1968

Preparation and Spectral Properties of Oxomolybdenum(v) Complexes.

Harry Edmond Pence II
Louisiana State University and Agricultural & Mechanical College

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Chemistry, inorganic

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PREPARATION AND SPECTRAL PROPERTIES OF OXOMOLYBDENUM(V) COMPLEXES

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy in The Department of Chemistry

by

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To Ginn
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The final creation of this dissertation has been assisted by many different individuals and it is appropriate to attempt to indicate some of these contributors and offer the sincere thanks of the author. The most important component of this assistance has been the continual encouragement offered by parents and family. Without this support the completion of this extensive period of training would have been impossible.

The author wishes to thank Dr. Joel Selbin for suggesting this project and providing enthusiastic direction and helpful advice during the course of the work. Also, it would be remiss of the author not to give recognition to the many faculty members and students, especially his lab partners, who have contributed to his understanding of various aspects of the problem by their suggestions and informal discussions. A particular debt of gratitude must be noted for the invaluable help and advice provided by Dr. David Ogden.

While indicating the many individuals who have helped to bring this project to fruition, it is necessary to express the admiration and appreciation felt for Dr. Robert Nauman. The National Science Foundation Programs which he has directed served as a unique opportunity for advanced training for many college chemistry teachers, of which the author was one.

The author wishes to thank the Charles E. Coates Memorial Fund for financial assistance in the publication of this dissertation.
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LIST OF COMMONLY USED SYMBOLS

AA  Acetylacetone or 2,4-pentanedione*
BF₃A  Benzoyl trifluoroacetone or 1-phenyl-4,4,4-trifluorobutane-1,3-dione
DBM  Dibenzoylmethane or 1,3-diphenylpropane-1,3-dione
Dq  A parameter used to indicate the magnitude of the energy separation between the d orbitals in a complex due to an octahedral array of ligands.
Ds and Dt Parameters used to indicate further removal of the degeneracy of the d orbitals as the symmetry is decreased from the octahedral case.
en  Ethylenediamine
F₆A  Hexafluoroacetylacetone or 1,1,1,5,5,5-hexafluoropentane-2,4-dione
kK  A unit of frequency, used in the electronic region of the spectrum, called the kiloKayser.
1kK = 1000 cm⁻¹
TF₃A  Thienyl trifluoroacetone or 1-(2-thienyl)-4,4,4-trifluorobutane-1,3-dione

* Since trivial nomenclature is used almost exclusively by inorganic chemists working with β-diketones the accepted practice has been followed in this dissertation. The correct IUPAC names are shown above.
ABSTRACT

Five new complexes of oxomolybdenum(V) have been prepared and examined by customary procedures to allow the assignment of correct formula and structure. The formulae of the new complexes are of the general type \([(C_{2}H_{5})_{4}N][MoOC\_3\_3L]\) or \([(C_{2}H_{5})_{4}N][MoOb\_3\_3L]\), where L is a β-diketone such as dibenzoylmethane, hexafluoroacetylacetone, phenyltrifluoroacetylacetone, or thenoyltrifluoroacetylacetone. The methods used to characterize the compounds were elemental analyses, infrared spectra (in the region 4,000 to 300 cm\(^{-1}\)), electronic spectra (in the region 10 to 45 kK), equivalent conductance, magnetic susceptibility, and electron paramagnetic resonance. Information gathered from all of the sources mentioned above was consistent with the proposal of paramagnetic, monomeric structure for all of the compounds.

In addition to the above materials, a new compound was prepared which was tenatively formulated as \([(C_{2}H_{5})_{4}N][MoOF_{3}\_3(C_{6}H_{5} COCHCO_{6}H_{5})]\). The amount of compound obtained was insufficient to allow the unambiguous characterization of the substance.

The electronic spectra of the compounds was studied as acetonitrile and methylene chloride solutions at room temperature and as mineral oil mulls at liquid nitrogen temperatures. The data obtained was examined and the effectiveness of various proposals concerning the energy levels in oxomolybdenum(V) species was evaluated. This allowed assignment of most of the prominent bands of the spectra.
The first d-d transition was observed at about 14 kK for the chloro complexes and assigned as the transition $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$.

The degeneracy of the $d_{xz}$ and $d_{yz}$ orbitals should be removed in this low symmetry, but it was not possible to unambiguously identify the splitting which would be expected in this case. A second group of bands in the neighborhood of 22 kK was assigned as a vibrational progression superimposed upon the $d_{xy} \rightarrow d_{x^2-y^2}$ transition. On the basis of various arguments it was possible to predict that the third and last d-d transition should be found at relatively high energy, where it would be hidden by more intense bands. Tentative assignments were also proposed for a ligand to metal charge transfer absorption and the $\pi_3 \rightarrow \pi_4$ intraligand transition.
GENERAL INTRODUCTION

For the past several years this research group has directed much effort toward preparing, characterizing and determining the spectral properties of transition metal oxocations. One particular system which has aroused considerable interest, not only in this laboratory but also in many others, is the oxovanadium(IV) or, as it is often called, the vanadyl ion. Since its electron configuration may be described as a sole d electron outside of an argon-like inner core, this should be a relatively simple system for spectra observation and interpretation. Unfortunately the problem has not proven to be as straightforward as might be hoped and a spirited controversy has developed in the literature concerning the correct assignment of the visible and ultraviolet absorption bands of complexes containing this species. The dispute has recently been summarized by two review articles which are recommended to the attention of the interested reader. The resulting interest has focused attention on other, similar systems which might clarify the vanadyl situation. One such system, the oxomolybdenum(V) or molybdenyl ion, is the topic of concern in this dissertation.

The crux of the "vanadyl question" has been the applicability of the Ballhausen and Gray (BG) assignments for

the spectrum of VO(H$_2$O)$_5^{2+}$ as a general model suitable for the explanation of many or all vanadyl complexes. This naturally leads one to question the Gray and Hare attempt to explain the visible and ultraviolet absorptions of (NH$_4$)$_2$MoOC$_5$$_5$ using the (BG) vanadyl energy diagram. Gray and Hare adopted this approach because information which is required for the molecular orbital calculation is lacking for molybdenum(V) and sufficient experimental data was not available to permit an empirical approach. Certain workers have already pointed out apparent inconsistencies in the GH scheme and it would seem that the time is ripe for a careful re-examination of their proposal. It would be especially helpful to examine the spectra of compounds which might serve as a test of their proposal.

Gray and Hare assumed that the [MoOC$_5$]$^{2-}$ ion would have a tetragonal structure ($C_{4v}$ symmetry) with a short Mo = O bond, analogous to the structures reported for vanadyl compounds from X-ray determinations. They used a coordinate system centered on the metal ion and arranged so that the oxo-group lies along the positive z axis and the chloro groups fall directly on the remaining Cartesian axes. The same coordinate system will be used throughout this dissertation. A Crystal Field Treatment (such as that presented in the appendix of this dissertation) predicts the splitting of the d-orbitals into four energy levels, one of which is degenerate. Figure 1, drawn from the Ballhausen and Gray paper$^3$, shows the removal of degeneracy as the symmetry

---

Figure 1. Energy Levels in Crystalline Fields of Oh and Compressed C4v Symmetry, with (−3Ds + 5Dt) > 0
of the ligand arrangement becomes octahedral ($O_h$ symmetry) and then tetragonal ($C_{4v}$ symmetry). For each level the figure indicates the appropriate d-orbital, the atomic symmetry designation of the orbital, and the energy as a function of $D_s$, $D_t$, and $D_q$.

$D_q$ is the familiar crystal field splitting parameter, which measures the d level separation due to an octahedral environment, while $D_s$ and $D_t$ are associated with the further removal of orbital degeneracy due to the descent in symmetry to a tetragonally distorted environment. The latter two constants will be discussed in more detail later.

From the simple diagram three d-d transitions are predicted:

- $d_{xz}$, $d_{yz}$ ($d_{xy}$ (energy = $3D + 5Dt$)), $d_{x^2-y^2}$ ($d_{xy}$ (energy = $10D_q$)), and $d_{z^2}$ ($d_{xy}$ (energy = $10D_q - 4Ds - 5Dt$)).

If all three transitions can be assigned it is possible to calculate the values for $D_q$, $D_s$ and $D_t$. The arrow pointing to the left indicates the absorption of energy, the ground state or orbital being written on the right. This convention will be followed throughout the dissertation.

The Gray-Hare molecular orbital diagram for the system is shown in Figure 2. Metal-Chlorine $\pi$ bonding is completely neglected, only oxygen $\pi$ orbitals being used in the diagram.

Seventeen electrons (10 from five chlorines, six from the axial oxygen, and one from the metal) are distributed in the orbitals of lowest energy to produce a ground state $^2B_2$, $[(\text{I}_a^b)^2 \text{ (II}_a^b)^2 \text{ (b}_1^b)^2 \text{ (e}_o^b)^4 \text{ (III}_a^b)^4 \text{ (b}_2) \text{]}$. The spectrum observed for the compound $[\text{NH}_4][\text{MoOCl}_5]$ is tabulated.

* Wherever it appears that no ambiguity might result the common practice of using the metal d orbital to represent the molecular orbital of which it is a principal constituent will be followed.
Figure 2. Molecular Orbital Diagram Proposed for $\left[ \text{MoOCl}_5 \right]^{2-}$ by Gray and Hare (ref. 4)
in Table 1, which also includes the GH assignments and the configuration of the excited state for each assignment. Bonding sigma orbitals are designated as IC (inner core), since they are presumed to be unimportant for transitions in the spectral range under consideration. The third d-d transition \( (d_z^2 \rightarrow d_{xy}) \) is not assigned and is presumed to be covered by the intense charge transfer bands.

Table I

Electronic Absorption Spectral Data for \((\text{NH}_4)_2\text{MoOCl}_5\) in 10 M HCl

Assignments according to Gray and Hare

<table>
<thead>
<tr>
<th>frequency(^*)</th>
<th>transition</th>
<th>excited state(^**)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.05</td>
<td>( ^2E(\text{I}) \rightarrow ^2B_2 )</td>
<td>((\text{IC})^{12}(e_\pi^4)(e^*)_\frac{\pi}{\pi} )</td>
</tr>
<tr>
<td>22.50</td>
<td>( ^2B_1 \rightarrow ^2B_2 )</td>
<td>((\text{IC})^{12}(e_\pi^4)(b^*_\frac{\pi}{\pi}) )</td>
</tr>
<tr>
<td>28.20</td>
<td>( ^2E(\text{II}) \rightarrow ^2B_2 )</td>
<td>((\text{IC})^{12}(e_\pi^3)(b_2^2) )</td>
</tr>
<tr>
<td>32.20</td>
<td>( ^2B_2 \rightarrow ^2B_2 )</td>
<td>((\text{IC})^{12}(e_\pi^3)(b_2)(e^*)_\frac{\pi}{\pi} )</td>
</tr>
<tr>
<td>41.70</td>
<td>( ^2E \rightarrow ^2B_2 )</td>
<td>((\text{IC})^{12}(e_\pi^3)(b_2^2)(b^*_\frac{\pi}{\pi}) )</td>
</tr>
</tbody>
</table>

\(^*\) frequencies are given in kilokaysers (kK), 1 kK = 1000 cm\(^{-1}\)

\(^**\) the ground state in each case is \((\text{IC})^{12}(e_\pi^4)(b_2)\)

By comparing the frequency of the first d-d band with the difference between the first and the second charge transfer bands it was possible to estimate the repulsion energy associated with placing a second electron into the \( d_{xy} \) orbital. A value of 8.4 kK was determined for ammonium oxopentachloromolybdate(V) by them\(^4\) compared with only 4.7 for \( \text{VO}((\text{H}_2\text{O})_5^{2+} \). On the other hand, Ballhausen
and Gray\textsuperscript{3} report a repulsion energy of 11.7 kK for $\text{VO(H}_2\text{O)}_5^{2+}$, obtained by comparing the positions of the first charge transfer band of $\text{VO}^{2+}$ with the first band of $\text{VOCl}_3$. Because of the larger size of the d orbitals of the molybdenum ion it would naturally be expected that the interelectronic repulsion would be lower for oxomolybdenum(V) compounds. This emphasizes the fact that the method used by Gray and Hare provides only an estimate of the repulsion energies and should be used with this in mind.

Spectral data for a number of different compounds have apparently been satisfactorily interpreted using the GH scheme.\textsuperscript{5,6} One of the strongest arguments in favor of arranging the d levels as proposed by Gray and Hare is the consistent observation of a low intensity visible band at a similar frequency ($\sim$14 kK) in a wide variety of oxomolybdenum(V) compounds. According to the GH model, this corresponds to a transition from $d_{xy}$ to $d_{xz, yz}$. The splitting between these levels is due to the tetragonal distortion, a distortion which Gray and Hare have attributed almost entirely to the ligand field of the oxygen. A natural result of this assumption is that all oxomolybdenum(V) complexes should have the first ligand field transition at about the same frequency, since the same agency is responsible in each case.


The first disagreement with the Gray and Hare model was reported by Allen et al.\textsuperscript{7}. These workers prepared and performed spectral measurements on a number of significant compounds. Some of their results are shown in Table II. The spectrum of the \([\text{WOCl}_5]^2^-\) anion was found to be very similar to that already described for \([\text{MoOCl}_5]^2^-\), i.e., two low intensity bands followed by three bands at higher energies which are very intense. By analogy with the GH scheme and on the basis of relative intensities Allen et al.\textsuperscript{7} assign the first two bands as ligand field transitions and the three bands at higher energies as charge transfer (C.T.) in origin. This is in qualitative agreement with the GH diagram but the model breaks down under more careful examination. The frequency of the lowest energy band is almost exactly the same for the tungsten and molybdenum complexes. If one accepts the Gray and Hare scheme, it follows that the energy gap between \(b_2^*\) and \(e^b_\Pi\) must also be the same in both complexes. If this were true, one would expect little change in the separation between \(b_2^*\) and \(e^b_\Pi\) for the two complexes and so the first two C.T. bands should occur at about the same frequency for \([\text{MoOCl}_5]^2^-\) and \([\text{WOCl}_5]^2^-\). However, all three charge transfer bands for the tungsten complex are observed to blue shift by 4000 to 5000 cm\(^{-1}\). Although the shift to higher energy is expected for the third band because of the increase in \(Dq\), which is usual when moving down a family in the transition

metals if other factors are constant, the large energy shift of
the first two charge transfer bands is inexplicible in terms of
the Gray and Hare MO proposal.

<table>
<thead>
<tr>
<th>complex</th>
<th>conditions</th>
<th>peak positions (kK) (molar extinction coeff. in parentheses)</th>
</tr>
</thead>
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<tr>
<td>$\overset{\text{I}}{\text{M}_2 \text{MoOCl}_5}$</td>
<td>aq. HCl</td>
<td>14.10 (11); 22.42 (10); 28.01 (570); 32.26 (5300); 40.00 (3600)</td>
</tr>
<tr>
<td>$\overset{\text{I}}{\text{M}_2 \text{MoOBr}_5}$</td>
<td>aq. HBr</td>
<td>14.29 (7); 21.28 (560); 2410 (3200); 26.53 (2500)</td>
</tr>
<tr>
<td>$\overset{\text{I}}{\text{M}_2 \text{WOC}_5}$</td>
<td>aq. HCl</td>
<td>14.20 (29); 25.19 (16); 32.79 (500); 37.17 (2700); 44.44 (3000)</td>
</tr>
</tbody>
</table>

The problem becomes even more acute if the spectrum of
the $[\text{MoOBr}_5]^2-$ anion is examined. Allen et al. found that the
d-d band (only one band is observed which appears to have the
appropriate intensity) is slightly blue shifted in this compound
compared to the chloro analogue. All three charge transfer bands
are red-shifted in the bromo complex. If the same reasoning is
applied to this system it is again evident that this observation
is irreconcilable with the GH proposal. Allen and his associates
conclude that "the $\pi$-electrons of the bromine atoms are involved
in at least some of the transitions". However, they do not
mention any possible effect on the d-d transition assignments.
Horner and Tyree also argue that halogen to metal \(\pi\)-bonding is important in oxomolybdenum complexes and find evidence that this is true not only in the chloro but also the bromo complexes. In a study of the spectra of niobium and tantalum oxohalometalates they found the charge transfer bands of the bromo complex to red shift compared to the chloro complex, just as had been observed by Allen et al. in the oxomolybdenum(V) complexes. They also noted a great similarity in the charge transfer bands for \(\text{MX}_6^-\) and \(\text{MOX}_5^2-\) (where M is Nb, Mo or W, and X is Cl or Br). They suggested that this similarity was difficult to explain unless the transitions involved molecular orbitals with considerable halogen character. As further evidence they note that the MO calculation for \([\text{VO(H}_2\text{O})_5]^{2+}\) ion predicts the energy of the oxygen \(\pi\) level as \(-132,000\ \text{cm}^{-1}\) and the energy of the vanadium 3d level as \(-113,000\ \text{cm}^{-1}\). They assume that the oxygen \(\pi\) level lies at about the same level in \([\text{MoOC}_5^-\text{Cl}]^2-\) and estimate the energy for the 4d electrons of molybdenum or niobium to be about \(-100,000\ \text{cm}^{-1}\). The energy of the chlorine \(\pi\) levels has been calculated as about \(-103,000\ \text{cm}^{-1}\) using a similar method of calculation. Since the chlorine \(\pi\) levels lie above the oxygen \(\pi\) levels by what is apparently a substantial amount, Horner and Tyree insist that the highest bonding molecular orbital levels in the energy diagram should be those arising from the Cl \(\pi\) levels. They conclude that


any interpretation of the charge transfer spectrum of MoOCl$_5^{2-}$ must consider chlorine π bonding.

Feenan and Fowles$^{10}$ also question the validity of the Gray-Hare assignments in connection with the spectra of certain compounds of the type MoOCl$_3^-$·2L and MoOCl$_3^-$·L' (where L is one of several unidentate ligands such as tetrahydrofuran, tetrahydridiophene, etc., and L' is a bidentate ligand such as 1,4-dioxane, 1,4-thioxane, etc.). A low intensity (extinction coefficient between 14 and 40) band is observed at about 13,000 cm$^{-1}$ in each case and this is assigned to the $d_{xz}$, $d_{yz}$ → $d_{xy}$ transition in accord with Gray and Hare. The second band ($\varepsilon_{\text{max}} = 11 - 18$) proves more difficult to explain satisfactorily. It is found at about 19 kK for oxygen ligands such as tetrahydrofuran and at about 15 kK for the sulfur analogues. Horner and Tyree$^5$ prepared similar compounds with L being triphenylphosphine oxide, triphenylarsine oxide, or dimethyl sulfoxide and reported a first band at 13.5 to 13.8 kK and the second at 22.3 to 22.7 kK. Feenan and Fowles suggest that the movement of the second band to higher energies as the ligand is changed from a thioether, to an ether and finally a phosphine or arsine oxide corresponds to the normal order of ligand field strength but the magnitude of the change is quite unexpected and perplexing.

The most persuasive evidence in support of the GH

scheme arises from investigations conducted by Wentworth and Piper\textsuperscript{11} on the spectra of oxopentahalomolybdenum(V) anions in host lattices at liquid nitrogen temperatures. Although unable to obtain oriented crystals suitable for polarized spectra, they suggest the higher intensity of the first band relative to the second is consistent with Gray and Hare's assignments since the selection rules in $C_{4v}$ symmetry allow $d_{x^2-y^2}$, $d_{xy}$, $d_{yz}$, but forbid the other possible $d$-$d$ transitions. The latter would be expected to gain intensity from vibrational interaction and so would be of lower intensity but not completely forbidden. The splitting parameter, $D_q$, is assigned a value of 2260 cm$^{-1}$ and comparison of this value with that determined for various hexachloromolybdates indicates a charge of slightly more than +4 on the molybdenum ion compared to the chloride ions. The first $d$-$d$ band is split for all three halogen derivatives and this is ascribed to the efforts of a vibrational progression superimposed on the electronic transition.

