ELECTRON SPIN RESONANCE STUDIES OF TRANSITION METAL COMPLEXES.

CHRISTOPHER CHIKE EZZEH

University of Windsor

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ELECTRON SPIN RESONANCE STUDIES
OF
TRANSITION METAL COMPLEXES

BY
CHRISTOPHER CHIKE EZZEH

A Dissertation
submitted to the Faculty of Graduate Studies
through the Department of Chemistry in
partial fulfillment of the requirements
for the degree of Doctor of Philosophy
at the University of Windsor
Windsor, Ontario
1975
To

MARY ANN

and

my parents

OBI AND MRS. JOHNSON WALTER EZZEH
FOREWORD

The work described in this thesis was undertaken by the author in the Chemistry Department of the University of Windsor, Ontario, between 1972 and 1974.

The author wishes to express his sincere appreciation to Professor Bruce R. McGarvey for suggesting this problem and for his available assistance and understanding patience during the course of this investigation. His gratitude goes also to Professor F. Holuj of the Physics Department for allowing him to use his spectrometer for liquid helium studies and to Dr. T. C. Kwan for his assistance in taking the spectra. The author's gratitude goes also to Drs. William E. Jones and M. Rafi Mustafa for the individual assistance and specially Dr. Mustafa for typing this thesis.

Christopher Chike Ezze
Windsor, Ontario
January 1975
ABSTRACT

ELECTRON SPIN RESONANCE STUDIES OF TRANSITION METAL COMPLEXES

In order to determine the charge transfer in the Mn-O bond the electron spin resonance study of the MnO$_4^{2-}$ ion in dilute single crystals of the orthorhombic host BaSeO$_4$ has been done at 4°K. The principal g and A values are $g_x = 1.9580 \pm 0.0004$, $g_y = 1.9655 \pm 0.0008$, $g_z = 1.9824 \pm 0.0004$, $\alpha_x = (126.0 \pm 0.4) \times 10^{-4}$ cm$^{-1}$, $\alpha_y = (84.2 \pm 0.4) \times 10^{-4}$ cm$^{-1}$ and $\alpha_z = (16.3 \pm 0.4) \times 10^{-4}$ cm$^{-1}$. The x, y and z axes are chosen so that the y axis is along the b crystallographic axis while the x and z axes are nine degrees away from the c and a crystallographic axes respectively. The principal x and z axes of the g and A values in the ac plane are found to differ by 4°. The ground state is shown to be the $d_{2z}$ orbital with a 2% admixture of $d_{x^2-y^2}$ orbital, similar to that of MnO$_4^{2-}$ in BaSO$_4$ but different from that of MnO$_4^{2-}$ in $K_2CrO_4$ where the ground state was shown to be the $d_{xy}$ orbital. It is shown that for MnO$_4^{2-}$ in BaSeO$_4$ the difference in the principal x and z axes of the g and A values is attributable to an admixture of the $d_{y^2}$ orbital with the $d_{xy}$ orbital which is estimated to be about 0.03% from the angular separation of the axes. An MO analysis of the ESR data for MnO$_4^{2-}$ in BaSeO$_4$ and BaSO$_4$ shows that the d orbital contribution to the molecular orbitals occupied by the unpaired electron are close to those of a +2 charged free ion. A further
analysis shows the pattern of charge transfer in the Mn-O bond. There is more σ charge transfer and less π charge transfer when MnO$_4^{2-}$ substitutes for the smaller SO$_4^{2-}$ than when it substitutes for the larger SeO$_4^{2-}$ ion.

Also the ESR of dilute single crystals of Fe(CN)$_5$NH$_3$$^+$ ion in Fe(CN)$_5$NO,2H$_2$O has been investigated at 40 K. The principal g values are $g_x = 0.845 \pm 0.001$, $g_y = 2.177 \pm 0.001$ and $g_z = 2.995 \pm 0.001$. The hyperfine interaction for the amine nitrogen was observed and found to be $0 < A_x < 2.2 \times 10^{-4}$ cm$^{-1}$, $0 > A_y > -3.7 \times 10^{-4}$ cm$^{-1}$ and $A_z = (+8.1 \pm 0.4) \times 10^{-4}$ cm$^{-1}$. The g values are consistent only with a ground state in which the unpaired electron is primarily in a d$_{xz}$ orbital rather than the expected d$_{x^2-y^2}$ orbital. The large anisotropy in the hyperfine interaction is explained as requiring a 20% transfer of electron spin to the amine nitrogen. This unusual ground state and covalency of the Fe-N bond suggest that NH$_3$ in this complex has a much stronger ligand field strength than is found in other complexes.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>I</strong></td>
<td></td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>A. Scope of this work</td>
<td>1</td>
</tr>
<tr>
<td>B. Historical</td>
<td>2</td>
</tr>
<tr>
<td>C. Charge transfer in metal-ligand bonds</td>
<td>4</td>
</tr>
<tr>
<td><strong>II</strong></td>
<td></td>
</tr>
<tr>
<td>ELECTRON SPIN RESONANCE SPECTROMETER</td>
<td>6</td>
</tr>
<tr>
<td><strong>III</strong></td>
<td></td>
</tr>
<tr>
<td>CRYSTAL STRUCTURES</td>
<td>9</td>
</tr>
<tr>
<td>A. General Description</td>
<td>9</td>
</tr>
<tr>
<td>B. Barium Selenate</td>
<td>9</td>
</tr>
<tr>
<td>C. Sodium Nitroprusside</td>
<td>11</td>
</tr>
<tr>
<td>D. Identification of Crystal Axes</td>
<td>12</td>
</tr>
<tr>
<td><strong>IV</strong></td>
<td></td>
</tr>
<tr>
<td>EXPERIMENTAL</td>
<td>13</td>
</tr>
<tr>
<td>A. Preparation of Single Crystals</td>
<td>13</td>
</tr>
<tr>
<td>1. Preparation of BaSeO$_4$</td>
<td>13</td>
</tr>
<tr>
<td>2. Growth of Single Crystals of Ba(Se,Mn)$_2$O$_4$</td>
<td>13</td>
</tr>
<tr>
<td>3. Preparation of Na$_3$Fe(CN)$_5$NH$_3$.3H$_2$O</td>
<td>14</td>
</tr>
<tr>
<td>4. Oxidation of Na$_3$Fe(CN)$_5$NH$_3$.3H$_2$O to Na$_2$Fe(CN)$_5$NH$_3$.H$_2$O</td>
<td>15</td>
</tr>
<tr>
<td>5. Growth of Single Crystals of Na$_2$Fe(CN)$_5$(NO,NH$_3$)$_2$.2H$_2$O</td>
<td>15</td>
</tr>
<tr>
<td>B. Operational Techniques</td>
<td>16</td>
</tr>
<tr>
<td><strong>V</strong></td>
<td></td>
</tr>
<tr>
<td>THE SPIN HAMILTONIAN FOR $d^1$ IONS IN A TETRAHEDRALLY DISTORTED ENVIRONMENT</td>
<td>18</td>
</tr>
</tbody>
</table>

vii
A. The General Hamiltonian

B. The Spin Hamiltonian

VI

EXPERIMENTAL RESULTS

A. Manganate Ion in Barium Selenate
   1. The ESR Spectra
   2. Determination of the Hyperfine Coupling Constant
   3. Determination of \( g \) Values
   4. Forbidden Transitions

B. Pentacyanoamminoferrate(III) Ion in Sodium Nitroprusside
   1. The ESR Spectra
   2. Determination of the \( g \) Values
   3. Nitrogen Hyperfine Splitting

VII

ANALYSIS OF THE SPIN HAMILTONIAN

PARAMETERS

A. The Crystal Field Approach to the Analysis of the Spin Hamiltonian Parameters for \( \text{MnO}_4^{2-} \) in \( \text{BaSeO}_4 \)

B. Molecular Orbital Theory

C. The Molecular Orbital Approach to the Analysis of the Spin Hamiltonian Parameters for \( \text{Fe(CN)}_5\text{NH}_3^{2-} \) ion in \( \text{Na}_2\text{Fe(CN)}_5\text{NO}.2\text{H}_2\text{O} \)

D. The Nitrogen Hyperfine Interaction

VIII

CONCLUSION
<table>
<thead>
<tr>
<th>Chapter</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>APPENDIX</td>
<td>82</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>89</td>
</tr>
<tr>
<td>VITA AUCTORIS</td>
<td>93</td>
</tr>
</tbody>
</table>
# Table of Contents

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>26</td>
</tr>
<tr>
<td>3</td>
<td>27</td>
</tr>
<tr>
<td>4</td>
<td>30</td>
</tr>
<tr>
<td>5</td>
<td>34</td>
</tr>
<tr>
<td>6</td>
<td>35</td>
</tr>
<tr>
<td>7</td>
<td>38</td>
</tr>
<tr>
<td>8</td>
<td>44</td>
</tr>
<tr>
<td>9</td>
<td>48</td>
</tr>
<tr>
<td>10</td>
<td>55</td>
</tr>
<tr>
<td>11</td>
<td>57</td>
</tr>
<tr>
<td>12</td>
<td>64</td>
</tr>
<tr>
<td>13</td>
<td>65</td>
</tr>
<tr>
<td>14</td>
<td>66</td>
</tr>
<tr>
<td>15</td>
<td>73</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

Figure  
1  Block diagram of X-band superheterodyne spectrometer used for ESR experiments at liquid helium temperatures  
2  X-band cavity system with horizontal crystal mount  
3  ESR spectrum of MnO$_4^{2-}$ in BaSeO$_4$ when the magnetic field is along the b axis of the crystal  
4  Typical spectrum of MnO$_4^{2-}$ in BaSeO$_4$ in the ac plane  
5  Plot of K in gauss versus $\theta$ for MnO$_4^{2-}$ in BaSeO$_4$ in the ac plane  
6  Plot of $g^2$ versus $\theta$ for MnO$_4^{2-}$ in BaSeO$_4$ in the ac plane  
7  Plot of $g^2K^2$ versus $\theta$ for MnO$_4^{2-}$ in BaSeO$_4$ in the ac plane  
8  The principal axes for MnO$_4^{2-}$ in (a) K$_2$CrO$_4$ and (b) BaSO$_4$  
9  ESR spectrum of Fe(CN)$_5$NH$_3^{2-}$ in Na$_2$Fe(CN)$_5$NO$_2$H$_2$O when the magnetic field is along the c axis of the crystal  
10 The ESR spectrum of Fe(CN)$_5$NH$_3^{2-}$ in Na$_2$Fe(CN)$_5$NO$_2$.2H$_2$O when the magnetic field is along the Fe-NH$_3$ bond axis  
11 Plot of $g$ versus $\theta$ for Fe(CN)$_5$NH$_3^{2-}$ in Na$_2$Fe(CN)$_5$NO$_2$.2H$_2$O for rotation in the ab plane
Figure

12 Plot of $q^2$ versus $\theta$ for Fe(CN)$_5$NH$_3^{2-}$ in Na$_2$Fe(CN)$_5$NO.2H$_2$O for rotation in the ab plane

13 Coordinate axes used in the MO calculations for MnO$_4^{2-}$

14 Coordinate axes used in the MO calculations for Fe(CN)$_5$NH$_3^{2-}$

15 Broadline NMR spectrum of powdered Na$_2$Fe(CN)$_5$NH$_3$.H$_2$O at room temperature
Chapter 1

INTRODUCTION

A. Scope of this work

The splitting of the d orbitals of metal ions by their environment has been a subject of interest to chemists. In octahedral and tetrahedral symmetries these orbitals are split into a group of three designated as $t_2$ and a pair designated as $e$. In an octahedral environment the $e_g$ orbitals are higher in energy than the $t_{2g}$ orbitals, while in a tetrahedral field the $t_2$ orbitals are higher in energy than the $e$ orbitals. Distortions from either octahedral or tetrahedral symmetries further split the energies of each group of orbitals. An understanding of the crystal field theory is useful in order to predict the number of unpaired electrons that a transition metal ion possesses in various crystal fields and hence the actual magnetic moments. Electron spin resonance studies of paramagnetic ions provide useful information about the wave function describing the unpaired electrons both in the ground state and in the excited electronic states. This information is obtained from the spin hamiltonian parameters that are directly determined by the experimental measurements.

The study of the complexes mentioned below was undertaken to determine their spin Hamiltonian parameters, to analyze these parameters in order to determine the ground state of the metal ions, and to perform a molecular orbital analysis of these parameters in order to determine the charge transfer in the metal-ligand bonds. These ions have been
studied in single crystals diluted with an isomorphic diamagnetic host to reduce interactions between neighboring paramagnetic ions. The principal ions studied in this work are the manganate ion in barium selenate and the pentacyanoammine ferrate(III) ion in sodium nitroprusside. Manganese(VI) has a $d^1$ configuration while iron(III) has a $d^5$ configuration. The $d^5$ configuration in an octahedral crystal field can be treated by the hole formalism so that it is similar to the $d^1$ system.

B. Historical

Since the discovery of the technique by Zavoisky\(^{(1)}\), ESR has provided much information on inorganic systems. Among the interesting systems studied are $d^1$ and $d^5$, which have been studied in some detail recently. Manganese(VI) is a $d^1$ system and its tetrahedral oxyanion has been studied in different hosts. Carrington et al.\(^{(2)}\) investigated the $\text{MnO}_4^{2-}$ ion in $\text{K}_2\text{CrO}_4$ host and their data were analyzed by Schonland\(^{(3)}\) who found the unpaired electron to be in the $d_{xy}$ orbital. The $\text{CrO}_4^{2-}$ ion in $\text{K}_2\text{CrO}_4$ has a site symmetry of $C_s$ and the $z$ axis was chosen as the principal axis that lies in the symmetry plane of the ion and comes closest to bisecting the angle between the two oxygen atoms in the plane. The $x$ and $y$ axes are perpendicular to this axis with one being in the plane of symmetry and the other perpendicular to it. In this study we have designated the $y$ axis to be the one perpendicular to the plane. Subsequent investigations of other $d^1$ tetrahedral oxyanions: $\text{MnO}_4^{2-}$ in $\text{BaSO}_4$ by Kosky et al.\(^{(4)}\), $\text{CrO}_4^{3-}$ in $\text{Ca}_2\text{PO}_4\text{Cl})$ and $\text{Ca}_5\text{(PO}_4)_3\text{Cl}$ by Banks, Greenblatt
and McGarvey\(^{(5,6)}\), and MoO\(_4^{3-}\) in CaWO\(_4\) by Azerbayejani and Merlo\(^{(7)}\) found the unpaired electron in the \(d_{z^2}\) orbital for these complexes. Ballhausen and Liehr\(^{(8)}\) have proposed an energy level scheme for the manganate and hypochromate ions in which the unpaired electron occupied one of the \(e\) orbitals. Since the \(d_{z^2}\) orbital is one of the \(e\) orbitals, it is apparent that these ESR results demonstrate the correctness of this energy level scheme. The fact that the unpaired electron of MnO\(_4^{2-}\) ion in K\(_2\)CrO\(_4\) and in BaSO\(_4\) occupies different \(d\) orbitals is puzzling since both host lattices belong to the same space group, \(P2_1\), and their oxyanion tetrahedra have similar bond angles as shown in Tables 1, 7 and 11. Kosky et al.\(^{(4)}\) suggested that the smaller size of SO\(_4^{2-}\) ion relative to the MnO\(_4^{2-}\) and CrO\(_4^{2-}\) ions might cause a different distortion for MnO\(_4^{2-}\) in BaSO\(_4\). Since SeO\(_4^{2-}\) ion is likely to be more nearly the size of the MnO\(_4^{2-}\) ion, it was decided to study the MnO\(_4^{2-}\) ion in single crystals of BaSeO\(_4\) to determine the effect that the lattice size has upon the distortion present in the MnO\(_4^{2-}\) ion.

A \(d^5\) system in an octahedral environment can be analyzed mathematically using the hole formalism. The first reported paramagnetic resonance work on a \(d^5\) system, Fe(CN)\(_6^{3-}\), was by Baker, Bleaney and Bowers\(^{(9)}\). Bleaney and O'Brien\(^{(10)}\) later developed the theory of the complex cyanides of the iron group. Since then a large number of \(d^5\) \((t_{2g})^5\) complexes have been studied. Among the most recently reported studies are: Ru\(^{3+}\) in Yttrium Gallium garnet\(^{(11)}\), Fe\(^{3+}\) complexes with sulfur-containing ligands\(^{(12)}\), Fe(III) \(N,N\)-dimethylldithiocarbamate\(^{(13)}\), Fe(phenanthroline)\(_2\)(CN)\(_2\)^+\(^{(14)}\) and trisbidentate
complexes of Fe(III), Ru(III), Os(III) with sulfur donor ligands. Most of these studies were done on frozen glasses or powders. Single crystal studies of the strong field d^5 complexes have been reported for Fe(CN)_6^{3-} and Mn(CN)_6^{4-} (9), Ru(H_2O)_6^{3+} (11), IrBr_6^{2-} and IrCl_6^{3-} (16), Ru(NH_3)_6^{3+} (17), Ru(acac)_3 (18), Os(P(C_2H_5)_2C_6H_5)_2 (19), and the formally d^5 complexes of Mn(CN)_5NO_2^-(20,21) and Cr(CN)_5NO_3^- (20,22,23). In many of these, the site symmetries are lowered as a result of geometric distortions such as inequivalent atom positions and this results in crystal field splittings of the t_2g orbitals of several hundred reciprocal centimeters. It thus appears that additional single crystal studies of iron complexes, such as Fe(CN)_5NH_3^2-, in which the major distortions from octahedral symmetry are attributable to a sixth inequivalent ligand in the first coordination sphere, would be valuable in interpreting the considerable data on powders and frozen glasses. This investigation would also provide some information about the wave functions for the three Kramers doublets that make up the \{(t_{2g})^5\} configuration. This can be obtained from a low temperature study of the complex ion of interest.

