of the g and chlorine hyperfine tensors was done in the single crystal. Also, the polycrystalline sample gave a spectrum at 77°K very similar to that found for γ -irradiated polycrystalline K₃RhCl₆·H₂O.

The assignment of the electron configuration of the hexachlororhodate radical as d^7 instead of d^9 is based mostly on physical reasoning, since both, depending on the distortion, could give an unpaired electron in the $d_g 2$ orbital and to first order, the g theory is the same. With this in mind, additional information was sought by irradiating K₂ [RhCl₅(H₂O)] where the distortion can be determined. Again the crystals were small and the signal too weak to follow throughout a rotation. Assuming the polycrystalline spectrum is from one species, the radical appears to have three g values, with a four-line pattern superimposed on the high-field line. This spectrum is consistent with [RhCl₅(H₂O)]³⁻ or possibly [RhCl₅]³⁻ formed by addition of an electron and tends to support the d^7 assignment for the hexachororhodate ion. B. Results

1. Powders at 77°K.--Shown in Figures 6.1(A) and 6.1(B) are first-derivative X-band powder spectra of γ irradiated $K_3 RhCl_6 \cdot H_2 O$ and of AgCl doped with Rh^{2+} , both measured at 77°K. The g values are nearly the same for both systems and because of the small nuclear magnetic moment of rhodium and its nuclear spin of 1/2, the rhodium hyperfine coupling is within the line width. The chlorine superhyperfine splitting, superimposed on the $g_{||}$ line, is not very well resolved in either case, but at higher gain all seven lines from two equivalent chlorines can be seen in the case of the AgCl lattice. The differences here could arise from two phenomena which are both dependent on the host lattice. First, the line width should differ for the two lattices since they would have different spinlattice relaxation times. Secondly, the degree of randomness in the orientation of the radicals should vary because of the different particle size of the powders and their different powdering characteristics.

Shown in Figure 6.2 is the first-derivative powder pattern of γ -irradiated K₂[RhCl₅(H₂O)] measured at X-band at 77°K. Because of the three g-value pattern (*i.e.*, g_{\perp} and g_{\perp} ' are nearly equal and greater than free spin and g_{\parallel} is less than free spin), it is evident that the radical, assumed to be [RhCl₅(H₂O)]³⁻ or [RhCl₅]³⁻, is slightly



at 77°K of γ -irradiated K₃RhCl₆·H₂O. (B) The firstderivative X-band polycrystalline spectrum of AgCl:Rh²⁺. At high field the seven-line pattern from the interaction with two equivalent ³⁵Cl nuclei is resolved with increased gain.





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distorted from its C_{4v} symmetry. Superimposed on the $g_{||}$ line is a four-line pattern having splittings which are consistent with an electron in a d_2^2 orbital interacting with the axial chlorine nucleus.

2. Single Crystal at 77°K. -- In cubic crystals with the NaCl structure, M²⁺ ions entering the lattice substitutionally are expected to trap a charge-compensating cation vacancy¹²⁰. This vacancy can distort the cubic (O_{μ}) crystalline field differently, depending on its orientation relative to the M^{2+} ion. If the direction of the line joining the M^{2+} ion and the trapped vacancy is parallel to one of the crystallographic axes, the crystalline field will experience a tetragonal distortion. Since cation vacancies along the three crystallographic axes are symmetrically equivalent, this type of distortion will result in three sites for the M²⁺-vacancy pairs, each with its unique axis directed along one of the crystallographic axes. On the other hand, if the direction of the M^{2+} vacancy pair is parallel to 110, the crystal field will have orthorhombic symmetry. In this case, symmetry arguments show that six sites are expected.

As shown below, the ESR results for Rh^{2+} doped into the AgCl lattice are consistent with the first case, where the cation vacancies are stabilized along the axes. Upon rotating the crystal about the *c* axis, three sets

of seven lines are seen, each belonging to a magnetically distinct site with its unique axis directed along one of the crystallographic axes. Thus, with H//a as shown in Figure 6.3, the sites along the b and c axes are perpendicular to the field and the site along a is parallel to the field. As the crystal is rotated about c toward the b axis, the site along c remains perpendicular to the field while the signals from the sites along the a and baxes move toward each other, becoming equivalent at 45° (see Figure 6.4). Since the components of the seven-line multiplet have intensity ratios 1:2:3:4:3:2:1 and the largest splitting occurs along the $g_{||}$ direction, it must arise from an unpaired electron in the d_z^2 orbital interacting with the two equivalent axial chlorine nuclei. Thus, the spin-Hamiltonian used to interpret the spectra is:

$$\mathcal{F} = g_{\|\|}^{\beta \hat{H}_{z} \hat{S}_{z} + g_{\|}} \beta (\hat{H}_{x} \hat{S}_{x} + \hat{H}_{y} \hat{S}_{y}) \\ + A_{\|\|}^{(35} \text{Cl}) \hat{S}_{z} \int_{n=5}^{6} \hat{I}_{z}^{n} \\ + A_{\|\|}^{(35} \text{Cl}) (\hat{S}_{x} \int_{n=5}^{6} \hat{I}_{x}^{n} + \hat{S}_{y} \int_{n=5}^{6} \hat{I}_{y}^{n})$$
(6.1)

where I^5 and I^6 are used to designate the spin on the two axial chlorine nuclei and the rhodium hyperfine terms have been omitted since its splitting was within the line width. In Table 6.1 are listed all the ESR parameters







ra	dicals n	neasured	at 77°K	•	
Complex	<i>g</i>	g⊥	<i>g</i> ⊥'	$A_{ }^{(35_{CL})}$ ax	A_{\perp} ⁽³⁵ Cl) _{ax}
Rh ²⁺ in AgCl (Powder)	2.002	2.430			****
γ-K ₃ RhCl ₆ H ₂ O (Powder)	2.007	2.460			
$\gamma - K_2 [RhCl_5 (H_2O)]$)]				
(Powder)	1.992	[,] 2.481	2.355	33.12 G	
Rh- in AgCl (single crys	tal)	• • • •			
	2.012	2.419		27.27 G	11.94 G

obtained from analysis of the single-crystal and powder spectra.

Table 6.1.--The ESR parameters for chlororhodate (II) radicals measured at 77°K.

C. Discussion

1. γ -Irradiated $K_3 RhCl_6 \cdot H_2O$.--The d^6 complex in $K_3 RhCl_6 \cdot H_2O$ is diamagnetic with completely filled t_{2g} orbitals. A paramagnetic radical can form from this ion upon γ irradiation by (1) loss of an electron, (2) capture of an electron, or (3) rupture of a bond. Using the g values predicted by the first-order expressions shown in Table 5.5 and other physical arguments, it is feasible to show that only one of the possible radicals which could result from these mechanisms is consistent with all the experimental data.