Of particular significance, in the work cited above, is the discussion of tetragonal distortion in the vanadyl and molybdenyl systems as measured by the parameters $D_q$, $D_s$ and $D_t$. As shown in the appendix of this dissertation, these terms are formulated using a crystal field approach so that

\begin{align*}
D_q &= \frac{1}{6} \rho_{4}^{xy} \\
D_s &= \frac{1}{7} \left(2\rho_{2}^{xy} - \rho_{2}^{z^+} - \rho_{2}^{z^-}\right) \\
D_t &= \frac{1}{21} \left(2\rho_{4}^{xy} - \rho_{4}^{z^+} - \rho_{4}^{z^-}\right)
\end{align*}

where $\rho_n = \text{eq} \left( \frac{e^n}{R^{n+1}} \right)$. Here $e$ represents the electronic charge and $q$ the effective ligand charge, while $R$ and $r$ are used to delineate the metal ion to ligand and the electron to metal distance, respectively. The positioning of the ligands with respect to the Cartesian coordinates is established as described previously (see pg. 2). To insure that these equations are consistent with earlier formulations of $D_s$ and $D_t$ it need only be noted that if both axial ligands exert identical fields the equations reduce to the form predicted by Piper and Carlin\textsuperscript{12} for the centric tetragonal field. If all of the ligands exert the same field $D_s$ and $D_t$ become zero and the equation for $D_q$ is that of a regular octahedral case\textsuperscript{12}.

One significant prediction is stressed by Wentworth and Piper: $D_s$ and $D_t$ should be negative quantities. Such a proposal follows naturally from the assumption of the overpowering importance of the oxygen field. Under these circumstances $\rho^{z+}_n$ must be larger than the other terms. In fact, the relative order of magnitude of the terms as enunciated in their paper is $\rho^{z+}_n \gg \rho^{z-}_n \sim \rho^{xy}_n$. Acceptance of this order leads naturally to the statement in question, since it follows that the two terms with negative values will overwhelm the positive term. This theory will be treated in some detail in the discussion section.

From the above information it would appear that some serious discrepancies remain to be rationalized before a completely

satisfactory solution of the optical and ultraviolet spectra of oxomolybdenum(V) complexes is obtained. Under these circumstances it is natural to turn to the results of Electron Paramagnetic Resonance (EPR) measurements to clarify the problem. Inspection of the literature in this field reveals further disagreement.

One of the first reports of EPR data for an oxomolybdenum(V) species was the work by Hare, Bernal, and Gray\textsuperscript{13}, who determined $g_{av.}$ (average) for $(\text{NH}_4)_2\text{[MoOC\ensuremath{\overset{\ne}{\overset{\nu}{\backslash}}}_5]}$ in concentrated acidic solution. The interpretation proposed was predicated upon the bonding model espoused by Gray and Hare\textsuperscript{4}. Values for $g_\perp$ and $g_{||}$ were not observed directly but rather were calculated using equations derived by Ballhausen and Gray\textsuperscript{3} with the energies of the d-d transitions taken according to the GH assignments. The $g$ value expressions for a $d^1$ transition metal oxocation in a $C_{4v}$ ligand field are\textsuperscript{3}

\[
g_\perp = 2 \left(1 - \frac{(C_1^*)^2 \xi}{\Delta E(2E(I) \leftarrow 2B_2)}\right)
\]

\[
g_{||} = 2 \left(1 - \frac{(C_1^*)^2 \xi}{\Delta E(2B_1 \leftarrow 2B_2)}\right)
\]

where $\xi$ is the spin-orbit coupling constant, $\Delta E$ represents the separation between the d levels of the symmetry indicated, and $C_1^*$ is the bonding coefficient for the antibonding levels. Using these relationships in conjunction with the equation

\[
g_{av.}^2 = \frac{1}{3} \left(2g_\perp^2 + g_{||}^2\right)
\]

Hare et al. obtain a value of 1.965 for $g_\parallel$ and 1.915 for $g_\perp$. The spin-orbit coupling constant is assumed to be reduced from an estimated value of 1030 cm$^{-1}$ in the free molybdenum(V) ion to only 240 cm$^{-1}$ in the complex. The explanation they offer for such an unbelievably large reduction is strong oxygen-to-metal $\pi$ bonding.

More recent results have failed to corroborate the values calculated by Hare et al. Gutowsky and co-workers were able to determine both $g_\parallel$ and $g_\perp$ from the EPR spectrum of the [MoOCl$_5$]$^{2-}$ anion in a host crystal lattice. The results, 1.9632 for $g_\parallel$ and 1.9400 for $g_\perp$, not only disagree by a substantial amount with the Hare etc. results but are opposite in order of magnitude. Spectral results and the fact that $g_{av}$ calculated from the crystal observation agrees with $g_{av}$ for the solutions verify that both research groups were observing the same entity. Gutowsky et al. suggest that the reversed relative magnitudes of the g values should be reflected in the bonding coefficients. The spin-orbit coupling parameter is given a value in the range 650 to 800 cm$^{-1}$. It is proposed that in-plane bonding is more important for molybdenyl than vanadyl complexes and that ligand spin-orbit effects are significant in the molybdenum complexes. The reversal in the relative magnitude of the g shifts is presumed to be a result of the large spin-orbit interaction and


and the general covalency of the complexes.

The relative magnitude of the g values for \((\text{NH}_4)_2[\text{MoOCX}_5]\) is verified by the experiments of Kon and Sharpless \(^{16}\). They examined the EPR spectra of \([\text{MoOCX}_5]^{2-}\) and \([\text{MoOBr}_5]^{2-}\) solutions in the appropriate concentrated acid at room temperature and also in frozen solutions (77°K). These observations allowed them to determine \(g_{\text{av.}}\) and \(g_{\|}\) directly and to calculate \(g_{\perp}\) from these results. Their values are shown in Table III, which also includes the other results discussed previously. As may be readily seen the values obtained using the Gray and Hare assignments seem to be in rather poor agreement with the results of more direct, and presumably more accurate, methods.

**TABLE III**

<table>
<thead>
<tr>
<th>compound</th>
<th>(g_{\text{av.}})</th>
<th>(g_{|})</th>
<th>(g_{\perp})</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{MoOCl}_5]^{2-})</td>
<td>1.947*</td>
<td>1.915</td>
<td>1.965</td>
<td>13</td>
</tr>
<tr>
<td>([\text{MoOCl}_5]^{2-})</td>
<td>1.947</td>
<td>1.9632*</td>
<td>1.9400*</td>
<td>15</td>
</tr>
<tr>
<td>([\text{MoOCX}_5]^{2-})</td>
<td>1.947*</td>
<td>1.960</td>
<td>1.936</td>
<td>16</td>
</tr>
<tr>
<td>([\text{MoOBr}_5]^{2-})</td>
<td>1.9463</td>
<td>1.9700</td>
<td>1.934</td>
<td>17</td>
</tr>
<tr>
<td>([\text{MoOCX}_5]^{2-})</td>
<td>1.993*</td>
<td>2.090*</td>
<td>1.945</td>
<td>16</td>
</tr>
</tbody>
</table>

* indicates values obtained by direct observation. The other values are calculated from the observed results.


Of special interest is the explanation proposed by Kon and Sharpless for the appearance of extra structure superimposed on the broad perpendicular band as observed in frozen solutions. This structure remained, even in samples which had been highly enriched with a molybdenum isotope having zero spin and so the bands cannot originate due to hyperfine splitting caused by molybdenum nuclei having non-zero spin. The data is best explained by superhyperfine interaction with the bromine ligands. Bromine consists primarily of nuclei having a spin of 3/2. The interaction most probably occurs due to $\pi$ bonding between the bromine p orbitals and the $d_{xy}$ orbital. In this same paper an explanation is proposed for the difficulties which have been encountered in the discussion of charge transfer bands of oxymolybdenum(V) when the GH energy levels are used. These authors indicate that compounds of this type exhibit anomalous g values, in that $g_{||}$ is greater than $g_{\perp}$ or $g_{||}$ is greater than 2.0023. Such results are presumed to indicate a low-lying excited electronic configuration in which an electron in a filled $b_1$, sigma orbital is excited to the $d_{xy}$ metal orbital. Such a transition would be expected to shift in just such a fashion as that noted by Allen et al. (see previous discussion) and would not be inconsistent with the arguments advanced in connection with the transition from an oxygen $\pi$ level. The relatively low intensity bands at 28 kK in the chloro and 21 kK in the bromo complexes (see Table I) are suggested as the $b_2 \rightarrow b_2^b$ charge transfer transitions. The low intensity would be expected since the exciting of an electron from $b_1$ to a $b_2$ state is forbidden due to symmetry arguments. As
support for their supposition these workers argue that the evidence shows that the metal-oxygen bond is predominant due to strong π bonding and that the metal-halogen bondings are easily dissociated and thus much weaker. Therefore the transfer of an electron from a sigma bonding orbital, which is usually presumed to require considerable energy, may occur at a much lower frequency than is usually expected.

A survey of the recent literature to find support for the Kon and Sharpless proposal discloses little concrete evidence. McClung, Dalton, and Brubaker\textsuperscript{17} have observed the electronic and EPR spectra of several complexes of the type $\text{M[Mo(OR)}_2\text{Cl}_4]$, where M is a large, organic cation, such as pyridinium, and R is a methyl or ethyl group. These authors suggest that the alkoxy groups are trans to each other and so the molecular symmetry is $D_{4h}$. In general the spectra consist of a low intensity band at about 14 kK ($\varepsilon = 15$ to 30) which is assigned as the $d_{xz}d_{yz} - d_{xy}$ transition. This suggests that the field of the methoxy groups is rather strong, for the degree of tetragonal distortion is equivalent to that observed for the oxomolybdenum complexes. Since $g_{||}$ is greater than $g_{\perp}$ (see Table III) the theory of Kon and Sharpless would seem to require a low energy charge transfer band with extinction coefficient in the range of 300 to 500. The only absorption which appears to suit this prediction is a low intensity band ($\varepsilon \approx 200$) at approximately 23 kK which is assigned as the second d-d transition, $d_{x^2-y^2} - d_{xy}$ by McClung et al. These
authors suggest that the $d_{z^2} \rightarrow d_{xy}$ as well as the charge transfer bands are "hidden" under this absorption. They fail to indicate that any asymmetry of the band or other evidence from the spectra leads them to this conclusion. The placing of the $d_{z^2} \rightarrow d_{xy}$ transition in this region is contrary to the work of Wentworth and Piper as well as certain arguments which will be advanced in the discussion section of this dissertation. In the absence of direct evidence such an assignment seems questionable. The existence of the charge transfer transition is more difficult to access. If it does exist, the intensity must be much lower than the range predicted by Kon and Sharpless since the band envelope almost surely contains the $d_{x^2-y^2} \rightarrow d_{xy}$ transition. In summary this evidence seems to be inconclusive.

Fowles and Frost have prepared and observed the electronic spectra of a number of complexes of oxotungstate(V) and (VI) and detected a low intensity charge transfer transition in each case. They state that it is not possible to determine whether the transition is from a sigma or a pi level on the basis of their observations.

Further EPR spectra of the oxohalomolybdenum(V) complexes have been measured by Dowsing and Gibson, who report agreement with the values reported in Table III (except for the results of Hare, Bernal, and Gray). Although these authors refer to the

paper by Kon and Sharpless they choose to ignore the opportunity to comment on the suggestion that one of the sigma bonding levels lies at relatively high energy. However, they do interpret their data in terms of the equations for $g_\parallel$ and $g_\perp$ proposed by Ballhausen and Gray (see pg.14), which do not permit any unusual disposition of the levels, and report that the agreement is satisfactory. It is particularly perplexing that $g_\parallel$ is found to be greater than $g_\perp$ for the compound (Et$_4$N)MoCl$_6$ by these workers. It would appear that consistency would require a high energy sigma bonding level in this case also but it is difficult to identify any agency equivalent to the intense field of the oxo group which might be responsible for such a modification of the expected order in this compound.

From the above discussion, an investigation which has as its primary purpose the scrutinization of both the Gray-Hare model and the suggested modifications of this model seems necessary. To achieve this goal, a study of certain $\beta$-diketone complexes of oxomolybdenum(V). was undertaken. This choice was dictated by several factors: (a) Ligands of this type have been used frequently by this group and are readily available; (b) A variety of $\beta$-ketoenolate ligands are at hand, allowing the preparation of a series of complexes; (c) The charge transfer spectra for these compounds should contribute a useful comparison with the charge transfer spectra of the analogous vanadyl complexes,
currently under investigation\textsuperscript{21}.

Since the reactions and properties of compounds of molybdenum(V)\textsuperscript{22} and oxomolybdenum(V)\textsuperscript{23} have recently been surveyed, a general discussion of this topic seems unnecessary. One very important property which does require consideration is the tendency of oxomolybdenum(V) to polymerize.

Magnetic\textsuperscript{13} and spectrophotometric\textsuperscript{24} measurements in hydrochloric acid solution agree that $[\text{MoOCl}_5]^{2-}$ is the principle species in concentrated acid (greater than 10M). It is proposed that upon dilution\textsuperscript{13} a paramagnetic dimer is formed which is the prevalent species in the concentration range 10 to 6 M. The formula $[\text{Mo}_2\text{O}_3\text{Cl}_8]^{2-}$ is proposed for this dimer. An oxygen bridge replaces an equatorial chloro group on each of the monomers. This is supported by the observation\textsuperscript{13} that the only electronic transition affected by dimer formation is $d_{x^2-y^2} \rightarrow d_{xy}$, which is localized in the plane perpendicular to the MoO$^{3+}$ axis. In acid concentrations less than 2 M only diamagnetic species are formed and the structure of these species is unknown.

Although various spectral and magnetic studies have been performed on solutions of oxomolybdenum(V) in hydrobomic acid there is not yet complete agreement on the species present. Some

\textsuperscript{21} Ogden, D., and Selbin, J., unpublished work.


workers\textsuperscript{25,26} report that these systems are not analogous to the hydrochloric acid system in that \([\text{MoOBr}_5]^{2-}\) is not present in even the most concentrated acid. On the other hand, the results of an EPR study are interpreted\textsuperscript{20} to signify that this species is dominant in acid concentrations greater than 9.4 M. As the acid concentration is decreased the tendency of the molybdenum to polymerize is reported by all workers but the identity of the resulting species is still in dispute.

The ability of \(\beta\)-diketones to coordinate with metal ions has been the subject of extensive investigation for many years. In general the ligands contain \(\beta\)-carbonyl groups with at least one proton on the gamma carbon so that keto-enol tautomerism is a possibility.

They act as a bidentate ligand with a wide variety of metal ions and form compounds which may be represented by the general formula:

\[
\begin{array}{c}
[H-C\begin{array}{cc}
\text{O} & \text{M} \\
\text{C} & \end{array} & \\
\text{R} & \end{array}
\]

\[
\begin{array}{c}
[H-C\begin{array}{cc}
\text{O} & \\
\text{C} & \end{array} & \\
\text{R} & \end{array}
\]

\[
\begin{array}{c}
[H-C\begin{array}{cc}
\text{O} & \\
\text{C} & \end{array} & \\
\text{R} & \end{array}
\]


Holm and Cotton\textsuperscript{27} have formulated the following generalizations concerning the structure of such complexes:

(a) The OCCCO portion of the chelate ring lies in the same plane, however, the OMO plane may be at an angle of ~160° to the mean plane of the ligand atoms\textsuperscript{28}; (b) The pairs of M-O, O-C, and C-C distances are of equal length to within experimental error; (c) The ring C-C and C-C distances are intermediate between single and double bond distances. This data requires the existence of some kind of resonance in the chelate ring, but the possibility of any substantial degree of "benzenoid" type resonance, as shown below, is discounted by most investigators.

![Diagram of chelate ring]

The most common methods used to prepare complexes of this kind are described by Fernelius and Bryant\textsuperscript{29}, and a recent article by Fackler\textsuperscript{30} provides references to more recently developed techniques as well as comments on the more traditional procedures. The latter review describes a wide variety of known complexes and, in combination with the monograph by Moshier and

\textsuperscript{29} Fernelius, W.C., and Bryant, B.E., \textit{Inorg. Syn.}, 5, 105 (1957).
and Sievers\(^{31}\), is an excellent introduction to the field. Symbols used for the \(\beta\)-diketones in this dissertation are those proposed by Fackler\(^{30}\).

Complexes of oxomolybdenum(V) with \(\beta\)-diketones have been studied comparatively little. A compound formulated as \(\text{Mo}_2\text{O}_3(\text{AA})_4\) has been prepared by Larson and Moore\(^{32}\); Rosenheim and Nernst\(^{33}\) have synthesized \(\text{MoO(OH)(AA)}_2 \cdot 4\text{H}_2\text{O}\); and the compound \(\text{MoO}_2(\text{AA})\) is reported by Morgan and Castell\(^{34}\). These appear to be the only complexes known prior to this work.

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A. Apparatus

Elemental Analyses

Carbon and hydrogen analyses were performed by Mr. R.L. Sieb of this department using a Carbon-Hydrogen Analyzer manufactured by Coleman Instruments Corp., Maywood, Ill. All other elemental analyses were determined by Micro-Tech Laboratories, Inc., Skokie, Illinois. This firm did not indicate the methods employed.

Infrared Spectra

Spectra were observed from 4000 to 650 cm\(^{-1}\) by means of a model IR-7 Spectrometer made by Beckman Instruments, Inc., Fullerton, California. This is a double monochromater prism-grating instrument which utilizes a prism for primary dispersion of the spectrum into broad bands which are then resolved by the grating. The specifications indicate a resolution of 0.3 cm\(^{-1}\) and a frequency accuracy better than ±2.0 cm\(^{-1}\) in the region of principal interest. The scan of a polystyrene film was used to check the calibration, no correction was necessary. The samples were ground with mineral oil ("Nujol") and the resulting mull was placed between sodium chloride plates.

Far infrared spectra (650 to 300 cm\(^{-1}\)) were also measured for most of the compounds using a Beckman model IR-10 spectrophotometer. In this region the wavenumber accuracy is specified to be ±4 cm\(^{-1}\). A scan of a polystyrene film was employed for calibration. The appropriate correction has been
applied to all of the reported spectra. Samples were run as Nujol mulls between cesium iodide plates.

**Electronic Spectra**

Solutions prepared with a variety of different solvents were examined in one centimeter cells. A Cary 14 spectrophotometer provided spectra in the region from 10 kK toward higher energy until solvent absorption precluded further measurement. The various solvents were all of reagent grade and used without further purification. In each case where spectra are reported a base line of solvent vs solvent was determined to allow elimination of spurious bands.

Low temperature spectra were obtained by means of the same instrument. The samples were mulled with mineral oil and smeared on a piece of filter paper which was taped to a special holder. The holder consisted of a brass plate shaped to fit into an optical Dewar flask. The walls of the Dewar are made of quartz which is transparent to visible and ultraviolet light to about 45 kK. The paper was placed over a hole in the plate which coincided with the light path of the instrument. The samples were initially placed below the level of the liquid nitrogen, but, when sufficient time had elapsed to ensure temperature equilibrium, the liquid was poured off so that the level was just below the light path. In this way interference from nitrogen bubbling was prevented. No improvement in resolution was noted when the sample was below the nitrogen, in opposition to the method described above, and so it was concluded that the temperature did not rise substantially under the conditions of the measurement.
A diffuse reflectance spectrum was observed for one compound by means of a point by point plot of the transmission as recorded on a Beckman DU, single-beam spectrophotometer. Magnesium carbonate was employed as a reference and the spectral range measured was 16.7 to 10.0 kK.

**Equivalent Conductance**

The resistance of solutions having concentrations of $10^{-3}$ to $10^{-4}$ M were determined by means of a model RC 16 conductivity bridge operating at 60 c.p.s. This bridge is manufactured by Industrial Instruments. The solvent was reagent grade acetonitrile from a freshly opened bottle. The cell and solutions were maintained in a thermostated oil bath (temperature 25°C) for half an hour prior to the measurement and during the actual observation of the resistance.