C. Charge Transfer in Metal-Ligand Bonds

Charge transfer in metal-ligand bonds has been estimated using the molecular orbital parameters determined from ESR studies. For transition metal complexes, molecular orbital models have been found appropriate because they take account of the atomic orbitals belonging to the ligand atoms and therefore introduce covalency to the bonding. The importance
of covalent bonding in these complexes is supported by the short metal-oxygen bonds for oxyanions and cations, large reductions of the metal spin orbit coupling parameters and hyperfine interaction with ligand nuclei that have nuclear moments, which show that the unpaired electron is delocalized. Owen(24) and Stevens(25) were the first to use the molecular orbital theory to calculate the effects on the magnetogyric ratio of the electron arising from covalent bonding in Cu(II) and Ni(II) compounds. Some d\(^1\) complexes for which the molecular orbital treatments have been given are: CrOCl\(_n\)\(^{(n-3)}\)\(^-\), \(n=4\) and 5 by Kon et al.(26), MoOCl\(_5\)\(^{2-}\), VOCl\(_3\)\(^-\) and VO(H\(_2\)O)\(_5\)\(^{2-}\) by DeArmond et al.(27), Ti(acac)\(_3\) by McGarvey(28) and CrCl\(_5\)(H\(_2\)O)\(^2-\) by Garrett et al. Most recently McGarvey(30) has performed a self consistent charge analysis on the ESR spin Hamiltonian parameters of CrO\(_4\)\(^{2-}\) and MoO\(_4\)\(^{3-}\). In this analysis MO mixing coefficients are calculated from the spin Hamiltonian parameters using excited state energies obtained from optical spectroscopy, values of the spin orbit coupling constant, \(\xi\), for the d orbital obtained from atomic spectroscopy and values of \(<r^{-3}>\) for the d orbital obtained from Hartree-Fock computations. The calculation is done for values of \(\xi\) and \(<r^{-3}>\) appropriate to different charges on the free metal ion and a Mulliken charge analysis is done on the resulting molecular orbitals. The computation is deemed self-consistent when the Mulliken charge on the metal ion equals the charge associated with the values of \(\xi\) and \(<r^{-3}>\) used. Such a method has been applied to determine the charge transfer in the Mn-O bond of the manganate ion in this study.
Chapter II

ELECTRON SPIN RESONANCE SPECTROMETER

Both the 300°K and 77°K electron spin resonance studies were done on a Varian E-12 spectrometer. The crystals investigated gave broad spectra at 77°K and none at 300°K because the spin lattice relaxation time, T₁, is short at these temperatures. Liquid helium temperature studies were done on a spectrometer built by Professor F. Holuj of the Physics Department of the University of Windsor. This was an X-band spectrometer. At low temperatures, the spin lattice relaxation time, T₁, is long, requiring the use of low powers. Measurements at low power makes it necessary to employ a superheterodyne system. Figure 1 shows a block diagram of the spectrometer used. 100 KHz field modulation was employed. A double Dewar system was used to hold the liquid helium. Liquid nitrogen was placed in the outer dewar while the inner dewar was evacuated to about 25 microns of mercury. This evacuation ensured a slow evaporation of the liquid helium.

A cylindrical cavity operating in the TE₀₁₁ mode, shown in Figure 2, was used. A single crystal was mounted so that it could be rotated at 4°K on a horizontal axis while the magnetic field could be rotated perpendicular to this axis. The crystal mount and gear system are also shown in Figure 2.
Figure 1. Block diagram of x-band superheterodyne spectrometer used for ESR experiments at liquid helium temperatures.
Figure 2. X-band cavity system with horizontal crystal mount.
Chapter III

CRYSTAL STRUCTURES

A. General Description

The interpretation of ESR results in the solid state requires a knowledge of the crystal structure of the substance studied. In single crystal ESR studies the paramagnetic ion is introduced as an impurity into a diamagnetic and isomorphic host whose crystal structure is known. Since the paramagnetic ion substitutes for the diamagnetic ion in the lattice, it is generally assumed that the site symmetry for the paramagnetic ion is the same as for the diamagnetic ion.

The two diamagnetic hosts used in these studies are BaSeO₄ and Na₂Fe(CN)₅NO·2H₂O. Both are orthorhombic and have four molecules per unit cell. Each has a site symmetry of Cs at the metal ion. The four molecules in the unit cell are related pairwise by inversion centers as discussed below. The pairs are interchanged by a reflection in a plane containing the unique crystal axis and one parallel to the molecular plane.

B. Barium Selenate

The complete crystal structure of BaSeO₄ has not been done but x-ray diffraction studies of powder samples show it to be isomorphic with barium sulfate with similar unit cell dimensions. The unit cell constants for BaSeO₄, BaSO₄ and K₂CrO₄ are given in Table 1. BaSeO₄ crystals belong
<table>
<thead>
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<th>Space Group</th>
<th>$\text{BaSO}_4^{(33)}$</th>
<th>$\text{BaSeO}_4^{(32)}$</th>
<th>$\text{K}_2\text{CrO}_4^{(34)}$</th>
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</thead>
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<td>8.98±0.02 Å</td>
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<td>Pnma</td>
<td>7.15 Å</td>
<td>7.35±0.01 Å</td>
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</tr>
</tbody>
</table>
to the orthorhombic space group Pnma, point symmetry mmm and have four molecules per unit cell. Each selenium atom is at the center of a distorted tetrahedron of four oxygen atoms, two of which lie in the ac plane which passes through the selenium nucleus. The other two are symmetrically situated above and below this plane with the line joining them parallel to the b axis. The site symmetry of each molecule is \( C_2 \).

In the space group Pnma, there is an inversion center at the point \( 0 \bar{z} 0 \). This inversion center relates the ion pair at the points \( x\bar{x}z \) and \( x(3/4)\bar{z} \) as well as those at \( (1/2-x)3/4(1/2+z) \) and \( (1/2+x)1/2(1/2-z) \). The two pairs are interchanged by a glide reflection across a plane parallel to the crystallographic ab plane. Thus in the mixed crystals, \( \text{Ba(Se,Mn)O}_4 \), there will be essentially two kinds of paramagnetic ions in the lattice, geometrically identical but distinguished by their differing orientations relative to the crystallographic axes.

C. Sodium Nitroprusside:

This crystal belongs to the space group Pnmm \(^{(35)}\) with the lattice constants: \( a = 11.8 \) \( \alpha \), \( b = 15.52 \) \( \alpha \) and \( c = 6.22 \) \( \alpha \). In the nitroprusside ion, the plane of symmetry includes the Fe-N axis. Two equatorial cyanides are above and two are below this plane which is parallel to the ab plane of the crystal. The Fe-N-O systems are linear and make angles of \( \pm 33^\circ \) with the crystallographic a axis. The equatorial cyanides are \( 90^\circ \) apart so that there is no crystallographic reason to expect a major distortion of the crystal field from the axial symmetry.
In the substituted crystal, Na$_2$Fe(CN)$_5$(NO, NH$_3$)$_2$H$_2$O, the $y$ principal axis should be perpendicular to the ab plane. The axis associated with the field parallel to the Fe - NH$_3$ direction should be about 133° from the $a$ axis.

In the Na$_2$Fe(CN)$_5$NO$_2$H$_2$O the molecule centered about the position $xy0$ and $\bar{x}\bar{y}0$ are related by inversion through the origin so also is the pair at ($\bar{k}$-$x$)($\bar{k}$+$y$)$\frac{1}{2}$ and ($\bar{k}$+$x$)($\bar{k}$-$y$)$\frac{1}{2}$. these two pairs are related by a glide reflection across either a plane parallel to the crystallographic bc plane or one parallel to the ac plane.

D. Identification of Crystal Axes:

BaSO$_4$ crystals grew prismatically elongated along the [010] direction with (101) denoting the predominant faces. These features were also expected for BaSeO$_4$. The long axis was identified as the $b$ axis for BaSO$_4$ (4). The same was assumed by us for BaSeO$_4$ crystals. The $a$ and $c$ axes were roughly identified by observing the interfacial angles.

Sodium Nitroprusside crystals are needle-like in habit along the $c$ axis. The predominant faces are (110). The $a$ and $b$ axes were identified by visually considering the interfacial angles.
Chapter IV

EXPERIMENTAL

A. Preparation of Single Crystals:

1. Preparation of BaSeO₄:

30g of Na₂SeO₄ were weighed out and dissolved in 600 ml of distilled water. To this solution were added 10 ml of 6N HCl. The solution was then heated almost to boiling and 130 ml of 0.5M BaCl₂ solution were added with stirring. The hot mixture was further stirred for ten minutes, covered and allowed to stand for 24 hours. The precipitate of BaSeO₄ was then filtered through a sintered glass funnel, washed with hot water and dried in an oven at 110°C.

2. Growth of Single Crystals of Ba(Se,Mn)O₄:

The first reported growth of single crystals of BaSO₄ and Ba(Se,Mn)O₄ was by Wagner(36). Patel and Koshy(37) subsequently grew single crystals of BaSO₄ by cooling a melt of an equimolar mixture of BaCl₂ and Na₂SO₄. In this study Wagner's method was used. This method requires a platinum crucible since the molten flux is caustic. A mixture containing 14% KCl, 30.8% NaCl and 29.2% BaSeO₄ was thoroughly mixed at room temperature and transferred to a platinum crucible. About 0.01g of KMnO₄ was added for each 25g of the starting material. The crucible was placed in a temperature-controlled furnace which was gradually heated to 780°C in air. This temperature was chosen after a few trial runs at various temperatures. Chloride ions liberated at this temperature reduced the permanganate to the
manganate. The contents of the crucible were allowed to remain at this temperature overnight and the furnace was cooled to 640°C at a rate of about 2.0 degrees per hour. The furnace was then allowed to cool to room temperature without control. The crystals were separated by dissolving the KCl-NaCl flux in hot water. The crystals grew as small prisms about 6 mm long and 1 to 2 mm thick. The color of the substituted crystals varied from pink to blue. The pink color is due to the presence of permanganate. The ESR signals observed at 40K indicated the presence of manganate ions. No attempt was made to determine the concentration of the manganate ion in the crystals.

3. Preparation of Na₃Fe(CN)₅NH₃·3H₂O:

Sodium pentacyanommino ferrate(III) was prepared according to Brauer by first preparing the diamagnetic Na₃Fe(CN)₅NH₃·3H₂O. 30g of sodium nitroprusside were weighed out and dissolved along with 4g of NaOH in 120 ml of distilled water. The mixture was cooled in an ice-water bath. At 0°C ammonia was introduced until the solution was saturated. During the operation the temperature was not allowed to exceed 20°C. The solution was then kept under loose cover for several hours at 0°C and the crystals which separated from the brownish yellow solution were collected by filtration. The remainder of the compound was precipitated from the solution by addition of methanol. The product, Na₃Fe(CN)₅NH₃·3H₂O, was purified by solution in some cold water, from which it was precipitated as fine yellow needles by careful addition of 90% alcohol. The crystals were dried for several days in a vacuum desiccator.
over calcium chloride.

4. **Oxidation of Na₃Fe(CN)₅NH₃.3H₂O to Na₂Fe(CN)₅NH₃.H₂O**

A solution of 20g of sodium nitrite in 50 ml of distilled water was treated at 0°C with 20 ml of 30% acetic acid and then with 30g of Na₃Fe(CN)₅NH₃.3H₂O prepared above. After two hours, a 1:1 mixture of alcohol and ether was added; this first precipitated a violet aquo complex salt (formed in a side reaction); further addition of alcohol-ether mixture precipitated the desired salt. This was purified by repeated solution in cold water and precipitation with alcohol. The dark yellow powder was dried to constant weight in vacuum over concentrated sulfuric acid.

5. **Growth of Single Crystals of Na₂Fe(CN)₅(NO₂NH₃).2H₂O**

To a saturated solution of sodium nitroprusside was added about 0.5% by weight of Na₂Fe(CN)₅NH₃.H₂O. The solution was thoroughly stirred and allowed to evaporate slowly over several days. The best crystals were obtained by evaporating ethanol-water solutions. The crystals grew as small prisms and varied in length and thickness. Well formed crystals 4 mm long and about 1 mm thick were used for ESR measurements.
B. Operational Techniques:

A well formed crystal of BaSeO$_4$ containing MnO$_4^{2-}$ ion was selected for the study. This crystal was mounted by means of '5 Minute Epoxy' (manufactured by Le Page's Ltd., Montreal) to the end of a polyethylene rod with the b axis of the crystal approximately parallel to the axis of the rod. The polyethylene rod was attached to the cavity by means of the gear system shown in Figure 2. The magnet can be rotated about an axis orthogonal to that of the rod. Thus a combined rotation can align the b axis along the magnetic field direction. When the alignment of the axis is correct, the four molecules in the unit cell will be magnetically equivalent, thus giving identical resonances. A slight rotation of the magnet was found necessary to correctly align the b axis parallel to the magnetic field. This is at the intersection of two planes in which the resonances of the molecules in the crystal coincide. These are the ab and bc planes. Along the ab plane the g values show an increase as the magnetic field moves away from the b axis towards the a axis. The maximum g value occurred when the magnetic field was along the a axis, $90^\circ$ away from the a and b axis lies the c axis. The a and c axes were used to define the ac plane. Except when the magnetic field is along the a or c axis in the ac plane, the four molecules divide into two magnetically inequivalent pairs and the resonances of each pair are resolved. Spectra were recorded at selected points in the ac plane.

The same procedure was employed for Fe(CN)$_5$NH$_3^{2-}$ ion in Na$_2$Fe(CN)$_5$NO$_2$H$_2$O crystal but the axes were differently labelled. The unique crystallographic axis was now the c axis.
Spectra were recorded at selected intervals in the ab plane.

The magnetic field of each ESR transition was determined by measuring the frequency of a proton resonance. The frequency of the proton oscillator was varied until the proton signal was observed on the oscilloscope. This frequency was measured with a Hewlett Packard No. 5253A Frequency counter. The value of the frequency so obtained was accurate to 1 kHz and since the magnetic field was homogeneous in this area it was not necessary to correct the value of the frequency for the probe position. The mechanical reproducibility of a given crystal setting was 0.5°.
THE SPIN HAMILTONIAN FOR $d^1$ IONS IN A TETRAHEDRALLY DISTORTED ENVIRONMENT

A. The General Hamiltonian:

The energy of a transition metal ion in a crystal field in the absence of an external magnetic field can be described by a quantum mechanical Hamiltonian which includes magnetic as well as electric interactions and can be written as:

$$\mathcal{H} = \sum_{i} \left( \frac{p_i^2}{2m} \right) - \sum_i (Ze^2/r_i) + \sum_{i,j} e^2/r_{ij} + \sum_{i,j} \lambda_{ij} L_i \cdot S_j - \sum_i e_i \varphi_c(r_i) + \mathcal{J}_{\text{quad}} \tag{6}$$

in which $\sum (p_i^2/2m)$ is the total electron kinetic energy of the paramagnetic ion, summed over each electron of the ion, $Ze^2/r_i$ is the coulomb attraction between the nucleus and these electrons, $e^2/r_{ij}$ is the coulomb repulsion between electrons and is summed only over pairs of electrons, $\sum_{i,j} \lambda_{ij} L_i \cdot S_j$ is the spin-orbit coupling with each $i$ and $j$ ranging over all electrons, $\sum_i S_i \cdot \mathbf{S}_i$ is the magnetic interaction between all electrons and the nucleus, $e_i \varphi_c(r_i)$ is the crystal field interaction and $\mathcal{J}_{\text{quad}}$ is the nuclear quadrupole interaction.

The first five terms represent the Hamiltonian for the free ion. The fifth term is the crystal field interaction, a term in which it is assumed that crystal field sources external to the ion give rise to electrostatic potential $\varphi_c$ at the ion with which each electron interacts. The
symmetry of the crystal field determines the nature of the resulting energy levels and the extent of the degeneracy remaining in them.

If the molecule is placed in a magnetic field $H$, two additional terms must be added to the Hamiltonian given by equation (6). These are:

$$\beta_e H^* (L + 2.0023S) = g_N \beta_N H^* I$$

in which $L$ and $S$ are the orbital angular momentum and the intrinsic spin vector operators respectively, $\beta_N$ and $\beta_e$ are the nuclear and electronic magnetons respectively and $g_N$ is the nuclear $g$ factor. $I$ is the nuclear spin vector operator. These terms result from the interactions of the electronic and the nuclear magnetic moments with the magnetic field.