The first possibility, the loss of an electron, would result in a d^5 ion with a ${}^2T_{2g}$ ground state. Because this state is triply degenerate, the ion would undergo distortion to remove the degeneracy. By comparing the experimental g values then with those predicted for a lowspin d^5 system under different distortions, the first possibility can be eliminated. Also, because the t_{2g} orbitals are not very sensitive to distortions, they give three orbital states which are close in energy. Since these states are short for such systems and thus resonance is usually observed only at temperatures much lower than 77°K.

In the second case, the addition of an electron would result in a species with an unpaired electron in the doubly degenerate e_g orbitals. Again the ion would undergo distortion to remove the degeneracy but, since these orbitals are sensitive to distortions, the resulting differences in orbital energy is enough for resonance to be observed at 77°K. Depending on the distortion, the electron could either be in a d_z^2 or $d_x^2_{-y}^2$ orbital. Using the spin-orbit coupling value of 1235cm^{-1} found for $\text{Rh}^{2+,121}$ and the approximate $\Delta E_x^2_{-xx}, yx$ value of 20,000 $\text{cm}^{-1,122}$, the predicted g values are relatively close to the experimental values. Also, with the unpaired electron in the d_x^2 orbital, there should be some interaction with the axial chlorine nuclei. This appeared to be the case in the single crystal.

For the last possible method of producing radicals, the only reasonable reaction would be the loss of a chlorine atom giving $[RhCl_5]^{3-}$. This ion would have the unpaired electron in the d_2^2 orbital as was found experimentally but the single axial chlorine would give only a four-line pattern which wasn't found experimentally.

Thus, the picture that emerges from this analysis is that the irradiation of $K_3RhCl_6 \cdot H_2O$ produces a $[RhCl_6]^{4-}$ ion by capturing an electron and this ion undergoes a distortion so that the unpaired electron is in the d_2^2 orbital. The $[RhCl_6]^{2-}$ ion formed by the ejection of an electron may also be present but, because of its preditably fast spin-lattice relaxation time, resonance isn't observed at $77^{\circ}K$.

2. γ -Irradiated K₂[RhCl₅(H₂O)].--A similar approach can be used to analyze the paramagnetic radicals produced in γ -irradiated K₂[RhCl₅(H₂O)]. The [RhCl₅(H₂O)]²⁻ ion is a d^6 system wherein the axial H₂O ligand removes the degeneracy of the t_{2g} orbitals. Although the H₂O ligand should give a greater crystal field splitting than chlorine according to the spectrochemical series, it is not uncommon that this ordering changes for nearly adjacent members of this series. Thus, without optical spectra for this compound, one cannot know with certainty whether the H₂O ligand acts to tetragonally elongate or compress the crystal field. Therefore, if an electron is removed from

the radical, the resulting $[RhCl_5(H_2O)]^-$ ion could have the unpaired electron either in the d_{xy} orbital or the doubly degenerate $d_{xz,yz}$ orbitals. However, the theoretical g values show that neither of these possibilities could give the experimental values and, as seen in the case of the isoelectronic $[RuCl_5(H_2O)]^{2-}$ ion in Chapter VII, the relaxation time would probably be too fast for resonance to be observed at 77°K.

If, on the other hand, an electron is captured by the complex, the $[RhCl_5(H_2O)]^{3-}$ species is formed. Since the experimental g values are only consistent with those predicted for the odd electron in the d_{g}^{2} orbital, either the H_2O ligand gives rise to tetragonally elongated crystal field or the H_0O ligand is lost to form the $[RhCl_5]^{3-1}$ species. In either case the axial symmetry of the ion must be lowered to account for the three q values. Such a distortion would not be surprising for these two radicals, since the unpaired electron in the d_2^2 orbital would overlap with the H_2^0 ligand in one case or have an unbonded lobe in the other case and therefore would be sensitive to external influences. These could arise either from the arrangement of the nearest neighbor ions or the hole produced by irradiation. Also, it should be noted that the chlorine splitting is consistent with that expected from the unpaired electron in the d_2 orbital. The four-line pattern, superimposed on the $g_{||}$ line, would arise from

the electron interacting with the single axial chlorine and the splitting, being greater than that found for the [RhCl₆]³⁻ ion, is consistent with the larger Rh-Cl_{ax} overlap expected for these ions.

Lastly, the radicals produced by the rupture of a bond are not consistent with the experimental results. The most likely bond breakage would result in the loss of the H_2O ligand but this would not yield a paramagnetic radical. The other likely bond rupture would result in the loss of the axial chlorine but no chlorine hyperfine structure would be found in this case.

In summary, the analysis of the ESR parameters shows that the $[RhCl_5(H_2O)]^{3-}$ or the $[RhCl_5]^{3-}$ radical, formed by the capture of an electron, are the only species consistent with the experimental data. The $[RhCl_5(H_2O)]^{-}$ species may also form but, due to fast relation times, its resonance would not be observed at 77°K.

3. $\underline{\operatorname{AgCl}:\operatorname{Rh}^{2+}}$.--For rhodium doped into AgCl, it is apparent from the analysis of the single crystal ESR spectra that the ion enteres the lattice substitutionally and, hence, is surrounded by a octahedron of chloride ions. The g values and seven-line hyperfine pattern arising from this radical indicate that the unpaired electron is in the d_g^2 orbital interacting with the two axial chlorine nuclei. Thus, the radical could result from Rh^{2+} , a d^7 system, with a tetragonal elongation or Rh°, a d^9 system, with a tetragonal compression. It should be noted that Wilkens, *et al.* have made a study of the temperature dependence of the *g* values for this system¹²³. They attributed their results to the Rh° ion experiencing a dynamic Jahn-Teller distortion and apparently failed to realize that their results could also have been explained by the Rh²⁺ ion undergoing a dynamic Jahn-Teller effect with the opposite distortions. Hence, before investigating the bonding in this radical, arguments will be presented for the Rh²⁺ assignment.