**Magnetic Susceptibility**

The magnetic moments of the molybdenum compounds were determined by the Gouy Method. The sample was tightly packed into a glass tube and the apparent change in mass due to an applied magnetic field was measured.

The balance was an Ainsworth type BCT with magnetic damping (sensitivity 0.05 mg). A model AL7500 Electromagnet produced by Alpha Scientific Laboratories, Inc., Berkeley, California, provided the field applied to the samples. The pole caps of this magnet are four inches in diameter and the air gap is approximately 1½ inches. The coils were connected in series to a variable output power supply which had been adjusted to a current of 8 amperes. According to information supplied with
magnet this should provide a field of approximately 6,000 gauss.
Since the magnet was air-cooled the current was applied intermittently
to prevent overheating and change in field strength.

A double-ended sample tube about 18 cm long was used.
The two ends had been separated by a glass partition and the
lower section sealed. The tube hung from the balance arm on a
nylon line, adjusted so that the partition in the center of the
tube was located at the center of the magnetic field. The amount
of tube hanging below the center of the poles should equal the
amount above the center partially eliminating any correction due
to the tube itself. A draft tube prevented disturbance of the
sample by stray air currents. A thermometer in the balance case
allowed determination of the temperature to within 0.5°C.

Electron Paramagnetic Resonance

The instrument used was a model JES-3BX, X-band
spectrophotometer produced by the Japan Electron Optics Laboratory,
Co., Ltd., Tokyo, Japan and the spectra were recorded as the first
derivative on an xy recorder manufactured by the Riken Denshi Co.,
Ltd., Tokyo, Japan, model XY-D5N. A modulation frequency of
100 kc/sec and modulation widths in the range of 5 to 20 gauss
proved satisfactory. The electromagnet is a low impedance
highly homogeneous field type capable of a maximum field of
13,000 gauss. It is water cooled.
B. Preparation of Compounds

All of the reagents and solvents used were reagent grade chemicals from common commercial sources, except for a few materials which were prepared by procedures found in the literature. The starting material for the majority of the complexes reported below was tetraethylammonium oxopentachloromolybdate(V), which was prepared as needed. This material was especially useful since it is relatively stable when dry and is soluble in several common solvents. For the attempts to prepare the bromo complexes the starting material was tetraethylammonium oxotetraphosphomolybdate(V) monohydrate, which was prepared using the procedures described by Bishop\(^1\).

To obtain either of the substances mentioned above oxotrihydroxomolybdenum(V) (or molybdanyl hydroxide), MoO(OH)\(_3\), was prepared first. Of the several procedures examined, that outlined by Bishop\(^1\) appeared most satisfactory, although the difficulty of filtering the sluggish brown precipitate which results is not exaggerated in his report. After drying and washing with acetone, this compound served as a suitable source for the oxomolybdenum(V) entity.

The method described by Bishop for the preparation of \([(C_2H_5)_4N]_2[MoOCl_4]_5\) presented some problems and so the procedure mentioned by Palmer\(^2\) for the synthesis of \((NH_4)_2MoOCl_5\) was adapted

\(^1\) Bishop, A.D., M.S. Thesis, Louisiana State University, Baton Rouge, Louisiana, 1962.

by the substitution of the appropriate number of moles of
tetraethylammonium bromide for ammonium carbonate, resulting
in a more straightforward method.

\[ ([C_2H_5]_4N)[MoOCl_3(F_6A)]^* \]

The liquid, hexafluoroacetylacetone, was added slowly to
a host, concentrated solution of \([([C_2H_5]_4N)[MoOCl_5]] \) in acetonitrile.
An excess of ligand (2 to 1 molar ratio) was used. The reaction
mixture turned red almost immediately. The solvent was partially
removed by warming under reduced pressure and the resulting precipitate
recovered by filtration. The crude material was stirred with hot
methylen chloride to dissolve the product, after which the unreacted
\([([C_2H_5]_4N)[MoOCl_5]]_2 \) was removed by filtration. The methylene
chloride was then partially removed by evaporation so that an orange,
crystalline product resulted when the liquid was placed in an ice
bath. The crystals were dessicated under a vacuum for 24 hours and
then submitted for analysis.

Calculated for \([([C_2H_5]_4N)[MoOCl_3(CF_3COClCOF_3)] \) %C 28.10,
%H 3.81 %Cl 19.14 %F 20.52 Found %C 27.96 %H 4.18 %Cl 19.25
%F 20.48

\([([C_2H_5]_4N)[MoOCl_3(TF_3A)] \)\]

A hot solution of thenoyltrifluoroacetone dissolved
in a minimum volume of acetonitrile was added to a hot solution of
\([([C_2H_5]_4N)[MoOCl_5]] \) in acetonitrile, while the latter was being stirred.
Two moles of ligand were used per mole of molybdenum(V) compound.

* A list of symbols and abbreviations is provided in the
  front of this dissertation.
The solvent was partially evaporated and the resulting red precipitate recovered by filtration. This product was washed several times with hot chloroform and then dried under a vacuum.

Calculated for \([(C_2H_5)_4N][MoOCl_3(C_4H_3SCOCHCOCF_3)]\)  
\% C 33.73  
\% H 4.25  
\% Cl 18.67  
\% F 10.00  
\% S 5.63  
Found  
\% C 33.51  
\% H 4.51  
\% Cl 18.78  
\% F 10.63  
\% S 5.74

The procedure employed was analogous to that described for the other compounds. A hot solution of benzoyltrifluoroacetone in acetonitrile was added to a hot solution of \([(C_2H_5)_4N][MoOCl_3]\) in the same solvent and the resulting red solution was evaporated to force a precipitate. The red precipitate was washed with cold p-dioxane, although caution is necessary since the compound will slowly dissolve in this solvent. Vacuum dessication was used for three days to attempt to remove water and any remaining solvent. The low chlorine analysis may indicate that some of the dioxane was not removed, although the other analyses appear satisfactory.

Calculated for \([(C_2H_5)_4N][MoOCl_3(C_6H_5COCHCOCF_3)]\)  
\% C 38.35  
\% H 4.64  
\% Cl 18.87  
\% N 2.48  
Found  
\% C 38.36  
\% H 4.88  
\% Cl 17.95  
\% N 2.70

\([(C_2H_5)_4N][MoOCl_3(DBM)]\)

The ligand in this case was dibenzoylmethane. The method was similar to that described above, however the solvent chosen was acetone. A deep red compound was recovered by partial evaporation of the red solution which resulted from the combination of the ligand
and the usual oxomolybdenum(V) compound. The crystalline product was washed several times with hot tetrahydrofuran.

Calculated for \([{(C_2H_5)_4N}][MoOC\_3(C_6H_5COCHCOC_6H_5)]\) % C 48.21 % H 5.46 % Cl 18.60 % N 2.45 Found % C 48.02 % H 5.63 % Cl 18.29 % N 2.67

Several efforts were made with each of the \(\beta\)-diketones, acetylacetone, benzoylacetonel and di-pi-valoylmethane, to prepare other compounds of this type, but it proved impossible to isolate any pure products. This was true even though in all cases the reaction solutions became red or orange, surely indicating appreciable reaction.

\([{(C_2H_5)_4N}][MoOBr_3(DBM)]\)

The ligand, dibenzoylmethane, was dissolved in a small amount of acetonitrile, then warmed and added to a concentrated solution of \([{(C_2H_5)_4N}][MoOBr_4 \cdot H_2O]\) in the same solvent. After partial evaporation a black crystalline compound formed which was washed several times with hot tetrahydrofuran. The product, a reddish-black material, was dried several days under a vacuum.

Calculated for \([{(C_2H_5)_4N}][MoOBr_3(C_6H_5COCHCOC_6H_5)]\) % C 39.17 % H 4.43 % Br 34.00 Found % C 39.08 % H 4.79 % Br 34.15

Despite efforts to prepare other bromo complexes with various \(\beta\)-diketones no further compounds could be isolated. In all cases a change in the color of the solution was noted and microscopic observation revealed very small amounts of reddish crystals in the precipitate which resulted when hexafluoroacetylacetone was used as a
ligand and the procedure followed was similar to that which had proven successful in the other cases. The amount of material was too small to recover by the methods used in this work.

**Attempts to prepare a Fluoro Complex**

The spectral measurements performed by Wentworth and Piper\(^3\) upon what was presumed to be the anion \([\text{MoOF}_5]^{2-}\) present in diluent crystals is the only report of a fluoro complex of oxomolybdenum(V) which could be located in the literature. Apparently neither this compound nor any of its possible derivatives have been isolated. Since the oxo-species of molybdenum(V) usually behaves as a class a acceptor\(^4\) (according to the criteria of Ahrland et al.\(^5\)) the possibility exists that halogen exchange might be successful if the fluoro complex is sufficiently stable. This expectation led to the experiment described below:

Approximately 0.25 g of \([\text{(C}_2\text{H}_5)_4\text{N}][\text{MoOCl}_3(\text{DBM})]\) was placed in a round bottom flask with 80 ml of alcohol and about 0.3 g of sodium fluoride. The mixture was refluxed for several days. During this period the red oxomolybdenum(V) compound dissolved to an increasing extent and the color of the solution faded from reddish-pink to yellow. When no trace of the red color could be discerned the reaction mixture was filtered to remove unreacted sodium fluoride and then evaporated to dryness. A heterogeneous yellow and white


residue remained. The product was dissolved in methylene chloride and unreacted sodium fluoride removed by filtering several times. When the methylene chloride solution was partially evaporated and placed in an ice bath, a yellow precipitate was recovered. Unlike any of the compounds prepared previously, this substance was only sparingly soluble in solvents such as acetonitrile, tetrahydrofuran, acetone and methylene chloride. Since it is unlikely that the exchange reaction was complete it would be expected that some chlorine would remain, causing the carbon and hydrogen analyses to be slightly less than the theoretical values. Based on this reasoning the reported values are in satisfactory agreement with the formulation of the compound as a monomer. However, other evidence, to be discussed later, is not completely consistent with this hypothesis.

Calculated for \([(C_2H_5)_4N][MoOF_3DBM]\] %C 52.88 %H 5.98

Found %C 51.29 %H 6.18

Some explanation is necessary for the choice of solvents in the preparations described above. It is well known that use of a basic solvent or addition of a base greatly enhances the possibility for the formation of \(\beta\)-diketone chelates. Since acetonitrile is a slightly acidic solvent it is to be expected that attempts to conduct reactions of that type in this medium will encounter difficulties. The reporting of the compounds above in no way indicates that these expected troubles failed to materialize. Indeed, it is felt that the failure to produce many of the compounds whose preparation was attempted may be traced directly to the problem of the solvent system.
To circumvent this problem several alternate methods were investigated. Complexes formed using water or ethanol as a solvent with the addition of a base such as sodium acetate yielded small amounts of red material which decomposed unless dried very quickly. No satisfactory formulation of these materials was possible which would agree with the reported analyses. It was impossible to determine if this was due to decomposition, incomplete purification, polymerization, or a combination of several of these factors.

Sodium salts were prepared for some of the \( \beta \)-diketones, but reaction of these substances with oxomolybdenum(V) produced a brown product which analyzed much lower in carbon and hydrogen than the monomer. Attempts to purify these substances failed to improve the situation and it is assumed that they are polymeric species. From some exploratory experiments it would appear that tetrahydrofuran offers the most promise for use as a solvent but the amount of product obtained is very small.

As may be concluded from the preceding commentary the choice of acetonitrile as a solvent was dictated more by the failure to find a more effective medium than by any intrinsic advantage of the substance itself.

C. Experimental Details, Results and Preliminary Discussion

Infrared Spectra

The recorded spectra are listed below for each of the compounds in the region 1700 to 650 cm\(^{-1}\). Intensities are indicated
by the abbreviations s - strong, m - medium, w - weak, sh - shoulder, br - broad, and v - very.

\[ (C_2H_5)_4N][MoO\ell_3(F_6A)] \]

1652 (m), 1623 (w), 1558 (w), 1537 (mw), 1487 (m), 1423 (w), 1394 (w), 1255 (s), 1212 (s), 1154 (vs), 1107 (w), 1066 (w), 1054 (w), 1000 (mw), 976 (m), 945 (w), 907 (w), 814 (m), 782 (w), 742 (w), 662 (m)

\[ (C_2H_5)_4N][MoO\ell_3(TF_3A)] \]

1597 (br, s.), 1589 (sh), 1547 (s), 1538 (sh), 1517 (m), 1482 (s), 1454 (s), 1406 (s), 1393 (sh), 1355 (m), 1345 (s), 1323 (sh), 1305 (br, s), 1258 (s), 1232 (s), 1205 (br, s), 1171 (m), 1150 (br, s), 1074 (w), 1012 (m), 999 (m), 965 (s), 935 (m), 899 (vw), 856 (m), 809 (m), 779 (mv), 774 (ms), 741 (m), 684 (mv), 646 (m)

\[ (C_2H_5)_4N][MoO\ell_3(BF_3A)] \]

1611 (s), 1595 (m), 1575 (s), 1540 (m), 1482 (m), 1451 (sh), 1392 (w), 1322 (s), 1313 (sh), 1290 (vs), 1252 (m), 1203 (s), 1184 (w), 1169 (w), 1143 (s, br), 1080 (m), 1023 (w), 1000 (mv), 966 (s), 944 (m), 900 (w), 820 (w), 782 (m), 742 (w), 708 (mv), 704 (sh)

\[ (C_2H_5)_4N][MoO\ell_3(DBM)] \]

1594 (m), 1589 (m), 1549 (s), 1519 (br, s), 1478 (s), 1453 (s), 1360 (vs), 1317 (s), 1303 (s), 1231 (m), 1181 (mv), 1157 (mv), 1125 (w), 1075 (sh), 1068 (mv), 1022 (mv), 999 (mv), 956 (s), 939 (mv), 927 (w), 889 (w), 815 (s), 789 (mv), 767 (m), 702 (w), 687 (m)
\[(\text{C}_2\text{H}_5\text{)}_4\text{N}[\text{MoOBr}_3(\text{DBM})]\]

1593 (m), 1586 (m), 1546 (s), 1517 (s), 1475 (s), 1452 (s), 1396 (vw), 1355 (s), 1315 (m), 1296 (m), 1255 (vw), 1229 (m), 1180 (m), 1156 (w), 1124 (vw), 1068 (w), 1021 (w), 997 (w), 955 (s), 938 (w), 815 (vw), 787 (w), 758 (m), 700 (vw), 662 (m).

suspected \[(\text{C}_2\text{H}_5\text{)}_4\text{N}[\text{MoOF}_3(\text{DBM})]\]

1598 (m), 1591 (m), 1554 (s), 1535 (s), 1481 (s), 1310 (m, br), 1237 (m), 1171 (w), 1127 (w), 1069 (m), 1022 (w), 1000 (w), 966 (w), 938 (s), 902 (s), 790 (w), 770 (m), 690 (w).

A complete assignment of all of the bands recorded above would require extensive calculations and contribute little toward the goal of this endeavor. For this reason no general interpretation will be attempted. However, it is customary to assign the stretching frequency of the metal-multiply bonded oxygen. It has been pointed out\(^6\) that this absorption is customarily found in the region 900 to 1100 cm\(^{-1}\) for oxometal cations, and that the intensity is usually much greater than any of the surrounding bands. In every case a strong absorption is found which fits this description and these are presumed to be the Mo=O stretches. A listing of these absorptions is found in Table IV.

Before proceeding it should be noted that the terms "metal-oxygen stretch" or "metal-halogen stretch" which are used throughout this section are only meant to designate vibrations of the entire molecules in which the amplitude of the vibration along a particular bond axis is sufficiently greater than the motion of the

balance of the molecule so that the total vibrational motion may be designated in terms of the predominant oscillation.

The spectrum obtained for the compound tentatively designated as \([(\text{C}_2\text{H}_3)_4\text{N}][\text{MoOF}_3(\text{DBM})]\) has two intense bands in this region, at 938 and 902 cm\(^{-1}\). Selbin\(^7\) has indicated that broad absorption bands in the region 920 to 800 cm\(^{-1}\) are characteristic of polymeric metal-oxygen chains. This is in keeping with other data to be presented later and with the low solubility of this compound in solvents which have proven very effective with compounds of this type. Another possibility exists which is also consistent with this data. Cotton\(^8\) has studied the characteristics of molybdenum-oxygen bonds and observed that for a species such as \([\text{MoO}_2]^2+\) or \([\text{MoO}_2]^+\) there should exist two metal-oxygen stretching frequencies, one due to the antisymmetric and the other the symmetric stretch. It is not possible to distinguish among these possibilities from the infrared data alone.

The spectral bands in the region 650 to 300 cm\(^{-1}\) are shown below. The absolute accuracy of the frequencies is estimated as ±6 cm\(^{-1}\) and the accuracy relative to the other spectra recorded is ±2 cm\(^{-1}\). The intensities are indicated by means of the same symbols listed in the previous section.

Although a complete assignment of all of the reported bands would require a normal coordinate calculation for these molecules, a less rigorous set of assignments for a few important vibrations is more than adequate for the purposes of this work. As has already been indicated the high intensity serves to identify the stretching vibration associated with the molybdenum to oxygen terminal bond, and similar indications may be used to identify the metal-halogen frequencies and the metal-chelate oxygen stretch.

Sabatini and Bertini have studied the far infrared spectra of compounds of $[\text{MoOCl}_3]^{2-}$ and $[\text{MoOBr}_3]^{2-}$ with various cations and indicate that the metal-chlorine stretching vibrations are observed.

as a very intense band at a frequency of 327 cm⁻¹. At liquid nitrogen temperatures a shoulder is detected which is also assigned as a molybdenum-chlorine stretching frequency. For the compound K[Pt (AA)Cl₂], Nakamoto and Behnke¹⁰ have used a normal coordinate treatment as a basis for assignments and report two strong absorptions at 339 and 327 cm⁻¹ which correspond to platinum-chlorine stretching frequencies.

Comparison of these reports with the spectra reported herein show definite parallels. In each of the chloro compounds a very intense absorption is observed in the region 318 to 345 cm⁻¹ and this is almost surely the metal-chlorine stretch. For the bromo compound no absorption is discovered in this region, which is to be expected since Sabatini and Bertini⁹ place the metal-bromine stretching frequencies in the neighborhood of 250 cm⁻¹, beyond the range of the instrumentation used. For one of the chloro compounds it appears that the chloro-molybdenum stretch is split into two components.

Determination of the metal-oxygen (chelate) stretch is more difficult. Nakamoto¹¹ has listed the frequencies for this vibration in a number of transition metal acetylacetonates and reports values from 422 to 500 cm⁻¹. All of these metals are in the II or III


oxidation state. The intensity of these bands varies but in all cases they are among the strongest absorptions in this region of the spectrum. The most likely source of confusion appears to be a ring deformation frequency which appears at a slightly higher frequency and is also fairly strong.

As a means of discriminating between these vibrations it must be noted that Nakamoto\textsuperscript{11} reports a shift in the metal-oxygen frequency upon the substitution of electron releasing or withdrawing groups for the methyl groups on the simple acetylacetonates. A CF\textsubscript{3} group has the effect of decreasing the Mo-O bond strength, (decreasing the frequency) whereas a phenyl group should strengthen the bond (increase the frequency). The ring deformation vibration should be less sensitive to this type of effect.

In each of the compounds a peak of higher intensity than those surrounding it is found between 585 and 605 cm\textsuperscript{-1}. This set of bands is assigned as the ring deformation for the following reasons: 1. The frequencies are much higher than those reported by Nakamoto for the M-O stretch. 2. Although the shift in frequency is in the direction predicted, the magnitude of the shift is less than half as great as that reported in other compounds\textsuperscript{11}. 3. The strongest evidence in favor of this assignment would be the existence of other bands which might be assigned to the metal-oxygen stretch and would avoid the first two objections. Such a set of absorption bands does exist.