**B. The Spin Hamiltonian:**

It is difficult to calculate the energy levels using the above Hamiltonian but since in ESR one is concerned only with the spin states of the electronic ground state, it is possible to integrate out the electronic functional variables and by second order perturbation theory derive a spin Hamiltonian. This Hamiltonian involves only spin operators, predicts the ground state spin states and for $S = \frac{1}{2}$ for one nucleus, has the form:

$$\mathcal{H}_S = \beta_e H^* g^* S + I^* g_S \Sigma$$

where $H^* g^* S$ is the magnetic Zeeman term in which $H$ is the external magnetic field, $g^*$ is the electronic spin vector and $g$ is a second order matrix. This term arises from the interaction of the magnetic field with the spin and orbital angular
momenta of the electron. The second term \( I \cdot \mathbf{A} \cdot \mathbf{S} \) is the hyperfine splitting term in which \( I \) and \( \mathbf{S} \) are the nuclear and electronic spin magnetic momentum vectors respectively and \( \mathbf{A} \) is a second order matrix. It can be shown that the hyperfine term can be written as a sum of two terms, one representing the anisotropic part which arises from the dipolar interaction between nuclear and electronic spins which are not too close to each other, and the other representing the isotropic part which arises from the Fermi contact interaction due to the electron density at the nucleus. The principal axes of the \( \mathbf{A} \) and the \( g \) matrices are usually oriented in the same or nearly the same direction. These axes can be conveniently determined by measuring the ESR spectra of a single crystal.
Chapter VI

EXPERIMENTAL RESULTS

A. Manganate Ion in Barium Selenate

1. The ESR Spectra

The crystal structure of Ba(Se,Mn)O₄ predicts that when the magnetic field is along the b axis of the crystal, the magnitudes of the direction cosines for the magnetic field relative to the molecular axes of all four molecules in the unit cell are identical and only six lines will be expected. These six lines are due to the hyperfine interaction of ⁵⁵Mn nucleus which has a nuclear spin of ⁵⁄₂ resulting in (2I + 1) lines. The six lines were observed as expected and the spectrum recorded in this orientation is shown in Figure 3. In the crystallographic ac plane, the six lines should split into two sets of six lines except when the magnetic field is along either of the other two crystallographic axes. This splitting of the six lines is caused by the fact that in this plane the four molecules now divide into two magnetically inequivalent pairs. Twelve lines are therefore to be expected but in general only eleven or ten lines were observed due to accidental overlap of one or two lines. A typical spectrum recorded in the ac plane is shown in Figure 4.

Since the molecular symmetry mirror plane coincides with the crystallographic mirror plane, two principal axes of g must lie in the plane. The exact orientation of these with respect to the crystallographic axes can be derived experimental-
Figure 3. ESR Spectrum of $\text{MnO}_4^{-}$ in $\text{BaSeO}_4$ when the magnetic field is along the $b$ axis of the crystal.
Figure 4. Typical ESR spectrum of $\text{MnO}_4^{2-}$ in $\text{BaSeO}_4$ for rotation in the ac plane.
ly by plotting $g^2$ as a function of the angle of rotation in a specific plane. These two principal axes must be orthogonal and the third principal axis must be orthogonal to the mirror plane. This third principal axis $g_y$ is parallel to the b crystallographic axis. The positions of each resonance line of the spectra recorded in the ac plane are given in Table 2. The line width of the spectra are about one gauss and the line shape is nearly gaussian.

2. Determination of the Hyperfine Coupling Constants

The angular dependence of $g$ and $A$ can be derived by perturbation theory from the spin Hamiltonian given in equation (8). The first order results are given as:

$$\hbar v(M_I) = g\beta H + KM_I$$  \hspace{1cm} (9)

$$g = \left(g_x^2 \cos^2 \alpha + g_y^2 \cos^2 \beta + g_z^2 \cos^2 \gamma \right)^{1/2}$$  \hspace{1cm} (10)

$$K = \left(g_x A_x^2 \cos^2 \alpha + g_y A_y^2 \cos^2 \beta + g_z A_z^2 \cos^2 \gamma \right)^{1/2} / g$$  \hspace{1cm} (11)

assuming $g$ and $A$ coaxial, where $\cos \alpha$, $\cos \beta$ and $\cos \gamma$ are the direction cosines between the principal axes and the magnetic field direction, $g_x$, $g_y$ and $g_z$ are the principal $g$ values, $A_x$, $A_y$ and $A_z$ are the principal $A$ values and $M_I$ is the azimuthal magnetic quantum number for the nucleus.

Experimentally we vary $H$ keeping $v$ constant. Solving equation (9) for $H$ gives

$$H = \left(\hbar v_0 / g\beta\right) - \left(K/g\beta\right)M_I$$  \hspace{1cm} (12)

where $v_0$ is the frequency of the spectrometer and $h$ is Planck's constant. Thus to first order, a spectrum of six equally spaced lines separated by $K/g\beta$ gauss and centered at
\( \nu / g \beta \) gauss is expected. When the hyperfine coupling is large compared to \( g \beta H \), equation (12) is no longer adequate and we must include second order terms from perturbation solution of equation (8). These terms are given in the Appendix.

Examination of these equations reveals that the second order terms depend on \( M^2 \) only and therefore accurate values of \( K/g \beta \) can be obtained from the equation

\[
-K/g \beta = \left\{ H_{M} - H_{-M} \right\}/2|M|
\]  

(13)

Since there are three values of \(|M_1|\) as given in Table 2, we obtain three measurements of \( K/g \beta \) from each spectrum using equation (13). The average \( K/g \beta \) values for different orientations of the magnetic field in the ac plane are given in Table 3 for each of the two resonances observed. Also the value of \( K/g \beta \) for the b axis is given.

The determination of \( K \) requires a value for \( g \). Since \( g \) need be known to only three or four significant figures for this purpose, second order corrections are not necessary and \( g \) was calculated from the value of the center field, \( \nu / g \beta \), for the six line spectrum.

One of the principal axes must be along the b axis and this has been designated the y axis. Therefore \( \lambda_y \) is the value of \( \lambda \) found for the magnetic field along the crystallographic b axis. The x and z principal axes must be in the ac plane and are found at the positions of the maximum and minimum \( K \) values. For a rotation of the magnetic field in an arbitrary crystal plane, equation (11) takes the form

\[
g^2 K^2 = (gK)^2_{\min} + \left( (gK)^2_{\max} - (gK)^2_{\min} \right) \cos^2(\theta - \theta_{\max})
\]  

(14)
TABLE 2

Resonance Positions in Gauss for Rotation in the ac Plane
and Along the b-Axis

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<tr>
<th>Angle</th>
<th>+5/2</th>
<th>+3/2</th>
<th>+1/2</th>
<th>-1/2</th>
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</tr>
<tr>
<td>Line I</td>
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<td></td>
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<td></td>
<td></td>
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<tr>
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<td>3398.4</td>
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<td>3479.6</td>
</tr>
<tr>
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<td>3348.2</td>
<td>3395.9</td>
<td>3442.2</td>
<td>3483.4</td>
<td>3523.7</td>
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<tr>
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<td>3393.9</td>
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<td>2526.3</td>
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</tr>
<tr>
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<td>3579.9</td>
<td>3672.9</td>
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<td>3489.4</td>
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<td>3680.6</td>
</tr>
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**TABLE 3**

Hyperfine Splitting Constants, $K/g\beta$, in Gauss for Rotation in the ac Plane for $\text{MnO}_4^{2-}$ at 4 $^\circ$K

<table>
<thead>
<tr>
<th>Angle</th>
<th>Line I</th>
<th>Line II</th>
</tr>
</thead>
<tbody>
<tr>
<td>-9</td>
<td>$17.6 \pm 0.2$</td>
<td>$45.3 \pm 0.5$</td>
</tr>
<tr>
<td>0</td>
<td>$28.2 \pm 0.7$</td>
<td>$28.2 \pm 0.7$</td>
</tr>
<tr>
<td>9</td>
<td>$45.3 \pm 0.5$</td>
<td>$17.6 \pm 0.2$</td>
</tr>
<tr>
<td>20</td>
<td>$67.6 \pm 0.7$</td>
<td>$28.9 \pm 0.7$</td>
</tr>
<tr>
<td>35</td>
<td>$95.8 \pm 0.5$</td>
<td>$61.1 \pm 0.7$</td>
</tr>
<tr>
<td>50</td>
<td>$118.1 \pm 0.7$</td>
<td>$90.2 \pm 0.7$</td>
</tr>
<tr>
<td>65</td>
<td>$132.7 \pm 0.2$</td>
<td>$113.7 \pm 0.2$</td>
</tr>
<tr>
<td>81</td>
<td>$137.9 \pm 0.2$</td>
<td>$130.4 \pm 0.2$</td>
</tr>
<tr>
<td>97</td>
<td>$132.2 \pm 0.2$</td>
<td>$138.1 \pm 0.2$</td>
</tr>
</tbody>
</table>

*b-axis*  

$91.8 \pm 0.2$

The angle is measured from the a axis.
where $\theta$ and $\theta_{\text{max}}$ are respectively the angles at which $(gK)$ was measured at any specified orientation, and the angle at which $(gK)$ is a maximum. $(gK)_{\text{max}}$ and $(gK)_{\text{min}}$ are the maximum and minimum values for $(gK)$. The best values of $(gK)_{\text{max}}^2$, $(gK)_{\text{min}}^2$ and $\theta_{\text{max}}$ were found by fitting the values of $K$ given in Table 3 to equation (14) with a least squares program written by Tepper (40) and slightly modified. The values of $A_X$, $A_Y$ and $A_Z$ and the angle $\alpha$ between the $z$ principal axis of the hyperfine tensor and the a crystallographic axis are given in Table 4. Figure 5 shows a plot of $K$ in gauss versus the angle $\theta$ in the ac plane. The z axis is chosen as the principal axis that lies in the symmetry plane of the ion and comes closest to bisecting the angle between the two oxygen atoms in the plane.

3. Determination of the $g$ Values:

The appropriate values of $g$ obtained by the first order equations must be corrected for second order terms. Using the estimated values of $A_X$, $A_Y$, $A_Z$, $g_X$, $g_Y$ and $g_Z$ the $g$ values, for the various orientations, corrected for second order effects were calculated. The second order equations are not strictly valid in this case because, as will be seen later, the principal $x$ and $z$ axes are not the same for both the $g$ and $A$ tensors. However since the angle between the principal axes is small, the error incurred in using these equations is not more than the normal errors in determining line positions. Thus when the magnetic field is along the $b$ axis of the crystal, the magnetic field $H$, for a specific value of $M_I$ is given by:

$$H(M_I) = \frac{h\nu_o}{g_Y\beta} - \frac{A_Y}{g_Y\beta} M_I - \frac{(A_Z^2 + A_Y^2)}{4g_Y\beta h\nu_o} [I(I + 1) - M_I^2] \quad (15a)$$

For two resonance lines of the same $M_I$, equation (15a) yields
Figure 5. Plot of $K$ in Gauss versus $\Theta$ for $\text{MnO}_4^{2-}$ in $\text{BaSeO}_4$ in the ac plane. $\Theta$ is measured from the a' axis.
<table>
<thead>
<tr>
<th></th>
<th>BaSeO$_4$</th>
<th>BaSO$_4$&lt;sup&gt;a&lt;/sup&gt;</th>
<th>K$_2$CrO$_4$&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g_x$</td>
<td>1.9580 ± 0.0004</td>
<td>1.9600</td>
<td>1.966</td>
</tr>
<tr>
<td>$g_y$</td>
<td>1.9655 ± 0.0008</td>
<td>1.9687</td>
<td>1.970</td>
</tr>
<tr>
<td>$g_z$</td>
<td>1.9824 ± 0.0004</td>
<td>1.9800</td>
<td>1.938</td>
</tr>
<tr>
<td>$\alpha(g_z)$</td>
<td>13.4 ± 0.5°</td>
<td>13°</td>
<td>-</td>
</tr>
<tr>
<td>$A_x$ (10$^{-4}$ cm$^{-1}$)</td>
<td>126.0 ± 0.4</td>
<td>128</td>
<td>33</td>
</tr>
<tr>
<td>$A_y$ (10$^{-4}$ cm$^{-1}$)</td>
<td>84.2 ± 0.4</td>
<td>79</td>
<td>25</td>
</tr>
<tr>
<td>$A_z$ (10$^{-4}$ cm$^{-1}$)</td>
<td>16.3 ± 0.4</td>
<td>48</td>
<td>135</td>
</tr>
<tr>
<td>$\alpha(A_z)$</td>
<td>9.2 ± 0.5°</td>
<td>13°</td>
<td>-</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reference (4)

<sup>b</sup> Reference (2)
\[
\frac{[H(M_\perp) + H(-M_\perp)]}{2} = H^0 - \frac{(A^2_x + A^2_y)}{4g_\beta h\nu_o} [I(I + 1) - M_\perp^2] \tag{15b}
\]

where \(H^0\) is \((h\nu_o/g_\beta \beta_0)\) from which \(g_y\) is calculated.

Equation (15b) was solved for \(H^0\) and evaluated using the estimated values of \(A_x, \ A_y\) and \(g_y\). Three values of \(H^0\) were obtained and their average used to calculate \(g_y\) corrected for second order effects.

For rotation in the ac plane the magnetic field \(H(M_\perp)\) is given by:

\[
H(M_\perp) = \frac{h\nu_o}{g_\beta} - \frac{KM_\perp}{g_\beta} - \frac{(A^2_x + A^2_y)}{4g_\beta h\nu_o} [I(I + 1) - M_\perp^2] \tag{16a}
\]

\[-\frac{g^2 A_y}{g^4} \frac{(A_x - A_z)^2}{2K^2g_\beta \nu_o} M^2_\perp \sin^2 \alpha \cos^2 \alpha \]

where \(\alpha\) is the angle between the z axis and the magnetic field, \(K\) and \(g\) are the hyperfine splitting constant and \(g\) values respectively for a specific orientation in the ac plane. Again, for two resonance lines of the same \(M_\perp\) values, equation (16a) yields:

\[
\frac{1}{2} [H(M_\perp) + H(-M_\perp)] = H^0 - \frac{(A^2_x + A^2_y)}{4g_\beta h\nu_o K^2} [I(I + 1) - M^2_\perp] \tag{16b}
\]

\[-\frac{g^2A_y}{g^4} \frac{(A_x - A_z)^2}{2g_\beta \nu_o K^2} \sin^2 \alpha \cos^2 \alpha \cdot M^2_\perp \]

The last two terms of equation (16b) were estimated from the values of \(A_x, A_y, A_z, g_x, g_y, g_z\) and the angle \(\alpha\) estimated from a plot of first order \(g^2\) versus the angle \(\theta\) defined above. Three values of \(H^0\) were obtained for a given orientation and their average was used to calculate the \(g\) values corrected for second order effects using equation (17)
\[ g = \frac{(2.0036 \times H_{DPPH})}{H^0} \]  

The values of \( H^0 \), \( g \), and \( g^2 \) so obtained are given in Table 5.

For a rotation of the magnetic field in an arbitrary crystal plane, equation (10) takes the form:

\[ g' = \left( g_{\text{min}}^2 + (g_{\text{max}}^2 - g_{\text{min}}^2) \cos^2(\theta' - \theta_{\text{max}}) \right)^{1/2} \]  

(18)

Using the computer program mentioned earlier the \( g \) values given in Table 5 were fitted to equation (18). The principal \( g \) values obtained have been given in Table 4. Figure 6 shows the plot of \( g^2 \) versus the angle \( \theta \) in the ac plane for the experimental and computer-fitted curves. Table 6 gives the values of \( g^2 k^2 \) in \( \text{cm}^{-2} \) used for the plot of \( g^2 k^2 \) versus the angle \( \theta \) in the ac plane shown in Figure 7.

