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BONDING AND SPECTRA OF COORDINATION COMPOUNDS

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BONDING AND SPECTRA OF COORDINATION COMPOUNDS

Robert Dean Feltham
(Thesis)

June 1957

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June 1957

ABSTRACT

The electron spin-resonance spectra of chromium dibenzene cation and similar compounds are used to establish the nature of the chemical bond between the chromium and the carbon atoms. These are found to be essentially "covalent" compounds, the electrons being spread out over all the atoms of the complex. The optical spectra, both visible and ultraviolet, are presented and related to the bonding and electron-spin resonance spectra. The transitions from approximately 10,000 to 2000 A are assigned in terms of molecular orbitals.

A comparative study of copper acetate and of copper bisacetylacetonate is made on the basis of the optical and spin-resonance spectra. The spectra are discussed in terms of a modified-ligand electrostatic field. The visible spectra are assigned to transitions between 3d levels of the copper ion, but ligand orbitals must be partly intermixed with these d orbitals in order to explain all the known data.

This model is then extended to the more complicated case of vanadyl chelates. The optical spectra of seven vanadium (IV) complexes with β-diketones are discussed. Their relationship to the molecular structure of the chelates is established and correlated with properties of the metal ion and the ligand. Electron spin-resonance spectra of both solutions and single crystals of vanadium (IV) chelates are presented and related to the optical spectra. The methods of preparation of these compounds are described.

The model developed from the discussion of vanadyl and copper chelates is extended to the chelates of all the metals of the first transition series. An explanation for the stabilities of complexes of these metals is offered in terms of this model.

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I. INTRODUCTION

The problem of major concern is how to describe accurately the physical and chemical properties of metal-ion complexes. This may be done in the framework of quantum mechanics. The problem then reduces to finding the stationary states of the compounds in question. In theory all molecular problems could be solved by starting with the nuclei and electrons of the particular molecule, and subsequently finding the correct Hamiltonian for the system. Then the stationary states of the system could be found directly. This has been done for only the simplest of systems, the hydrogen molecule, and this only with a considerable amount of work.

Because of the mathematical difficulties of the problem, many approximations must be made. One of the most rewarding methods for making approximations is the development of a model. The first statement that may be made about a model is that, since it is an approximation, in general it will be incorrect in at least some aspect. The usefulness of a model then is to lead to successively better models, the hope being that eventually a model will be developed that does give correct descriptions of the systems under consideration. Some of the more useful models will be discussed in detail.

Pauling was one of the first to interpret the bonding in metal-ion complexes in terms of the covalent bond.[1] In valence-bond formulation the covalent bonds used by the metal are the s, p, and d orbitals, hybridized according to the symmetry of the molecule. These hybrids of orbitals available do, indeed, account for the observed symmetry, and often account for the observed magnetism and stability of the complexes. However, with the development of new techniques such as electron spin resonance and nuclear magnetic-resonance absorption for the investigation

of the orbital ground states of these molecules, it has been found that Pauling's formulation of the bonding in these compounds is inadequate to explain the observed properties.

Van Vleck used crystalline electric fields to explain the magnetic susceptibility of paramagnetic salts.[2] The first to employ this theory in interpreting the visible spectra of these salts were Van Vleck[3] and Hartmann.[4] Hartmann treated the visible spectra of $Ti^{+3}(3d^1)$ as transitions between the d levels split by the surrounding electric fields of the ligands.[5] Hartmann later extended this treatment to $V^{+3}(3d^2)$, and $Ni^{+2}(3d^8)$.[6,7] If the parameters of this theory (r_{ab}, the distance between the ligand and metal ion, and μ_b, the dipole moment of the ligand) evaluated by independent means, are used to calculate the energies of the transitions, it is found that the agreement is poor. One may still partially account for these discrepancies by electrostatics. However, the results of electron resonance can be calculated in terms of the observed visible spectra. It is found empirically that the crystalline-field description is still incomplete, and the final explanation must include some "covalent bonding," which has been included in the form of LCAO MO's (linear combination of atomic orbitals, molecular orbitals).