If for the moment we accept the assignments of metal-halogen and ring deformation frequencies outlined above, an examination of
the far infrared spectra of \([(C_2H_5)_4N][MoOC\&_3(TF_3)A]\) and
\([(C_2H_5)_4N][MoOC\&_3(BF_3)A]\) discloses only bands at 512 and 515 cm\(^{-1}\)
respectively, which stand out above the surrounding bands and are
not yet assigned. It is not unreasonable to assume that the electron
releasing power of the thenoyl group will be similar to that of the
phenyl group (especially if one keeps in mind that our method of
observation is not very sensitive) so that the similarity in values
would be in keeping with a Mo-O stretch. If this is true one would
expect to find a band of reasonable intensity at higher frequency
in the dibenzoylmethane complexes and at lower frequencies in the
hexafluoroacetylacetone complexes.

Both of the dibenzoylmethane complexes have a pair of bands,
either of which might be the metal-oxygen absorption. However, the
first of these is only slightly higher in frequency than the bands
assigned at 512 and 515 cm\(^{-1}\), so it seems probable that the higher energy
band is the molybdenum-oxygen (chelate) stretch in both of these
compounds. This proposition is supported by the fact that the higher
energy band is greater in intensity than the lower energy band. Also,
Nakamoto\(^{11}\) reports a similar doublet for the complex of dibenzoylmethane
with copper(II), in which he assigns the higher frequency band as
the metal-oxygen stretch.

The hexafluoroacetylacetone complex also has a pair of bands
which might be the vibration in question. Although both of them are
equal in intensity, the higher frequency absorption is at 520, which
is higher, not lower, than the frequencies assigned previously for
the complexes with benzoyltrifluoroacetylacetone and thenoyltrifluoro-
acetylacetone. As has been pointed out above it is expected that the
band should be at lower energy, so the absorption at 499 cm\(^{-1}\) is
almost surely the molybdenum-oxygen(chelate) stretch for this compound.

As a check on the accuracy of the proposed assignments, note
that the frequency shift of the metal-oxygen band is 48 cm\(^{-1}\) when the
frequency in the hexafluoroacetylacetone complex is compared with
that of the dibenzoylmethane complex. Nakamoto\(^{11}\) lists the shifts
of this type as being 47 cm\(^{-1}\) for the copper(II) complexes and
61 cm\(^{-1}\) for nickel(II). A summation of all the assignments attempted
is shown in Table IV.

Table IV
Stretching Frequencies Assigned for the New Oxomolybdenum(V) Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mo-O</th>
<th>M-Cl</th>
<th>Mo-O(chelate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[\text{C}_2\text{H}_5\text{N}]MoOCl(_3)(F(_6\text{A})) ]</td>
<td>976</td>
<td>345</td>
<td>499</td>
</tr>
<tr>
<td>[\text{C}_2\text{H}_5\text{N}]MoOCl(_3)(TF(_3\text{A})) ]</td>
<td>965</td>
<td>340</td>
<td>512</td>
</tr>
<tr>
<td>[\text{C}_2\text{H}_5\text{N}]MoOCl(_3)(BF(_3\text{A})) ]</td>
<td>966</td>
<td>335</td>
<td>515</td>
</tr>
<tr>
<td>[\text{C}_2\text{H}_5\text{N}]MoOCl(_3)(DBM) ]</td>
<td>956</td>
<td>318 &amp; 333</td>
<td>547</td>
</tr>
<tr>
<td>[\text{C}_2\text{H}_5\text{N}]MoOBr(_3)(DBM) ]</td>
<td>955</td>
<td>---</td>
<td>550</td>
</tr>
<tr>
<td>[\text{C}_2\text{H}_5\text{N}]MoOF(_3)(DBM) ]</td>
<td>938</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

Electronic Spectra

For all of the compounds except \[\text{C}_2\text{H}_5\text{N}\]MoOF\(_3\)(DBM) \] the
spectra were obtained for solutions in both acetonitrile and methylene
chloride as well as in mineral oil mulls at liquid nitrogen temperatures. One centimeter cells were used for all of the solution spectra. The frequencies of the absorption bands are shown in tabular form (see Table V). In addition this table lists the extinction coefficients for the bands as observed in acetonitrile. In many cases extinction coefficients were also determined in methylene chloride and they were generally smaller in this solvent. Finally, the spectra of the acetonitrile solutions are shown in Figures 3 thru 7. The spectra of the methylene chloride solutions were very similar in appearance.

Unfortunately the amount of \( [\text{C}_2\text{H}_5]_4\text{N}[\text{MoOF}_{3}(\text{DBM})] \) available was not sufficient to obtain spectra of the weaker bands. Strong peaks were observed at 29.2 and 40.0kK for this compound, just as in the other metal complexes in which dibenzoylmethane is present as a ligand. The failure to obtain spectra of the weaker bands is very unfortunate, since this might have provided an important indication of the actual nature of this material.

The \( \beta \)-diketones were observed spectrally as solutions using acetonitrile as a solvent. The frequencies of the absorptions are reported in Table VI.

For future reference it must be pointed out that for each of the complexes for which electronic spectra are reported there exists a set of three to four bands in the region 10 to 21kK which are observed to have relatively low extinction coefficients (30 to 550). The group of bands will be designated as "weak bands" for the
purposes of referral in the discussion later on in the dissertation.
The pair of bands in the neighborhood of 23kK having extinction
coefficients of 400 to 20,000 will be designated as "moderate bands" and the remaining peaks, having very high intensity, in the region beyond 28kK will be called "strong bands".

Table V

Electronic Spectra of the New Oxomolybdenum(V) Compounds

<table>
<thead>
<tr>
<th>CH₃CN solution*</th>
<th>CH₂CL₂ solution</th>
<th>mull at 77°K</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(C₂H₅)₄N][MoOCCL₃(F₆A)]</td>
<td>----</td>
<td>12.1</td>
</tr>
<tr>
<td>12.9 (sh)***</td>
<td>----</td>
<td>12.9</td>
</tr>
<tr>
<td>14.2 (30)</td>
<td>14.1</td>
<td>14.5</td>
</tr>
<tr>
<td>18.9 (80)</td>
<td>18.9</td>
<td>18.7</td>
</tr>
<tr>
<td>20.3 (80)</td>
<td>20.3</td>
<td>20.3</td>
</tr>
<tr>
<td>23.7 (sh)</td>
<td>23.8</td>
<td>23.6</td>
</tr>
<tr>
<td>25.4 (2,600)</td>
<td>25.4</td>
<td>25.1</td>
</tr>
<tr>
<td>28.5 (sh)</td>
<td>31.9</td>
<td></td>
</tr>
<tr>
<td>32.2 (11,000)</td>
<td>35.1</td>
<td></td>
</tr>
<tr>
<td>39.7 (sh)</td>
<td>38.6</td>
<td></td>
</tr>
<tr>
<td>40.5 (sh)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>42.7 (12,000)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table V (continued)

<table>
<thead>
<tr>
<th></th>
<th>CH₃CN solution</th>
<th>CH₂Cl₂ solution</th>
<th>mull at 77°K</th>
</tr>
</thead>
<tbody>
<tr>
<td>([(C₂H₅)₄N][MoOCl₃(TF₃A)]]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>13.7</td>
<td>13.7</td>
<td>11.6</td>
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<tr>
<td></td>
<td>18.9 (300)</td>
<td>18.8</td>
<td>13.2</td>
</tr>
<tr>
<td></td>
<td>20.1 (400)</td>
<td>20.2</td>
<td>18.1</td>
</tr>
<tr>
<td></td>
<td>23.8 (20,000)</td>
<td>23.5</td>
<td>20.0</td>
</tr>
<tr>
<td></td>
<td>24.9 (sh)</td>
<td>24.8</td>
<td>21.5</td>
</tr>
<tr>
<td></td>
<td>28.2 (sh)</td>
<td>27.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>29.1 (39,000)</td>
<td>29.0</td>
<td>23.4</td>
</tr>
<tr>
<td></td>
<td>31.7 (36000)</td>
<td>31.3</td>
<td>24.7</td>
</tr>
<tr>
<td>([(C₂H₅)₄N][MoOCl₃(BF₃A)]]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>12.7</td>
<td>13.9</td>
<td>11.8</td>
</tr>
<tr>
<td></td>
<td>13.8</td>
<td>13.9</td>
<td>14.1</td>
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<tr>
<td></td>
<td>19.2 (180)</td>
<td>19.1</td>
<td>19.0</td>
</tr>
<tr>
<td></td>
<td>20.5 (200)</td>
<td>20.5</td>
<td>20.4</td>
</tr>
<tr>
<td></td>
<td>24.1 (4000)</td>
<td>23.9</td>
<td>21.9</td>
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<tr>
<td></td>
<td>25.1 (4000)</td>
<td>24.9</td>
<td>23.5</td>
</tr>
<tr>
<td></td>
<td>26.1 (4000)</td>
<td>26.0</td>
<td>24.9</td>
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<tr>
<td></td>
<td>29.9 (sh)</td>
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<td>26.1</td>
</tr>
<tr>
<td></td>
<td>29.9 (sh)</td>
<td>30.0</td>
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<td></td>
<td>33.6 (40,000)</td>
<td>33.1</td>
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</tr>
<tr>
<td></td>
<td>38.2 (sh)</td>
<td>37.6</td>
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**Table V (continued)**

<table>
<thead>
<tr>
<th>CH₃CN solution</th>
<th>CH₂Cl₂ solution</th>
<th>mull at 77⁰K</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>[(C₂H₅)₄N]</em>[MoOCl₃(DBM)]*</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>12.8</td>
<td>11.7</td>
</tr>
<tr>
<td>13.6 (30)</td>
<td>13.7</td>
<td>14.2</td>
</tr>
<tr>
<td>18.4 (50)</td>
<td>18.4</td>
<td>18.0</td>
</tr>
<tr>
<td>19.7 (50)</td>
<td>19.6</td>
<td>19.2</td>
</tr>
<tr>
<td>22.2 (420)</td>
<td>22.2</td>
<td>21.6</td>
</tr>
<tr>
<td>23.7 (420)</td>
<td>23.5</td>
<td>23.2</td>
</tr>
<tr>
<td>29.2 (11,000)</td>
<td>29.4</td>
<td>25.4</td>
</tr>
<tr>
<td>32.8 (15,000)</td>
<td>31.2</td>
<td></td>
</tr>
<tr>
<td>35.5 (sh)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>39.4 (sh)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| *[(C₂H₅)₄N]*[MoOBr₃(DBM)] | | |
| 12.8 (sh) | | 11.8 |
| 14.1 (41) | 14.1 | 14.0 |
| 18.2 (550) | 18.2 | 17.7 |
| 21.8 (6000) | 21.5 | 19.5 |
| 22.7 (6000) | 23.7 | 21.1 |
| 27.3 (sh) | 27.0 | 22.5 |
| 29.4 (50,000) | 29.4 |
| 35.6 (sh) | |
| 40.0 (40,000) | 40.0 |

* Extinction coefficients are given in parentheses after the frequencies in acetonitrile solution, sh indicates shoulder.

** All frequencies are in kK units, 1kK = 1000 cm⁻¹.
Table VI

<table>
<thead>
<tr>
<th></th>
<th>Electronic Spectra of the Ligands Used in this Investigation**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dibenzoylmethane</td>
<td>27.2* (sh), 29.5, 34.1 (sh), 40.3</td>
</tr>
<tr>
<td>Benzoyltrifluoroacetone</td>
<td>28.3 (sh), 30.6, 39.1 (sh)</td>
</tr>
<tr>
<td>Hexafluoroacetylacetone</td>
<td>32.1 (sh), 32.7, 38.2, 39.0</td>
</tr>
<tr>
<td>Thenyltrifluoroacetone</td>
<td>28.2 (sh), 31.1, 334 (sh), 39.1</td>
</tr>
</tbody>
</table>

* All frequencies are in kK units, 1 kK = 1000 cm⁻¹.

** In acetonitrile solution.

A diffuse reflectance spectrum was obtained for the compound [([C₂H₅]₄N)[MoOCl₃(DBM)] to determine if the weak shoulder noted on the band at 13.7 kK for this compound might become more prominent when observed by this method. Although a slight indication of the shoulder was noted, there was not much improvement in the band compared with the solution observations and the resolution was not comparable with the mulls reported in Table V. A value of 13.2 kK was determined for the maximum of the broad band by means of diffuse reflectance observations.
Figure 3

Electronic spectrum of \([\text{C}_2\text{H}_5\text{N}]\text{MoC_3A(F}_6\text{A})\) in acetonitrile solution. Concentrations are \(4.5 \times 10^{-3}\) M in the region 10 to 22kK and \(1.15 \times 10^{-4}\) M in the region 22 to 45kK.
Figure 4

Electronic spectrum of [(C₂H₅)₄N][MoOCl₆(THF)₃] in acetonitrile solution. Concentrations are 2.34 x 10⁻⁴ M in the region 10 to 21 kK and 1.9 x 10⁻⁵ M in the region 21 to 45 kK.
Figure 5

Electronic spectrum of $[\{(C_2H_5)_4N\}[MoOC\ell_3(BF_3)]]$ in acetonitrile solution. Concentrations are $2.80 \times 10^{-3} \text{M}$ in the region 10 to 22kK and $1.2 \times 10^{-5} \text{M}$ in the region 22 to 45kK.
Figure 6

Electronic spectrum of $[(C_2H_5)_4N][MoOCl_3(DBM)]$ in acetonitrile solution. Concentrations are $3.23 \times 10^{-3} \text{M}$ in the region 10 to 26kK and $4.1 \times 10^{-5} \text{M}$ in the region 26 to 45kK.
Figure 7

Electronic spectrum of \([(C_2H_5)_4N][MoOBr_3(DBM)]\) in acetonitrile solution. Concentrations are $1.40 \times 10^{-3}$ M in the region 10 to 20 kK, $1.40 \times 10^{-4}$ M in the region 20 to 25 kK, and $9.1 \times 10^{-6}$ M in the region 25 to 45 kK.
EQUIVALENT CONDUCTANCE

The theory of simple conductometric measurements is treated in many standard analytical and physical chemistry texts and so only a brief outline is included here.

The resistance, \( R \), of a solution between two electrodes of surface area, \( A \), and separated by a distance, \( \ell \), is given by the equation

\[
R = \rho \left( \frac{\ell}{A} \right)
\]

The proportionality constant, \( \rho \), is called the specific resistance. Since the conductance is the inverse of the resistance, the reciprocal of the above expression defines the conductance of a solution. It follows that the inverse of the specific resistance is the specific conductance. It is the common practice to evaluate the ratio \( \ell/A \) for a given cell, by observing the resistance of a solution of known specific conductance. The ratio for a particular cell is called the cell constant.

Usually chemists prefer to use the equivalent conductance rather than the specific conductance. If the concentration, \( C \), is expressed as gram-equivalents of solute per liter, the relation between equivalent and specific conductance is

\[
\Lambda = \frac{1000}{\rho C}
\]

Substituting the expression for \( \rho \) produces the following equation for equivalent conductance:

\[
\Lambda = \frac{1000}{\frac{\ell}{A} \cdot \frac{1}{RC}}
\]
The cell used in these determinations has a volume of about 15 ml and is equipped with two platinized platinum electrodes. A rough measurement indicates the radius of the electrodes is about 1 cm and the distance between them is about 0.85 cm. It is estimated from these values that the cell constant should be approximately 0.3.

To accurately determine the cell constant a 0.011N solution of potassium chloride in water was prepared and the resistance of the solution measured. The equivalent conductance of this standard\textsuperscript{12} was 141.0. A value of 0.295 was obtained for the cell constant using this calibration, which compares well with the estimate.

Results of the measurements performed on the oxomolybdenum(V) compounds are shown in Table VII. These values may be compared with results quoted by Drago and Purcell\textsuperscript{13} for a number of one to one electrolytes. The range of equivalent conductances for these known compounds was 168 to 208. Judged on this basis the results obtained in this investigation appear to generally support the contention that these compounds are monomeric, one to one electrolytes, although the conductance of \([\text{CH}_3\text{N}]\text{MoOCl}_3\text{F}_6\text{A}\)] is rather high and may indicate some further dissociation.


Table VII
Equivalent Conductances of Oxomolybdenum(V) Complexes at 25°C

<table>
<thead>
<tr>
<th>Compound</th>
<th>Equivalent Conductance (ohms$^{-1}$ cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(C$_2$H$_5$)$_4$N][MoOC$_3$(F$_6$A)]</td>
<td>210</td>
</tr>
<tr>
<td>[(C$_2$H$_5$)$_4$N][MoOC$_3$(TF$_3$A)]</td>
<td>150</td>
</tr>
<tr>
<td>[(C$_2$H$_5$)$_4$N][MoOC$_3$(BF$_3$A)]</td>
<td>150</td>
</tr>
<tr>
<td>[(C$_2$H$_5$)$_4$N][MoOC$_3$(DBM)]</td>
<td>174</td>
</tr>
<tr>
<td>[(C$_2$H$_5$)$_4$N][MoOBr$_3$(DBM)]</td>
<td>193</td>
</tr>
</tbody>
</table>
MAGNETIC SUSCEPTIBILITY

The theory of magnetic susceptibility is treated in detail in several standard texts. If a cylindrical sample is suspended in a magnetic field so that one end is in an area of high intensity and the other is in a region of negligible intensity the force acting on the sample, F, is given by the equation:

\[ F = \frac{1}{2}A \left( H^2 - H_0^2 \right) \left( K - K' \right) + \delta \]

where
- \( A \) - cross-sectional area of the sample
- \( H \) - higher intensity field strength
- \( H_0 \) - lower intensity field strength
- \( K \) - magnetic susceptibility of the sample per unit volume
- \( K' \) - magnetic susceptibility of the atmosphere per unit volume
- \( \delta \) - force due to the sample tube alone

It is assumed that the sample is of uniform cross-section so that the factor \( \frac{1}{2}A(H^2 - H_0^2) \) may be treated as a constant and a density factor is introduced to transform the volume susceptibility of the sample to gram susceptibility. Now the equation has the form:

\[ 10^6 \chi_g = \frac{\alpha + \beta}{w} \frac{F'}{\delta} \]

where
- \( \chi_g \) - gram susceptibility of the sample
- \( \alpha \) - constant due to displaced air
- \( \beta \) - tube calibration constant


F' - force exerted on the sample in mg (i.e. observed force minus δ)

w - weight of the sample in grams

To determine the correction due to the displaced air, α, the tube is filled to the mark with water and the volume determined by the weight of the water. A volume of 0.2871 mL results (average of two determinations) when this method is used. Figgis and Lewis\textsuperscript{14} state that the volume susceptibility of air is 0.029 × 10\textsuperscript{-6} c.g.s units/cm\textsuperscript{3} at 20°C. The product of the tube volume and the atmospheric susceptibility is 0.0083 × 10\textsuperscript{-6}, the value of α. Since this is at the limits of accuracy of the procedure this constant was ignored in the calculations below.

Evaluation of β is usually performed by observations on a sample of known susceptibility; either cobalt tetrakis(thiocyanato) mercurate(II)\textsuperscript{16} or tris(ethylenediamine)nickel(II)thiosulphate\textsuperscript{17} is suitable for this purpose. The latter compound was chosen because it is a d\textsuperscript{8} system and should yield values similar to those expected for the new compounds to be investigated. It was prepared as described by Adams and Raynor\textsuperscript{18}.

The Gouy tube was packed by adding a small amount of material, then tapping it against the desk top at least 100 times.

\textsuperscript{17} Ogden, D., Dissertation Victoria University of Manchester, 1966.
This process was continued until the solid reached a small mark scribed in the glass. The compound used for calibration was fine-grained and packed well without grinding, however, in most cases, it was necessary to grind the substance in a mortar and pestle before packing. During the filling process care was exercised to prevent fingerprints on the glass and when the packing was complete the tube was wiped with a clean, lint-free cloth to remove any foreign matter picked up during the tapping. Nitric acid or acetone was used to clean the tube and it was dried in an oven at 100°C prior to each determination.