Single crystal ESR studies of \( \text{MnO}_4^{2-} \) ion have been reported by Carrington et al. (2) in a \( \text{K}_2\text{CrO}_4 \) host lattice and by Kosky et al. (4) in a \( \text{BaSO}_4 \) host lattice. The principal \( g \) and \( A \) values in these two host lattices have been given in Table 4 for comparison with the corresponding values for the \( \text{BaSeO}_4 \) host lattice. The space group and unit cell parameters for these three hosts have been given in Table 1. Figure 8a shows one of the chromate tetrahedra projected onto (100) and Figure 8b shows one of the sulfate tetrahedra projected onto (010). It is assumed that since \( \text{BaSO}_4 \) and \( \text{BaSeO}_4 \) are isomorphic Figure 8b will apply to \( \text{BaSeO}_4 \). The bond angles and the bond distances for all three ions are listed in Table 7. \( O_1 \) and \( O_{II} \) are the two oxygen atoms in the molecular symmetry plane and \( O_{III} \) for \( \text{SO}_4^{2-} \) and \( \text{CrO}_4^{2-} \) represent the two oxygen atoms above and below this plane. For \( \text{SeO}_4^{2-} \), space group \( \text{Pmmn} \),
Figure 6. Plot of $g^2$ versus $\theta$ for $\text{MnO}_4^{2-}$ in $\text{BaSeO}_4$ in the ac plane. $\theta$ is measured from the a axis.
TABLE 5

The Values $H^0$ in Gauss and the Corresponding $g$ and $g^2$

Values for Rotation in the ac Plane at 4 °K

at a Frequency of 9.425 GHz

<table>
<thead>
<tr>
<th>Angle</th>
<th>$H^0$</th>
<th>$g$</th>
<th>$g^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-9</td>
<td>3422.5 ± 0.7</td>
<td>1.9822 ± 0.0004</td>
<td>3.9289</td>
</tr>
<tr>
<td>0</td>
<td>3423 ± 3</td>
<td>1.982 ± 0.002</td>
<td>3.9283</td>
</tr>
<tr>
<td>9</td>
<td>3427.9 ± 0.9</td>
<td>1.9790 ± 0.0005</td>
<td>3.9165</td>
</tr>
<tr>
<td>20</td>
<td>3434.5 ± 0.1</td>
<td>1.9752 ± 0.0001</td>
<td>3.9016</td>
</tr>
<tr>
<td>35</td>
<td>3444.1 ± 0.2</td>
<td>1.9697 ± 0.0001</td>
<td>3.8798</td>
</tr>
<tr>
<td>50</td>
<td>3455.6 ± 0.2</td>
<td>1.9632 ± 0.0001</td>
<td>3.8540</td>
</tr>
<tr>
<td>65</td>
<td>3462.4 ± 0.5</td>
<td>1.9593 ± 0.0003</td>
<td>3.8388</td>
</tr>
<tr>
<td>81</td>
<td>3464.3 ± 0.2</td>
<td>1.9582 ± 0.0001</td>
<td>3.8347</td>
</tr>
<tr>
<td>97</td>
<td>3459.4 ± 0.2</td>
<td>1.9610 ± 0.0001</td>
<td>3.8456</td>
</tr>
</tbody>
</table>

Line II

<table>
<thead>
<tr>
<th>Angle</th>
<th>$H^0$</th>
<th>$g$</th>
<th>$g^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-9</td>
<td>3427.9 ± 0.9</td>
<td>1.9790 ± 0.0005</td>
<td>3.9165</td>
</tr>
<tr>
<td>0</td>
<td>3423 ± 3</td>
<td>1.982 ± 0.002</td>
<td>3.9283</td>
</tr>
<tr>
<td>9</td>
<td>3422.5 ± 0.7</td>
<td>1.9822 ± 0.0004</td>
<td>3.9289</td>
</tr>
<tr>
<td>20</td>
<td>3424 ± 2</td>
<td>1.9815 ± 0.0009</td>
<td>3.9262</td>
</tr>
<tr>
<td>35</td>
<td>3426 ± 1</td>
<td>1.9801 ± 0.0007</td>
<td>3.9208</td>
</tr>
<tr>
<td>50</td>
<td>3437.3 ± 0.7</td>
<td>1.9736 ± 0.0004</td>
<td>3.8952</td>
</tr>
<tr>
<td>65</td>
<td>3448.3 ± 0.2</td>
<td>1.9673 ± 0.0001</td>
<td>3.8703</td>
</tr>
<tr>
<td>81</td>
<td>3458.9 ± 0.2</td>
<td>1.9613 ± 0.0001</td>
<td>3.8467</td>
</tr>
<tr>
<td>97</td>
<td>3464.3 ± 0.9</td>
<td>1.9582 ± 0.0005</td>
<td>3.8347</td>
</tr>
</tbody>
</table>
Table 6
Values of $g^2K^2$ for $\text{MnO}_4^{2-}$ in $\text{BaSeO}_4$ for the rotation in the ac plane and at a Frequency of 9.425 GHz

<table>
<thead>
<tr>
<th>Angle</th>
<th>$g^2K^2 \times 10^{-4}$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Line I</td>
</tr>
<tr>
<td>-9</td>
<td>0.104</td>
</tr>
<tr>
<td>0</td>
<td>0.267</td>
</tr>
<tr>
<td>9</td>
<td>0.687</td>
</tr>
<tr>
<td>20</td>
<td>1.618</td>
</tr>
<tr>
<td>35</td>
<td>3.016</td>
</tr>
<tr>
<td>50</td>
<td>4.518</td>
</tr>
<tr>
<td>65</td>
<td>5.656</td>
</tr>
<tr>
<td>81</td>
<td>6.092</td>
</tr>
<tr>
<td>97</td>
<td>5.636</td>
</tr>
</tbody>
</table>

The angle is measured from the a axis.
Figure 7. Plot of $g^2 k^2$ versus $\theta$ for MnO$_4^{2-}$ in BaSeO$_4$ in the ac plane. $\theta$ is measured from the a axis.
Figure 8. The principal $g$ axes in the symmetry plane, for $\text{MnO}_4^{2-}$ in (a) $\text{K}_2\text{CrO}_4$ and (b) $\text{BaSO}_4$. 
TABLE 7

Bond Angles and Bond Distances for $SO_4^{2-}$, $SeO_4^{2-}$ and $CrO_4^{2-}$ Tetrahedra

<table>
<thead>
<tr>
<th>Bond Angles</th>
<th>Bond Distances</th>
</tr>
</thead>
<tbody>
<tr>
<td>$SO_4^{2-}$</td>
<td></td>
</tr>
<tr>
<td>$O_{III} - S - O_{III}$</td>
<td>106°</td>
</tr>
<tr>
<td>$O_{III} - S - O_{I}$</td>
<td>108°</td>
</tr>
<tr>
<td>$O_{I} - S - O_{II}$</td>
<td>114°</td>
</tr>
<tr>
<td>$O_{II} - S - O_{III}$</td>
<td>111°</td>
</tr>
<tr>
<td>$S - O_{III}$</td>
<td>1.48 Å</td>
</tr>
<tr>
<td>$S - O_{I}$</td>
<td>1.50 Å</td>
</tr>
<tr>
<td>$S - O_{II}$</td>
<td>1.52 Å</td>
</tr>
</tbody>
</table>

$SeO_4^{2-}$ (a)

<table>
<thead>
<tr>
<th>Bond Angles</th>
<th>Bond Distances</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_{I} - Se - O_{II}$</td>
<td>116°</td>
</tr>
<tr>
<td>$O_{I} - Se - O_{III}$</td>
<td>109°</td>
</tr>
<tr>
<td>$O_{I} - Se - O_{IV}$</td>
<td>112°</td>
</tr>
<tr>
<td>$O_{II} - Se - O_{III}$</td>
<td>112°</td>
</tr>
<tr>
<td>$O_{II} - Se - O_{IV}$</td>
<td>106°</td>
</tr>
<tr>
<td>$O_{III} - Se - O_{IV}$</td>
<td>106°</td>
</tr>
<tr>
<td>$Se - O_{I}$</td>
<td>1.57 Å</td>
</tr>
<tr>
<td>$Se - O_{II}$</td>
<td>1.57 Å</td>
</tr>
<tr>
<td>$Se - O_{III}$</td>
<td>1.64 Å</td>
</tr>
<tr>
<td>$Se - O_{IV}$</td>
<td>1.66 Å</td>
</tr>
</tbody>
</table>

$CrO_4^{2-}$

<table>
<thead>
<tr>
<th>Bond Angles</th>
<th>Bond Distances</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_{III} - Cr - O_{III}$</td>
<td>105°</td>
</tr>
<tr>
<td>$O_{III} - Cr - O_{I}$</td>
<td>109°</td>
</tr>
<tr>
<td>$O_{I} - Cr - O_{II}$</td>
<td>111°</td>
</tr>
<tr>
<td>$O_{II} - Cr - O_{III}$</td>
<td>112°</td>
</tr>
<tr>
<td>$Cr - O_{III}$</td>
<td>1.65 Å</td>
</tr>
<tr>
<td>$Cr - O_{I}$</td>
<td>1.60 Å</td>
</tr>
<tr>
<td>$Cr - O_{II}$</td>
<td>1.50 Å</td>
</tr>
</tbody>
</table>

(a) Bond angles and distances for $SeO_4^{2-}$ were taken from reference 41 for $H_2SeO_4$. 
$O_{III}$ and $O_{IV}$ are the counterparts of $O_{III}$ but they are not identical to each other since they have different bond distances and angles. The site symmetry for $CrO_4^{2-}$ and $SO_4^{2-}$ is $C_s$. The principal $g$ value directions for $MnO_4^{2-}$ ion in $K_2CrO_4$ have been shown in figure 8a while those for $MnO_4^{2-}$ ion in $BaSO_4$ are shown in Figure 8b. Both the $g_z$ and $g_x$ principal axes lie in the bc plane with the $g_z$ axis displaced $5^\circ$ from a line bisecting the $O_{III}^{-}Cr-O_{III}^{-}$ bond angle. The $g_y$ principal axis direction is parallel to the a crystallographic axis. The $g_z$ values for $MnO_4^{2-}$ in both $BaSO_4$ and $BaSeO_4$ are the maximum values while the $g_z$ value for $MnO_4^{2-}$ in $K_2CrO_4$ is the minimum value. However, it has been found in $BaSeO_4$ that the maximum $g$ value and the minimum hyperfine constant are directed $4^\circ$ away from each other. This indicates that in the ac plane the principal axes of the $g$ and $A$ values are not the same. This has also been observed for $MnO_4^{2-}$ in $K_2CrO_4$. The maximum value of the hyperfine splitting constant is along the z direction for $MnO_4^{2-}$ in $K_2CrO_4$ while the minimum value is along the z direction for both $BaSO_4$ and $BaSeO_4$ hosts. Thus, as for the $g$ values, the maxima and minima for the hyperfine splitting constants are reversed.

4. Forbidden Transitions:

When the magnetic field is along the a axis, some of the 'forbidden transitions', $\Delta M_s = 1; \Delta M_I = 1$, which were less intense in other orientations, now become more intense than normal transitions. The small value of the hyperfine splitting constant relative to the quadrupole interaction gave rise to these large quadrupole induced transitions.
However, the large overlap of the two resonances (forbidden and allowed) in this region precluded a careful orientation study thus making it difficult to obtain the values for the quadrupole terms in the spin Hamiltonian.

B. Amminopentacyanoferrate (III) ION in Sodium Nitroprusside:

1. The ESR Spectra:

The crystal structure of the host, sodium nitroprusside, predicts that if Fe(CN)$_5$NH$_2^-$ ion is substituted as expected, the four molecules in the unit cell will be magnetically equivalent when the magnetic field is along the unique crystallographic axis and thus will give rise to a single resonance signal. This unique crystallographic axis is the c axis and the ESR spectrum recorded when it is along the magnetic field is shown in Figure 9. The line width of this spectrum is 6 gauss. In the crystallographic ab plane this single resonance splits into two lines since the four molecules in the unit cell now occur as two magnetically equivalent pairs. For all orientations in this plane, except when either of the two crystallographic axes are along the magnetic field, two lines were observed. Iron-57 has a nuclear spin of 1/2 but its abundance is too small to give any observable hyperfine splitting. The only hyperfine splitting observed is that due to $^{14}$N of the NH$_3$ group which is resolvable only when the magnetic field is near the z principal direction. The spectrum recorded when the magnetic field is along this direction is shown in Figure 10. The splitting was too small to be observed.
Figure 9. ESR spectrum of $\text{Fe(CN)}_5\text{NH}_3^{2-}$ in $\text{Na}_2\text{Fe(CN)}_5\text{NO}.2\text{H}_2\text{O}$ when the magnetic field is along the c axis of the crystal.
Figure 10. The ESR spectrum of Fe(CN)$_5$NH$_3$$^{2-}$ in Na$_2$Fe(CN)$_5$NO.2H$_2$O

when the magnetic field is along the Fe-NH$_3$ bond axis
in the other two principal directions of \( g \). In addition to these lines, some weak sharp lines were observed in some orientations. These weak lines were attributed to a strong field \( d^5 \) iron species by reason of the large variation in the \( g \) values with orientation. These may result from \( \text{Fe(CN)}_5\text{NH}_3^+ \) ion doping into the site such that the \( \text{NH}_3 \) group occupies the position of a CN group instead of the preferred NO site. It was not possible to analyze these weak lines well enough to characterize their principal \( g \) values.

2. Determination of the \( g \) Values:

The angular dependence of the \( g \) value has been given in equation (10). Since two resonance lines were observed for the two pairs of magnetically inequivalent molecules during the rotation in the \( ab \) plane, the magnetic field of each line was determined by measuring the frequency of the proton nuclear magnetic resonance. Six reliable values were obtained for one line and four values for the other line and with a knowledge of the point of intersection of these lines, these values were combined for the \( g \) analysis. The values of these magnetic fields used in the combined \( g \) analysis are given in Table 8. Since DPPH (diphenylpicrylhydrazyl) was used as a reference, the \( g \) values were calculated from equation (17). Using the computer program mentioned earlier the experimental \( g \) values were fitted to equation (18). The plots of the \( g \) angle \( g^2 \) against the angle \( \theta \), defined with respect to the \( z \) axis, are shown in Figures 11 and 12 respectively.

As expected, both the ESR lines coincided in the \( c \) direction, which will be called the \( y \) direction in the complex.
Table 8

H in Gauss and g Values used for the Combined g analysis for Fe(CN)$_5$NH$_3$$^{2-}$ in the ab Plane
Spectrometer Frequency 9.489 GHz

<table>
<thead>
<tr>
<th>Angle</th>
<th>H (in Gauss)</th>
<th>g</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2263 ± 0.5</td>
<td>2.9959 ± 0.001</td>
</tr>
<tr>
<td>15</td>
<td>2336.4 ± 2</td>
<td>2.9018 ± 0.002</td>
</tr>
<tr>
<td>30</td>
<td>2580.5 ± 5</td>
<td>2.6273 ± 0.005</td>
</tr>
<tr>
<td>44</td>
<td>3017.8 ± 8</td>
<td>2.2465 ± 0.006</td>
</tr>
<tr>
<td>45</td>
<td>3062.5 ± 12</td>
<td>2.2138 ± 0.008</td>
</tr>
<tr>
<td>59</td>
<td>4025.9 ± 10</td>
<td>1.6840 ± 0.004</td>
</tr>
<tr>
<td>60</td>
<td>4036.7 ± 21</td>
<td>1.6795 ± 0.008</td>
</tr>
<tr>
<td>75</td>
<td>6040.2 ± 19</td>
<td>1.1224 ± 0.004</td>
</tr>
<tr>
<td>89</td>
<td>8004.3 ± 20</td>
<td>0.8470 ± 0.002</td>
</tr>
<tr>
<td>104</td>
<td>6258.3 ± 12</td>
<td>1.0833 ± 0.002</td>
</tr>
</tbody>
</table>

The angle is measured from the z principal axis.
Figure 11. Plot of $g$ versus $\theta$ for Fe(CN)$_5$NH$_3^{2-}$ ion in Na$_2$Fe(CN)$_5$NO.2H$_2$O for rotation in the ab plane.
Figure 12. Plot of $g^2$ versus $\theta$ for $\text{Fe( CN)}_5\text{NH}_3^{2-}$ ion in $\text{Na}_2\text{Fe( CN)}_5\text{NO}.2\text{H}_2\text{O}$ for rotation in the ab plane.
The two other principal directions are in the ab plane making angles of ±31° and ±59° to the a axis. The principal axis at 31° will be called the z direction and is associated with the Fe - NH₃ direction in the complex ion. The other principal axis in this plane at -59° will be called the x direction.

3. Nitrogen Hyperfine Splitting:

When the magnetic field is near the z principal axis three hyperfine lines are observed. Nitrogen-14 has a nuclear spin $I = 1$. This splits the single resonance of iron into three components. The three lines were measured with proton NMR and the central line was used to calculate the g value. The hyperfine splitting constant was determined by taking the average of the differences between the two outer lines and the central line. This was found to have a value of 5.8 gauss. Attempts to obtain the extrapolated values of the hyperfine splitting in the other principal directions by plotting $g^2k^2$ versus $\cos^2 \theta$ were unsuccessful because both $g^2$ and $k^2$ decreased rapidly making extrapolation uncertain. In these directions the line widths were used to estimate an upper limit on the magnitude of the hyperfine interaction by taking one half of the line width. These values as well as the principal g values and the orientation of the z and x principal axes with respect to the a axis are given in Table 9.
TABLE 9

Principal $g$ and $A$ Values for $\text{Fe(CN)}_5\text{NH}_3^{2-}$ at $4{\,}^\circ\text{K}$

\begin{align*}
g_x &= 0.8470 \pm 0.002 \\
g_y &= 2.177 \pm 0.001 \\
g_z &= 2.9959 \pm 0.001 \\
A_x \leq & \quad 2.2 \times 10^{-4} \text{ cm}^{-1} \\
A_y \leq & \quad 3.7 \times 10^{-4} \text{ cm}^{-1} \\
A_z &= 8.1 \pm 0.4 \times 10^{-4} \text{ cm}^{-1} \\
\theta_z &= 31{\,}^\circ \\
\theta_x &= 59{\,}^\circ
\end{align*}

where $\theta_z$ and $\theta_x$ are the angles between the $z$ and $x$ axes and the $a$ axis of the crystal respectively.
Chapter VII

ANALYSIS OF THE SPIN HAMILTONIAN PARAMETERS

Two approaches have been used in the analysis of the spin Hamiltonian parameters. These are the Crystal Field Theory and the Molecular Orbital Theory. The Crystal Field Theory treats the interaction between the metal ion and the ligand as purely electrostatic, the ligand atoms or ions being represented as point charges. It does not take into account the partly covalent nature of the metal-ligand bonds. On the other hand, the Molecular Orbital Theory takes into account the metal-ligand interaction which it describes in terms of molecular orbitals formed by the overlap of ligand and metal orbitals. The use of these two methods in the analysis of the spin Hamiltonian is discussed below.