It would be hoped that a general method might be found for predicting and explaining the physical and chemical properties of inorganic compounds as the method of molecular orbitals does for organic compounds. However, it should be apparent to anyone who has been reading the recent literature that even these usual methods of quantum mechanics have been proving inadequate to describe accurately some properties of organic compounds, especially the electronic spectra. It is the hope of the author that a general method for ordering the excited electronic states of inorganic compounds has been found, and a model derived that will at least qualitatively account for the observed physical and chemical properties.

Metal-ion chelates and "sandwich" π complexes were chosen for this particular study because they usually remain as units throughout many differing conditions. If the structure of the chelate is known from x-ray analysis of the crystalline solid, and the electronic spectra are shown to be identical in the solid, solution, and gaseous phases, then one may

be fairly confident that this is the configuration in solutions, and for those chelates or π complexes that sublime, even in gaseous phase. Copper (II) ($3d^9$) and vanadium (IV) ($3d^1$) were chosen because of their rather simple electronic configurations. Most of these compounds are relatively stable, and are easily prepared as described in the next section.

II. PREPARATION OF METAL CHELATES

Vanadyl Chelates

The first report in the literature of the preparation of vanadyl bisacetylacetonate was by Morgan and Moss.[8] They reported the formation of the monohydrate as well. The most recent and complete studies were done by Jones.[9] He reports that the following method of preparation is satisfactory: dissolve the ligand in ethanol, add this to a solution of vanadyl sulfate in dilute sulfuric acid, and neutralize with 10% Na_2CO_3. Generally the chelate settles out as an oil which then solidifies.

Pfeiffer et al. have made a thorough study of vanadyl complexes with aldimines.[10] They also report the formation of vanadium bissalicylaldehydeethylenediimine dichloride. Unless otherwise specified the method of Jones was used for preparing the chelates described here.

Vanadyl Bisacetylacetonate

This compound is soluble in most organic solvents such as benzene, chloroform, acetone, dioxane, and pyridine, and is slightly soluble in water. The color is a deep blue to blue-green. It readily forms weak solvates.

Anal. Calcd. for $C_{10}H_{14}O_5V$: C, 45.29; H, 5.32. Found: C, 45.48; H, 5.41.

Vanadyl Bisdibenzoylmethanate

This is in general more insoluble than the acetylacetonate (less than 0.01 M in $CHCl_3$). It has a light apple-green color.

Anal. Calcd. for $C_{30}H_{22}O_5V$: C, 70.19; H, 4.32. Found: C, 69.92; H, 4.30.

Vanadyl Bisbenzoylacetonate

The compound is dark green in color. It is soluble in the same solvents as the acetylacetonate, but not to the same extent.

Anal. Calcd. for $C_{20}H_{18}O_5V$: C, 61.70; H, 4.66. Found: C, 61.56; H, 4.70.

Vanadyl Bistrifluoroacetylacetonate

This compound is a light apple-green in color. It is slightly soluble in water as well as in the usual organic solvents. It is less stable to hydrolysis than the other chelates.

Anal. Calcd. for $C_{10}H_8F_6O_5V$: C, 32.19; H, 2.16; F, 30.55. Found: C, 33.92; H, 2.93; F, 29.00.

Vanadyl Bissalicylaldehydethylenediiminate

This is a dark-green compound which is quite soluble in the usual organic compounds.

Anal. Calcd for $C_{16}H_{14}N_2O_3V$: C, 57.66; H, 4.23; N, 8.48. Found: C, 57.29; H, 3.98; N, 8.43.

Other Compounds

Bisacetylacetonethylenediimine

The Schiff's base was prepared by dissolving acetylacetone and ethylenediamine in ethanol and allowing them to react. The compound was crystallized by evaporating to a small volume and cooling. The product was yellow. It was recrystallized from methylcyclohexane, giving a white crystalline product.

Anal. Calcd for $C_{12}H_{20}N_2O_2$: C, 64.26; H, 8.98; N, 12.49. Found: C, 64.70; H, 9.11; N, 12.44.

Copper Bisacetylacetonethylenediiminate

This compound was prepared according to the method of McCarthy.[11] The compound has a deep wine color and is soluble in most of the usual solvents except carbon tetrachloride.