A typical set of results for the calibration is as follows (each observation is the average of three readings recorded to the nearest tenth of a milligram):

1. weight of the empty tube out of the field 160.1 mg
2. weight of the empty tube in the field 160.5
3. weight of the tube and the solid out of the field 275.2
4. weight of the tube and the solid in the field 278.0

These results indicate a tube correction (#2 - #1) of 0.4 mg. The apparent paramagnetism of the tube was probably due to the presence of paramagnetic or ferromagnetic material in the glass (see ref.14, p 413) since changing the position of the tube did not remove the correction. The weight of the sample in this case is (#3 - #1) 0.1151 g. The force exerted by the field on the paramagnetic substance is equal to the weight change when the field is applied to the sample (#4 - #3) minus the tube correction obtained above.
The result is $2.8 - 0.4 = 2.4\ mg$. The gram susceptibility of Ni(en)$_3S_2O_3$ is $10.84 \times 10^{-6}$ at 298°K. (see ref. 18 p 150).

Inserting these numbers into the equation stated earlier one obtains:

$$\beta = \frac{10^6 \chi \cdot w}{P} = \frac{10.84 \times 0.115\ g}{2.4\ g} = 0.520$$

Values of 0.520, 0.527 and 0.508 were determined for three different tube packings. The value of $\beta$ used for the determinations below is 0.518, the average of the above.

To test the accuracy of the procedure using this apparatus a sample of Co[Hg(SCN)$_4$] was prepared according to the literature\textsuperscript{19} and the gram susceptibility was determined as described above. Observed results were $14.9 \times 10^{-6}$ and $15.2 \times 10^{-6}$ or an average value of $15.0 \times 10^{-6}$. The reported value (ref. 14, p 415) is $16.44 \times 10^{-6}$.

A freshly open bottle of ferrous ammonium sulfate was determined to have a gram susceptibility of $30.4 \times 10^{-6}$ compared to the reported value (ref. 14, p 415) of $32.3 \times 10^{-6}$.

As a final test the magnetic moment of a sample of vanadyl acetylacetonate, which had been recrystallized from acetonitrile, was determined. The procedure is shown in detail since it is rather similar to that used for the molybdenum compounds. As before each observation is the average of three readings rounded to the nearest tenth of a milligram.

1. weight of the empty tube out of the field 159.5 mg
2. weight of the empty tube in the field 160.1
3. weight of the tube and the solid without field 444.0
4. weight of the tube and the solid with the field 447.0

tube correction = 0.5 mg; weight of sample = 284.7; \( F' = 2.2 \) mg

\[
10^6 \chi_g = \frac{\beta F'}{w} \\
= \frac{0.518 \times 2.2 \text{ mg}}{0.2847} \\
= 4.00
\]

Multiply by the molecular weight of the compound to obtain the molar susceptibility of the compound, \( \chi_M \)

\[
\chi_M = 4.00 \times 10^{-6} \times 265 \\
\chi_M = 1.060 \times 10^{-6}
\]

The molar susceptibility obtained above must be corrected for the diamagnetism of substance using the values of Pascal's Constants from Selwood\textsuperscript{15}.

<table>
<thead>
<tr>
<th>Element</th>
<th>Correction</th>
</tr>
</thead>
<tbody>
<tr>
<td>vanadium(IV)</td>
<td>-7.00</td>
</tr>
<tr>
<td>oxygen (3 x 1.72)</td>
<td>+5.16</td>
</tr>
<tr>
<td>carbon (5 x 6.00)</td>
<td>-30.00</td>
</tr>
<tr>
<td>hydrogen (7 x 2.93)</td>
<td>-20.51</td>
</tr>
<tr>
<td>total diamagnetic correction</td>
<td>-52.35</td>
</tr>
</tbody>
</table>

This correction is subtracted from the molar susceptibility to obtain the actual molar susceptibility, \( \chi_M' \).
\[ 10^6 \chi_M' = 1060 - (-52.35) = 1112 \]
\[ \mu_{\text{eff.}} = 2.84 \left( T \times \chi_M' \right)^{\frac{1}{2}} \]
\[ = 2.84 \left( 301.7 \times 1112 \times 10^{-6} \right)^{\frac{1}{2}} \]
\[ = 1.65 \text{ B.M.} \]

As a comparison, Figgis and Lewis\(^{14}\) report a value of 1.72 B.M.

Results

Below is a Table of the values obtained for the magnetic moments of the compounds which have been prepared in sufficient quantity to permit use of the procedure. Each value is the average of two determinations. The maximum uncertainty is probably ±0.2 Bohr Magnetons.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Magnetic Moment (Bohr Magnetons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{C}_2\text{H}_5]_4\text{N}[\text{MoOCl}_3(\text{F}_6\text{A})])</td>
<td>1.75</td>
</tr>
<tr>
<td>([\text{C}_2\text{H}_5]_4\text{N}[\text{MoOCl}_3(\text{TF}_3\text{A})])</td>
<td>1.85</td>
</tr>
<tr>
<td>([\text{C}_2\text{H}_5]_4\text{N}[\text{MoOCl}_3(\text{BF}_3\text{A})])</td>
<td>1.77</td>
</tr>
<tr>
<td>([\text{C}_2\text{H}_5]_4\text{N}[\text{MoOCl}_3(\text{DBM})])</td>
<td>1.63</td>
</tr>
<tr>
<td>([\text{C}_2\text{H}_5]_4\text{N}[\text{MoOBr}_3(\text{DBM})])</td>
<td>1.69</td>
</tr>
</tbody>
</table>
ELECTRON PARAMAGNETIC RESONANCE

The effect of the ligand field in a complex ion upon the metal orbitals is most frequently studied by ultraviolet-visible spectroscopy; however, another valuable method for detecting the effect of coordination is electron paramagnetic resonance (EPR) spectroscopy. A very brief discussion of some of the relevant features of this method, drawn from standard references, is included herein.

A free electron possesses a magnetic moment which may be regarded as arising from the spinning motion of the electronic charge. If the electron is placed in a magnetic field the energy is given by the equation

\[ E = -\mu H \cos \theta \]

where \( E \) is the energy in ergs, \( \mu \) is the magnitude of the magnetic dipole moment in ergs per gauss, \( H \) is the magnetic field strength in gauss and \( \theta \) is the angle between the magnetic moment and the direction of the external field. The orientation of the magnetic moment of the electron is quantized in such a way that only two energy values are possible. These two orientations are described by the spin quantum numbers.


number, $m_s$, which has values of $+1/2$ and $-1/2$ only. The usual convention is to assume that the external magnetic field is applied along the z axis and so the total angular momentum of the electronic system along the z axis, $S_z$, is of special interest. If the electron is in an atomic orbital the total angular momentum will be determined by not only the spin momentum but also the orbital momentum, which is indicated by the quantum number, $m_l$. For the unbound electron the latter effect is negligible and so values of $+1/2\hbar$ and $-1/2\hbar$ are the only possibilities for $S_z$. The relation between the magnetic moment and the total angular momentum of the electron is expressed by

$$\mu_z = -\frac{g_e \mu_B}{\hbar} S_z$$

where $g_e$ represents the Lande g factor, a proportionality constant between the magnetic moment and the magnetic momentum for the unbound electron, and $\mu_B$ is the Bohr magneton ($e\hbar/2m_e$). Insertion of this relation into the energy equation mentioned previously produces

$$E = \frac{g_e \mu_B H z S_z}{\hbar}$$

Thus, two energy states are possible for the free electron in a magnetic field: $+\frac{1}{2}g_e \mu_B H_z$ and $-\frac{1}{2}g_e \mu_B H_z$. Transitions between these states are possible by a flipping of the direction of the electron's angular momentum vector, the energy of the transition being given by

$$\Delta E = g_e \mu_B H_z$$
or if the Planck relation is applied

\[ h\nu = g_e \mu_B H \]

The frequency for such a transition, \( \nu \), is in the microwave region of the electromagnetic spectrum when the magnetic field is of the order of several thousand gauss.

The experimental procedure employed is to place the sample in a microwave cavity where it is subjected to constant frequency radiation, and then to apply a magnetic field which is varied until absorption occurs. Both the field and the frequency must be adjusted from one sample to another so that neither one alone is adequate to specify the position of a given absorption. Instead the value of \( g \) in the equation \( h\nu = g_e \mu_B H z \) is used. This factor equals 2.002319 for an unbound electron, but when the electron is in the orbitals of an atomic nucleus the value may be altered appreciably. Changes in the \( g \) value can yield valuable information concerning the magnetic fields which are affecting the electron in an atomic or molecular system.

The actual spectrum is greatly simplified because paired electrons do not give rise to an EPR signal. This restriction is due to the fact that if one of the electrons experiences a "flip" (transition) both electrons will possess the same set of quantum numbers. This is forbidden by the Pauli Principle. Observations of electron paramagnetic resonance are limited to materials having one or more unpaired electrons, that is, paramagnetic substances.
One further factor must be mentioned before proceeding to a description of the actual spectra. If the unpaired electron under observation is in an orbital of atomic nucleus with a magnetic moment, the two energy levels may be split into a series of sublevels. This effect, known as hyperfine splitting, occurs because an atomic nucleus having a spin of \(I\) will have \((2I + 1)\) components of the spin in the \(z\) direction which may interact with the electron magnetic energy levels to produce \((2I + 1)\) new energy sublevels from each of the original levels.

Since 75% of the molybdenum nuclei have zero spin \((^{94,96,98,100}_{\text{Mo}})\) these nuclei have no magnetic moment and no hyperfine splitting results. However, 25% of the nuclei have a spin of \(5/2\) \((^{95,97}_{\text{Mo}})\) and hyperfine interaction between these nuclei and their electrons is to be expected. The resulting energy level diagram is shown in Figure 8. Although two different isotopes are present with spin of \(5/2\) the magnetic moments of the two are so similar that no further splitting of the twelve levels listed is observed experimentally.\(^{23,24}\)

The energy of a given sublevel is obtained from the equation

\[
E(m_s, m_I) = g \mu_B^* z \frac{m_s}{s} + C m_I m_s
\]

here \(m_s\) is the quantum number for the \(z\) component of electron spin momentum, \(m_I\) is the quantum number for the \(z\) component of nuclear


Hyperfine splitting of the energy levels of an electron bound to a nucleus having a spin of 5/2 and in the influence of an external magnetic field. The first column (A) represents the unperturbed energy levels, the second column (B) shows the splitting of this level due to an applied external field and the third column (C) demonstrates the hyperfine splitting of the electronic energy levels because of a nuclear spin of 5/2.
spin and \( \mathcal{Q} \) is the hyperfine coupling constant. The allowed transitions between the various energy levels are determined by the selection rules \( \Delta m_s = \pm 1 \) and \( \Delta m_I = 0 \). Thus the only allowed absorptions are \( E'_1 \rightarrow E''_1 \), \( E''_2 \rightarrow E''_1 \), \( E''_3 \rightarrow E''_1 \), \( E''_4 \rightarrow E''_9 \), \( E''_5 \rightarrow E''_8 \), and \( E''_6 \rightarrow E''_7 \). The transition energies may be readily calculated from the energy values given in the Figure. For instance:

\[
E''_1 - E''_1 = \left( \frac{3}{2} g \mu_B H_z + \frac{5}{4} \mathcal{Q} \right) - \left( -\frac{1}{2} g \mu_B H_z - \frac{5}{4} \mathcal{Q} \right)
\]

\[
\Delta E = g \mu_B H_z + \frac{5}{2} \mathcal{Q}
\]

If the process is continued for all of the transitions it is determined that six lines are predicted and that the separation between each line is equal to \( \mathcal{Q} \).

To recapitulate, the above treatment predicts a single intense absorption, corresponding to \( E''_2 \rightarrow E''_1 \) in the diagram, associated with electrons moving about molybdenum(V) nuclei having a spin of zero. On either side of this line should be found three lower intensity bands caused by interaction between the electrons and molybdenum nuclei having a spin of 5/2. This prediction satisfactorily explains the observed spectrum, which is shown in Figure 9.

Although the instrument used in these experiments has an accurate frequency calibration device, comparable field intensity readings are not directly available. For calibration purposes a capillary tube containing a manganese(II) salt diluted in magnesium oxide powder is inserted in the cavity and this signal is superimposed
Figure 9. EPR Spectrum of $\left[\left(\text{C}_2\text{H}_5\right)\text{N}\right]\left[\text{MoOCl}_3\text{(DBM)}\right]$ in Degassed Acetone Solution
on that of the sample. A system of six, equal intensity lines is observed for this marker. The separation between the third and fourth lines (counting from the low magnetic field side) is 86.7 gauss and the g value for the fourth line is 1.98. From a simple proportion based on the distance between the third and fourth signals, the difference in magnetic field (86.7 gauss), and the distance between the signal to be measured and the fourth line of the marker it is possible to calculate the difference in field intensity, $\Delta H$, between the sample and the reference line.

For the manganese(II) line

$$h\nu = g_{1} \mu_{B} H$$

and for the sample (relative to the fourth signal of the marker)

$$h\nu = g \mu_{B} (H - \Delta H)$$

solving the above for $g$

$$g = \frac{h\nu}{\mu_{B} (H - \Delta H)}$$

inserting the value of $H$ from the first equation

$$g = \frac{h\nu}{\mu_{B} \left( \frac{h\nu}{g_{1} \mu_{B}} - \Delta H \right)}$$

dividing the numerator and denominator by $\mu_{B}$

$$g = \frac{h\nu}{\frac{h\nu}{g_{1} \mu_{B}} - \Delta H}$$

substitution of observed values into this equation allows determination
of the $g$ value. As an example the following data is found for

$$[\text{Et}_4\text{N}][\text{MoOCl}_3(\text{F}_6\text{A})]$$

$$\nu = 9410 \text{ megacycles}$$

$$h = 6.63 \times 10^{-27} \text{ erg} \cdot \text{ sec}$$

$$\mu_B = 9.27 \times 10^{-21} \text{ erg/gauss}$$

$$g_1 = 1.98$$

$$H = 57 \text{ gauss}$$

substituting

$$g = \frac{6.63 \times 10^{-27} \text{ erg} \cdot \text{ sec} \times 9.41 \times 10^9 \text{ sec}^{-1}}{9.27 \times 10^{-21} \text{ erg/gauss}}$$

$$= \frac{6.63 \times 10^{-27} \text{ erg} \cdot \text{ sec} \times 9.41 \times 10^9 \text{ sec}^{-1}}{1.98 \times 9.27 \times 10^{-21} \text{ erg/gauss}}$$

$$g = 1.947$$

The values obtained are shown in Table IX. Average hyperfine splitting values in gauss were determined by measuring the separation of the first and last line of the hyperfine spectrum, comparing this with the splitting between the third and fourth lines of the marker to obtain the field in gauss and then dividing by five. Several attempts were made to locate a signal for the compound tentatively identified as $$[(\text{C}_2\text{H}_5)_4\text{N}][\text{MoOF}_3(\text{DBM})]$$ but all were unsuccessful.

**Table IX**

Electron Paramagnetic Spectral Results for the New Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>$g_{av}$</th>
<th>$Q_{av}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Et}_4\text{N}][\text{MoOCl}_3(\text{F}_6\text{A})]$</td>
<td>1.947</td>
<td>51 gauss</td>
</tr>
</tbody>
</table>
Table IX (continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$g_{av}$</th>
<th>$\alpha_{av}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Et$_4$N][MoOCl$_3$(DBM)]</td>
<td>1.945</td>
<td>55</td>
</tr>
<tr>
<td>[Et$_4$N][MoOBr$_3$(DBM)]</td>
<td>1.982</td>
<td>49</td>
</tr>
</tbody>
</table>

Summation

The experimental evidence presented in the preceding section is entirely consistent with the proposal that all of the compounds except that prepared by fluorine exchange are monomeric oxomolybdenum(V) complexes. The analytical data is in good agreement with values expected for such compounds, whereas, if the species were dimeric substantial changes would be evident in the theoretical values. The bulk magnetic susceptibility results are also within experimental error of the value of 1.73, which is the spin-only result expected for a d$^1$ system. Finally the presence of sharp infrared absorptions in the region 900 - 1000 cm$^{-1}$, probably the metal-oxygen stretch, and the absence of broad absorptions in the region 800 - 900 cm$^{-1}$, usually associated with oxo bridging in dimeric substances, appears to confirm that the substances are monomeric in the solid state.

The same description seems to be satisfactory for solutions of these materials. This is evidenced by the paramagnetism of the compounds, as detected by electron paramagnetic resonance, and the fact that electronic spectra of the solutions are similar to those
observed for the solids as mulls or by diffuse reflectance. Equivalent conductance also corresponds to this assignment.

In summation the evidence reported above gives strong support to the assignment of monomeric, paramagnetic nature to all of the compounds prepared in this investigation (except one) regardless of whether they are in solution or the solid state. The lone exception is the complex identified as \([(C_2H_5)_4N][MoOF_3(DBM)]\). The failure to observe a signal by means of EPR is indicative of either molybdenum(VI) or some dimeric species, but in the absence of further supporting evidence it is dangerous to make any proposal based only on the absence of a signal. It is obvious that further work is required on this compound and this will be discussed in the final section of this dissertation.
DISCUSSION

This section is intended to be a detailed explanation of the electronic spectra of the new compounds described previously, especially with regard to the effectiveness of the Gray and Hare scheme as a suitable model for the elucidation of these results. It is assumed that the evidence presented earlier is sufficient to support the proposal that the complexes are monomeric, paramagnetic, oxomolybdenum(V) species and so this will be treated as an established fact. Since it has not yet been completely characterized, the compound produced by fluorine exchange will not be discussed in any detail and it is not included in any of the general conclusions advanced in the course of the following commentary. In the absence of any contrary data, a gross octahedral configuration is presumed for the new complexes.

Assignment of a coordinate system appropriate for the new species is complicated by the fact that it is not known if the β-diketone is attached to the metal only in the plane perpendicular to the oxo group or if one of the chelate oxygens is trans to the oxo group. As will be explained later, the former assumption is more consistent with the intensities of the bands which are presumed to be d-d transitions, and, based on this supposition, the coordinate system shown in Figure 10 is chosen.

Using this model requires $C_5$ symmetry for molecules in which $R_1$ and $R_2$ are identical, or $C_1$ symmetry in the event that
Figure 10. Coordinate System Used in C₃ Symmetry
they are different. The $C_s$ character table appropriate for the coordinate system adopted is given below:

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_s$</td>
<td>E</td>
<td>$\sigma_{xz}$</td>
</tr>
<tr>
<td>A'</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>A''</td>
<td>1</td>
<td>-1</td>
</tr>
</tbody>
</table>

From this table it may be readily seen that $d_{x^2-y^2}$, $d_z^2$ and $d_{xz}$ belong to the A' representation and $d_y$ and $d_{xy}$ belong to the A'' representation. The change in the arrangement of the axes must be accompanied by a re-evaluation of the ordering of the energies of the metal d orbitals. Some adjustment of the array of d levels used in $C_4v$ symmetry is probably required to harmonize with the new disposition of the axes.

Since the $d_{x^2-y^2}$ orbital points between all of the ligands in the equatorial plane and away from the axial ligands, especially the oxo group, this will become the ground state orbital. The $d_{xz}$ and $d_{yz}$ levels also point between all of the ligands but will be higher in energy due to their having considerable electron density in the vicinity of the oxo group. These two levels, which are degenerate in $C_4v$ symmetry, will still be very similar in energy, but should differ slightly since the environments are not exactly the same. It is not possible, using simple Crystal Field arguments, to decide the exact magnitude of the splitting, or which one will be lower in energy, but the energy difference is expected to be
rather small. Because it points directly at the equatorial ligands the $d_{xy}$ orbital should be next and the $d_{z^2}$ level is surely highest in energy, pointing directly at the oxo group.

To summarize the qualitative arguments presented above, the major changes in the arrangement of the metal d orbitals as the symmetry is changed from $C_{4v}$ to $C_s$ and the axes revised to correspond to the new symmetry is the certainty that the degeneracy of the $d_{xz}, d_{yz}$ level is removed and the exchange of positions of the $d_{xy}$ and $d_{x^2-y^2}$ orbitals, so that the latter becomes the ground state.