A. The Crystal Field Approach to the Analysis of the Spin Hamiltonian Parameters for MnO$_4^{2-}$ in BaSeO$_4$:

This theory predicts a splitting of the d orbital levels in a tetrahedral molecule such that the orbitals belonging to the E irreducible representation lie lower in energy than the T$_2$ irreducible representation. The single d electron may be either in the d$_{z^2}$ or d$_{xy}$ orbital. The axes are chosen so that the z axis is an improper rotation axis for the D$_{2d}$ symmetry while the x and y axes are in the mirror planes. A comparison of the spin Hamiltonian parameters for MnO$_4^{2-}$ in both BaSO$_4$ and BaSeO$_4$ listed in Table 4 shows that they are similar.
Kosky et al. have analyzed the spin Hamiltonian parameters for \( \text{MnO}_4^{2-} \) in \( \text{BaSO}_4 \) considering the two possible ground states of \( d_z^2 \) and \( d_{xy} \) orbitals. Their results show that while physically meaningful parameters were obtained assuming \( d_z^2 \) ground state, no physically reasonable parameters were obtained assuming \( d_{xy} \) as the ground state. Thus their analysis favors the \( d_z^2 \) ground state for \( \text{MnO}_4^{2-} \) in both \( \text{BaSO}_4 \) and \( \text{BaSeO}_4 \). In this study it was found that the linewidths of the ESR spectra are narrower than those found in the studies of Kosky et al. and Banks et al. These narrower lines resulted in greater accuracy in the determination of \( g \) and \( A \) values and hence, to the finding that their principal axes are not the same. This requires us to assume no higher a local symmetry than the site symmetry \( C_2 \). In this symmetry group the \( d_z^2, d_{x^2-y^2} \) and the \( d_{xz} \) orbitals belong to the same irreducible representation if the symmetry plane is taken to be in the \( xz \) plane. The \( d_{xy} \) orbital must lie close in energy to the \( d_z^2 \) orbital since liquid helium temperatures were required to observe a resonance signal, indicating a short spin-lattice relaxation time, \( T_1 \). The general \( d \) orbitals can be written as:

\[
\begin{align*}
\psi_{z^2} &= a_d z^2 + b_d x^2-y^2 + c_d xz \\
\psi_{x^2-y^2} &= a_{x^2-y^2} + b_{x^2-y^2} + c_{x^2-y^2} \\
\psi_{xz} &= a_{xz} + b_{xz} + c_{xz} \\
\psi_{xy} &= e_d xy + f_d yz \\
\psi_{yz} &= e_d yz + f_d xy
\end{align*}
\]
Normalization and orthogonalization require that

\[ \begin{align*}
ab_1 + ba_1 + cc_1 &= 0; \\
ac_2 + bb_2 + ca_2 &= 0; \\
ab_1b_2 + b_1c_2 + c_1a_2 &= 0; \\
ab_1a_2 + b_1b_2 + c_1c_2 &= 1; \\
e^2 + f^2 &= 1. 
\end{align*} \]

If the ground state is \( \psi_2^2 \), perturbation method can be used to estimate the effects of the spin-orbit terms since the mixing of the closest state, \( \psi_{xy} \), by spin-orbit coupling gives terms of small magnitude. The resulting two Kramers doublets were obtained by McGarvey (42) and are given by:

\[ \psi_+ = \psi_{x^2}^+ + iA \psi_{xy}^+ - iB \psi_{yz}^+ - (1/2)C \psi_{x^2-y^2}^- + (1/2)D \psi_{xz}^- \\
+ (i/2)E \psi_{xy}^- + (i/2)F \psi_{yz}^- \]

\[ \psi_- = \psi_{x^2}^- + iA \psi_{xy}^- + iB \psi_{yz}^- + (1/2)C \psi_{x^2-y^2}^+ - (1/2)D \psi_{xz}^+ \\
+ (i/2)E \psi_{xy}^+ + (i/2)F \psi_{yz}^+ \]

where \( \psi_+ \) and \( \psi_- \) are spin up and spin down wave functions,

\[ A = \left( \frac{2be + cf}{2} \right) \frac{\xi}{\Delta E_{xy}}; \]

\[ B = \left( \frac{ce - 2bf}{2} \right) \frac{\xi}{\Delta E_{yz}}; \]

\[ C = \left[ c(\sqrt{3}b_1 - a_1) - c_1(\sqrt{3}a - b) \right] \frac{\xi}{\Delta E_{x^2-y^2}}; \]

\[ D = \left[ e(\sqrt{3}a + b - fc) \right] \frac{\xi}{\Delta E_{xz}}; \]

\[ E = \left[ f(\sqrt{3}a + b) + ec \right] \frac{\xi}{\Delta E_{yz}}; \]

\[ F = \left[ e(\sqrt{3}a + b) - fc \right] \frac{\xi}{\Delta E_{yz}} \]

and \( \xi \) is the spin orbit coupling constant, \( \Delta E_{yz} \), \( \Delta E_{xy} \), \( \Delta E_{xz} \) and \( \Delta E_{x^2-y^2} \) are the energy differences between the ground state.
state \( \psi_z^2 \) and the states \( \psi_{yz}, \psi_{xy}, \psi_{xz} \) and \( \psi_{x^2-y^2} \).

The actual values of the coefficients in equation (20) depend strongly upon the choice of the coordinate axes \( x \) and \( z \). Since there is no symmetry requirement for choosing these axes, we shall choose the most convenient which is the axes that makes \( c = 0 \). This is convenient because it eliminates one variable and the axes will be approximately the same as the principal axes of the \( A \) tensor since the major contribution to off-diagonal terms in the \( A \) comes from the admixture of \( d_{xz} \) into the ground state. Also this choice eliminates terms involving \( a_1, b_1, c_1, a_2, b_2 \) and \( c_2 \) from the resulting equations so that only two independent orbital coefficients (\( b \) and \( f \)) will appear in these equations.

The \( g \) values are then found by operating within the ground state doublet \( \psi^+ \) with the magnetic Zeeman operator,

\[
\beta \hbar (b + 2.0023 g) \text{ and this gives:}
\]

\[
g_z = 2.0023 - 8b^2 [\eta_2 + f^2 (\eta_1 - \eta_2)]
\]

\[
g_x = 2.0023 - 2(\sqrt{3}a + b)^2 [\eta_1 + f^2 (\eta_2 - \eta_1)]
\]

\[
g_y = 2.0023 - 2(\sqrt{3}a - b)^2 \eta_3
\]

\[
g_{xz} = 4bef(\sqrt{3}a + b)(\eta_2 - \eta_1)
\]

where \( g_{yz} \) is the off-diagonal element of \( g \) tensor in the \( xy \) plane and \( \eta_1 = \xi/\Delta E_{yz}, \eta_2 = \xi/\Delta E_{xy}, \eta_3 = \xi/\Delta E_{xz} \).

Similarly the \( A \) values were found by McGarvey \(^{(42)} \) to be:

\[
A_z = -K + P((4/7)(1 - 2b^2) + (\eta_3/7)(\sqrt{3}a - b)(\sqrt{3}a + 3b)
\]

\[
+ (1/7)(\sqrt{3}a + b)(\sqrt{3}a - 3b)[\eta_1 + f^2 (\eta_2 - \eta_1)]
\]
\[ A_x = -K + P\{(2/7)(1 - 2b^2) - (4\sqrt{3}/7)ab - (4\sqrt{3}/7)ab \times \{n_2 + \frac{f^2}{b(n_1 - n_2) - (n_3/7)(\sqrt{3}a - b)(\sqrt{3}a + 3b)} + (g_x - 2.0023)\}; \]

\[ A_y = -K + P\{(2/7)(1 - 2b^2) + (4\sqrt{3}/7)ab + (4\sqrt{3}/7)ab \times \{n_2 + \frac{f^2}{b(n_1 - n_2) - (1/7)(\sqrt{3}a + b)(\sqrt{3}a - 3b)} + (g_y - 2.0023)\}; \]

\[ A_{xz} = (2/7)efbP(n_2 - n_1)(15\sqrt{3}a + 11b); \]

\[ A_{zx} = 2efbP(n_2 - n_1)[2b(a + \sqrt{3}b) - (a/7)(3a + \sqrt{3}b)] \]

where \( P = 2.0023g_N^B g_{e_n}^e < r^{-3}>_{ave} \) and \( K \) is the Fermi contact term.

In deriving equations (21) and (22) it was assumed that \( \xi/\Delta E_{x^2-y^2} = n_3 \). This quantity may be approximated because it appears only in terms whose values are small.

To diagonalize the \( g \) tensor, the \( x \) and \( z \) axes must be rotated. The angle through which they must be rotated is given by:

\[ \tan 2\phi = \frac{2g_{xz}}{(g_x - g_z)} \]

(23)

To solve for seven unknowns in equations (21) and (22), it was assumed that the values of \( A_x, A_y, A_z, g_x, g_y \) and \( g_z \) are the same as the principal values determined experimentally and that \( \phi \) is equal to the angle between the principal \( z \) axes for the \( g \) and \( A \) tensors. Equations (21) and (22) were solved by successive approximations. \( A_z \) was assumed positive and \( A_x \) and \( A_y \) negative since assuming \( A_z \) negative resulted in a smaller
value for \( P \) indicating considerable delocalization of the unpaired electron. The values of the parameters obtained by the solution of the above equations are given in Table 10. In obtaining the parameters given in this Table, it was assumed that the difference between the coordinate systems of equations (21) and (22) and the principal axes of the \( A \) tensor was negligible. This assumption can be checked by using these parameters to calculate the angle \( \phi(A) \) between the principal \( z \) axis and the coordinate \( z \) axis. The angle of rotation needed to diagonalize the hyperfine term of equation (22) is given by:

\[
\tan 2\phi(A) = \frac{2(A_Z A_{ZX} + A_X A_{XZ})}{A_Z^2 - A_X^2 + A_{XZ}^2 - A_{2X}^2}
\]

(24)

Using the parameters given in Table 10 a value of 0.14° is obtained for \( \phi(A) \), which is less than the experimental error.

The above analysis is similar to that done by Kosky et al.\(^{(4)}\) for \( \text{MnO}_4^{2-} \) in \( \text{BaSO}_4 \) and by Banks et al.\(^{(5)}\) for \( \text{CrO}_4^{3-} \) in \( \text{Ca}_2\text{PO}_4\text{Cl} \) except for the assumption of a lower symmetry. These workers did not detect any difference in the principal axes of the \( S \) and \( A \) values and therefore assumed an effective symmetry of \( C_{2v} \) which requires \( f = 0 \) in equations (21) and (22). The results of their analysis are also given in Table 10 for comparison with the results obtained in this study. In these analyses the unpaired electron was found to be located primarily in a \( d_{z^2} \) orbital. The values of \( b^2 \) found for \( \text{MnO}_4^{2-} \) in both \( \text{BaSO}_4 \) and \( \text{BaSeO}_4 \) are found to be larger than that found for \( \text{CrO}_4^{3-} \) in \( \text{Ca}_2\text{PO}_4\text{Cl} \). These values indicate a relatively small admixture of \( d_{x^2-y^2} \) orbital for \( \text{CrO}_4^{3-} \) but larger for \( \text{MnO}_4^{2-} \) in the ground state. In \( \text{CrO}_4^{3-} \) in \( \text{Ca}_2\text{PO}_4\text{Cl} \) the
<table>
<thead>
<tr>
<th></th>
<th>MnO$_4^{2-}$</th>
<th>CrO$_4^{3-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BaSeO$_4$</td>
<td>BaSO$_4$</td>
</tr>
<tr>
<td>$K$ (10$^{-4}$ cm$^{-1}$)</td>
<td>59.7</td>
<td>48</td>
</tr>
<tr>
<td>$P$ (10$^{-4}$ cm$^{-1}$)</td>
<td>141.7</td>
<td>179</td>
</tr>
<tr>
<td>$\eta_1$</td>
<td>0.00657</td>
<td>0.0061</td>
</tr>
<tr>
<td>$\eta_2$</td>
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<td>0.12</td>
</tr>
<tr>
<td>$\eta_3$</td>
<td>0.00775</td>
<td>0.0069</td>
</tr>
<tr>
<td>$b^2$</td>
<td>0.017</td>
<td>0.023</td>
</tr>
<tr>
<td>$f^2$</td>
<td>0.0003</td>
<td>&lt; 0.0001</td>
</tr>
</tbody>
</table>

a. This work
b. Reference 4
c. Reference 5
d. Reference 6
e. Assumed equal in analysis
accidental equality of the terms \((\sqrt{3}a + b)^2\eta_1\) and \((\sqrt{3}a-b)^2\eta_3\) gave rise to axial symmetry. This is not so for \(\text{MnO}_4^{2-}\) in both \(\text{BaSO}_4\) and \(\text{BaSeO}_4\). Thus as a result of the smaller \(b^2\) value there is a lesser admixture of \(d_{x^2-y^2}\) orbital in the ground state of \(\text{CrO}_4^{3-}\) than in that of \(\text{MnO}_4^{2-}\). For the two host lattices, \(\text{BaSO}_4\) and \(\text{BaSeO}_4\), the \(A\) values are highly anisotropic and this arises from the larger \(b^2\) values. The large value of \(\eta_2\) for both ions relative to the values of \(\eta_1\) and \(\eta_3\) confirm the assumption that \(AE_{xy}\) is small and hence the distortion from tetrahedral symmetry is not large.

The difference in the ground states for \(\text{MnO}_4^{2-}\) in \(\text{BaSO}_4\), \(\text{BaSeO}_4\) and in \(\text{K}_2\text{CrO}_4\) is puzzling. The three host lattices belong to the same space group and their oxyanion tetrahedra have similar bond angles. Before this work was done it was thought that the different ground states of \(\text{MnO}_4^{2-}\) in \(\text{BaSO}_4\) and in \(\text{K}_2\text{CrO}_4\) could be due to shorter bond distances of \(\text{SO}_4^{2-}\). \(\text{K}_2\text{MnO}_4\) and \(\text{KMnO}_4\) crystalise in the same space group, \(\text{Pmna}\), and their bond angles and bond distances are listed in Table 11. The bond angles of these oxyanions are essentially tetrahedral. The Mn-O bond distance for \(\text{MnO}_4^{2-}\) is slightly larger than those of \(\text{MnO}_4^{2-}\). The longer bond distance of \(\text{MnO}_4^{2-}\) is probably due to the extra electron which expands the metal ion, but does not distort the bond angles of the oxyanion. In \(\text{K}_2\text{CrO}_4\), \(\text{BaSO}_4\) and \(\text{BaSeO}_4\) the bond angles are similarly distorted from the tetrahedral angles. The bond distances of \(\text{SeO}_4^{2-}(41)\) and \(\text{CrO}_4^{2-}\) are slightly shorter than those of \(\text{MnO}_4^{2-}\) while that of \(\text{SO}_4^{2-}\) is much shorter. Thus in the substitution of \(\text{MnO}_4^{2-}\) in \(\text{BaSO}_4\) the distortion could have resulted in a different anisotropy and
TABLE 11

Bond Angles and Bond Distances for MnO$_4^-$ and MnO$_4^-$ Tetrahedra

<table>
<thead>
<tr>
<th>Bond Angles</th>
<th>Bond Distances</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$<em>{\text{III}}$ - Mn - O$</em>{\text{III}}$ 109$^\circ$</td>
<td>Mn - O$_{\text{III}}$ 1.66 Å</td>
</tr>
<tr>
<td>O$<em>{\text{III}}$ - Mn - O$</em>{\text{I}}$ 110$^\circ$</td>
<td>Mn - O$_{\text{I}}$ 1.65 Å</td>
</tr>
<tr>
<td>O$<em>{\text{I}}$ - Mn - O$</em>{\text{II}}$ 110$^\circ$</td>
<td>Mn - O$_{\text{II}}$ 1.67 Å</td>
</tr>
<tr>
<td>O$<em>{\text{II}}$ - Mn - O$</em>{\text{III}}$ 108$^\circ$</td>
<td></td>
</tr>
</tbody>
</table>

(a) G. Palenik, Inorg. Chem. 6, 503 (1967)

(b) M. Greenblatt, E. Banks, and B. Post, Acta Crystallogr. 23, 166 (1967)
hence a different ground state. Both $\text{SeO}_4^{2-}$ and $\text{CrO}_4^{2-}$ have comparable lattice size yet $\text{MnO}_4^{2-}$ has the same ground state in $\text{BaSeO}_4$ as in $\text{BaSO}_4$. Thus the different ground state in $\text{K}_2\text{CrO}_4$ cannot be due solely to the difference in the size of the host anion.