In the melt, the Rh³⁺ ion would first be reduced to Rh²⁺. This ion, according to the analysis above for γ -irradiated K₃RhCl₆·H₂O and K₂[RhCl₅(H₂O)], should be stable in an octehedral field of chloride ions. Also, there is a history of other metal (II) ions being stabilized in the AgCl lattice 124-127, (including the analogous $d^7 \operatorname{Co}^{2+}$ ion) by charge compensation involving cation vacancies. If now the Rh²⁺ ion were to be further reduced to Rh°, some additional overall stabilization of the system should occur. However, there appears to be no decrease in lattice energy resulting from such a reduction, since charge compensation would also be needed for the Rh° ion. Also, the [Rh°Cl₆]⁶⁻ complex should be less stable than the Rh²⁺ complex, since it involves two more electrons in antibonding molecular orbitals. Hence, it is difficult to see why the Rh²⁺ ion would be further reduced to the Rhº ion.

Thus, assuming the ion to be Rh^{2+} with a tegragonally elongated field, the unpaired electron would be in an antibonding $|E_g, d_z^2\rangle$ orbital. This symmetry assignment for the orbital, however, assumes that the ion would essentially have \mathcal{O}_h symmetry, since the distortion is probably small as evidenced by the fact that it is dynamic at higher temperatures. The $|E_g, d_z^2\rangle$ molecular orbital is composed mostly of the d_z^2 orbital but has some ligand orbital character. The form of the orbital is

$$|E_{g}, d_{z}^{2}\rangle = \alpha |5d_{z}^{2}\rangle - \alpha' [(1/2\sqrt{3})$$

$$(2\sigma_{5}^{+}2\sigma_{6}^{-}\sigma_{1}^{-}\sigma_{2}^{-}\sigma_{3}^{-}\sigma_{4}^{-})], \qquad (6.2)$$

where $\sigma = n |_{3p_z} \rangle_i + (1-n^2)^{1/2} |_{3s} \rangle_i$ and i = 1 - 4 designate the equatorial ligand orbitals while i = 5,6 designate the axial orbitals. It is not possible to derive coefficients for this orbital using the metal *A*-tensor theory, since the rhodium hyperfine splittings are within the line width and could not be evaluated. However, it is possible to estimate the degree of covalency in this orbital using the ligand hyperfine splittings.

The principal values for the chlorine superhyperfine splitting tensor are (in units of $1 \times 10^{-4} \text{ cm}^{-1}$)

$$\begin{bmatrix} A_{z} & & \\ & A_{x} & \\ & & A_{y} \end{bmatrix} = \begin{bmatrix} +25.61 \\ & +13.48 \\ & & +13.48 \end{bmatrix}. (6.3)$$

Although there are eight possible sign combinations for the principal elements, only the choice with all signs positive is consistent with the assumptions that (1) the spin transferred to the p_z orbital is positive (2) the spin-polarization of the $p_{\pi x}$ and $p_{\pi y}$ orbitals would be small, and (3) the isotropic chlorine hyperfine interaction should be large and positive, since the chlorine 3s orbitals are directly involved in the bonding.

The principal elements of the chlorine hyperfine interaction tensor can be expressed in terms of the isotropic contribution A_g , the direct dipolar interaction A_d between the electron in the d_z^2 orbital of Rh and the chlorine nucleus, the dipolar interaction A_p between the electron in the $3p_z$ orbital of chlorine and the chlorine nucleus, and the dipolar interaction $A_{\pi x}$, $A_{\pi y}$ between the polarized electron density in the chlorine p_x and p_y orbital and the chlorine nucleus. As a result of the relationship between the direction cosines of the three chlorine p dipolar terms, only two independent values $(A_p - A_{\pi x})$ and $(A_{\pi y} - A_{\pi x})$ can be determined, such that

$$\begin{bmatrix} A_{z} & 0 & 0 \\ 0 & A_{z} & 0 \\ 0 & 0 & A_{y} \end{bmatrix} = A_{s} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$+ A_{d} + A_{p} - A_{\pi} \begin{bmatrix} 2 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \\+ A_{\pi y} - A_{\pi x} \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{bmatrix}. \quad (6.4)$$

The $A_d = 0.26 \times 10^{-4} \text{ cm}^{-1}$ term has been calculated from $A_d = gg_n \beta \beta_n r^{-3}$ using the Rh-Cl_{ax} distance of 2.150 Å, which was estimated from the Ag-Cl interatomic distance by allowing for the smaller Rh ionic radius⁸⁰. The three observed principal components lead to $A_s = 17.52 \times 10^{-4} \text{ cm}^{-1}$, $(A_p - A_{\pi x}) = 3.78 \times 10^{-4} \text{ cm}^{-1}$, and $(A_{\pi y} - A_{\pi x}) = 0.0 \text{ cm}^{-1}$. Thus the values $A_{\pi y}$ and $A_{\pi x}$ are equal, as expected for an O_h ion with the unpaired electron in the $|E_g, d_z^2\rangle$ antibonding orbital. Also, for this type of orbital, the $A_{\pi x}$ and $A_{\pi y}$ values are expected to be negative and small relative to the A_p term²⁴. Hence, they will be considered to be approximately zero, giving $A_p = 3.78 \times 10^{-4} \text{ cm}^{-1}$. With this quantity and A_s , one can obtain information about the $|E_a, d_z^2\rangle$ antibonding orbital.

In order to correlate these experimental quantities to bonding parameters, it is necessary to develop theoretical expressions for A_g and A_p . This can be done using the spin-Hamiltonian expression determined for the hyperfine splitting arising from electron density in the axial chlorine σ orbitals. The Hamiltonian will have axial symmetry about the z axis and can be expressed as

$$\hat{\mathcal{H}}_{L} = A_{||} \hat{s}_{z} \hat{i}_{z}^{+} A_{\perp} (\hat{s}_{x} \hat{i}_{x}^{+} \hat{s}_{y}^{-} \hat{i}_{y}^{-}) .$$
 (6.5)

Focusing attention then on the hyperfine splitting resulting from one of the axial chlorine orbitals, the expectation value of the Hamiltonian leads to the approximate expression

$$\langle E_{g}, d_{z}^{2} | \hat{\mathcal{H}}_{L} | E_{g}, d_{z}^{2} \rangle \stackrel{\approx}{=} (\alpha^{2}/3) \langle \sigma_{6} | \hat{\mathcal{H}}_{L} | \sigma_{6} \rangle.$$
 (6.6)