Anal. Calcd. for $C_{12}H_{18}N_2O_2Cu$: C, 50.41; H, 6.34; N, 9.80. Found: C, 49.64; H, 6.21; N, 9.33.

III. THEORETICAL TREATMENT OF THE BONDING IN TRANSITION-METAL COMPLEXES

Introduction

Consider for a moment what determines the geometrical arrangement of atoms in a metal chelate. First, because usually these ligands are all good electron donors, the ligands repel one another. If ligand-ligand repulsion is most important, the geometry will be such as to minimize this repulsion. Secondly, if covalent bonding is not important, the d electrons present will orient themselves in such a manner as to minimize the electrostatic repulsions between the ligands and themselves. If there is a small amount of covalent bonding, then this model may still be used, modified by slight mixing of ligand orbitals. If covalent bonding is most important, then the geometry will be that in which the strongest covalent bonds may be formed, and the repulsive terms mentioned above will be secondary effects. Because the ligand electrostatic field is considered to have the most important effect in the observed electronic properties of these compounds, this theory is presented first.

Ligand Field Theory

In order to decide how the d orbitals are arranged energy-wise, only the symmetry of the molecule need be known. The assumption is then made that the ligand electrons appear as an average negative potential field, so far as the central atom's electrons are concerned. This perturbing potential can be expressed in spherical harmonics.[14,15]

The energies of these levels are found by calculating the integrals: $\int \Psi_i V' \psi_j d\tau$. This has been done by Holmes[14] and Belford.[15] If the radial wave functions are used and the integrations performed, it is found that the energies obtained are incorrect.[15] However, it is convenient to express the data in terms of the potential parameters.

If the metal ion has only d orbitals of low enough energy to be considered for the ground state and low-lying excited states, then the relative energies of these orbitals may be found without specific calculations. Since the electrostatic field due to the ligands is assumed to

be the only energy effect of importance, the energies of the d orbitals may be discussed solely in these terms. If the spatial distribution of an electron in the various d orbitals is considered, then the effect of a negative charge (or charges) on their energies may readily be seen.

The major symmetry axis is defined in the following discussion as the z axis of the molecule. Because for the chelates concerned, the metal atom is located at the center of symmetry of the molecule, the molecular and metal axes coincide, and the molecular and metal z axis are one and the same. If there are four donor atoms in the complex, then there are two types of geometrical arrangements of interest, square-planar and tetrahedral. Five d orbitals in a square of four negative charges no longer have the same energy. The $d_{x^2-y^2}$ has the highest energy because it is nearest the negative charges. The d_{xy} orbital is next in energy since it is still in the plan of the negative charges but has nodes along the two axes described by the four charges. The d_{z^2} is next to the lowest in energy because it has only a small probability in the plane of the charges. The lowest-energy d orbitals are the degenerate d_{xz}, d_{yz} orbitals, which have nodes in the plane of negative charges.

If there are five donor atoms, the geometrical arrangement of interest is the tetragonal pyramid. The relative energies of the d orbitals are the same as for four square planar charges, except for the effect of an additional charge along the symmetry axis. The effect of this charge is to decrease the energy of the d_{xy} orbital relative to that of the d_{z^2}. In the limit of this charge as the predominant effect, the order of the d orbitals would be the same as for two negative charges in the linear triatomic arrangement. The $d_{x^2-y^2}$, d_{xy} orbitals would be of lowest energy, the d_{xz}, d_{yz} next, and d_{z^2} of the highest energy.

The only geometrical arrangement of interest for six negative charges is at the corners of an octahedron. If the six negative charges are identical, then the triply degenerate d_{xz}, d_{yz}, d_{xy} orbitals are of lowest energy, and the doubly degenerate d_{z^2}, $d_{x^2-y^2}$ of the highest energy. For four equivalent and two nonequivalent charges the energies of the d orbitals lie somewhere between those for an octahedral arrangement and for a square planar arrangement, or alternatively between those for

an octahedral and those for a linear triatomic arrangement. Figure 1 summarizes these qualitative arguments. The energies for a tetrahedral arrangement are just the reverse of those for an octahedral arrangement. The effect of a basic solvent on the orbitals of the chelates in question will be assumed to be the addition of one or two negative charges along the symmetry (z) axis of the molecule.