A. Assignment of the "Weak" Intensity Bands

In a $d^1$ system, such as oxomolybdenum(V), only three d-d transitions are possible: $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$, (which may be split into two bands by the low symmetry), $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{z^2} \rightarrow d_{x^2-y^2}$. The intensities of ligand field absorptions are quite low, the extinction coefficients being always less than 500 and frequently having values and an order of magnitude smaller. It is logical to look for these transitions in the region of the spectrum where bands, previously designated as "weak bands", have been observed.

The first, and most definite, assignment which can be made in this region is to ascribe the broad, weak band centered at about 14 kK in all of the complexes as the $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ excitation. This is consistent with the work of Gray and Hare, if the change in coordinate system is taken into account. As was
pointed out in the introduction, the existence of a band of this type, at this frequency in so many different oxomolybdenum(V) complexes is impossible to explain unless the origin of the absorption is closely related to the tetragonal distortion resultant from the presence of the oxo group. The invarience of the frequency when dealing with so many different ligands eliminates the possibility that it might be connected with the ligand and at the same time prevents the assignment of this band as \( d_{xy} - d_{x^2-y^2} \), for the difference in energy between these two levels is equal to 10Dq. A change in the ligand should produce a corresponding change in 10Dq, and the failure to observe such a change eliminates the latter possibility.

Having arrived at a firm assignment for the peak, it is next necessary to inquire if any evidence is observed for the splitting, which might exist between the \( d_{xz} \) and \( d_{yz} \) levels. It is to be expected that difficulty would be encountered in observing any separation because of the broad envelope of vibrational components which compose the transition. Unless the frequency difference is large the overlap of the two band envelopes will make resolution difficult. A shoulder is observed on the 14kK band for all of the compounds in mulls at 77\(^\circ\)K and is frequently observed in solution spectra. This may represent the expected splitting. On the other hand there exist two further possibilities: it may be only a particularly prominant vibrational transition or it may be a metal-to-ligand transition. No evidence is available which allows evaluation of
these possible choices.

The next problem is to ascertain the identity of the pair of bands which appear in the region 18 - 21 kK and are more intense than the band previously mentioned. Several possibilities exist. The \( d_{xy} - d_{x^2-y^2} \) transition almost surely exists in this area and the two bands observed in solution may simply be vibrational components of this single, d-d transition. A second possibility would place all the ligand field bands at low energy, assigning one of the absorptions to the \( d_{xy} - d_{x^2-y^2} \) and the other to \( d_{z^2} - d_{x^2-y^2} \). Finally it might be feasible to explain them as a combination of the \( d_{xy} - d_{x^2-y^2} \) and an intraligand transition from a singlet to a triplet state. The validity of each of these possibilities must be examined.

The possibility of detecting a singlet to triplet transition in the absorption spectrum of a transition metal complex is usually not considered. Very weak singlet to triplet absorptions have been reported in some organic molecules\(^1\) but up until now there have been no such definite assignments reported for the absorption spectra of transition metal complexes. There is, however, research being completed in this laboratory\(^2\) which is consistent with such an assignment for a low intensity peak found in the electronic absorption spectra of a large number of \( \beta \)-ketoenolates of the vanadyl ion.

2. Ogden, D., and Solbin, J., unpublished work.
Since the oxomolybdenum(V) system bears such a close resemblance to oxovanadium(IV) it is reasonable to attempt to find support for this contention in the present work. Unfortunately, the spectra reported fail to contribute to the problem. Definite assignment of singlet-triplet character in these spectra is not possible, judging from the best evidence available.

The basis for the statement made above is twofold: The extinction coefficients for most bands in the region where such a transition might be found are much too high (as great as 550) and the agreement of the frequencies is poor when compared with Ogden and Selbin's values for the presumed singlet-triplet absorption. The failure to agree with the results of Ogden and Selbin might easily be explained by the effect of the different metal ions on the β-diketones but the intensity argument is difficult to overlook.

One other chance for the singlet-triplet assignment is the band at 20 to 22 kK which is visible only in mulls at liquid nitrogen temperatures. Lacking any accurate measure of the intensity it is difficult to exclude such a hypothesis but, as nearly as may be determined from the mull spectra, it is similar in intensity to the two bands previously examined. It will be seen shortly that these bands are consistent with the postulation of vibrational structure of a d-d transition. Under these circumstances it is not possible to completely eliminate the singlet-triplet possibility, but it does appear unlikely.

The position of the $d_{z^2} \rightarrow d_{x^2-y^2}$ excitation is a matter of
some debate. On the basis of theoretical arguments the equivalent transition has been placed at very high frequencies by Ballhausen and Gray\(^3\) in \(\text{VO(H}_2\text{O})_5^{2+}\), by Gray and Hare\(^4\) in \([\text{MoOCl}_5]^2^-\), and by Wentworth and Piper\(^5\) in \([\text{MoOX}_5]^2^-\) (where \(X\) is Cl, Br, or F). As has been pointed out by Selbin, Maus, and Johnson\(^6\), the frequency of this transition is expected to be higher in the acetylacetonate complex of vanadyl than in the pentaaquo complex. Despite this there has been a tendency to assign the transition at low frequencies in \(\beta\)-diketone complexes. A similar trend is found for the molybdenyl complexes, as was noted in the introduction of this dissertation while discussing the work of McClung et al.\(^7\). It is apparent that the location of the \(d_{z^2} \rightarrow d_{x^2-y^2}\) transition at frequencies as low as 18 or 19 kK might be given some credance by various workers and so the validity of such an assignment must be considered.

One approach is to tentatively place the transition at about 20 kK and test the hypothesis by determining values for \(D_q\), \(D_s\), and \(D_t\) from the equations of Wentworth and Piper\(^5\). Suppose the following assignments are made for the complex \([\text{(C}_2\text{H}_5\text{)}_4\text{N}]\text{[MoOC}_2\text{F}_3\text{]}\):\[
\begin{align*}
\text{d}_{xz}, \text{d}_{yz} & \rightarrow \text{d}_{x^2-y^2} & 13.8 \text{ kK} \\
\text{d}_{xy} & \rightarrow \text{d}_{x^2-y^2} & 19.2 \text{ kK} \\
\text{d}_{z^2} & \rightarrow \text{d}_{x^2-y^2} & 20.5 \text{ kK}
\end{align*}
\]

The energies of these transitions are given in terms of the constants $D_q$, $D_s$ and $D_t$ in the following way:

$\begin{align*}
&d_{xz}, d_{yz} \leftarrow d_{x^2-y^2} - 3D_s + 5D_t \\
&d_{xy} \leftarrow d_{x^2-y^2} \quad 10D_q \\
&d_{z^2} \leftarrow d_{x^2-y^2} \quad 10D_q - 4D_s - 5D_t
\end{align*}$

Simple algebraic solution yields $D_q = 19.2 \text{ kK}$, $D_s = -2.2 \text{ kK}$ and $D_t = +1.4 \text{ kK}$. The arguments expounded by Wentworth and Piper for the acentric, tetragonal case (see introduction pg. 12) should still be applicable if it is possible to assume that the ligand field exerted by the planar chloro groups is not much different from the field resulting from the oxygens of the chelate. The failure to discover significant separation of the $d_{xz}$ and the $d_{yz}$ levels and the fact that the $g_{av}$ values obtained by electron paramagnetic resonance measurements are very similar to those reported for $[\text{MoOCl}_5]^{2-}$ seems to sustain this supposition as being a valid first approximation. Within the limits of this approximation the conclusion of Wentworth and Piper is inescapable: $D_s$ and $D_t$ must both be negative quantities. It might be argued that the simplification introduced here, in combination with the generally disputable nature of the premises basic to Crystal Field Theory, make the reliability of the conclusion only provisional, but the disparity between prediction and observation is so great that the theory appears sufficiently conclusive to eliminate the possibility of assigning the $d_{z^2} \leftarrow d_{x^2-y^2}$ transition in the 20kK region of the spectrum.
The use of Ds and Dt values as a test for a set of assignments is very useful, but this is not as satisfactory as a method which might allow the prediction of the frequencies to be expected for one or more bands. In an effort to accomplish this end the Crystal Field approach to ligand field transitions was examined with some care for the case of the acentric, tetragonal field (presumably the symmetry of the [MoOCl₆]²⁻ ion) and the results are derived in Appendix I. As is demonstrated in this treatment the energies of the d levels may be delineated in terms of either of two different sets of constants: Dq, Ds and Dt or \( \alpha_2 \) and \( \alpha_4 \). Direct calculation of any of these parameters has proven highly inaccurate, but the idea presented itself that if the relationship among the various levels might be graphically represented, and if certain values obtained directly from experiment might be applied to this graphical presentation, the possibility exists that plausible, numerical predictions might be forthcoming for at least one of the ligand field transitions. Such a manipulation is best predicated upon the energies stated in terms of the alpha constants. To simplify these energy expressions to the state where only two variables are necessary the following assumptions are made:

a. Various ratios between \( \alpha_2 \) and \( \alpha_4 \) are presented in the literature, but all of the values suggested are between \( \alpha_2 = \alpha_4 \) and \( \alpha_2 = 3\alpha_4 \). Graphs were constructed based on both of these extremes and the graph resulting when \( \alpha_2 = 3\alpha_4 \) is shown here, since it places \( d_{z^2} \) at a lower energy. That is, it is more favorable
to the assignment which is in contention.

b. The field exerted by the ligands in the equatorial plane, as indicated by $\alpha_{4}^{xy}$, is set at a constant value, equivalent to that of the actual complex.

c. The axial chloro ligand is assumed to exert a field equal to that of the equatorial ligands (i.e., $\alpha_{4}^{xy} = \alpha_{4}^{z+}$).

d. The effect of varying the field of the remaining axial group (the oxo group) can now be measured by allowing the ratio $\alpha_{4}^{z+}/\alpha_{4}^{xy}$ to vary from zero to three.

The assumptions described above produce a graphical picture of the energy level changes resultant from holding the ligand field intensity of the chloro groups constant for the ion $[\text{MoOCl}_{4}]^{2-}$ and allowing the oxo group to approach along the Z axis from an infinite distance to a position at which it produces a very intense field.

The equations describing the energies of the metal d orbitals in terms of the constants $\alpha_{4}^{xy}$ and $\alpha_{4}^{z+}$ are:

\[
E(d_{xy}) = \frac{3}{21} \alpha_{4}^{xy} - \frac{17}{21} \alpha_{4}^{z+}
\]
\[
E(d_{xz}, d_{yz}) = -\frac{19}{21} \alpha_{4}^{xy} + \frac{5}{21} \alpha_{4}^{z+}
\]
\[
E(d_{x^2-y^2}) = \frac{38}{21} \alpha_{4}^{xy} - \frac{17}{21} \alpha_{4}^{z+}
\]
\[
E(d_{z^2}) = -\frac{3}{21} \alpha_{4}^{xy} + \frac{24}{21} \alpha_{4}^{z+}
\]

The graph shown in Figure 11 is the result of this approach. It must be emphasized that, although the method employed has been described in terms of a specific complex anion, the results are general and may be applied to any other system of this same symmetry.
Figure 11. Graphical Representation of the Effect of the Field Intensity of an Axial Ligand Upon the Energies of the Metal d Orbitals. An Acentric Tetragonal Arrangement is assumed. The Dashed Line Indicates the Position of the [MoOCl₅]⁻ anion on the Graph. For this Compound $\alpha_{4y}^{x^+}$ has a Value of 13.5 kK.
which is characterized by a single intense ligand group which may be presumed to act as the source of the predominant coulombic field. By appropriate modifications similar representations may be obtained which may be utilized for the interpretation of other symmetries, such as $D_{4h}$. The energy axis is measured in terms of the parameter $\alpha_{4}^{xy}$, which is proportional to $Dq$.

$$Dq = \frac{1}{6} \alpha_{4}^{xy}$$

Using the observed value of $Dq$ for a compound and choosing a point on the graph where the ratio of the frequency of the $d_{xz},d_{yz} \rightarrow d_{xy}$ to the $d_{x^2-y^2} \rightarrow d_{xy}$ transition is correctly represented the value of the ratio of $\alpha_{4}^{z^+/\alpha_{4}^{xy}}$ and the frequency for the $d_{z^2} \rightarrow d_{xy}$ transition are obtained. For the complex $[\text{MoOC\text{\text{\text{\text{-}}}5}]^{2-}$ the ratio is 2.0 and the predicted frequency of the transition $d_{z^2} \rightarrow d_{xy}$ is 50 kK.

Before using these results one must reconsider the method and decide if it is sufficiently valid to provide a trustworthy estimate of the position of the absorption peak in question. Particular note must be taken of two of the assumptions required in the preparation of the graph. First, the axial chloro group has been treated as a source of electrical repulsion equivalent to the equatorial ligands. In fact, the presence of the strongly bonding oxo group trans to the chloro group should increase the metal-halogen distance compared to that found for the equatorial halogens, decreasing the ligand field strength of the former group. This would, in turn, cause a lowering of the energy of the
$d_{z^2}$ level. On the other hand, the relationship between $\alpha_2$ and $\alpha_4$, which serves as a basis for the diagram, is chosen to give a minimum value for the energy of the $d_{z^2}$ level. It is intended that these two effects should cancel each other out and it is probable that if an error results, it is one of underestimating the energy of the level rather than overestimation.

The fallacy inherent in the Crystal Field Theory itself is more difficult to assess. The failure of this theory to provide any avenue for the introduction of covalent bonding is commonly offered as one of its principle shortcomings, but the ramifications of this oversight in the case of the $d_{z^2}$ are difficult to ascertain. As has been indicated previously the sigma bonding between the metal and the oxo group is predominantly by means of the molecular orbital which has the $d_{z^2}$ metal orbital as an important component. Similarly, a molecular orbital composed partially of the $d_{xz}$ and $d_{yz}$ metal orbitals is the principle source of pi bonding between two groups. Pi bonding to any of the other ligands is considered to be relatively unimportant from the viewpoint of its effect on the metal. This leads one to believe that the major result of covalency in the compound under discussion will be to change the energy of the $d_{xz}$ and $d_{yz}$ orbitals. The sigma bonding in which the $d_{z^2}$ is involved should preclude any important pi bonding. On the basis of this reasoning the Crystal Field Theory should provide a reasonably correct description of this orbital, at least as far as may be determined by the use of very qualitative arguments.
The conclusion reached from the rather lengthy digression above is that the \( d_{z^2} \) metal orbital lies at comparatively high energy in the ion \([\text{MoOCl}_5]^{2-}\) as far as can be determined by elementary Crystal Field calculations. A number of limitations must be noted in the approach used, but an evaluation of these approximations, on the basis of qualitative arguments leads one to believe that the \( d_{z^2} \rightarrow d_{xy} \) absorption should be found at high frequencies, perhaps as high as 50 kK. The similarity between the observed spectrum of the \([\text{MoOCl}_5]^{2-}\) ion and the complexes of the type \([\text{MoOCl}_3 L^-]\) (where \( L \) is a \( \beta \)-diketone anion) suggests that the analogous transition, \( d_{z^2} \rightarrow d_{x^2-y^2} \), in the latter complexes will also lie at very high frequencies, probably covered by the profusion of intense bands found at energies greater than 20 kK.

The preceding arguments render unlikely, if not untenable, any assignments of the bands at 18 to 20 kK which ascribes them to intraligand singlet-triplet or \( d_{z^2} \rightarrow d_{x^2-y^2} \) and gives support to the third possibility offered, namely, that the bands in this region represent only the \( d_{xy} \rightarrow d_{x^2-y^2} \) transition, split into several components by vibronic interaction. The splitting between the bands, including the absorption observed only in the mulls at liquid nitrogen temperatures, is between 1.2 and 1.6 in every case except \([\text{(C}_2\text{H}_5)_4 N][\text{MoOCl}_3(\text{DBM})]\), where a very indistinct band at 20.0 kK is separated by only 0.8 kK from the band at 19.2 and \([\text{(C}_2\text{H}_5)_4 N][\text{MoOBr}_3(\text{DBM})]\), which has only two bands in this region instead of three, the separation being 1.8 kK. The infrared spectrum
of the compounds (see pg.36) includes a number of intense absorptions in the region 1,400 to 1,600 cm\(^{-1}\) (1.4 to 1.6 kK) which might explain a splitting of this magnitude.

If the explanation of the set of three bands presented above is correct the separation between the first and second bands (counting from the higher frequency side) should be greater than the difference between the second and third bands. Observed splittings do not agree with this prediction as well as might be hoped, but the variation is within the limits of error of the measurements.

The best possible explanation concerning the bands found below 21 kK in the new oxomolybdenum(V) complexes has been deduced to be the assignment of all of the prominent bands as \(d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}\) or the \(d_{xy} \rightarrow d_{x^2-y^2}\) transitions. This is consistent with the predictions of Gray and Hare.

A brief pause is necessary at this point to reconsider the assumption that the \(\beta\)-diketone chelate is bonded to the metal so that both points of attachment are in the equatorial plane. Using this model the symmetry of the complexes is \(C_2\) for symmetrical \(\beta\)-diketones and \(C_1\) if the \(\beta\)-diketone is not symmetric. Placement of one of the chelate oxygens trans to the oxo group would have produced complexes of the same symmetry, \(C_2\), regardless of the type of \(\beta\)-diketone used. Commonly used symmetry arguments, such as are described in Cotton's exceptionally useful book on group theory,\(^8\)

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prove that all electronic transitions are allowed in any polarization if the symmetry is \( C_1 \), but in \( C_3 \) symmetry transitions are allowed in either the \( z \) orientation or the \( x \) and \( y \) orientation. The intensities are expected to be lower in the latter case because the transitions are not completely allowed. Comparison of the spectra of the four compounds of the type \([\text{MoOCl}_3(R_1\text{COCHCOR}_2)]^-\) will show that if presumably equivalent bands are compared the intensity is always greater when \( R_1 \) is different from \( R_2 \) than when they are the same. This fact is the basis for presuming that the chelation occurs only in the plane of the molecule.

B. Assignment of the "Moderate" Bands

The group of two or three bands observed in the region 21 to 26 kK has previously been designated as "moderate bands" because they are found to have intensities intermediate between the weakest and strongest bands in the spectrum. The absence of any absorption bands in this region of the spectrum for the free ligands indicates that these are not intraligand transitions. It is highly probable that these absorptions are charge transfer transitions from the ligand to the metal. These arise when one of the electrons in a filled molecular orbital is excited to one of the orbitals consisting primarily of a metal d level. The possibility also exists that the origin might be metal to ligand, but the observations of Mitchell and Williams\(^9\) on the spectra of a variety of molybdenum(V)

complexes led them to conclude that only the ligand to metal transition was intense enough to be readily detected.

Three different proposals have been made concerning the filled molecular orbital having the highest energy in oxomolybdenum(V) complexes: Gray and Hare\(^\text{10}\) suggested a pi level associated with the oxo group was highest in energy, Kon and Sharpless\(^\text{11}\) proposed a sigma level associated with the bonding of the planar ligands, and Allen \textit{et al.}\(^\text{12}\) placed a pi chloro level as the highest filled molecular orbital. The merits of some of these models has already been discussed in the literature (as reported in the introduction), and these findings must be briefly reviewed below in addition to investigating new arguments which might cast further light on the problem.

Allen \textit{et al.}\(^\text{12}\) and Horner and Tyree\(^\text{13}\) have presented very cogent criticisms of the placement of the pi oxo levels above all of the other filled molecular orbitals. The blue shifts of the charge transfer bands of the \([\text{WOCl}_5]^2^-\) anion and the red shift of the charge transfer bands of \([\text{MoOBr}_5]^2^-\), both relative to the absorptions observed for \([\text{MoOCI}_5]^2^-\), are impossible to explain using the Gray and Hare scheme. On the basis of these arguments

\begin{itemize}
\end{itemize}
the Gray and Hare model is judged to be the least satisfactory with regard to the placement of the filled molecular orbitals.