Several terms have been dropped in this approximation, resulting in the following errors: (1) a relative large error arises from omitting the $\langle d_z^2 | \hat{\mathcal{H}}_L | \sigma_\delta \rangle$ term which could not be evaluated since good δd_z^2 wave-functions were not available for Rh^{2+} , (2) a small error has been introduced by omitting the $\sum_{i=1}^{2} \langle \sigma_i | \hat{\mathcal{H}}_L | \sigma_\delta \rangle$ terms since the large interatomic distances involved here make the r^{-3} dependent quantities quite small, and (3) the omission of the $\langle d_z^2 | \hat{\mathcal{J}}_L | d_z^2 \rangle$ term results in essentially no error in the calculation since it corresponds to A_d and therefore has been accounted for in the experimental A_p value. Evaluation of the above approximate expression for

$$\left\langle E_{g}, d_{z}^{2} | \hat{\mathcal{H}}_{L} | E_{g}, d_{z}^{2} \right\rangle \text{ leads to}$$

$$A_{g} = (\alpha^{2}/3)(1-n^{2})A_{g}^{\circ}, \qquad (6.7)$$

and

$$A_{p} = (\alpha^{2}/3)(n^{2})A_{p}^{\circ} , \qquad (6.8)$$

where $A_{g}^{\circ}({}^{35}\text{Cl}) = (8\pi/3)_{g_{g}g_{n}\beta\beta_{n}} |\psi_{3s}(0)^{2}| = 1570 \times 10^{-4}\text{cm}^{-1}$ and $A_{p}^{\circ}({}^{35}\text{Cl}) = (2/5)_{g_{g}g_{n}\beta\beta_{n}} \langle r^{-3} \rangle_{3p} = 46.75 \times 10^{-4}\text{cm}^{-1}$ have been determined from the $|\psi_{3s}(0)|^{2}$ and $\langle r^{-3} \rangle_{3p}$ values found from Hartree-Fock calculations of the free chlorine atoms with configurations $(3s3p^{6})$ and $(3s^{2}3p^{5})$, respectively¹⁰⁷. The ³⁵Cl values have been used since the ³⁷Cl structure could not be resolved experimentally and thus the measured splittings are considered to arise largely from the dominant ³⁵Cl isotope. Evaluation of these expressions gives

$$f_s$$
 (%) = 1.12% $\alpha^2 = 0.276$
 f_{p_s} (%) = 8.09% $n^2 = 0.878$

with a hybridation ratio p/s = 7.22.

The $[Rh(CN)_4Cl_2]^{4-}$ ion is the only other Rh^{2+} complex reported which shows axial ligand spin density¹²². This compound, produced by electron irradiation of the $[Rh(CN)_6]^{3-}$ ion in a KCl host lattice, gives quite similar spin densities for the axial chlorine ligands, $f_{p_2}(%) =$ ll.4% and $f_g(%) = 1.2$ %. These values, along with the similar g values, $g_{||} = 1.995$ and $g_{\perp} = 2.297$, provide an additional argument for the Rh²⁺ assignment in the hexachlororhodate complex. Also of interest is the $A_{\parallel}|^{(103}\text{Rh}) = -40.8 \times 10^{-4} \text{cm}^{-1}$ and $A_{\perp}(^{103}\text{Rh}) = -36.9 \times 10^{-4}$ values found for the $[\text{Rh}(\text{CN})_4\text{Cl}_2]^{4-}$ complex. These values give an $A_{iso}(^{103}\text{Rh}) = -38.2 \times 10^{-4} \text{cm}^{-1}$ and indicate that there is unpaired spin density in the Rh 5s orbital. This result is consistent with symmetry considerations. Since the complex has D_{4h} symmetry, the odd electron is in an $|A_{1g}\rangle$ molecular orbital. This type of orbital has 5s character and explains the isotropic rhodium splitting. In $[\text{RhCl}_6]^{4-}$, however, the complex has only a slight distortion from the O_h point symmetry group and thus the odd electron is essentially in an $|E_g, d_z^2\rangle$ orbital. An orbital with this symmetry, on the other hand, has no 5s character and therefore gives small rhodium splittings that are within the line-width.

CHAPTER VII

OTHER SYSTEMS

Included in this chapter are systems whose ESR spectra were not fully analyzed--either as a result of experimental difficulties or inherent shortcomings in the system. For each system discussed, there will be given the objectives for the investigation, the results, and an evaluation of the system with regard to future study. Suggestions for future work are given where the system appeared promising.

A. Chlororuthenate (III) Complexes

One of the main objectives in this investigation was to find the ruthenium hyperfine splittings, since none had been reported before in halometallate complexes. In fact, the only ruthenium hyperfine structure observed thus far has been for Ru^{3+} in $\operatorname{Co}(\operatorname{NH}_3)_6\operatorname{Cl}_3^{128,3}$, in $\operatorname{Al}_2\operatorname{O}_3^{129}$, and in the YGa and YAl garnet lattices ¹³⁰.

The $[RuCl_5(H_2O)]^{2-}$ ion in the $(NH_4)_2[InCl_5(H_2O)]$ lattice proved to be the most promising Ru^{3+} system investigated here. As the sample was cooled, using the helium flow system, resonance was first observed at about 20°K and at 12°K the resolution of the signal became

sufficient for an ESR study. However, the single crystal rotations could not be completed successfully since the crystal holder would freeze into one position as a result of the cold helium vapors mixing with the atmospheric humidity. Thus the results of the single crystal study, although quite informative, are only for unknown arbitrary orientations as is shown in Figure 7.1(A). The spectrum shows two six-line patterns, each superimposed on a strong central line and having about 7% of its intensity. This type of pattern is characteristic of species occupying two inequivalent sites in each of which the odd electron interacts with the ruthenium nucleus. Since ruthenium has two isotopes each of spin 5/2, ⁹⁹ Ru with a 12.81% natural abundance and ¹⁰¹Ru with a 16.98% natural abundance, and both isotopes give practically the same splitting, they appear experimentally as a six-line pattern arising from a 29.79% occurring isotope. Thus the six hyperfine lines should have, as found experimentally, an intensity of about 7% of the central line.

There were two types of doped $(NH_4)_2[InCl_5(H_2O)]$ crystals investigated by ESR. Some had areas of intense red color while others appeared more homogeneously light red throughout. Only in the latter case could the ruthenium hyperfine splitting be resolved. Apparently in the former case the $[RuCl_5(H_2O)]^{2-}$ ions are so close to one another that the hyperfine lines have been so



Figure 7.1--(A) The X-band spectrum at 9° K of the $[RuCl_5(H_2O)]^{2-}$ ion in the $(NH_4)_2[InCl_5(H_2O)]$ matrix with *H* at an arbitrary orientation. The upward and downward arrows designate the $101,99_{Ru}$ hyperfine lines for two magnetically inequivalent sites. (B) The powder spectrum of this sytem at 9° K.
broadened as to not be observable. It was found in these crystals that, for the most part, there appeared to be two magnetically distinct sites, but in some orientations there appeared to be four magnetically distinct sites with two sets of sites being nearly equivalent. It should be of interest then to see if these results can be related to the crystal structure of the host lattice.