If a symmetry of C_{4v} (tetragonal pyramid) is assumed for vanadyl chelates, then the five d orbitals are split into four levels, one still doubly degenerate. If the solvent effect is used to identify the transitions, the three absorptions present in the visible region are tentatively identified. There is some ambiguity in this identification, because the first thought might be that the field would be near $D_{\infty h}$, but on looking at the tetragonal potential one finds that the axial term is reduced by a factor of two, since there is only one ligand along the z axis. This means that even though the vanadyl oxygen is closer and has a higher charge than the other oxygens, its effect in comparison with the other ligands cannot compensate for this factor of two present in the octahedral complexes. Therefore, the field was identified as being somewhere between octahedral and square planar.

The perturbing term in the Hamiltonian assumed to describe the ligand field is

$$V = D(x^4 + y^4 + z^4 - 3/5\, r^4) + A(2z^2 - x^2 + y^2) + Q(z^4 + 6x^2y^2 - 3/5\, r^4),$$

where D, A, and Q are parameters depending on the radius and the charge. The order of increasing energy of the d orbitals is d_{xz}, d_{yz}; d_{xy}; d_{z^2}; $d_{x^2-y^2}$. From the crystal field calculations it is found that the energies in terms of the potential parameters are:

Energy	d Orbitals
6 Dq - 60 Ap - 14 Qq	$x^2 - y^2$, where $q \propto \overline{r^4}$
6 Dq + 60 Ap + 6 Qq	z^2, and $p \propto \overline{r^2}$
-4 Dq - 60 Ap + 16 Qq	xy
-4 Dq + 30 Ap - 4 Qq	xz, yz

If one electron is placed in the lowest energy level, all the observed electronic properties due to the metal ion may presumably be calculated.

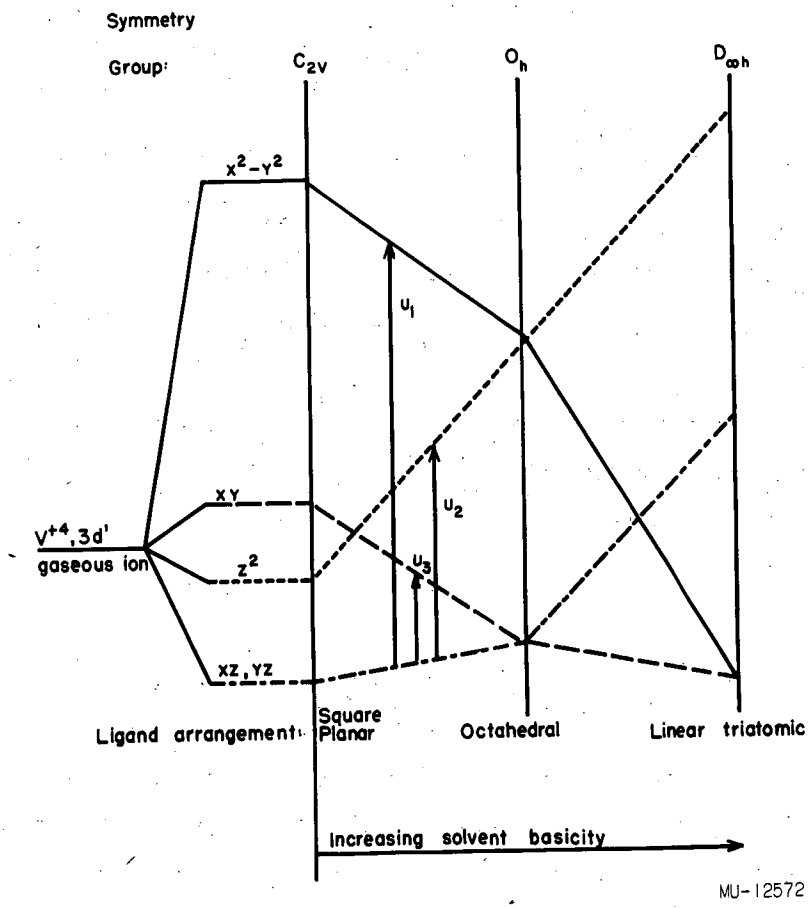


Fig. 1. Effect of ligand field on the energies of d orbitals.