B. Molecular Orbital Theory:

In the previous studies of $\text{MnO}_4^{2-}$ in $\text{BaSO}_4$ and $\text{K}_2\text{CrO}_4$ the authors did not perform a molecular orbital analysis to determine the charge transfer in the Mn–O bond. Because of the accuracy in the determination of the spin Hamiltonian parameters in this study, a molecular orbital analysis similar to that done by McGarvey\(^{(30)}\) on $\text{CrO}_4^{3-}$ was carried out to determine the charge transfer in the $\text{MnO}_4^{2-}$. The coordinate axes in the complex are taken to be those shown in Figure 13. The angle $\theta$ is chosen so that the $z$ axis is an improper rotation axis for the $D_{2d}$ symmetry while the $x$ and $y$ axes are in the mirror plane. In $\text{MnO}_4^{2-}$, the Mn(VI) is surrounded by four oxygen atoms in a distorted tetrahedral configuration. Each oxygen atom is assumed to have available the $2p_x$, $2p_y$, and $2p_z$ orbitals for the formation of molecular orbitals with the $d$ orbitals of the central ion. The molecular orbitals are chosen for the $D_{2d}$ symmetry since it is assumed that these are good enough for our calculations.

The localized antibonding molecular orbitals are:

$$A_1 = \beta_2 z^2 - (1/2) \beta_2' z^2 (p_x^1 - p_x^2 - p_x^3 + p_x^4);$$

$$E_{xz} = \alpha_{xz} d_{xz} + (\alpha_{xz}'/2) \cos \omega (p_x^1 - p_z^4) - (\alpha_{xz}'/2\sqrt{2}) \sin \omega x (p_x^1 - p_x^4 - \sqrt{3} p_y^2 + \sqrt{3} p_y^3);$$
Figure 13: Coordinate axes used in the MO calculations for MnO$_4^-$
\[ E_{yz} = \alpha_{yz} \sigma_{y} - (\alpha'_{yz}/\sqrt{2}) \cos \omega (p_z^2 - p_z^3) - (\alpha'_{yz}/2\sqrt{2}) \sin \omega \times (p_x^3 - p_x^4 - \sqrt{3}p_y^1 + \sqrt{3}p_y^4); \]

\[ B_1 = \alpha_{x^2-y^2} d_{x^2-y^2} - (\alpha'_{x^2-y^2}/2) \cos \rho (-p_x^1 - p_x^2 + p_x^3 - p_x^4) \]

\[ - (\alpha'_{x^2-y^2}/2) \sin \rho (-p_z^1 + p_z^2 + p_z^3 - p_z^4); \]

\[ B_2 = \beta_{xy} \sigma_{xy} - (\beta'_{xy}/2) ( -p_y^1 + p_y^2 + p_y^3 - p_y^4) \]

The angles \( \omega \) and \( \rho \) are molecular orbital parameters and their values are chosen to maximize the overlap integrals. The orbitals are designated by the irreducible representations of the \( D_{2d} \) symmetry to which they belong. In the previous work on \( \text{CrO}_4^{3-} \), it was assumed that distortion from tetrahedral symmetry was so small that \( \alpha_{xz} \) is equal to both \( \alpha_{yz} \) and \( \alpha_{x^2-y^2} \) and that \( \beta_{xy} \) is equal to \( \beta_{xy} \). The analysis was then done in terms of the simpler equations applicable to the axial symmetry of \( D_{2d} \). In this approach \( g_4 \) and \( A_4 \) were obtained by averaging the experimental \( x \) and \( y \) values. This calculation was done for \( \text{MnO}_4^{2-} \) in \( \text{BaSO}_4 \) and \( \text{BaSeO}_4 \) and the resulting charges for the manganese ion are reported later in Tables 13 and 14 as \( q_{axial} \). The larger anisotropies observed for \( \text{MnO}_4^{2-} \) suggested that an alternative method of calculation might be appropriate.

The parameters that were obtained in the previous analysis and listed in Table 10 may be approximately calculated from the molecular orbitals in the following manner:
\[ P = 2.0023 g_N \delta e \delta_N < A_1 | x^{-3} | A_1 > = \beta_2^2 P_d \]

\[ P_d = 2.0023 g_N \delta e \delta_N < d_z^2 | x^{-3} | d_z^2 > \]

\[ \eta_1 = (1/3) < A_1 | l_x | E_{yz} > < E_{yz} | l_x | A_1 > / \Delta E_{yz} \]

\[ = (\xi_d / \Delta E_{yz}) \{ P_\pi (z^2) P_\sigma (yz) - \alpha_{yz} \alpha'_{yz} \beta_{z^2} \beta'_{z^2} [\cos \omega - (\sqrt{3}/2) \times \sin \theta \sin \omega] / \sqrt{6} \} \]

\[ \eta_2 = (1/4) < A_1 | l_z | B_2 > < B_2 | l_z | A_1 > / \Delta E_{xy} \]

\[ = (\xi / \Delta E_{xy}) \{ P_\pi (xy) P_\sigma (x^2 - y^2) - \alpha_{x^2 - y^2} \alpha'_{x^2 - y^2} \beta_{xy} \beta'_{xy} \times (\sin \theta \sin \varphi - \cos \theta \cos \varphi) / 2 \} \]

\[ \eta_3 = (1/3) < A_1 | l_y | E_{xz} > < E_{xz} | l_y | A_1 > / \Delta E_{xz} \]

\[ = (\xi / \Delta E_{xz}) \{ P_\pi (z^2) P_\sigma (xz) - \alpha_{xz} \alpha'_{xz} \beta_{z^2} \beta'_{z^2} [\cos \omega - (\sqrt{3}/2) \times \sin \theta \sin \omega] / \sqrt{6} \} \]

where \( \xi_d \) is the spin orbit coupling constant for the \( d \) electron and \( P_\sigma \) and \( P_\pi \) are the charge densities on the manganese ion in the \( E \) and \( A_1 \) orbitals respectively. Mulliken\(^{(43)}\) defined these terms as:

\[ P_\sigma = \alpha^2 - \alpha' \alpha s_A \]
\[ P_\pi = \beta^2 - \beta' \beta s_E \]

\( \alpha, \alpha', \beta \) and \( \beta' \) have been defined in equation (25). \( s_A \) and \( s_E \) are the overlap integrals whose values have been calculated from the overlap integrals of Jaffe\(^{(44)}\) and Jaffe and Doak\(^{(45)}\) who gave the values of the integrals \( \int d_z^2 p_x^1 d\tau \) and \( \int d_y^2 p_z^2 d\tau \). The spin orbit contribution of the ligand oxygen atom has not been taken into account because of its relatively small value compared to that of the manganese ion. The angle \( 2 \theta \) is the
angle between two bonds and is taken as 109.5° for these calculations. Following the procedure of McGarvey (30) the contribution of the excited state, arising from the promotion of a bonding electron in the \( ^{+}E_{xz,yz} \) orbital to the \( A_1 \) orbital, to the spin Hamiltonian parameters is considered. The wave function of the \( ^{+}E_{yz} \) bonding molecular orbital is given as:

\[
^{+}E_{yz} = \alpha_0 y_z + (\alpha'_0 / \sqrt{3}) \cos \omega (p_x^2 - p_z^2) + (\alpha'_0 / 2 \sqrt{2}) \sin \omega (p_x^2 - p_y^2 - \sqrt{3} p_y^1 + \sqrt{3} p_y^4) \tag{28}
\]

The additional contribution to the parameter \( \eta_1 \) is:

\[
\Delta \eta_1 = -(\xi d / \Delta E_{yz}^+) \{ \Pi_{s}(z^2) [1 - \Pi_{o}(yz)] + \alpha_0 y_z + \alpha'_0 \beta_{z} z \beta'_{z} z \times [\cos \omega - (\sqrt{3}/2) \sin \theta \sin \omega] / \sqrt{6} \} \tag{29}
\]

Similar expressions are obtained for \( \Delta \eta_2 \) and \( \Delta \eta_3 \). In obtaining equation (29) use was made of the fact that the orthogonality of \( E_{yz} \) and \( ^{+}E_{yz} \) requires that

\[
(1 - \Pi_{o}) = \alpha^2 - \alpha_a \gamma \Sigma \tag{30}
\]

The number of electrons in the metal d orbitals of the \( \sigma \) bonding orbitals is

\[
6 - 2 \Pi_{o}(xy) - 2 \Pi_{o}(yz) - 2 \Pi_{o}(x^2-y^2) \tag{31}
\]

and for the bonding \( \pi \) orbitals is

\[
4 - 2 \Pi_{s}(xy) - 2 \Pi_{s}(z^2). \tag{32}
\]

The effective charge, \( Q \), on the manganese ion is given by:

\[
Q = -3 + 2 \Pi_{o}(xz) + 2 \Pi_{o}(yz) + 2 \Pi_{o}(x^2-y^2) + 2 \Pi_{s}(xy) + 2 \Pi_{s}(z^2) \tag{33}
\]

From this molecular orbital analysis the only values that can be determined are those of \( \Pi_{s}(z^2) \), \( \Pi_{o}(xz) \) and \( \Pi_{o}(yz) \). \( \Pi_{s}(xy) \) has, therefore, been estimated as equal to \( \Pi_{s}(z^2) \) while \( \Pi_{o}(x^2-y^2) \) has been taken as the average of the values of
$P_o(xz)$ and $P_o(yz)$. The values of the spin orbit coupling constant, $t_d$, for the $d$ orbitals of manganese ion can be calculated from the spectroscopic tables (46) and the values of $P_d$ can be determined from Hartree-Fock computations (47).

The values of $\Delta E_{xz}$ and $\Delta E_{yz}$ for $\text{MnO}_4^{2-}$ in $\text{BaSO}_4$ have been obtained from spectroscopic studies (4) and the same values have been assumed for $\text{MnO}_4^{2-}$ in $\text{BaSeO}_4$ crystals. Overlap integrals can be estimated from tables (44, 45) using shielding parameters obtained by Clementi and Raimondi (48). The values of these parameters used in the computations are given in Table 12. Following the work (30) on $\text{CrO}_4^{3-}$, a self consistent method in which the values of the parameters given in Table 12 for an assumed charge are used to calculate the charge density in each orbital. This calculated charge density is then compared with the assumed charge. The values of $\omega$ and charge densities in the individual molecular orbitals obtained by using equation (31) are given in Table 13 for the case of $\Delta E_{xy, yz}$ equal to infinity and $\Delta E_{xz, yz}^{\pm}$ equal to 33,000 cm$^{-1}$. Values of $\omega$ obtained using the axial approximation employed on $\text{CrO}_4^{3-}$ are given for comparison. For $\text{MnO}_4^{2-}$ in $\text{BaSO}_4$ there is no solution of the equation for an assumed charge of +1.

The values of $\omega$ obtained from the self consistent method and the molecular charge densities are given in Table 14. The values of $\omega$ and $\omega_{axial}$ are seen to be very similar indicating that their determination is not too sensitive to the different approximations used in the two methods of computation. The values of $P_o$ are found to be slightly higher when estimated by the axial approximation and the values of $P_{\pi}$ are lower.
TABLE 12
Parameters used in MO Computations

<table>
<thead>
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<th>Charge</th>
<th>+1</th>
<th>+2</th>
<th>+3</th>
<th>+4</th>
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<tbody>
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<td>$\xi_d$ (cm$^{-1}$)</td>
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<td>297</td>
<td>361</td>
<td>405</td>
</tr>
<tr>
<td>$P_d$ (10$^{-4}$ cm$^{-1}$)</td>
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<td>187</td>
<td>211</td>
<td>235</td>
</tr>
<tr>
<td>$s_A$</td>
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<td>0.044</td>
<td>0.042</td>
<td>0.039</td>
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<tr>
<td>$s_E$</td>
<td>0.142</td>
<td>0.134</td>
<td>0.125</td>
<td>0.118</td>
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<tr>
<td>$\Delta E_{xz}$ (cm$^{-1}$)</td>
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<td>10,064</td>
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<tr>
<td>$\Delta E_{yz}$ (cm$^{-1}$)</td>
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<tr>
<td>$\Delta E_{xz, yz}$ (cm$^{-1}$)</td>
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<td></td>
<td>$\geq$33,000</td>
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</tr>
</tbody>
</table>
TABLE 13
MO Results for MnO$_4^{2-}$ in BaSO$_4$ and BaSeO$_4$

<table>
<thead>
<tr>
<th>Assumed Charge</th>
<th>$\Delta E_{xz,yz}^\pm$ (cm$^{-1}$)</th>
<th>$P_{\sigma}(xz)$</th>
<th>$P_{\sigma}(yz)$</th>
<th>$P_{\pi}(z^2)$</th>
<th>$Q$</th>
<th>$Q_{axial}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaSeO$_4$</td>
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<tr>
<td>+4</td>
<td>$\infty$</td>
<td>0.474</td>
<td>0.415</td>
<td>0.583</td>
<td>1.418</td>
<td>1.656</td>
</tr>
<tr>
<td>+3</td>
<td>$\infty$</td>
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<td>0.398</td>
<td>0.651</td>
<td>1.515</td>
<td>1.689</td>
</tr>
<tr>
<td>+2</td>
<td>$\infty$</td>
<td>0.461</td>
<td>0.397</td>
<td>0.738</td>
<td>1.790</td>
<td>1.916</td>
</tr>
<tr>
<td>+1</td>
<td>$\infty$</td>
<td>0.445</td>
<td>0.379</td>
<td>0.852</td>
<td>2.028</td>
<td>2.114</td>
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<tr>
<td>+4</td>
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<td>0.578</td>
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<td>0.651</td>
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<tr>
<td>+1</td>
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<td>0.538</td>
<td>0.852</td>
<td>2.930</td>
<td>2.949</td>
</tr>
<tr>
<td>BaSO$_4$</td>
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<td></td>
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<tr>
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<td>$\infty$</td>
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<td>0.291</td>
<td>0.744</td>
<td>1.081</td>
<td>1.135</td>
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<td>+3</td>
<td>$\infty$</td>
<td>0.304</td>
<td>0.270</td>
<td>0.832</td>
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<td>0.481</td>
<td>0.744</td>
<td>2.188</td>
<td>2.170</td>
</tr>
<tr>
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<td>0.459</td>
<td>0.832</td>
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<td>0.437</td>
<td>0.946</td>
<td>2.543</td>
<td>2.575</td>
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</table>
### TABLE 14

Self Consistent Values for MnO$_4^{2-}$

<table>
<thead>
<tr>
<th>$\Delta E^{+}_{xz,yz}$</th>
<th>$Q$</th>
<th>$Q_{\text{axial}}$</th>
<th>$P_{\sigma}(xz)$</th>
<th>$P_{\sigma}(yz)$</th>
<th>$P_{\pi}(z^2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BaSeO$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\infty$</td>
<td>1.830</td>
<td>1.930</td>
<td>0.458</td>
<td>0.394</td>
<td>0.757</td>
</tr>
<tr>
<td>33,000</td>
<td>2.557</td>
<td>2.607</td>
<td>0.604</td>
<td>0.559</td>
<td>0.690</td>
</tr>
<tr>
<td></td>
<td>BaSO$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\infty$</td>
<td>1.564</td>
<td>1.585</td>
<td>0.281</td>
<td>0.244</td>
<td>0.996</td>
</tr>
<tr>
<td>33,000</td>
<td>2.445</td>
<td>2.445</td>
<td>0.473</td>
<td>0.447</td>
<td>0.895</td>
</tr>
</tbody>
</table>
but the differences are not large. The value of $\Delta E^{\pm}_{xz, yz}$ is not known but the value of 33,000 cm$^{-1}$ assumed is not unreasonable on the basis of the spectroscopic studies(4) and the values of $\mu$ obtained with it are therefore, thought to be close to the correct values.