The crystal structure shows $(NH_A)_2[InCl_5(H_2O)]$ to be orthorhombic with four molecules per unit cell¹³¹. The H₂O molecules in each unit cell are not distributed randomly among the six corners of the $[InCl_5(H_2O)]^2$ -octehedra but occupy a particular corner in the symmetry plane. Also, every $[InCl_5(H_2O)]^{2-}$ ion is related to another ion in the cell by a C_2 screw axis and the only symmetry individual sites have is the mirror plane. Thus, if the $[RuCl_5(H_2O)]^{2-}$ ion were to enter the lattice with its $Cl-Ru-H_2O$ bond along the $Cl-In-H_2O$ direction, and to assume the geometry of the site, there should be only two magnetically distinct sites and each site should give rise to a three g-value ESR pattern. But, since four magnetically distinct sites appear in some orientations, the $[RuCl_5(H_2O)]^{2-}$ ion apparently does not have exactly the same orientation in the lattice as the $[InCl_5(H_2O)]^{2-}$ ions. Further information about the site symmetry of the ion in the lattice can only be obtained by examining the g values.

Because no complete analysis of the singlecrystal spectra was made, the powder spectrum must be relied on for this information. The powder spectrum shown in Figure 7.1(B) for a 2500 gauss sweep shows only two g values and sweeping the field further did not reveal a third g value. This result would indicate that the $[RuCl_{5}(H_{2}O)]^{2}$ ion has retained its molecular C_{4v} symmetry (noting that the ion actually has C_{2v} symmetry if the hydrogen atoms of the water molecule are included but these are not considered significant for the covalent bonding in the complex). Any lowering of the C_{4v} symmetry should produce a three g-value pattern. On the basis of the powder pattern, the values $g_{||} = 3.013$ and $g_{|} = 2.216$ have been assigned. It is difficult to understand these g values, however, using first-order g theory for a lowspin d^5 system having $C_{d,n}$ symmetry.

In order to derive first-order g expressions for the $[\operatorname{RuCl}_5(\operatorname{H}_2 O)]^{2^-}$ ion, one must have some idea of the ordering of molecular orbital energy levels. In such an ion, the axial $\operatorname{H}_2 O$ molecule removes the degeneracy of the t_{2g} orbitals. However, not having optical spectra for this compound, or analogous compounds, one cannot know with certainty whether the b_2^* orbital would be of higher energy relative to the e^* orbitals, or if the opposite situation occurs. Considering then the first possibility, the b_3^* orbital would contain the unpaired

electron giving rise to the following first-order g-value expressions:

$$g_{||} = 2.0023 - 8\lambda/(\Delta E_{b_1^* - b_2^*})$$
(7.1)

$$g_{\perp} = 2.0023 + 2\lambda/(\Delta E_{b_2^*-e^*})$$
 (7.2)

From these expressions, one would expect $g_{||}$ to be less than and g_{\perp} to be greater than the free-spin value. Obviously, if the unpaired electron is in the b_2^* molecular orbital, the first-order expression for $g_{||}$ does not adequately describe the situation. Focusing then on the $g_{||}$ value of 3.0134, there apparently must be greater mixing of the filled b_1 orbital with the b_2^* orbital than of the b_2^* orbital with the empty b_1^* orbital. For this situation one should add the term $+8\lambda/(\Delta E_{b_2^*-b_1})$ to the $g_{||}$ expression as was done by Kon and Sharpless³⁷ to explain the $g_{||}$ value for $[\text{CrOCl}_5]^{2^-}$. For $g_{||}$ of $[\text{RuCl}_5(\text{H}_2\text{O})]^{2^-}$, however, it is difficult to see how this term could make a large enough contribution to account for the experimental value.

For the other possible distortion, where the b_1^* orbital is lower in energy than the e^* orbitals, the odd electron would be in the doubly-degenerate e^* orbitals. The molecule should, in this case, undergo a Jahn-Teller distortion to remove the degeneracy. This would result in a lowering of symmetry for the ion and should give rise to three g values. Therefore, neither possibility seems to adequately explain the experimental g values, suggesting that a third g value having a value much less than 2.0023 might be found at very high field.

As indicated by the above discussion, the limited analysis of this system has raised some interesting questions. Further analysis of the system must include a complete single-crystal study. Since the $[\operatorname{RuCl}_5(\operatorname{H}_2\operatorname{O})]^{2-}$ ion tends to enter the lattice in clusters, very low amounts of the dopant (0.1%-0.01%) should be used in making the crystals. To circumvent the problem involving singlecrystal rotation with the helium flow system, perhaps passing warm helium gas across the cavity opening would help. If this problem cannot be alleviated, the work could probably be done with the Andonian Dewar.

Also investigated was the $[RuCl_6]^{3-}$ ion doped into KCl and NaCl. These systems, however, did not give a signal even at 10°K. Because the complex is d^5 and doped into highly symmetric cubic lattices, Jahn-Teller distortions are necessary to remove the orbital degeneracy. Since this type of distortion results only in small shifts in energy, the three orbitals will be close in energy and connected by spin-orbit coupling. Under these conditions, the ESR signal is only obtainable at low temperatures where the spin-lattice relaxation time is longer. Thus, it is not surprising that the signal was not observed

even at 10°K. With regard to future work, it might be necessary to go to 4.2°K to see the signal; only the Andonian Dewar system can approach this temperature.

The last ruthenium-containing system to be studied was the complex in single crystals grown from the melt of AgCl containing RuCl₂. This system was an attempt to make the ruthenium analogue of the $d^7 \operatorname{Rh}^{2+}$ ion doped into the AgCl lattice. Since the d^7 system for ruthenium is Ru^+ , this ion would not need charge compensation to enter the AgCl lattice. Thus it was felt, since the Rh²⁺ ion shows that a d^7 system can be stabilized in the AgCl matrix, that Ru³⁺ might be reduced in the AgCl melt to the Ru⁺ ion. The single crystals produced were a very dark burgandy color, indicating that a reaction occurred in the melt. However, the ESR spectra were not consistent with a paramagnetic ruthenium ion even at 13°K. But the crystal did give a signal which was observable even at 77°K. The spectrum consists of two portions, (1) a low-field pattern which is more intense and extends from about 2500 gauss to 3000 gauss and (2) a high-field pattern which has broad lines that start at 3300 gauss and end at about 4050 gauss. When the field was along any of the crystal axes the lowfield pattern consisted of two sets of doublets with the low-field doublet having about one half the peak height of the doublet at higher field. This pattern is consistent with a Ag²⁺ ion with the odd electron in the $d_x^2 - u^2$ orbital. The ESR parameters measured for this radical at 77°K are:

$$g_{||} = 2.527$$
 $A_{||} = -68.46$ G
 $g_{\perp} = 2.292$ $A_{||} = -105.60$ G

The high-field pattern has not been identified but it does not appear to contain the six-line hyperfine structure expected for a ruthenium radical. Since the primary concern here was to make a ruthenium-containing radical, a further study was not made. However, there are very few Ag^{2+} ions reported which have the odd electron in a $d_x^2-y^2$ orbital and hence this radical might merit future study.