The only other interaction that can affect the energy of this electron is spin-orbit coupling. This results from the interaction of the spin magnetic moment with the magnetic field set up by the orbital motion of the electron. This energy is considered small in comparison with the ligand field, and will now be considered as a perturbation. The perturbing term in the Hamiltonian is of the form $\lambda L \cdot S$ where λ is the spin-orbit coupling parameter. The unperturbed wave functions are

$$d_{xy}\alpha,\ d_{xy}\beta \quad \text{or } \sqrt{15/16\pi}\ \sin^2\theta \sin 2\phi(\alpha,\beta)\ ,$$
$$d_{xz}\alpha,\ d_{xz}\beta \quad \text{or } \sqrt{15/4\pi}\ \sin\theta\cos\theta\sin\phi\ (\alpha,\beta),$$
$$d_{yz}\alpha,\ d_{yz}\beta \quad \text{or } \sqrt{15/4\pi}\ \sin\theta\cos\theta\sin\phi\ (\alpha,\beta),$$
$$d_{z^2}\alpha,\ d_{z^2}\beta \quad \text{or } \sqrt{5/16\pi}\ (3\cos^2\theta - 1) \quad (\alpha,\beta);\ \text{and}$$
$$d_{x^2-y^2}\alpha,\ d_{x^2-y^2}\beta \ \text{or } \sqrt{15/16\pi}\ \sin^2\theta\cos 2\phi \quad (\alpha,\beta)\ .$$

Standard perturbation theory permits expansion of the eigenfunctions of the perturbed Hamiltonian in terms of eigenfunctions of the solved Hamiltonian given:[16]

$$\Psi S_1 = \Sigma_i\, c_i\ (S+\alpha,\ \text{or}\ \beta)\ \psi_i + \psi_0\, S$$

where $c_i = \langle \psi_i S_{1,2} \,|L\cdot S|\, \psi_0 S\rangle \frac{\lambda}{E_i}$. Noting that spin and angular functions are separate one needs only to compute $\langle \psi_1 \,|L|\, \psi_2\rangle$,$\langle S_{1,2} |\sigma| S\rangle$. These elements are from Condon.[17] The spin and orbital matrices are shown in Table I. Our perturbed eigenfunctions are listed in Table II.

If a magnetic field is applied to this unpaired electron, the spin degeneracy is removed. The energy difference between these two spin levels has the form $g\beta H$. The value of g for a free electron or an electron in an S state is 2.0023 (g_0). If there is some spin-orbital coupling, then the energy separation may be written as $(g_0 + \Delta g)\beta H$. Here Δg represents the field due to the orbital magnetic moment. It can be shown the $\Delta g_i = \langle L_{i\alpha}\rangle - \langle L_{i\beta}\rangle$. To find this contribution we need only find the matrix elements $\langle m|L_z|m\rangle$ and $\langle m|L_{x\ \text{or}\ y}|m\rangle$,

Table I

Matrix elements for d orbitals

$$\lambda\langle j|L_i|xy\rangle \qquad \langle s|\sigma|\alpha\rangle$$

$$\begin{array}{c|ccc} & x & y & z \\ \hline xz & -\lambda & 0 & 0 \\ yx & 0 & i\lambda & 0 \\ x^2-y^2 & 0 & 0 & 2\lambda \\ z^2 & 0 & 0 & 0 \end{array} \qquad \begin{array}{c|cc} & \alpha & \beta \\ \hline x & 0 & 1 \\ y & 0 & -i \\ z & 1 & 0 \end{array}$$

z quantization

$$\lambda\langle j|L_i|x^2-y^2\rangle \qquad \langle s|\sigma|\beta\rangle$$

$$\begin{array}{c|ccc} & x & y & z \\ \hline xz & 0 & -i\lambda & 0 \\ yz & \lambda & 0 & 0 \\ xy & 0 & 0 & -2\lambda \\ z^2 & 0 & 0 & 0 \end{array} \qquad \begin{array}{c|cc} & \alpha & \beta \\ \hline x & 1 & 0 \\ y & -i & 0 \\ z & 0 & -1 \end{array}$$