Tables 13 and 14 show that the effective charge on Mn(VI) ion is about 2. Since the effective charge is lowered the d orbital radius increases as the covalency of the bond increases. The $P$ value defined in equation(26)is proportional to $r^{-3}$. Hence the $P$ value will decrease with increasing charge transfer. The $P$ values are $287 \times 10^{-4}$ cm$^{-1}$ for Mn(VI) ion and $189 \times 10^{-4}$ cm$^{-1}$ for Mn(II) ion. The experimental values of $141.7 \times 10^{-4}$ cm$^{-1}$ for MnO$_4^{2-}$ in BaSeO$_4$ and $179 \times 10^{-4}$ cm$^{-1}$ for MnO$_4^{2-}$ in BaSO$_4$ indicate that the effective charges are more nearly +2 than the formal charge of +6. It appears that for MnO$_4^{2-}$ the high oxidation number requires some charge transfer to stabilize the complex ion. Although the effective charge on manganese is the same in both BaSeO$_4$ and BaSO$_4$ lattices, there is a change in the pattern in which the charge transfer takes place. Table 10 shows that more charge transfer takes place through the $\sigma$ orbitals and less through the $\pi$ orbitals when MnO$_4^{2-}$ substitutes for the smaller SO$_4^{2-}$ ion than when it substitutes for the larger SeO$_4^{2-}$ ion. Very little charge transfer via the $\pi$ orbitals is indicated in the BaSO$_4$ by the data.
C. The Molecular Orbital Approach to the Analysis of the Spin Hamiltonian Parameters for Fe(CN)$_5$NH$_3$$^{2-}$ in Na$_2$Fe(CN)$_5$NO, 2H$_2$O:

In the previous studies on strong field $t_{2g}^5$ systems (9-16) it was always assumed that distortions from octahedral symmetry were of the type that kept the principal axes coincident with the bond axes and, therefore, the appropriate d orbitals to be used in the theory were $d_{xy}$, $d_{xz}$ and $d_{yz}$. The system studied here does not meet this condition since the site symmetry requires that the x and y axes bisect the equatorial Fe-CN bond angles. There is only one plane of symmetry in the host crystal, but $C_{2v}$ symmetry will be assumed in the following discussion. The molecular orbitals for the $t_{2g}$ set of orbitals can be written as:

$$|x^2-y^2> = \alpha d_{x^2-y^2} - (\alpha_1/2)(p_x^3 + p_y^4 - p_x^5 - p_y^6)$$

$$- (\alpha_2/2) (-p_x^3 + p_y^4 - p_x^5 + p_y^6)$$

$$|xz> = \beta d_{xz} - (\beta_1/2)(p_x^3 + p_z^4 - p_x^5 + p_z^6)$$

$$- \beta_2 p_x^1 + \beta_3 p_x^2$$

$$|yz> = \gamma d_{yz} - (\gamma_1/2)(p_z^3 - p_x^4 + p_z^5 - p_x^6)$$

$$- \gamma_2 p_y^1 + \gamma_3 p_y^2$$

(32)

The coordinate axes are those shown in Figure 14. The z axis is along the Fe-NH$_3$ bond axis while the x and y axes are in the molecular plane. If now the spin orbit coupling and tetragonal distortion effects are taken into account the two
Figure 14. Coordinate axes used in the MO calculations for $\text{Fe(CN)}_5\text{NH}_3^{2-}$.
Kramers doublets can be written as:

\[ \psi_+ = d |xz\rangle + ie |yz\rangle - f |(x^2-y^2)\rangle \]
\[ \psi_- = d |xz\rangle - ie |yz\rangle - f |(x^2-y^2)\rangle \]

where \( |xz\rangle \) represents the molecular orbital with +1/2 spin belonging to the irreducible representation of \( \psi_{xz} \). The one electron hole formalism is used here to represent the \( t_{2g}^5 \) configuration. The constants \( d, e \) and \( f \) are found by degenerate perturbation theory to be

\[ f = \frac{\eta_2}{\eta_3} \left[ \frac{1}{2} \frac{\eta_1 \eta_3}{\eta_2} - E \right] \]  
\( (34a) \)

\[ e = \frac{2}{\eta_3} \frac{((1/4) \eta_1^2 + [1 + (1/2) \epsilon] E - E^2) d}{[1 + (1/2) \epsilon + (1/2)(\eta_1 \eta_2/\eta_3) - E]} \]  
\( (34b) \)

\[ d^2 + e^2 + f^2 = 1 \]  
\( (34c) \)

\[ E = (1/3) [1 + (3/2) \epsilon)] + x \]  
\( (34d) \)

where

\[ x = (2/3) [1 + (3/4) \epsilon^2 + (3/4)(\eta_1^2 + \eta_2^2 + \eta_3^2)] \] \[ \cos(\phi/3, \phi/3 + 120, \phi/3 + 240) \]

\[ \cos \phi = [(1 - (9/4) \epsilon^2 + (9/8)(\eta_1^2 - \eta_2^2 + \eta_3^2) + (9/8)(\eta_2^2 - \eta_3^2) - (27/16) \epsilon(\eta_2^2 - \eta_3^2)] \] \[ -(27/8) \eta_1 \eta_2 \eta_3]/[1 + (3/4) \epsilon^2 + (3/4)(\eta_1^2 + \eta_2^2 + \eta_3^2)] \] \( (3/2) \)

\[ \eta_1 = \xi_1/\Delta; \quad \eta_2 = \xi_2/\Delta; \quad \eta_3 = \xi_3/\Delta \] and \( \epsilon = \delta/\Delta \)

\[ \Delta = E_{x^2-y^2} - (E_{xz} - E_{yz})/2 \] and \( \delta = E_{yz} - E_{xz} \)

The spin orbit coupling constants \( \xi_n \) are defined as

\[ \xi_1 = a_1 \xi_{3d}; \quad \xi_2 = a_2 \xi_{3d}; \quad \xi_3 = b \xi_{3d} \]

\( E_{x^2-y^2} \) is the energy of the \( |x^2-y^2\rangle \) orbital while \( E_{yz} \) and
$E_{xz}$ are the energies of $|yz\rangle$ and $|xz\rangle$ molecular orbitals in the absence of the spin orbit coupling.

Since only three $g$ values are obtained experimentally, it has been necessary in the following analysis of the $g$ values to make the usual simplifying assumption that

$$\eta_1 = \eta_2 = \eta_3.$$  

From equation (33) the following expressions for the $g$ values can be obtained:

$$g_x = 2.0023(d^2 - e^2 - f^2) - 4efk$$
$$g_y = 2.0023(d^2 - e^2 - f^2) + 4efk$$
$$g_z = 2.0023(d^2 + e^2 - f^2) + 4dek$$

(35)

where $k = i\langle xz|\hat{L}_z|yz\rangle = i\langle yz|\hat{L}_x|x^2-y^2\rangle = i\langle xz|\hat{L}_y|x^2-y^2\rangle$. Consistent with the assumption about $\eta$, it has been assumed that $k$, the orbital reduction parameter, is the same for all three molecular orbitals. In deriving equation (35), it was also assumed that the second order contribution from the $e_g$ orbitals can be neglected compared to the very large first order contributions from the $t_{2g}$ orbitals.

Using the experimental values of $g$, equation (35) can be solved for $d, e, f$ and $k$. Furthermore from $d, e,$ and $f$, values can be obtained for $\eta$ and $\varepsilon$ using equation (34). The magnitude of $g_z$ can be as large as 3.0 only if $f$ in equation (35) is small and this is so if $\eta$ is positive. $\varepsilon$ must also be positive to keep $|g_y|$ greater than $|g_x|$. Only two solutions are possible for equations (34) and (35), one for $g_x$ assumed positive and the other for it assumed negative. Assuming $g_x$ negative gives a $k$ value greater than unity and therefore this solution is rejected. The values obtained for the para-
meters are given in Table 15.

The value of \( k \) obtained in this study is close to 0.875, the value reported by Bleaney and O'Brien for \( \text{Fe(CN)}_6^{3-} \). Oosterhuis (50) has studied the Mössbauer hyperfine spectrum of powdered \( \text{Na}_2\text{Fe(CN)}_5\text{NH}_3\cdot\text{H}_2\text{O} \) and fitted his results to equations similar to those developed here. Although he assumed the \( |xy\rangle \) orbital to be the lowest in energy, his results would equally well fit the above interpretation with the parameters: \( d=0.90, e=0.42, f=0.15 \) which are surprisingly close to the values obtained in the present study.

The values of \( \Delta \) and \( \delta \) could not be obtained without an independent determination of the spin orbit coupling parameter \( \xi \). Haberditzl et al. (51) have reported the magnetic moment of iron in \( \text{Na}_2\text{Fe(CN)}_5\text{NH}_3\cdot\text{H}_2\text{O} \) to be 2.32 Bohr magnetons at 295K. Our values of \( k, \eta \) and \( \varepsilon \) will predict this value when the value of the spin orbit coupling parameter is 325 cm\(^{-1}\) which is fairly close to 278 cm\(^{-1}\) reported by Bleaney and O'Brien (10) for \( \text{Fe(CN)}_6^{3-} \). Since the free ion values of the spin orbit parameter for \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \) are 400 and 460 cm\(^{-1}\) respectively (52), the value obtained in this study indicates considerably more covalency than the value of \( k \) would indicate.

Thornley (53) and Cotton (54) have shown that the neglect of configuration interaction in the theoretical treatment of octahedral complexes produces \( k \) values that seriously underestimate the covalency. The values of \( \Delta, \sigma \) and the energy of the excited Kramers doublet are found to be:
TABLE 15

Molecular Orbital Parameters for Fe(CN)$_5$NH$_3^{2-}$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k$</td>
<td>0.893</td>
</tr>
<tr>
<td>$d$</td>
<td>0.891</td>
</tr>
<tr>
<td>$e$</td>
<td>0.385</td>
</tr>
<tr>
<td>$f$</td>
<td>0.241</td>
</tr>
<tr>
<td>$n$</td>
<td>0.578</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>0.656</td>
</tr>
</tbody>
</table>
\[ \Delta = 560 \text{ cm}^{-1} \]
\[ \delta = 500 \text{ cm}^{-1} \]
\[ E_2 - E_1 = 530 \text{ cm}^{-1} \]
\[ E_3 - E_1 = 930 \text{ cm}^{-1} \]

if \( \xi = 325 \text{ cm}^{-1} \). \( E_1 \) is the energy of the lowest Kramers doublet.

The most surprising aspect of the above results is the ground state. It is generally acknowledged that the ligand field strength of \( \text{NH}_3 \) is considerably less than that of \( \text{CN}^- \), so that one would have expected the \( |x^2-y^2> \) hole orbital to be the most stable instead of the least stable as found here. Also the fact that \( \delta \) is comparable to \( \Delta \) is unexpected since the structure of the host lattice, \( \text{Fe(CN)}_5\text{NO}^2^- \), approximates four fold symmetry so well. The stability of the \( |xz> \) and \( |yz> \) holes over the \( |x^2-y^2> \) hole could be explained in part by noting that the bond angle between \( \text{Fe-N-O} \) and the equatorial \( \text{Fe-C-N} \) bonds is \( 96^\circ \) and assuming that the \( \text{Fe(CN)}_5\text{NH}_3^2^- \) ion adopts this geometry when incorporated in the same lattice. Such a distortion stabilizes the \( |xz> \) and \( |yz> \) orbitals and destabilizes the \( |x^2-y^2> \) orbital. It is hard to accept this as a valid explanation because it is difficult to believe that such a small distortion is more important energetically than the difference in ligand field strengths between \( \text{NH}_3 \) and \( \text{CN}^- \). Further if such distortions are so important, it is hard to understand why the Moessbauer results (50) for \( \text{Na}_2\text{Fe(CN)}_5\text{NH}_3\cdot\text{H}_2\text{O} \) agree so well with the results obtained in this study since the ion is in different lattices. Thus it is difficult to avoid the conclusion that
the NH₃ group in this complex is acting as a more basic ligand than it appears to do in other complexes.

D. The Nitrogen Hyperfine Interaction:

Using the two Kramers doublets given in equation (33) and the appropriate hyperfine operators the spin Hamiltonian parameters for the hyperfine interaction were obtained by McCarvey (42) as:

\[
\begin{align*}
\Lambda_x &= (d^2-e^2)K_{xz} - f^2 K_{x^2-y^2} + (2d^2+e^2-3ed)P_L \\
&\quad - (d^2-e^2-f^2-2ef)P_M \\
\Lambda_y &= (d^2-e^2)K_{xz} - f^2 K_{x^2-y^2} - (d^2+2e^2-3ed)P_L \\
&\quad - (d^2-e^2+f^2-2ed)P_M \\
\Lambda_z &= (d^2+e^2)K_{xz} - f^2 K_{x^2-y^2} - (d^2+e^2-10ed)P_L \\
&\quad + 2(d^2+e^2-f^2+2ed)P_M
\end{align*}
\]

where

\[
P_L = (2/5)g_e g_N \beta_e \beta_N <r^{-3}>_{2p} \beta_L^2
\]

\[
P_M = g_e g_N \beta_e \beta_N R_{3}\beta L^2
\]

\(g_e\) and \(g_N\) are the electronic and nuclear \(g\) factors, \(\beta_e\) and \(\beta_N\) are the Bohr and nuclear magnetons respectively, \(<r^{-3}>_{2p}\) is the average value of \(r^{-3}\) in a nitrogen 2p orbital and \(R\) is the Fe-N internuclear distance. \(K_{xz}\) is the Fermi contact interaction induced by the spin in \(|xz\rangle\) or \(|yz\rangle\) orbitals and \(K_{x^2-y^2}\) is the interaction induced by the spin in the \(|x^2-y^2\rangle\) orbital. In equation (32) the assumption is made that \(\beta\) is equal to both \(\alpha\) and \(\gamma\) while \(\beta_L\) is equal to \(\beta_2\) and \(\gamma_2\) of the ligand molecular orbitals.
The analysis of the hyperfine interaction is difficult because reliable values of $\lambda_x$ and $\lambda_y$ are not available neither are the signs for any of the hyperfine terms.

Reasonable estimates of $K_{xz}$ and $P_L$ could be arrived at by considering the range of possible solutions for equation (36). $P_L$ is small and can be readily estimated to be $0.26 \times 10^{-4}$ cm$^{-1}$ by assuming $R = 1.95$ Å and $\beta^2$ equal to unity. It is readily established that positive values of $P_L$ are only possible if $\lambda_z$ is positive. Further studies\(^{(20,55)}\) of the hyperfine interaction of $^{13}$C and $^{14}$N in Cr(CN)$_5$NO$^-$ show that $K_{xz}$ and $K_{x^2-y^2}$ are negative and that $|K_{x^2-y^2}|$ is less than $|K_{xz}|$.

If this restriction is placed on the above solutions, it is found that $\lambda_x$ must be positive and $\lambda_y$ negative and $P_L$ must be between $2.7 \times 10^{-4}$ cm$^{-1}$ and $5.0 \times 10^{-4}$ cm$^{-1}$ to be consistent with the above results. $K_{xz}$ must be between 0 and $-5.0 \times 10^{-4}$ cm$^{-1}$ with the larger magnitude values associated with the smaller values of $P_L$.

Morton\(^{(56)}\) has reported a value of 3.101 7, u. for $<r^{-3}>_{2p}$ which would make $P_L$ equal to $15.9 \times 10^{-4}$ cm$^{-1}$ if $\beta_L^2$ is equal to one. Thus the experimental estimates of $P_L$ predict values of $\beta_L^2$ between 0.17 and 0.31. This is a larger covalency than normally found in metal-ammonia bonds, but is however consistent with the conclusion in this study from g values that the NH$_3$ is interacting more strongly than one would expect.

This conclusion seems difficult to accept and appears more plausible if the NH$_3$ has lost a proton to become NH$_2^-$ which is a much stronger base than NH$_3$. Herington\(^{(57,58)}\)
has reported the reaction of pentacyanammino ferrate(III) with aromatic amines and claimed the formation of complicated complexes. Thus with aniline, $\text{Na}_2\text{Fe(CN)}_5\text{NH}_3\cdot\text{H}_2\text{O}$ forms $\text{Na}_2\text{Fe(CN)}_5\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{NHPh}$. The possibility of the formation of $\text{Na}_2\text{Fe(CN)}_5\cdot\text{NH}_2\cdot\text{H}_3\text{O}$ was made probable by the fact that $\text{Na}_2\text{Fe(CN)}_5\cdot\text{NH}_3\cdot\text{H}_2\text{O}$ undergoes color changes from reddish-yellow in strongly alkaline solutions to deep blue in acidic solutions. Attempts to determine this acid-base equilibrium by measuring the NMR shift of the amine hydrogen as a function of pH failed because water was in such a high concentration that the rapid exchange between the amine hydrogen and the water protons made it impossible to observe any resonance due to the amine hydrogen. In order to determine whether $\text{NH}_3$ was present in the solid $\text{Na}_2\text{Fe(CN)}_5\cdot\text{NH}_3\cdot\text{H}_2\text{O}$ as $\text{NH}_2$ with the proton abstracted by the water of hydration, a broad line NMR study of the powder was undertaken. The spectrum recorded at room temperature is shown in Figure 15. This spectrum shows a pattern typical of two protons and a sharp resonance at the center. The two proton pattern was analyzed and fitted to that expected for two protons separated by a distance of 1.62 Å, a value equivalent to that found in hydrates. The central resonance line has a wing typical of an axially symmetrical system that has a perpendicular and parallel shifts. Since water of hydration is normally hydrogen bonded and does not move freely, it is unlikely that the sharp resonance can be attributed to the hydronium ion. Thus it appears that the sharp resonance must be due to the $\text{NH}_3$ which is not
expected to be rigidly bound. It is, therefore, inevitable to conclude that the ammino group is not present as NH$_2$ in this complex.

That the NH$_3$ is interacting strongly in this complex could be understandable by considering the role of the CN$^-$ ion. The cyanide ion has a pair of degenerate, normally unoccupied, antibonding $\pi$-orbitals. These have the appropriate symmetry to combine with $t_{2g}$ orbitals of the iron. These $\pi$-orbitals enable the cyanide ion to act as an electron acceptor. This increases the effective charge on the iron and hence results in a stronger interaction between the NH$_3$ and the iron.
Chapter VIII

CONCLUSIONS

The electron spin resonance spectra have been investigated for manganate ions in barium selenate and for ammonium pentacyanoferrate (III) in sodium nitroprusside. Both the crystal field theory and the molecular orbital approaches have been used to analyze the spin Hamiltonian parameters. For the manganate ions in barium selenate the spin Hamiltonian parameters are shown to be consistent only with a ground state in which the unpaired electron is in a $d_{z^2}$ orbital with a 2% admixture of $d_{x^2-y^2}$ orbital. The difference in the principal x and z axes for the $g$ and the $A$ tensors has been shown to be attributed to the admixture of the $d_{yz}$ orbital with the $d_{xy}$ orbital. This has been estimated to be 0.03% from the angular separation of the axes. The molecular orbital coefficients, $\alpha$ and $\beta$, together with an estimate of the overlap integrals have been used to determine the charge densities on the metal ion. From the charge densities the formal charge on manganese was calculated by a self consistent method. It was found that the formal charge on Mn(VI) is about +2 which is in line with similar values found for other ions of high oxidation numbers $(28,59,60)$.