B. RhCl₃ in NaF

This system was studied in an effort to obtain the fluorine analogue of $AgCl:Rh^{2+}$, *i.e.*, $[RhF_6]^{4-}$ in NaF. Since Chan and Shields were successful in doping the V²⁺ ion into crystals of LiF and NaF grown from the melt, using mixtures of the alkaline fluoride and VCl_3^{132} , the same result might be expected with $RhCl_3$. However, the Rh^{2+} ion apparently did not enter the lattice since there was no observable signal even at 10°K. The problem here might be a result of the Na⁺ ion having too small a radius to be replaced by the larger Rh^{2+} ion. Since this system would be of considerable interest, further work would seem in order. Crystals of KF are deliquescent and present problems in sample handling, but RbF and CsF do not have this problem and, with their larger cationic radii, would be reasonable crystals to try.

C. $[\text{ReF}_6]^{2-}$ in Cs₂GeF₆

Most of the ESR studies of the Re⁴⁺ ion have been done on the $[\text{ReCl}_6]^{2-}$ ion in the K_2PtCl_6 lattice¹³³⁻¹³⁵. These investigations were done at 4.2K° and did not show any ligand hyperfine structure--probably as a result of the large line widths (25 gauss) and small ligand hyperfine splittings. Only small ligand hyperfine splittings would be expected for such a system since the three unpaired electrons in the t_{2g} orbitals, bonding only with ligand π orbitals, cannot interact directly with the ligand σ bonding orbitals.

The $[\operatorname{ReF}_6]^{2^-}$ system was made, then, as a fluorine analoque to the $[\operatorname{ReCl}_6]^{2^-}$ system. Also, because of the much greater magnetic moment of fluorine, ligand hyperfine structure should probably be observable and hence the π bonding in this ion could be studied. Unfortunately, crystals of Cs₂GeF₆ doped with $[\operatorname{ReF}_6]^{2^-}$ showed no ESR signal even when cooled to 9°K. Since the $[\operatorname{ReF}_6]^{2^-}$ ion has such a light pink color, one could not be certain if the ion had entered the Cs₂GeF₆ lattice. Therefore, a 1% aqueous solution of the $[\operatorname{ReF}_6]^{2^-}$ complex was made and examined at temperatures down to 9°K. This also did not give a signal. Since the $[\text{ReCl}_6]^{2-}$ study was done at 4.2°K, future work on the $[\text{ReF}_6]^{2-}$ ion must also probably be done at this temperature.

D. γ -Irradiated K₄Fe(CN)₆

As shown previously, the d^6 K₃Co(CN)₆ complex, when γ irradiated at 77°K, gave a d^7 system in which the odd electron interacted with two equivalent nitrogens. Hence the K_4 Fe(CN)₆ complex, also a d^6 system, could possibly form a similar radical under these conditions. The powder spectrum for γ -irradiated K₄Fe(CN)₆ is shown in Figure 7.2. The low-field portion of the spectrum consists of three lines, while at higher field there is another line. Gradual warming of the samples showed that the outer two lines of the low field pattern slowly lost their intensity until only the central line of this pattern, along with the line at higher field, remained at 210°K. Warming further, this remaining signal continued to lose intensity until it was gone at 250°K. Thus, the central line of the low-field pattern and the line at higher field seem to arise from the same radical. The observed g values for this radical, $g_{||} = 2.0017$ and $g_{|} = 2.0998$, are consistent with a d^7 system having the odd electron in the d_z^2 orbital. Therefore, it appears that the $d^7 [Fe(CN)_6]^{5-}$ ion



Figure 7.2--The X-band powder spectrum of $K_4Fe(CN)_6 \gamma$ irradiated and measured at 77°K.

forms but, contrary to the d^7 hexacyanocobaltate (II) ion, there is no interaction with the two axial nitrogens.

Root and Symons have γ irradiated [Fe(CN)₆]⁴⁻ doped into KCl¹³⁶. In this case they found a radical with very similar g values, $g_{||}$ = 1.999 and $g_{|}$ = 2.095, but which showed a triplet splitting from the odd electron interacting with one nitrogen nucleus. The g values for their radical are again consistent with a d^7 system having the unpaired electron in the d_{g}^{2} orbital but in this case one of the axial CN groups apparently rotates to give a metal-nitrogen bond. One possible explanation for this is that in hte KCl lattice there is expected to be a cation vacancy along the axial NC-Fe-CN bond direction and perhaps reorientation of the nearest CN group would better stabilize this vacancy. Also, by increasing the period of irradiation they found wing lines appearing on either side of the low-field pattern. These lines, which they attribute to a different species or possibly a radical pair, are probably the same wing lines found in the low-field portion of the spectrum for γ -irradiated K₄Fe(CN)₆. Finally, Root and Symons report that they did not obtain any radicals when pure K_4 Fe(CN)₆ was irradiated. Although they don't mention the temperature of irradiation explicitly, it appears to be room temperature; this and their short radiation period probably explain the discrepancies between their results and ours.

No single-crystal ESR studies of γ -irradiated $K_4 Fe(CN)_6$ were done since the system did not provide an analogue to the $[Co(CN)_4(NC)_2]^{4-}$ radical and, without enriching the sample with ¹³C or ⁵⁷Fe, very little could be learned about the bonding in the ion. However, if future work were to include ⁵⁷Fe or ¹³C enrichment, this could be an interesting system to study.

E.
$$\gamma$$
-Irradiated K_2 Ni(CN) $4 \cdot H_2O$
and Na₂Ni(CN) $4 \cdot 3H_2O$

Krigas initiated ESR studies of a series of irradiated cyanides, $K_2M(CN)_4 \cdot nH_2O$, where M = Pt, Pd, Ni¹³⁷. This is an interesting series of complexes since crystal structure investigations show that the square planar tetracyanometallate ions are stacked one upon another along the fourfold axis of the ion. In his work, Krigas found that crystals of $K_2Pt(CN)_4 \cdot 3H_2O$ crumbled upon irradiation and gave unusable spectra.