It is more difficult to form an estimate of the validity of the Kon and Sharpless\textsuperscript{11} proposal. As has been pointed out earlier there is no commentary on their work available in the literature. Their suggestion is attractive because it not only satisfies the objections put forth by Allen \textit{et al.}\textsuperscript{12}, but also provides an easy explanation of the comparatively low intensity of the first charge transfer band in the spectra of complexes such as [MoOCl\(_5\)]\(^2^-\) and [MoOBr\(_5\)]\(^2^-\). The transition is forbidden on the basis of symmetry arguments and so would be expected to have low intensity. Also, Cotton and co-workers\textsuperscript{14} have recently performed extended Hückel-type MO calculations on bis(β-ketoenelate) complexes of copper(II) and found sigma ligand orbitals which lie above the pi orbitals. The difference between the copper(II) system and the oxomolybdenum(V) system is so great that it is apparent that no grounds exist for direct comparison, but the results do suggest the possibility that the usual presumption that pi ligand levels will lie above sigma ligand levels should be exercised with considerable care. It is unfortunate that the issue is further confused in the case of Cotton's work by the failure to observe any indication of one of the two transitions predicted to originate from these sigma orbitals.

The present author has encountered a number of questions

with regard to the Kon and Sharpless\textsuperscript{11} proposition which he has been unable to answer satisfactorily. The problems which they represent are most perplexing and present a considerable stumbling block to the complete acceptance of the Kon and Sharpless Theory.

These workers argue that the sigma levels are at high energy in the oxomolybdenum(V) complexes because of the effect of the strongly bonding oxo group. Yet they find no evidence of this effect in the complex $\text{VO(H}_2\text{O)}^{2+}$. It would seem that the d orbitals of vanadium(IV) should overlap better with the oxygen orbitals because they are smaller than the molybdenum orbitals. Also the aquo groups may not be capable of bonding as strong as that of the chloro groups. On this basis the sigma orbitals should more likely be found at high energy values in the vanadyl complex, contrary to the apparent observations.

Kon and Sharpless\textsuperscript{11} also state that the reports of a number of compounds (such as those described in this dissertation) formed by the replacement of the chloro groups of $[\text{MoOCl}_5]^{2-}$ with various ligands is indicative of the weakness of the metal-halogen bonds. As has been pointed out by many authors the results of substitution or exchange reactions are a measure of the kinetic stability of bonds and frequently give an erroneous picture of bond strength. Thermodynamic stability is the property which must be considered to evaluate the energy of the bonds. Infrared observations are a much better measure of bond strength than suppositions based on reaction products.
The infrared frequencies of the metal-halogen bonds in the anions \([\text{MoOCl}_5]^2-\) and \([\text{MoOBr}_5]^2-\) have already been determined\(^{13a}\) and found to be very similar to the values reported for other metal complexes. Far infrared studies of the new complexes reported herein indicate slightly higher stretching frequencies for the metal-halogen bonds than in the pentahalo species and values for the metal-oxygen(chelate) stretch higher than any reported by Nakamoto\(^8\). The infrared results would seem to indicate the bonds are as strong or stronger in the oxomolybdenum complexes than in other species where no oxo group is present.

A final problem arises from the requirement that the metal-halogen bonds in the plane become weakened by the oxo group to a greater extent than the axial halo group. Normally it is the group trans to an intensely bonding group which is affected in this way.

If pi orbitals from the equatorial ligands and the axial halo group are highest in energy, all of the problems examined above are avoided and the only obstacle is the lack of a satisfactory explanation for the low intensity of the ligand to metal transition in the pentahloxomolybdenum(V) ions. Acceptance of this idea is especially welcome since the similarity between the spectra of halo and oxohalo complexes of various metal ions, as noted by Horner and Tyree\(^{14}\), is not consistent with the Kon and Sharpless proposal.

The best conclusion which can be reached on the basis of the available evidence is that the ligand-to-metal transitions observed in the oxopentahalomolybdate(V) complexes as well as the new compounds which are the subject of this dissertation consist primarily of the excitation of an electron from a \( \pi \) orbital associated with ligands other than the oxo group to a molecular orbital which has as its predominant component the metal \( d_{x^2-y^2} \) or \( d_{xy} \) orbital (depending on whether the symmetry is \( C_s \) or \( C_{4v} \)). Such a conclusion must be accepted as being only tentative until enough information concerning the \( 4d \) orbitals is available to allow an appropriate calculation which will cast more light on the problem.

C. Construction of an Empirical Orbital Diagram

The situation has by this point become sufficiently complex to require the construction of a molecular orbital diagram. The order of the molecular orbitals which are principally composed of metal \( d \) orbitals has been established and it has been decided that only \( \pi \) ligand orbitals are important in the interpretation of the electronic spectra. The \( \beta \)-diketone \( \pi \) system is usually represented as five molecular orbitals, the first three of which are filled, bonding levels and the other two empty antibonding levels. These energy levels will be designated by the greek letter \( \pi \), followed by an appropriate numerical subscript, i.e., the lowest energy orbital is \( \pi_1 \). Chlorine \( \pi \) levels are also possible in the diagram and will be indicated as \( \pi(C\ell) \) where required. The \( \pi \) oxo levels
are surely required and will be designated as $\pi$(oxo). To organize all of these levels into a diagram it is essential to assign relative energy values. The only means at hand to accomplish this are qualitative arguments based on general chemical and spectral information. It is also necessary to examine the extent of $\pi$ bonding between the metal and the various ligands and estimate the effect of any such overlap on the molecular orbitals.

The half-filled $d_{x^2-y^2}$ metal orbital must lie above any of the filled ligand $\pi$ orbitals or else an electron will tend to be transferred to the metal ion, reducing it. If the lowest $d$ level, $d_{x^2-y^2}$, is higher in energy than the lowest empty ligand $\pi$ orbital, which is $\pi_4$, the tendency will be for the metal electron to shift onto the ligand, oxidizing the metal. The failure of either of these potentialities to materialize is good evidence that the $d_{x^2-y^2}$ orbital lies between the empty and filled ligand orbitals.

The fact that bands which might be assigned as ligand-to-metal transitions are discovered at lower frequencies in the present compounds than in [MoOC\(_2\)]\(_2\)\(^{-}\) is most readily explained by placing the $\pi_3$ level of the \(\beta\)-diketone above the $\pi$ chloro level. On the basis of the arguments propounded by Horner and Tyree, it is most reasonable to place the $\pi$ oxo orbital at very low energy.

It has been seen so far that qualitative arguments are suitable for arranging most of the molecular orbitals considered to be important into an array based upon the energy of the levels.
The most difficult problem still remains: "Does the $\pi_4^*$ ligand orbital have energy greater or less than that of the $d_{xz}$ and $d_{yz}$ levels?".

A possible clue to the solution of the problem has been found in the work reported by Barnum. He studied the spectra of acetylacetonato complexes of many different trivalent metal ions from the first row of the periodic table, especially with regard to the frequency of the absorption in the complex which appeared to be the $\pi_4^* - \pi_3$ transition of the ligand. Barnum maintains that only $\pi$-bonding is important in determining the shift of $\pi_4^* - \pi_3$ for the systems he investigated.

Shifts in this band relative to the value in the free ligand had previously been studied by a number of research groups without the discovery of any single factor which is predominant in the determination of the direction of the frequency shift. Holm and Cotton make the general statement that "$\lambda_{max}$ of the main absorption band is a sensitive function of a number of parameters, the most important being probably cation charge, cation size, and its distortion effect on the ring $\pi$-system, and the $\pi$-bonding ability of the metal ion". However, they attempted to organize observations involving such a wide variety of metal ions that their failure does not exclude the existence of some valid correlation if a less diverse series of compounds is chosen.

The application of Barnum's approach to the system of interest herein is made rather complicated by the fact that both \( \pi_3 \) and \( \pi^* \) may interact with the chloro \( \pi \) orbitals to produce several MO's because of the effects of pi-bonding with the metal.

As a first approximation it is profitable to ignore these possibilities and consider only the effect of the ligand \( \pi \)-orbital overlap with certain of the metal \( d \) orbitals. Having observed the results in this admittedly simple case, it should be easier to understand the application of the method to more complicated cases which may correspond more closely to the situation actually encountered.

The results of pi-bonding upon the frequency of the \( \pi_3 \) to \( \pi^* \) intraligand transition are dependent on the energy of the \( d \) orbitals involved in the pi-bonding relative to the empty ligand level. Two general situations are conceivable, as is shown in Figure 12. The \( d_{\pi} \) level may be above (possibility A) or below (possibility B) the energy of the empty ligand level, \( \pi^* \).

It may be readily seen that in the first case both of the ligand levels will be depressed in energy by interaction with the \( d \) orbitals, but since the energies of the \( d_{\pi} \) and \( \pi^* \) orbitals are more similar than those of \( d_{\pi} \) and \( \pi_3 \) the effect will be larger in the former case. The result of the interaction is to raise the energy of the \( d_{\pi} \) orbital(s) and to decrease the energy difference between \( \pi_3 \) and \( \pi^* \).

If similar logic is applied to the case represented by possibility B the result is to increase the energy difference between
Figure 12. Effect of Metal-Ligand $\pi$-Bonding on the Energy of the $\pi_4^* - \pi_3$ Transition of a Complexed $\beta$-Diketone
and $\pi_3$ while the position of the $d_{\pi}$ orbital(s) is changed only slightly.

The above arguments may be summarized as follows: The change in frequency of the $\pi_3^* \rightarrow \pi_3$ transition of a $\beta$-diketone as compared to the frequency of that same transition in the free (or noncomplexed) ligand may be interpreted as being indicative of the relative energies of $d$ orbitals which are $\pi$-bonding with the ligand in cases where it may be presumed that metal-ligand $\pi$-bonding is the predominant cause of the frequency shift.

If the results of Barnum's approach are applicable to the oxomolybdenum(V) system, the statement used as the summary can be very useful as the foundation of a treatment which will determine the relative positions of the empty molecular orbitals, but if the results of Holm and Cotton are closer to a correct assessment of the number of variables involved the situation becomes too entangled for solution by deduction from the available evidence. The choice lies between an admission of defeat and an argument which can be considered as tentatively acceptable. The preference of the author is to explore the avenue leading to a possible result, attempting to ascertain the validity of the model when it has been completely articulated.

To apply a treatment similar to that of Barnum it is necessary to introduce the possibility of removing the degeneracy of the ligand $\pi$ orbitals and to assign the intraligand transition(s). Accomplishment of these goals is required to complete construction
of the empirical molecular orbital diagram.

D. Analysis of the Ligand Group Orbitals

The possibility of interaction between the pi molecular orbitals of \( \beta \)-diketone ring systems has been explored in some detail and it has been predicted that in systems where metal-ligand \( \pi \)-bonding occurs and two or more ketoenolate rings are bound to the metal, it is possible to remove the degeneracy of the \( \pi \) levels in the various ring systems. Although the agreement between the calculations and the observed spectra has sometimes been poor\(^{17}\) the results in many cases have correctly predicted splittings which were actually observed\(^{2,15,18,19}\). The presence of only one chelate ring in the complexes being discussed here prevents any specific application of the results obtained by the above workers, but interaction between the \( \beta \)-diketone system and the filled \( p_z \) chloro orbitals is a possibility.

The molecular orbitals which might result from pi bonding involving the metal d-orbitals, the \( \pi \) system in the chelate and the \( p_z \) chloro levels was approximated by constructing a diagram of the ketoenolate \( \pi \)-level, then adding to the diagram all possible arrangements of the \( p_z \) orbitals from the planar chloro groups which


would give different molecular orbitals. It is considered unnecessary to include the possibility of \( \pi \)-bonding for the \( p_x \) and \( p_y \) chlorine orbitals or the in-plane chelate orbitals. The only metal orbitals available for overlap with the ligand MO's which will be produced are \( d_{xz} \) and \( d_{yz} \), and it must be kept in mind that these \( d \) orbitals are strongly involved in \( \pi \)-bonding to the oxo group.

A typical ligand \( \pi \) orbital is shown in Figure 13; a more extensive diagram showing all of the resultant orbitals is found in Appendix II. The phase of the chelate orbitals at the various atoms is determined by the results of a Hückel MO calculation on the acetylacetonate ion performed by Forster.\(^{17} \) Amplitudes are not considered. The symmetry of the ligand orbitals is evaluated using the character table on page 82.

The result of constructing all of the probable ligand orbitals which might be involved in \( \pi \)-bonding with the \( d_{xz} \) and \( d_{yz} \) metal orbitals is the observation that two filled \( \pi \) orbitals of \( a' \) symmetry and one of \( a'' \) may exist. The \( a' \) orbitals may interact only with the \( d_{xz} \) orbital and the \( a'' \) only with \( d_{yz} \) because the ligand orbitals must have the same symmetry as the metal orbitals in order for interaction to occur resulting in a molecular orbital.

Four ligand orbitals are produced by the combination of \( r \) and the chloro \( p_z \) orbitals, all having \( a'' \) symmetry. These may form molecular orbitals only with the \( d_{yz} \) metal orbital.

Having created a model suitable for the introduction of \( \pi \)-bonding between the metal and ligands other than the oxo group
Figure 13. Ligand Group Orbitals Formed by the Combination of the Chloro $p_z$ and $\beta$-Diketone $\pi$ Orbitals
the next step is to assign, if possible, the frequency of the \( \pi_4^* - \pi_3 \) transition and determine the extent of shifting which has occurred, comparing this value to that of the free ligand. The magnitude of the shift should be indicative of the extent of the \( \pi \)-bonding and the direction of the shift should, as has been previously explained, be evidence of the position of the \( d_{xz} \) and \( d_{yz} \) orbitals relative to \( \pi_4^* \).

E. Assignment of the \( \pi_4^* - \pi_3 \) Intraligand Transition

In \([\text{C}_{2}H_{5}]_{4}N\text{MoOC}_{2}F_{3}(F_{6}A)\] this assignment seems to be very straightforward. Only one intense band is observed near the region where the absorption is to be expected, the band at 32.2 kK*. The only other band intense enough to be considered as the intraligand transition is at 42.7 kK. The frequency of the absorption in the free ligand is 32.7 kK. As has been emphasized earlier any \( \pi \)-bonding between the metal and ligands other than the oxo group is expected to be very weak. There are no grounds for disputing the Gray and Hare assumption that the oxo group has the predominant effect. This leads to the belief that any shift of the \( \beta \)-diketone energy levels due to \( \pi \)-bonding should be rather small. It seems almost certain that the absorption band at 32.2 kK is the transition in question. The important facts to note are the small size of the shift and the decrease in frequency.

A similar situation prevails for the compound \([\text{C}_{2}H_{5}]_{4}N\text{MoOBr}_{3}(\text{DBN})]\. The only strong band is at 29.4 kK. This represents

* All frequencies mentioned are values from acetonitrile solutions unless otherwise noted.
a slight decrease in frequency compared to the free ligand value (29.5 kK). In fact, the size of the shift is smaller than the accuracy expected in determining the frequencies.

The spectrum of [(C₂H₅)₄N][MoOCl₃(DBM)] is difficult to interpret alone because intense bands exist at 32.8 and 29.2, either of which might be assigned as \( \pi^* \rightarrow \pi \). It would be expected that the transition would have a similar energy in this compound to that suggested above for the same transition in the bromo analogue. This favors the assignment of the band at 29.2 kK. The possibility is supported by the fact that the 29.2 kK band shifts slightly to higher frequencies in a less polar solvent, such as methylene chloride, while the band at 32.8 is decreased in frequency by 1.6 kK when observed in methylene chloride. The direction of the shift in the former instance is more consistent with the behavior expected for a \( \pi^* \rightarrow \pi \) transition. The band at 29.2 kK is almost surely this transition for the compound under examination. It should be noted that a slight decrease in frequency (29.5 to 29.2 kK) is measured in this band relative to the free ligand.

For both [(C₂H₅)₄N][MoOCl₃(TF₃A)] and [(C₂H₅)₄N][MoOCl₃(BF₃A)] two intense bands are detected, either one of which might be the intraligand transition in question. In both cases the higher frequency band shifts in the opposite direction from that expected for a \( \pi^* \rightarrow \pi \) transition when the solvent polarity is decreased. Therefore, the lower frequency bands (29.1 and 29.9) are chosen as the correct assignments. These bands are both slightly lower than
the free ligand transitions (31.1 and 30.6 kK respectively).

To summarize the above assignments, in every case the band indicated to be the $\pi_4^* - \pi_3$ transition is discovered at slightly lower frequency than the corresponding transition in the uncomplexed ligand. This data may be interpreted to complete the molecular orbital diagram which was begun earlier.

The small size of the shift observed in the intraligand transition is very encouraging toward the application of the Barnum approach to the system. As has repeatedly been emphasized, the oxo group is responsible for most of the metal-ligand pi bonding and any effect arising from $\pi$-bonding involving the other ligands must be expected to be slight. The decrease observed in these cases may be considered as tentative evidence that both $d_{xz}$ and $d_{yz}$ lie slightly above the $\pi_4^*$ ligand orbital.

Determination of whether any mixing exists between the chloro groups and the chelate $\pi$ system is inconclusive. The $\pi_4^*$ $\beta$-diketone orbital has $a''$ symmetry and so may overlap slightly with the $d_{yz}$ orbital. As will be shown below this alone is sufficient to explain the frequency shifts noted above. On the other hand, the group of bands ("moderate intensity") previously assigned as ligand-to-metal must be explained. If no ligand orbital mixing is allowed there should exist only two transitions of this type, one from a chloro level and one from $\pi_3$. Instead as many as three transitions are found, and the energies of these bands is somewhat lower than might be anticipated for an excitation
originating in a chloro level, if the value of the ligand-to-metal transition of the compound \((\text{NH}_4\text{)}\text{MoOC}_2\), which presumably has its origin in a pi chloro level, might be used as a measure. The frequency separation is smaller than might be expected for orbitals resulting from ligand orbital mixing, but the variation in the separation is too large to be explained as vibrational splitting. In the face of such unsatisfactory arguments it is presumed that the simplest solution is the best choice, although further examination of the problem should be attempted at some later time.

A test is possible to examine the validity of the approach based on the work of Barnum. Consider the effect of pi bonding on the \(d_{yz}\) and \(\pi_4^*\) orbitals only. Increased overlap between these orbitals should cause the \(d_{yz}\) orbital to increase slightly in energy and the \(\pi_4^*\) level to decrease slightly. Since the \(d_{yz}\) orbital is the same entity in all of the chloro complexes and the \(\pi_4^*\) is very similar in nature for all of the \(\beta\)-diketones, it seems a logical assumption to presume the extent of the overlap between these orbitals will be largely determined by the energy of the \(\pi_4^*\) level. The more similarity in energy between the two orbitals in a given compound, the greater the expected mixing. Delocalization of the electron density in the ring pi system is accomplished by the presence of aromatic groups, but not by the fluoro groups. On the basis of this reasoning the \(\pi_4^*\) level should lie at lowest energy, i.e., least overlap, in the dibenzoylmethane complex and at highest energy in the hexafluoro complex, i.e., greatest overlap.
This suggests that the shift in the $\pi^4 \rightarrow \pi_3$ transition should be greatest in the latter case and smallest in the former with the remaining compounds having intermediate values. Considering the magnitude of the effect being measured the results are very encouraging. The only compound to fall seriously out of line is $[(C_2H_5)_4N][MoOC\ell_3(BF_3A)]$. This is not difficult to understand. The band measured in this compound is a shoulder on a more intense absorption and some margin for error can be allowed on this basis. Agreement is by no means excellent, but the rough correlation is encouraging.

Another test of the model is to determine if a shift in the $d_{yz} \rightarrow d_{x^2-y^2}$ transition follows the pattern predicted above. Using the main peak, rather than the small shoulder, agreement is again found. The highest frequency is observed for the compound $[(C_2H_5)_4N][MoOC\ell_3(\text{F}_6\text{A})]$ and the lowest for $[(C_2H_5)_4N][MoOC\ell_3(\text{DBM})]$. It would be naive to present these results as a verification of the approach used, but the agreement is sufficiently good to countenance further investigations using this method.