$$\lambda\langle j|L_i|-1\rangle \qquad \langle s|\sigma|\alpha\rangle$$

$$\begin{array}{c|ccc} & x & y & z \\ \hline -1 & 0 & 0 & 0 \\ x^2-y^2 & \frac{\lambda}{\sqrt{2}} & \frac{i\lambda}{\sqrt{2}} & 0 \\ xy & \frac{\lambda}{\sqrt{2}} & \frac{i\lambda}{\sqrt{2}} & 0 \\ z^2 & \frac{\sqrt{6}\lambda}{2} & \frac{-i\sqrt{6}\lambda}{2} & 0 \end{array} \qquad \begin{array}{c|cc} & \alpha & \beta \\ \hline x & 0 & 1 \\ y & 1 & 0 \\ z & 0 & -i \end{array}$$

y (or x) quantization

$$\lambda\langle j|L_i|0\rangle \qquad \langle s|\sigma|\beta\rangle$$

$$\begin{array}{c|ccc} & x & y & z \\ \hline +1 & \frac{-\sqrt{+6}\lambda}{2} & \frac{+i\sqrt{6}\lambda}{2} & 0 \\ -1 & \frac{\lambda\sqrt{+6}}{2} & \frac{+i\sqrt{6}\lambda}{2} & 0 \end{array} \qquad \begin{array}{c|cc} & \alpha & \beta \\ \hline x & 1 & 0 \\ y & 0 & -1 \\ z & i & 0 \end{array}$$

Table II

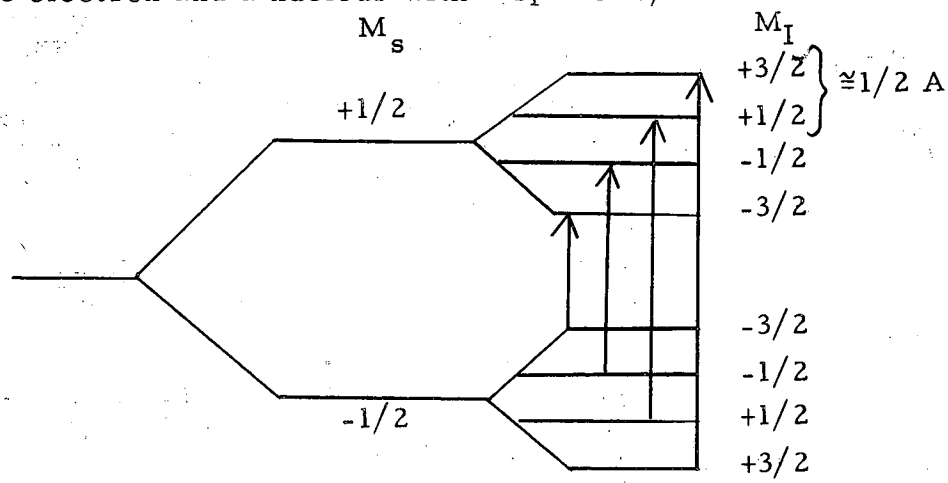
Eigenfunctions of the perturbed Hamiltonian[a]