In the present work, an effort was made to extend the previous studies by examining the ESR spectra of irradiated $K_2Pd(CN)_4 \cdot H_2O$ and $K_2Ni(CN)_4 \cdot H_2O$. Crystals of these compounds also tended to crumble upon irradiation so they were covered with Pliobond Glue. This procedure alleviated the problem somewhat but the palladium compound gave unusable spectra as had been found for the platinum compound. The nickel compound, on the other hand, gave strong lines which, at X-band, extended from 2800 gauss to 3300 gauss. With H//a there seem to be two main portions to the spectrum, a triplet at low field and a very complex pattern at higher field. The triplet appears to originate from the interaction of an unpaired electron with a nitrogen nucleus; because of this and a g value greater than the free-spin value, the pattern could arise from the d^7 $[Ni(CN)_4(NC)]^{2-}$ radical. Rotating the crystal about the a axis showed that lines move between the two portions of the spectra but because there were so many lines in the high-field portion, it was impossible to follow the lines completely. Irradiation of the Na₂Ni(CN)₄·3H₂O compound also gave strong lines and, in this case, the patterns were less complex and the crystals did not crumble.

The Pt and Pd anologues gave unusable spectra and the Ni systems alone were of limited interest since no 61 Ni hyperfine splitting was observable, so no further work was done on this series. If, however, these compounds were enriched with 13 C (and 61 Ni in the case of the nickel complexes) the radicals formed could probably be identified and their bonding characterized.

F. <u>Y-Irradiated Magnus'</u> Green Salt

Upon γ irradiation of $K_2 PtCl_4$ at 77°K, Krigas found that a (Pt₂) radical formed¹³⁷. The (PtCl₄)³⁻₂ structure was assigned to this radical and it was suggested that the formation of dimer species resulted from

the short Pt-Pt (4.13\AA) distance between the square planar units within the lattice.

Applying this hypothesis then, there should be a considerable likelihood that a (Pt_2) radical would form in irradiated Magnus' green salt, $[Pt(NH_3)_4][PtCl_4]$, where the Pt-Pt distance is only 3.25A^{O138} . Because Magnus' green salt is very slightly soluble, it is virtually impossible to obtain sizable crystals by evaporation techniques. The diffusion technique used appears to be the best method available for growing crystals of this material but it yielded crystals only large enough for Q-band study. Irradiation of the powder gave a weak signal which provided no evidence for dimer species and which appeared to decay rapidly upon warming. Since the Q-band spectrometer is not adapted for work at $77^{\circ}K$, no further investigation was made.

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APPENDICES

APPENDIX A

The following is a listing of a subroutine used to correct the experimental ESR parameters $(A_{||}, A_{|}, g_{||}, g_{|})$ of $[NbOF_5]^{3-}$ for second-order effects. The subroutine was used with a minimization program which adjusted the ESR parameters so as to give the smallest error between the experimental resonance line positions and those determined from the second-order expressions for the parallel and perpendicular spectra. An estimate of the quadrupole coupling constant can be determined by including it as an adjustable parameter.

SUBROUTINE SECORD

```
SUBROUTINE SECORD (XA, ERROR)
    DIMENSION XA(4), XB(4)
    DIMENSION HPARA(10) + HPERP(10) + SMALLM(10)
    COMMON/SCALE/XBEG(5) • STDEV(5)
    DATA HPARA/1957.31, 2264.56, 2581.79, 2908.18, 3245.08, 3591.23,
   $3947.18, 4312.86, 4687.92, 5072.61/
    DATA HPERP/2594.46, 2679.63, 2792.78, 2932.04, 3094.30, 3278.32.
   T3482.24.3709.78, 3954.31, 4214.59/
    DATA SMALLM/4.5,3.5,2.5,1.5,.5,-5,-1.5,-2.5,-3.5,-4.5/
    DO 3 I = 1.4
  3 XB(I)=XBEG(I)+XA(I)*STDEV(I)
    H=6.626196E-27
    V=9.25825E+9
    BIGI=4.5$B0HR=9.274096E-21
    Q = 0
    GPARA=XB(1) $ A=XB(2) $ B=XB(3) $ GPERP=XB(4)
    ERROR=0.0
    DO 10 I=1,10
 10 ERROR=ERROR+(H*V-((GPARA*ROHR*HPARA(I))+(A*SMALLM(I))+(B**2/(2.0*H
   1*V))*(BIGI*(BIGI+1.0)-SMALLM(I)**2)))**2
    DO 11 J=1.10
    JJ=J
 11 ERROR=ERROR+(H*V-((GPERP*BOHR*HPERP(J))+(B*SMALLM(JJ))+((A**2+B**2
   2)/(4.0*H*V))*(BIGI*(BIGI+1.0)-SMALLM(JJ)**2)+((((Q**2)*SMALLM(JJ))
   3/(2.0*B))*(2.0*BIGI*(RIGI+1.0)-(2.0*SMALLM(JJ)**2)-1.0)))**2
    PRINT 999, ERROR, XB, D
999 FORMAT(//2X, +THE NEW PARAMETERS+/10X, +ERROR=+G15.9./5X, +GPARA=+F10
   1.7.3X,*APARA=*E12.5,3X,*APERP=*E12.5/,10X*GPERP=*F10.7.5X*Q=*E12.5
   2)
    RETURN
    END
```

APPENDIX B

The following is a listing of the subroutine used to determine the molecular orbital coefficients and the charge of the central metal ion for $[VOF_5]^{3-}$ and $[NbOF_5]^{3-}$. This subroutine was used with a minimization program which adjusted the coefficients $(\beta_1, \beta_2, \text{ and } \epsilon)$ to give the best agreement between the experimental ESR parameters $(A_{||}, A_{|}, g_{||}, \text{ and } g_{|})$ and those determined from the second order molecular orbital expressions of DeArmond, et al. for these parameters. Included before the listing is an explanation of the input and output data.