The completed molecular orbital diagram, representing the ultimate summation of the extensive empirical discussions of this dissertation, is found in Figure 14. Only orbitals presumed to be important in the assignment of the electronic transitions in the region 10 to 45 kK are included.
Figure 14. Empirical Molecular Orbital Diagram for the New Oxomolybdenum(V) Compounds
SUGGESTIONS FOR FUTURE WORK

There are a number of areas connected with the work reported in this dissertation which might serve as avenues for further study. Although most of the prominent bands in the spectra of the complexes have been assigned, a few intense high frequency bands have not been discussed. The reason for ignoring these absorptions is simple; the state of the art is not yet adequate to attempt to explain these cases using the type of qualitative arguments which have been used effectively for the other bands. There is no consensus of opinion on the assignments of bands in this region which can be applied to the present case. Different workers, using different methods of calculation do not agree on the best assignment. As the situation becomes clarified, these bands should be re-examined, and further assignments attempted.

To make the task of classification simpler for these bands and to provide a further test for the assignments of the electronic spectra proposed in the preceding discussion, it would be very helpful to have spectra from other β-diketone complexes of oxomolybdenum(V). It might be possible to discover some new plan of attack which would make the preparation of further new compounds a reality. Similar preparative work should be tried with the oxotungsten(V) complexes and compounds involving molybdenum(VI). These species would provide a useful comparison for the compounds already available.
Calculations involving the new compounds have not been attempted and an effort should be made to apply some of the more common mathematical models to this system. As may be noted throughout the dissertation the results of such calculations are not infallible, but they do provide a useful tool for the further elucidation of the spectra observed.

One result of this work which the author definitely intends to re-investigate at the earliest opportunity is the identification of the material produced by halogen exchange. If this is truly a fluoro compound, as the evidence seems to indicate strongly, it is unique in the field of oxomolybdenum(V) chemistry and it would be very interesting to examine the spectra of this species. It is also possible that it might serve as a test of some of the assignments proposed previously.

Another experimental field which was not considered in the present work is the possibility of obtaining luminescence spectra. An unsuccessful attempt was made but this failure is not considered to be discouraging. A more carefully prepared attempt might well be successful.

As a final suggestion for future endeavors the author directs further attention to the work of Barnum, which has been applied to the present case with some apparent success. A detailed analysis of this method, especially with a view toward testing the fundamental assumptions, might add a potent tool to the procedures currently used for the investigation of charge transfer spectra.
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APPENDIX I

EFFECT OF A TETRAgonAL CRYSTALLINE FIELD UPON METAL d-ORBITALS

The effect upon the d-orbitals of a metal ion due to the electrostatic potential arising from a tetragonal distribution of ligands will be to remove some of the degeneracy of these levels. The extent of this splitting may be determined by application of first order perturbation theory, as described by Companion and Komarynsky. The following treatment is based on that method supplemented by readings in several standard reference works.

In principle the energy of any system may be determined by solution of the Schroedinger Equation

\[ \hat{H} \psi = E \psi \]

to obtain the eigenvalues, E, which correspond to the energy. Although this statement is rigorously true the problem of solution can be so difficult as to be impossible unless certain simplifying assumptions are made. For a metal ion in a tetragonal field the Hamiltonian operator for the system may be assumed to consist of two parts

\[ \hat{H} = \hat{H}_0 + \hat{V} \]


where $H_0$ is the Hamiltonian operator for the free ion and $V$ is the potential caused by the ligands. The effect of the second term should be much smaller than the first so that the ligand potential may be considered as a perturbation of the energy of the free metal ion.

If the energy of the unperturbed system is arbitrarily taken to be zero, the energy of the complex, relative to the free ion, is calculated by evaluating the effect of the electrostatic ligand potential upon the d-orbitals. This results from a solution of the secular determinant represented as

$$\begin{bmatrix}
H_{pq} - S_{pq} E_k
\end{bmatrix} = 0$$

which is written in expanded form as

$$\begin{vmatrix}
H_{11} - S_{11} E_k & H_{12} - S_{12} E_k & H_{13} - S_{13} E_k & \cdots & \cdots \\
H_{21} - S_{21} E_k & H_{22} - S_{22} E_k & \cdots & \cdots & \cdots \\
\vdots & \vdots & \ddots & \ddots & \ddots \\
H_{nl} - S_{nl} E_k & \cdots & \cdots & \cdots & H_{nm} - S_{nm} E_k
\end{vmatrix} = 0$$

The definitions for the terms used are

$$H_{pq} = H_{qp} = \int \psi^*_p \psi_q \, dv$$

and

$$S_{pq} = S_{qp} = \int \psi^*_p \psi_q \, dv$$

For this problem the eigenfunctions ($\psi$'s) are chosen to be the real d orbitals. As will be seen shortly, these functions will produce a completely diagonalized secular determinant for this case, which allows easy solution without the necessity of applying group theory. The d orbitals used as a basis set are
written in terms of a radial distribution function, \( R_{3d} \), (which gives the probability of finding an electron at a distance, \( r \), from the nucleus) and a set of spherical harmonics, \( Y_{1m} \) (which describe the directional properties of the orbitals).

\[
\begin{align*}
\psi_1 &= d_{x^2-y^2} = R_{3d}(1/2)[Y_{22} + Y_{22}^*] \\
\psi_2 &= d_{xz} = R_{3d}(1/2)[Y_{21} + Y_{21}^*] \\
\psi_3 &= d_{z^2} = R_{3d} Y_{20} \\
\psi_4 &= d_{yz} = R_{3d}(-i/2)[Y_{21} + Y_{21}^*] \\
\psi_5 &= d_{xy} = R_{3d}(-i/2)[Y_{22} + Y_{22}^*]
\end{align*}
\]

These functions for the \( d \) orbitals are orthogonal and normalized so that

\[
S_{pq} = \delta_{pq} = \begin{cases} 
1 & \text{if } p=q \\
0 & \text{if } p \neq q
\end{cases}
\]

The function \( \delta_{pq} \) is called the Kronecker Delta. If this condition is applied the determinant is simplified to

\[
\begin{vmatrix}
H_{11} = E_k & H_{12} & H_{13} & H_{14} & H_{15} \\
H_{21} & H_{22} - E_k & H_{23} & H_{24} & H_{25} \\
H_{31} & H_{32} & H_{33} - E_k & H_{34} & H_{35} \\
H_{41} & H_{42} & H_{43} & H_{44} - E_k & H_{45} \\
H_{51} & H_{52} & H_{53} & H_{54} & H_{55} - E
\end{vmatrix} = 0
\]

Evaluation of the energy of the \( d \) orbitals relative to the free metal ion values requires three steps: 1. description of the ligand potential, \( V \); 2. determination of the integrals, \( H_{pq} \) (defined above); and 3. solution of the determinant for the eigenvalues, \( E_k \).
It is characteristic of the Crystal Field Approximation that the perturbing potential is presumed to arise solely from the electrostatic repulsion produced by the ligands, which are considered to act as hard, nonoverlapping spheres. No provision is made in this treatment for covalent bonding; the ligands are presumed to be point charges.

There is abundant evidence to prove that covalent bonding is important in coordination compounds. This evidence is summarized in numerous standard references so it would be redundant to discuss it in this treatment. It must be understood at the outset that the approximations of the Crystal Field Theory do not correspond with the best available information concerning chemical bonding in complexes, but in the absence of more precise treatments it has produced results which are in qualitative agreement with experimental data.

The total electrostatic potential of the ligands is conveniently represented as the summation of the effects of the individual species.

\[ V = \sum_{i=1}^{6} V_i \]

The potential due to a single ligand, \( V_i \), acting as a point charge on the electrons is the relation

\[ V_i = \frac{Z_i e}{r_{ij}} \]

where \( Z_i e \) and \( e \) are the charges of the ligand and the electron

respectively and $r_{ij}$ is the distance from the ligand to the electron. The distance term may be expressed as an expansion centered on the metal ion as its origin, using normalized harmonic functions to match the symmetry of the system:

$$\frac{1}{r_{ij}} = \sum_{\ell=0}^{\infty} \sum_{n=-\ell}^{\ell} \frac{4\pi}{2\ell+1} \frac{r_{<}^{\ell}}{r_{>}^{\ell+1}} Y_{\ell m}^{\ast}(\theta_i, \phi_i) Y_{\ell m}(\theta_j, \phi_j)$$

where $r_{<}$ is the radial vector connecting the origin to the electron, or the vector between the origin and the ligand, whichever is shorter, and $r_{>}$ is the larger of these two distances. $Y_{\ell m}(\theta_i, \phi_i)$ and $Y_{\ell m}(\theta_j, \phi_j)$ are spherical harmonics which involve the angles $\theta_i$ and $\phi_i$ or $\theta_j$ and $\phi_j$ respectively, as shown in Figure 15. Since the Crystal Field Theory allows no orbital overlap between the metal and the ligands, cases where the metal ion to electron distance is greater than the metal ion to ligand distance may be ignored. Thus for all cases of interest $r_{<}$ is the length of the vector connecting the origin and the electron (henceforth designated $r$) and $r_{>}$ is the distance from the origin to the ligand (designated $R_{j}$). It is now possible to write the total ligand field potential

$$V = \sum_{i=1}^{6} \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \frac{4\pi Z_i e^2}{2\ell+1} \frac{r_{<}^{\ell}}{R_{j}^{\ell+1}} Y_{\ell m}^{\ast}(\theta_i, \phi_i) Y_{\ell m}(\theta_j, \phi_j)$$

This rather imposing infinite series is simplified by the observation that all harmonics of odd order are ineffective for incompletely filled d-orbitals and, if only d-orbitals are involved, the terms greater than fourth order exert no influence.
Figure 15. Coordinate System Used for Metal Ion and Ligands
The integrals, $H_{pq}$, may now be calculated by inserting the d wave functions and the ligand potential into

$$H_{pq} = \int \psi_p^* \psi_q \, dv$$

These expressions may become quite involved as is shown by the resulting statement of $H_{33}$

$$H_{33} = \sum_{i=1}^{4} \sum_{n=0,2,4} \frac{4\pi Z_i e^2}{(2\ell+1)^{3/2}} \frac{Y_{lm}^*(\theta_i, \phi_i)}{R_3} \int R_0^{R_3 d} R_2 \frac{r^\ell}{R_3^{\ell+1}} \, dr$$

If the possible mathematical expressions for $Y_{lm}^*(\theta, \phi)$ are inserted and the integrations are examined it becomes apparent that the integrals become zero except those for which $Y_{lm}^* = Y_{00}^*$, $Y_{20}^*$, $Y_{40}^*$ and integration of these terms yields $1/2, \sqrt{5}/2\pi$ and $3/7\pi$ respectively. The equation is simplified still further by the introduction of a new term, $\alpha_{\ell i}^i$, the radial integral, which is equal to

$$\alpha_{\ell i}^i = \frac{Z_i e^2}{R_3^{\ell+1}} \int R_0^{R_3 d} r^\ell \, dr$$

These substitutions produce the expression

$$H_{33} = \sum_{i=1}^{6} \frac{\sqrt{2\pi}}{35} \frac{Y_{00}^*(\theta_i, \phi_i)}{\alpha_0^i} + \frac{\sqrt{5\pi}}{21} \frac{Y_{20}^*(\theta_i, \phi_i)}{\alpha_2^i} + \frac{\sqrt{7\pi}}{40} \frac{Y_{40}^*(\theta_i, \phi_i)}{\alpha_4^i}$$

Again values for the spherical harmonics may be found in Pauling and Wilson (if it is kept in mind that $Y_{lm}^* = \theta_{\ell m} \phi_{\ell m}$) to be

---

\[ Y_{00}^{20}(\theta_1, \rho_1) = \frac{1}{2\sqrt{\pi}} \]
\[ Y_{20}^{20}(\theta_1, \rho_1) = \frac{\sqrt{5}}{4\sqrt{\pi}} (3\cos^2 - 1) \]
\[ Y_{40}^{20}(\theta_1, \rho_1) = \frac{9}{16\sqrt{\pi}} \left( \frac{35}{3} \cos^4 - 10 \cos^2 + 1 \right) \]

In a similar fashion the other \( H_{pq} \) integrals may be evaluated.

To facilitate the calculation of these rather complicated functions, Companion and Komarynsky \(^1\) have redefined the integrals in terms of certain ligand position functions, \( D_{1m} \) and \( G_{1m} \), which greatly simplify the evaluation of the integrals. The expressions for these functions are stated wherever appropriate, but the reader is referred to the original article for a complete list.

To determine the splitting of the d-orbitals in a centric, tetragonal ligand field it is necessary to define a set of ligand coordinates, determine the values of the ligand position functions, and evaluate the integrals by insertion of these functions. Then the secular determinant may be solved for the energies of the orbitals. The coordinate system chosen for the tetragonal system is shown in Figure 16.

The values of the \( D_{2m} \) functions are determined to be:
\[
D_{00} = 6 \sum_{1} C_{0}^{i}
\]
\[
D_{00} = 4C_{L}^{0} + 2C_{S}^{0}
\]
where \( L \) and \( S \) discriminate between the values of the near and distant ligands.
Figure 16. Ligand Coordinates for the Centric Tetragonal Field

<table>
<thead>
<tr>
<th></th>
<th>$\Theta_i$</th>
<th>$\Phi_i$</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0</td>
<td>R_l</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>180</td>
<td>R_s</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>90</td>
<td>0</td>
<td>R_l</td>
</tr>
<tr>
<td>D</td>
<td>90</td>
<td>180</td>
<td>R_l</td>
</tr>
<tr>
<td>E</td>
<td>90</td>
<td>270</td>
<td>R_l</td>
</tr>
<tr>
<td>F</td>
<td>90</td>
<td>90</td>
<td>R_l</td>
</tr>
</tbody>
</table>
All of the other $D_{lm}$ terms and all of the $G_{lm}$ terms are equal to zero.

The above results are now substituted into the equations for $H_{pq}$ in Table II.

\[
D_{20} = \sum_{i=1}^{6} \alpha_i^2 (3 \cos^2 \theta_i - 1)
\]

\[
D_{20} = 4\alpha_2^S - 4\alpha_2^L
\]

\[
D_{40} = 6 \alpha_4^i \left( \frac{35}{3} \cos^4 \theta - 10 \cos^2 \theta + 1 \right)
\]

\[
D_{40} = 4\alpha_4^L + \frac{16}{3} \alpha_4^S
\]

\[
D_{44} = 6 \sum_{i=1}^{6} \alpha_4^i \sin^4 \theta_i \cos^4 \phi_i
\]

\[
D_{44} = 4\alpha_4^L
\]

No diagonalization of the determinant is required for all off-diagonal
terms evaluate to zero. The eigenvalue solutions are the values of the five integrals listed above and by referring to the original numbering of the d orbitals the following equivalence is established:

$$H_{11} = E(d_{x^2-y^2}); H_{22} = E(d_{xz}); H_{33} = E(d_{z^2}); H_{44} = E(d_{yz});$$
$$H_{55} = E(d_{xy}).$$

As a check on the result it is noted that if $$\alpha_L^L = \alpha_S^S$$ the energies are exactly the same as those calculated for the perfect octahedral field!

It is possible to discuss the crystalline field in terms of $$\alpha_0^0, \alpha_2^2$$ and $$\alpha_4^4$$ or to formulate a new set of constants related to the original values. One such set of constants are $$A_2$$ and $$A_4$$, used by Hougen et al.\(^7\). The most common set of parameters is $$Dq, Ds, \text{and} Dt$$, as defined by Moffitt and Ballhausen\(^2\) and further discussed by Piper and Carlin\(^8\). In the latter paper the following definitions are proposed for these parameters in a tetragonal field:

$$Dq = \frac{1}{6} Z \langle r^4/r^5 \rangle_{xy}$$
$$Ds = \frac{2}{7} Z [\langle r^2/r^3 \rangle_{xy} - \langle r^2/r^3 \rangle_z]$$
$$Dt = \frac{2}{21} Z [\langle r^4/r^5 \rangle_{xy} - \langle r^4/r^5 \rangle_z]$$

where $$Z$$ is the charge magnitude, $$Ze^2$$, and the $$r$$'s are the radial vectors as defined previously in this derivation. From the definition of $$\alpha$$ used here

$$\alpha_L^L = \frac{Z e^2}{R_{i+1}} \int_C R_{3d}^2 r^L r^2 dr$$

---

one obtains

\[ \alpha^L_\ell = \frac{1}{\ell+1} \langle r^\ell / R^{\ell+1} \rangle \]

Restating the parameters in terms of this result produces

\[ D_q = \frac{1}{6} \alpha_4^L \]
\[ D_s = \frac{2}{7} (\alpha_2^L - \alpha_2^S) \]
\[ D_t = \frac{2}{21} (\alpha_4^L - \alpha_4^S) \]

Now shifting our zero, which had been defined as the energy of the free metal ion, upwards by \( 4\alpha_0^L + 2\alpha_0^S \), to emphasize the orbital splittings, and substituting the \( D_q, D_s \) and \( D_t \) values in the energy equations produces the energy relationships in terms of the new parameters:

\[ E(d_{x^2-y^2}) = 6D_q + 2D_s - D_t \]
\[ E(d_{xz}, d_{yz}) = -4D_q - D_s + 4D_t \]
\[ E(d_{z^2}) = 6D_q - 2D_s - 6D_t \]
\[ E(d_{xy}) = -4D_q + 2D_s - D_t \]

which correspond to the values obtained by Piper and Carlin\(^7\).

In an acentric, tetragonal field (i.e., the axial ligand distances are not equal) the \( \alpha_\ell^S \) terms must be separated into \( \alpha_\ell^{-} \) and \( \alpha_\ell^{+} \) slightly increasing the complexity of the energy stated in terms of these parameters, but if \( D_s \) and \( D_t \) are redefined as proposed by Wentworth and Piper\(^9\) i.e.

\[ D_q = \frac{1}{6} \alpha_4^L \]
\[ D_s = \frac{1}{7} (2\alpha_2^L - \alpha_2^2 - \alpha_2^2) \]
\[ D_t = \frac{1}{21} (2\alpha_4^L - \alpha_4^2 - \alpha_4^2) \]

the energy levels in terms of these parameters remain the same.
APPENDIX II

LIGAND GROUP ORBITALS POSSIBLE FOR THE NEW OXOMOLYBDENUM(V) COMPLEXES (see page 107)

\[ \alpha' \pi_3^+ p_1 + p_2 \]

\[ \alpha'' \pi_4^+ p_1 - p_2 \]

\[ \alpha' \pi_3^- p_1 - p_2 \]

\[ \alpha'' \pi_4^- p_1 + p_2 \]

\[ \alpha'' \pi_4^- p_1 - p_2 \]

\[ \alpha'' \pi_4^+ p_1 + p_2 \]
VITA

Harry Edmond Pence II was born on February 4, 1937 in Martins Ferry, Ohio and received his elementary and secondary education at Grover Village public school and Warren Consolidated High School, respectively. In 1958, he was granted the degree of Bachelor of Science by Bethany College, Bethany, West Virginia, and began graduate work at West Virginia University that same year. Work for the degree of Master of Science was completed in 1961 and the degree was awarded in 1962.

While in graduate school he married Virginia Lee Walliser and since that time has had two daughters, Roberta Lynn and Laura Ellen. A third child is expected momentarily.*

In 1961, Mr. Pence joined the faculty of Washington and Jefferson College, Washington, Pennsylvania and taught chemistry and Science courses at that institution for five years. During the summer of 1962, he attended the Louisiana State University as a National Science Foundation Research Participant and continuing support during the next four summers permitted him to complete many of the requirements for the degree of Doctor of Philosophy. He resigned from W and J in June, 1966, with the rank of Assistant Professor and commenced full time work at Louisiana State University where he is presently a candidate for the Ph.D. degree.

* Note added in proof: Heather Elaine joined the Pence family on July 29, just after the completion of this dissertation.
Candidate: Harry Edmond Pence

Major Field: Chemistry

Title of Thesis: Preparation and Spectral Properties of Oxomolybdenum(V) Complexes

Approved:

[Signatures]

Major Professor and Chairman
Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Date of Examination:

September 11, 1967