$\Psi_{z^2\alpha} = d_{z^2\alpha}$		$\Psi_{z^2\beta} = d_{z^2\beta}$
$\Psi_{xy\alpha} = d_{xy\alpha}$	$+ \frac{\lambda\beta}{2\Delta_{xz,\,yz}} (d_{yz} - d_{xz})$	$+ \frac{\lambda\beta d_{x^2-y^2}}{\Delta_{xy,\,x^2-y^2}}$
$\Psi_{xy\beta} = d_{xy\beta}$	$+ \frac{\lambda\beta}{2\Delta_{xz,\,yz}} (d_{yz} - d_{xz})$	$- \frac{\lambda\beta d_{x^2-y^2}}{\Delta_{xy,\,x^2-y^2}}$
$\Psi_{x^2-y^2\alpha} = d_{x^2-y^2\alpha}$	$+ \frac{\lambda\beta}{2\Delta_{xz,\,yz}} (d_{yz} - d_{xz})$	$- \frac{\lambda\alpha d_{xy}}{\Delta_{xy,\,x^2-y^2}}$
$\Psi_{x^2-y^2\beta} = d_{x^2-y^2\beta}$	$+ \frac{\lambda\alpha}{2\Delta_{xz,\,yz}} (d_{yz} - d_{xz})$	$+ \frac{\lambda\beta d_{xy}}{\Delta_{xy,\,x^2-y^2}}$
$\Psi_{-1\,\alpha} = \alpha/\sqrt{2}\,(d_{yz} - d_{xz})$	$+ \frac{\lambda\beta}{\sqrt{2}} \left(\frac{d_{x^2-y^2}}{\Delta_{x^2-y^2;\,xz,\,yz}}\right.$	$\left. + \frac{d_{xy}}{\Delta_{xy;\,xz,\,yz}}\right)$
$\Psi_{-1\beta} = \beta/\sqrt{2}\,(d_{xz} - d_{xz})$	$+ \frac{\lambda\alpha}{\sqrt{2}} \left(\frac{d_{x^2-y^2}}{\Delta_{x^2-y^2;\,xz,\,yz}}\right.$	$\left. + \frac{d_{xy}}{\Delta_{xy;\,xz,\,yz}}\right)$
$\Psi_{-1\alpha} = \alpha/\sqrt{2}\,(d_{xz} - d_{yz})$	$- \frac{\lambda\beta}{\sqrt{2}} \left(\frac{d_{x^2-y^2}}{\Delta_{x^2-y^2;\,xz,\,yz}}\right.$	$\left. + \frac{d_{xy}}{\Delta_{xy;\,xz,\,yz}}\right)$
$\Psi_{-1\beta} = \beta/\sqrt{2}\,(d_{xz} - d_{yz})$	$- \frac{\lambda\alpha}{\sqrt{2}} \left(\frac{d_{x^2-y^2}}{\Delta_{x^2-y^2;\,xz,\,yz}}\right.$	$\left. + \frac{d_{xy}}{\Delta_{xy;\,xz,\,yz}}\right)$

[a]Here Δ represents the energy separation of the d orbitals.

which depend on the angle between the direction of the magnetic field and the molecular axis. Table III lists these matrix elements. It can be seen that if the ground state is Ψ_{-1} then $g_{\parallel}$ is 2.0023, and $g_{\perp}$ depends on the energy separation Δ.

If there are nuclei present that have magnetic moments, there are further splittings of the electron spin levels. For any nuclear spin I there are 2I + 1 orientations of this spin in a magnetic field. This changes the effective magnetic field that the electron moves in. The energy levels for one electron and a nucleus with a spin of 3/2 are



If there are several equivalent nuclei, then they may be taken to have an effective spin that is equal to the sum of all the spins (two protons with a spin of 1/2 each = the total spin of 1). The only difference in the spectrum between a total spin of three times 1/2, and one nucleus with a spin of 3/2 is the intensity ratios of the hyperfine components. For a single nucleus, all orientations are equally probable, while for several nuclei, the probabilities of the various orientations follow the binomial coefficients. The above diagram shows the allowed transitions ($\Delta m_I = 0$, $\Delta m_s = \pm 1$). It can also be seen that the various transitions occur at different frequencies. The interaction between electron spin and nuclear spin may be expressed as $A \cdot I \cdot S$.[41] A is a parameter that depends on the radial wave function. For an ion in solution, this term is zero unless there is some "s" character in the wave function. That is, the only contribution to this term (A) is at $r = 0$.

Table III

Matrix elements for $\langle m | L_z | m \rangle$ and $\langle m | L_{x \text{ or } y} | m \rangle$

Ψ_m	L_z	$L_{y \text{ or } x}$
Ψ_{xy}	$\frac{-8\lambda}{\Delta_{x^2-y^2}}$	$\frac{-2\lambda}{\Delta_{xz,\ yz}}$
$\Psi_{x^2-y^2}$	$\frac{8\lambda}{\Delta_{xy}}$	$\frac{+2\lambda}{\Delta_{xz,\ yz}}$
Ψ_{-1}	0	$\left(\frac{1}{\Delta_{x^2-y^2}} + \frac{1}{\Delta_{xy}}\right)\lambda$
Ψ_{+1}	0	$-\left(\frac{1}{\Delta_{x^2-y^2}} + \frac{1}{\Delta_{xy}}\right)\lambda$
Ψ_{z^2}	0	0
	$\Delta_{g_{\parallel}}$	$\Delta_{g_{\perp}}$

In using this Hamiltonian one assumes the ligand field to be more important than spin-orbit coupling and covalent bonding.[18] In a system such as the vanadyl ion, which remains as a unit throughout so many chemical reactions, this last assumption may be very bad indeed. The effect of covalent bonding is considered in the next section.