INPUT

$GPARA = g_{ }$	$EAPARA = A cm^{-1}$
$\mathbf{GPERP} = g_{\perp}$	EAPERP = A_{\perp} cm ⁻¹
$CAPPA = \kappa$	$DELTEl = \Delta E_{(b_2 \rightarrow b_1)} \text{ cm}^{-1}$
$SB1 = S_{b_1}$	DELTE2 = $\Delta E_{(b_2 \rightarrow e)}$ cm ⁻¹
$SB2 = S_{b_{g_{g_{g_{g_{g_{g_{g_{g_{g_{g_{g_{g_{g_$	$\text{SIGMAM} = \lambda_M \text{ cm}^{-1}$
$SE = S_e^{2}$	$SIGMAL = \lambda_L \ cm^{-1}$
	$P = P cm^{-1}$

h

OUTPUT

$B1 = \beta_1$	$B1B = \beta_1^{2}$
$BlP = \beta'_1$	$BlPB = \beta_1^{,b}$
$B2 = \beta_2$	$B2B = \beta_2^b$
$B2P = \beta'_2$	$B2PB = \beta_2^{b}$
$\mathbf{E} = \mathbf{\varepsilon}$	$EB = \varepsilon^{b}$
$EP = \varepsilon'$	$EPB = \epsilon'^{b}$

Q = charge on the central metal ion.

SUBROUTINE MOCOEFF

```
SUBROUTINE MOCOEFF(AX, ANS)
     DIMENSION XA(3) • XB(3)
     COMMON/TIME/TIMELIM.TREG.TEND, ANOW. IMP. IPP, IVP, IXP
     COMMON/DATA/DELTE1, DELTE2, GPARA, GPERP, EAPARA, EAPERP, SIGMAM,
    65IGMAL · CAPPA · P · SB1 · SB2 · SE
     COMMON/XREG/XREG(5)/SCALE/SCALE(5)
     COMMON/QROOT/ IFORB, XX
     DATA INDEX/0/
     AA=0.0 $ 88=0.0 $ CC=0.0
     DO 3 I=1.3
   3 XB(I) = XREG(I) + XA(I) + SCALE(I)
     B_1 = XB(1) $ B_2 = XB(2) $ E = XB(3)
     B1P=QROOT(1.0.-?.0*B1*SB1.B1**2-1.0)
     IF (IFORB.EQ.1) AA=XX
     B2P=QROOT(].0.-2.0*B2*SB2.B2**2-1.0)
     JF(IFORB.EQ.1) BB=XX
     EP=QROOT(1.0,-2.0*E*SE,E**2-1.0)
     IF (IFORB.E0.1) CC=XX
     TDGPARA=-2.0*(2.0*SIGMAM*B2*B1-SIGMAL*B2P*B1P)*(2.0*B2*B1-2.0*B1*
    182P*S82-2.0*B2*B1P*S81-B1P*82P)/DELTE1
     TDGPERP= -(2.0*SIGMAM*B2*E)*(B2*E-B2*EP*SE-E*B2P*SB2)/DELTE2
     TAPARA=-P# (CAPPA+B2++2+ (4.0+B2++2/7.0)+2.0023-GPARA+ (3.0+(2.0023
    1-GPERP)/7.0)+6.0*SIGMAM*B2*E*(B2*EP*SE+E*B2P*SB2)/(7.0*DELTE2)+2.0
    2*(2.0*SIGMAM*B2*B1-SIGMAL*B2P*B1P)*(2.0*B2*B1P*SB1*2.0*B1*B2P*SB2*
    381P#82P)/DFLTE1)
     TAPERP=-P#(CAPPA#B2##2-(2.0#B2##2/7.0)+(11.0#(2.0023-GPERP)/14.0)+
    111.0*(SIGMAM*B2*E)*(B2*EP*SE+E*B2P*SB2)/(7.0*DELTE2))
     FDGPARA=GPARA-2.0023
     EDGPERP=GPFRP-2.0023
     ANS=((TPGPARA-EDGPARA)/EDGPARA)##2+((TDGPERP-EDGPERP)/EDGPERP) ##2+
    1((TAPARA-EAPARA)/EAPARA)##2+((TAPERP-EAPERP)/EAPERP)##2
     INDEX=INDEX+1
     BNOW=SECOND (AZZZ)
     IF (IVP.EQ.1) PRINT 200, INDEX, BNOW
200 FORMAT(* VALUE200: INDEX, BNOW = *, I5, 3X, F8.3)
   5 IF(IFORB.E0.1) GO TO 100
     IF (IVP.EQ.1)PRINT 202
IF (IVP.EQ.1) PRINT 9999. ANS, XR, B1P, B2P, EP, ANOW
9999 FORMAT (//2X+*THE NEW PARAMETERS*/10X+*ERROR=*G15.9+/5X+*B1=*F10.7
    1•5X•*82=*F10•7•5X•*E=*F10•7•/5X•*R1P=*F10•7•5X•*82P=*F10•7•5X•
    2 \neq EP = \neq F10.7, T120, \neq ANOW = \neq F6.3
```

```
CALL COEFF (B1+B1P+SB1+B1B+B1PB)
    CALL COEFF (B2+B2P+SB2+ B2B+B2PB)
    CALL COEFF ( E, EP, SE, EB, EPB)
    Q1=2.0*(818**2+818*81P8*581)
    Q2=2.0*(B2B**2+B2B*B2PB*$B2)
    Q3=4.0*(E8**2+E8*EP8*SE)
    Q4=B2P##2-B2#B2P#SB2
    Q=4.0-Q1-Q2-Q3+Q4
    203 FORMAT (//5X+#Q=#F10.7,5X+#Q1=#F10.7,5X,#Q2=#F10.7,5X+#Q3=#F10.7.
   V5X,*Q4=*F10.7,/5X,*B1B=*F10.7,5X,*B2B=*F10.7,5X,*EB=*F10.7,/5X.
   Z*B1PB=*F10.7.5X,*B2PB=*F10.7.5X.*EPB=*F10.7)
    INDEX=0
    RETURN
100 DD=AA+BB+CC
    ANS=ANS+10000000.0*DD+100000.0*DD**2
    IF (IVP.EQ.1)PRINT 201
201 FORMAT (//T25+*.....FORBIDDEN REGION......*)
    IF(IVP.EQ.1)PRINT 9999,ANS,X8,B1P,B2P,EP,ANOW
 99 RETURN
    END
    FUNCTION QROOT (A, B, C)
    COMMON/QROOT/ IFORB, XX
    IFORB=0
    YY = (B + 2 - 4 \cdot 0 + A + C)
    IF(YY.LT.0.0) IFORB=1
    XX = ABS(YY)
    QROOT = (-B + SQRT(XX)) / (2.0 + A)
    RETURN
    END
    SUBROUTINE COEFF (A.B.S.C.D)
    XX = (B*S-A)/(A*S-B)
    YY=ABS(1.0/(1.0+2.0*S*XX+XX**2))
    C=SQRT(YY)
    D=C+XX
    RETURN
```

```
END
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