One significant difference between the manganate ion in barium selenate and in barium sulfate is in the value of $K$, the isotropic term. This value can be used to calculate
\( \chi \), a quantity defined by Abragam et al.\(^{61} \) as characteristic of the central density of unpaired spin as:

\[
\chi = \frac{(4\pi/S)}{\langle \Psi | \sum_{i} \delta(r_i) S_{zi} | \Psi \rangle}
\]

\( \chi \) values obtained are:

\[
\chi = -1.64 \text{ for MnO}_4^{2-} \text{ in BaSO}_4
\]
\[
\chi = -2.04 \text{ for MnO}_4^{2-} \text{ in BaSeO}_4
\]

McGarvey\(^{49} \) has demonstrated that the value of \( \chi \) is nearly constant for a given configuration with similar ligands unless there is mixing of 3d and 4s orbitals. Such a mixing is symmetry-forbidden for the \( d_{xy} \) ground state observed for \( \text{MnO}_4^{2-} \) in \( \text{K}_2\text{CrO}_4 \) so that the value of \( \chi = -1.91 \) in this system can be used as a measure of that portion of \( \chi \) resulting from indirect polarization of inner s orbitals of manganese. Such a mixing would produce a positive contribution to \( \chi \).

It would appear that such a mixing is negligible for \( \text{MnO}_4^{2-} \) in \( \text{BaSeO}_4 \) but a small admixture of about 0.1\% occurs for \( \text{MnO}_4^{2-} \) in \( \text{BaSO}_4 \).

For \( \text{Fe(CN)}_5\text{NH}_3^{2-} \) in \( \text{Na}_2\text{Fe(CN)}_5\text{NO.2H}_2\text{O} \), the spin Hamiltonian parameters are shown to be consistent only with a ground state in which the unpaired electron is primarily in a \( d_{xz} \) orbital rather than the expected \( d_{x^2-y^2} \) orbital. The molecular orbital analysis of the spin Hamiltonian parameters has shown that there is a larger covalency than normally found in the metal-ammonia bonds and this is consistent with the conclusion that the \( \text{NH}_3 \) is interacting more strongly in this complex than one would expect.
Appendix

DERIVATION OF SECOND ORDER TERMS FOR S=1/2 IN RHOMBIC SYMMETRY

The spin Hamiltonian for this system is

\[ H = \beta (g_x H_x S_x + g_y H_y S_y + g_z H_z S_z) + A_x S_x I_x + A_y S_y I_y + A_z S_z I_z \]

We will quantize \( S \) and \( I \) in a coordinate system such that \( S \cdot g \cdot H \) and \( S \cdot A \cdot I \) give no off diagonal terms that involve two states with the same eigenvalue of \( S \).

We will choose this \( x'y'z' \) coordinate system with different choices of \( S \) and \( I \):

\[ S_x = S_{x'} \cos \omega \cos \gamma - S_{y'} \sin \gamma + S_{z'} \sin \omega \cos \gamma \]

\[ S_y = S_{x'} \cos \omega \sin \gamma + S_{y'} \cos \gamma + S_{z'} \sin \omega \sin \gamma \]

\[ S_z = S_{x'} \sin \omega + S_{z'} \cos \omega \]

Now \( H_x = H \sin \alpha \cos \phi \)

\( H_y = H \sin \alpha \sin \phi \)

\( H_z = H \cos \alpha \)
so that
\[ S \cdot g \cdot H = (g_x \sin \omega \cos \gamma \sin \alpha \cos \phi + g_y \sin \omega \sin \gamma \sin \alpha \sin \phi + g_z \cos \omega \cos \alpha)S_z \]
\[ + (g_x \cos \omega \cos \gamma \sin \alpha \cos \phi + g_y \cos \omega \sin \gamma \sin \alpha \sin \phi - g_z \sin \omega \cos \alpha)S_x \]
\[ + (-g_x \sin \omega \sin \gamma \cos \alpha \cos \phi + g_y \cos \omega \sin \gamma \sin \alpha \sin \phi)S_y \]
The \( S_y \) term shall be equal to zero when
\[ -g_x \sin \gamma \cos \phi + g_y \cos \omega \sin \phi = 0 \]
or when \( \tan \gamma = (g_y / g_x) \tan \phi \)
i.e., \[ \sin \gamma = g_x \sin \phi / (g_x^2 \cos^2 \phi + g_y^2 \sin^2 \phi)^{1/2} \]
and \[ \cos \gamma = g_x \cos \phi / (g_x^2 \cos^2 \phi + g_y^2 \sin^2 \phi)^{1/2} \]
Thus \( S_x \) term becomes
\[ (g_x^2 \cos^2 \phi + g_y^2 \sin^2 \phi)^{1/2} \cos \omega \sin \alpha - g_z \sin \omega \cos \alpha \]
which becomes zero when
\[ \tan \omega = [(g_x^2 \cos^2 \phi + g_y^2 \sin^2 \phi)^{1/2} / g_z] \tan \alpha \]
Also the \( S_z \) term becomes
\[ [g_x^2 \sin^2 \alpha \cos^2 \phi + g_y^2 \sin^2 \alpha \sin^2 \phi + g_z^2 \cos^2 \alpha]^{1/2} = g \]
Therefore \( \beta S \cdot g \cdot H \) becomes \( g \beta HS_z \), and the first order solution is
\[ E = \pm (1/2) g \beta H \]
Now to keep \( S \cdot A \cdot I \) from mixing up terms with the same eigenvalues of \( S_z \), we must choose \( \omega_I \) and \( \gamma_I \) to make the \( S_z, I_x, \) and \( S_z, I_y \) terms zero. The \( S_z, I_x \) term is
\[ A_x \sin \omega \cos \omega \cos \gamma I \cos \gamma I + A_y \sin \omega \sin \gamma \cos \omega I \sin \gamma I - A_z \cos \omega \sin \omega I \]
whereas \( S_z, I_y \) term is
\[ -A_x \sin \omega \cos \gamma \sin \gamma I + A_y \sin \omega \sin \gamma \cos \gamma I \]
This term is zero when
\[ \tan \gamma_I = (A_y / A_x) \tan \gamma = [(g_y A_y) / (g_x A_x)] \tan \phi \]
i.e., when
\[ \sin \gamma_I = \left[ g_x A_y \left( g_x^2 A_x^2 \cos^2 \phi + g_y^2 A_y^2 \sin^2 \phi \right) \right]^{1/2} \sin \phi \]

\[ \cos \gamma_I = \left[ g_x A_x \left( g_x^2 A_x^2 \cos^2 \phi + g_y^2 A_y^2 \sin^2 \phi \right) \right]^{1/2} \cos \phi \]

Then from \( S_z, I_x \) term we get

\[ (A_x^2 \cos^2 \gamma + A_y^2 \sin^2 \gamma)^{1/2} \sin \omega \cos \omega I - A_z \cos \omega \sin \omega I = 0 \]

which yields

\[ \tan \omega I = \frac{[(A_x^2 \cos^2 \gamma + A_y^2 \sin^2 \gamma)^{1/2} / A_z] \tan \omega}{[(g_x^2 A_x^2 \cos^2 \phi + g_y^2 A_y^2 \sin^2 \phi)^{1/2} / (g_x A_z)] \tan \omega} \]

The \( S_z, I_z \) term is then

\[ A_x \sin \omega \cos \gamma I \sin \gamma_I + A_y \sin \omega \sin \gamma I \sin \gamma_I + A_z \cos \omega \cos \omega I \]

\[ = \frac{(g_x^2 A_x^2 \sin^2 \phi A_x \sin^2 \phi + g_y^2 A_y^2 \sin^2 \phi + g_z^2 A_z^2 \cos^2 \phi)^{1/2}}{(g_x^2 \cos^2 \phi A_x \cos^2 \phi + g_y^2 \sin^2 \phi + g_z^2 \cos^2 \phi)^{1/2}} = k \]

To get the second order terms, we must find \( S_x, I_y \) and \( S_y, I_z \) terms of \( S \cdot A \cdot I \). The \( S_x, I_z \) term becomes

\[ A_x \cos \omega \cos \gamma I \sin \gamma_I + A_y \cos \omega \sin \gamma I \sin \gamma_I - A_z \sin \omega \cos \omega I \]

which is equal to

\[ \frac{g_y g_z}{g_k} (A_x^2 - A_z^2) \sin \phi \cos \phi \]

where \( g_{\perp} = (g_x^2 \cos^2 \phi + g_y^2 \sin^2 \phi)^{1/2} \) and

\[ A_{\perp} = (g_x^2 A_x^2 \cos^2 \phi + g_y^2 A_y^2 \sin^2 \phi)^{1/2} / g_{\perp} \]

The \( S_y, I_z \) term becomes

\[ -A_x \sin \gamma I \cos \gamma I + A_y \cos \gamma I \sin \gamma_I \]

which is equal to

\[ \frac{g_x g_y}{g_{\perp} g_k} (A_y^2 - A_x^2) \sin \phi \sin \phi \cos \phi \]

Also the \( S_x, I_x \) term becomes
\[ A_x \cos \omega \cos \gamma \cos \omega I \cos \gamma I + A_y \cos \omega \sin \gamma \cos \omega I \sin \gamma I + A_z \sin \omega \sin \omega I \]

which is equal to

\[
\frac{A_z A_\perp}{K}
\]

Similarly

\[
S_y I_x = -A_x \sin \gamma \cos \omega I \cos \gamma I + A_y \cos \omega \sin \gamma I \cos \gamma I
\]

\[
= \frac{g_x g_y g_z A_z}{g_\perp^2 g K \perp} \left( A_y^2 - A_x^2 \right) \cos \omega \sin \phi \cos \phi
\]

\[
S_x I_y = -A_x \cos \omega \cos \phi \sin \gamma I + A_y \cos \omega \sin \gamma I \cos \gamma I
\]

\[
= 0
\]

\[
S_y I_y = A_x \sin \gamma I + A_y \cos \gamma I
\]

\[
= A_x A_y / A_\perp
\]

\[
= g_\beta H S_z \perp + K_{zz} S_z \perp I_z \perp + K_{xz} S_x \perp I_z \perp + K_{yz} S_y \perp I_z \perp + K_{xx} S_x I_x \perp + K_{yy} S_y I_y \perp
\]

where \( K_{xz} \) etc have been defined earlier. For the spin functions

\( M_S M_I \) the first order energies are

\[ E = g_\beta H M_S + K M_S M_I \]

whereas the second order energy terms are found from

\[
E = \sum_n \frac{< \psi_o | H | \psi_n > < \psi_n | H^\dagger | \psi_o >}{E_o - E_n}
\]

where the summation does not include \( n = 0 \).

For \( S = 1/2 \) consider the \( M_S = -1/2 \) state. We have carefully arranged so that there are no terms in the summation that include the \( S = 1/2 \) state. Therefore for \( M_S = -1/2 \) we get to second order:
\[
E(-1/2, M_I) = -(1/2)g\beta H - (1/2)KM_I - \frac{(K_{xz} + K_{yz})}{4(g\beta H + KM_I)}M_I^2
\]

\[
- \frac{[(K_{xx} - K_{yy})^2 + K_{yz}^2]}{16[g\beta H + KM_I - (1/2)K]} [I(I + 1) - M_I(M_I + 1)]
\]

\[
+ \frac{[(K_{xx} + K_{yy})^2 + K_{yx}^2]}{16[g\beta H + KM_I - (1/2)K]} [I(I + 1) - M_I(M_I - 1)]
\]

If we ignore KM_I and K compared to g\beta H, we get

\[
E(-1/2, M_I) = -(1/2)g\beta H - (1/2)KM_I - \frac{K_{xx}K_{yy}}{4g\beta H} M_I^2
\]

\[
- \frac{(K_{xx}^2 + K_{yy}^2 + K_{yx}^2)}{8g\beta H} [I(I + 1) - M_I^2] - \frac{(K_{xz} + K_{yz})}{4g\beta H} M_I^2
\]

Similarly

\[
E(+1/2, M_I) = (1/2)g\beta H + (1/2)KM_I - \frac{K_{xx}K_{yy}}{4g\beta H} M_I^2
\]

\[
+ \frac{(K_{xx}^2 + K_{yy}^2 + K_{yx}^2)}{8g\beta H} [I(I + 1) - M_I^2] + \frac{(K_{xz} + K_{yz})}{4g\beta H} M_I^2
\]

Therefore for \(\Delta M_S = \pm 1\), \(\Delta M_I = 0\) transition, we get

\[
h\nu(M_I) = g\beta H + KM_I + \frac{(K_{xx}^2 + K_{yy}^2 + K_{yx}^2)}{4g\beta H} [I(I + 1) - M_I^2]
\]

\[
+ \frac{(K_{xz} + K_{yz})}{2g\beta H} M_I^2
\]

where \(K_{xx} = A_2A_\perp/K\); \(K_{yy} = A_xA_\perp/A_\perp\);

\(K_{yx} = [(g_xg_\perp g_\perp^2 A_\perp)/(g^2g_\perp K_A_\perp)](A_\perp^2 - A_x^2) \cos \phi \sin \phi \cos \phi\)

\(K_{xz} = [(g_\perp^2)/(g^2K)](A_\perp^2 - A_x^2) \sin \phi \cos \phi\)

\(K_{yz} = [(g_xg_\perp)/(g_\perp K)](A_\perp^2 - A_x^2) \sin \phi \sin \phi \cos \phi\)

For the MnO\(_{4}^{2-}\) system we will take the b-crystallographic direction to be the y direction. Then for the magnetic field along the b axis, \(\alpha = 90^\circ\), \(\phi = 90^\circ\), and hence
\[ K_{xx} = A_z A_y / A_y = A_z, \quad K_{yy} = A_x A_y / A_y = A_x, \quad K_{yx} = K_{yz} = 0, \text{ and hence} \]

\[ h\nu(M_I) = g_y B_H + A_y M_I + \frac{(A_z^2 + A_x^2)}{4 g_y B_H} [I(I + 1) - M_I^2] \]

or \[ H(M_I) = \frac{h\nu}{g_y B_H} - \frac{A_y}{g_y B_H} \cdot \frac{(A_z^2 + A_x^2)}{4 g_y \beta h \nu_o} [I(I + 1) - M_I^2] \]

For two lines of similar \(|M_I|\) values we have

\[ \frac{(H_{M_I} + H_{-M_I})}{2} = H^o - \frac{(A_z^2 + A_x^2)}{2 g_y \beta h \nu_o} [I(I + 1) - M_I^2] \]

The last term in the above equation is estimated from the \(A_z, A_x\) and the first order values of \(g_y, H^o\). \(H^o\) is then calculated from which \(g_y\) can be obtained.

For rotation in the \(xz\) plane \(\phi = 0^\circ\), so that

\[ K_{xx} = A_z A_x / K \text{ where } K = (g_x^2 A_x^2 \sin^2 \alpha + g_z^2 A_z^2 \cos^2 \alpha)^{1/2} / g \text{ and} \]

\[ g = (g_x^2 \sin^2 \alpha + g_z^2 \cos^2 \alpha)^{1/2} \]

Also \(K_{yy} = A_x A_y / A_x = A_y; K_{yx} = K_{yz} = 0 = K_{yzy}; \text{ and} \)

\[ K_{xz} = \frac{g_x g_z}{g_x^2} (A_x^2 - A_z^2) \sin \alpha \cos \alpha \]

Therefore

\[ h\nu(M_I) = g B_H + K M_I + \frac{(A_z^2 X^2 + A_x^2 Y^2)}{4 g B H K^2} [I(I + 1) - M_I^2] \]

\[ + \frac{g_x^2 g_z^2 (A_x^2 - A_z^2)^2}{2 g_x^4 k^2 g B H} M_I^2 \sin^2 \alpha \cos^2 \alpha \]

which on transposition gives
\[ H(M_I) = \frac{h\nu_0}{g\beta} - \frac{KM_I}{g\beta} - \frac{(A_x^2 + A_y^2 + A_z^2)^2}{4g\beta K^2 h\nu_0} [I(I + 1) - M_I^2] \]

\[ - \frac{g_x^2 g_z^2 (A_x^2 - A_z^2)}{q^4} \frac{(A_x^2 - A_z^2)^2}{2K^2 g\beta h\nu_0} M_I^2 \sin^2 \alpha \cos^2 \alpha \]

For two lines of similar \(|M_I|\) values the above equation becomes

\[ \frac{(H_{M_I} + H_{-M_I})}{2} = H^0 - \frac{(A_x^2 + A_y^2 + A_z^2)^2}{2g\beta K^2 h\nu_0} [I(I + 1) - M_I^2] \]

\[ - \frac{g_x^2 g_z^2 (A_x^2 - A_z^2)}{g^4 K^2 g\beta h\nu_0} M_I^2 \sin^2 \alpha \cos^2 \alpha \]

The last two terms are estimated with values of \(A_x\), \(A_y\), \(A_z\) and the first order values of \(g_x\), \(g_y\) and \(g_z\). \(H^0\) is calculated from which \(g\) can be obtained. The average value of \(g\) for each orientation was taken as the \(g\) value corrected for second order.

Near the maximum and minimum \(\sin^2 \alpha \cos^2 \alpha = 0\) and we can use the same technique to calculate \(g\) that was used for the \(b\)-axis. In between, it is best to calculate the correction terms and \(\alpha\) from the approximate values.
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