LCAO Molecular Orbital Treatment of Vanadyl Chelates

Introduction

This approach to molecular wave functions, along with the valence-bond approach, is the classic quantum-mechanical method for describing molecular states. It has long been known that of the two methods, valence bond as usually applied is suitable to simple homopolar bonds, while LCAO is a more general method. Because it is known that ligand-field theory does explain the general features of the electronic spectra of these compounds, the crystal field modified with LCAO MO's was chosen as the type of approach most appropriate for these polar covalent bonds.

Basis Wave Functions

Because molecular orbital formation is here considered as a perturbation on the crystalline-field wave functions, atomic orbitals must serve as the basis for the molecular wave functions. The first assumption is that all closed shells may be ignored. All atomic orbitals with energies greater than that of the 3d orbitals are considered to contribute a negligible amount to bonding and to excited molecular states. In the geometry of the molecule, the vanadium atom is assumed to be at the center of a square of oxygen atoms, and the fifth oxygen is along the z axis. The ligand hybrid orbitals used were chosen on the basis of this geometry so as to maximize the molecular bonding.

The vanadium ion therefore has available five 3d orbitals, designated as $d_{x^2-y^2}$, d_{xy}, d_{xz}, d_{yz}, and d_{z^2}. Each of the ligand oxygens is assumed to have two sp^2 hybrids and a p_z orbital available for bonding, called σ, t, and π respectively. A sigma-bonding

skeleton is assumed for all except V-O bonds. Each carbon atom has a p_z orbital. These are designated as c_1 through c_6. The atomic orbitals used for bonding from the vanadyl oxygen are the three 2p orbitals (π_a, π_b, p_z) and one 2s (S) orbital. A schematic diagram of the metal^{+n} bisacetylacetonate is pictured in Fig. 2. Only the d_{xz}, d_{yz}, and vanadyl orbitals have been omitted for the sake of clarity. Using this picture one easily sees which atomic orbitals remain essentially unchanged and which are involved in molecular orbitals.

Variation Calculation

If these orbitals are used as the basis wave functions, the required molecular eigenfunctions can be expanded according to $\bar{\Psi} = \Sigma_i b_i \phi_i$. The molecular Hamiltonian will have the symmetry of the molecule, which is C_{2v}. If the variation theorm, $\int \bar{\psi}_i H \bar{\psi}_i \geq E$, is applied, a 31-by-31 secular determinant is obtained which needs to be factored. The following discussion uses theorems from group theory, which will be found in any standard treatment of group theory.[19]

Because an eigenfunction of the Hamiltonian must belong to one of the irreducible representations of Hamiltonian symmetry, symmetry orbitals may first be obtained by applying $\Sigma_R \chi_R \phi_i = \Sigma_j b_j \phi_j$ (Table IV), where R represents a particular irreducible representation, χ_R is the character in the representation, and i, j, n, and m label the various basis wave functions of irreducible representations. There are no off-diagonal elements between members of different irreducible representation, because the integrals $\int \bar{\psi}^n_{R_i} H \psi^m_{R_j} d\tau$ and $\int \psi^n_{R_i} \psi^m_{R_j} d\tau$ vanish except for $R_i \times R_j = A_{1g}$. This effectively factors the determinant into irreducible subdeterminants.

Solution of the Secular Determinant

The Hamiltonian that is assumed to describe the metal-ion complexes of the first transition series with β-diketones is $H = \frac{\hbar^2}{2m} \nabla^2 + \Sigma_i \frac{e^2}{r_i} + V'$. In order to get even qualitative ideas about

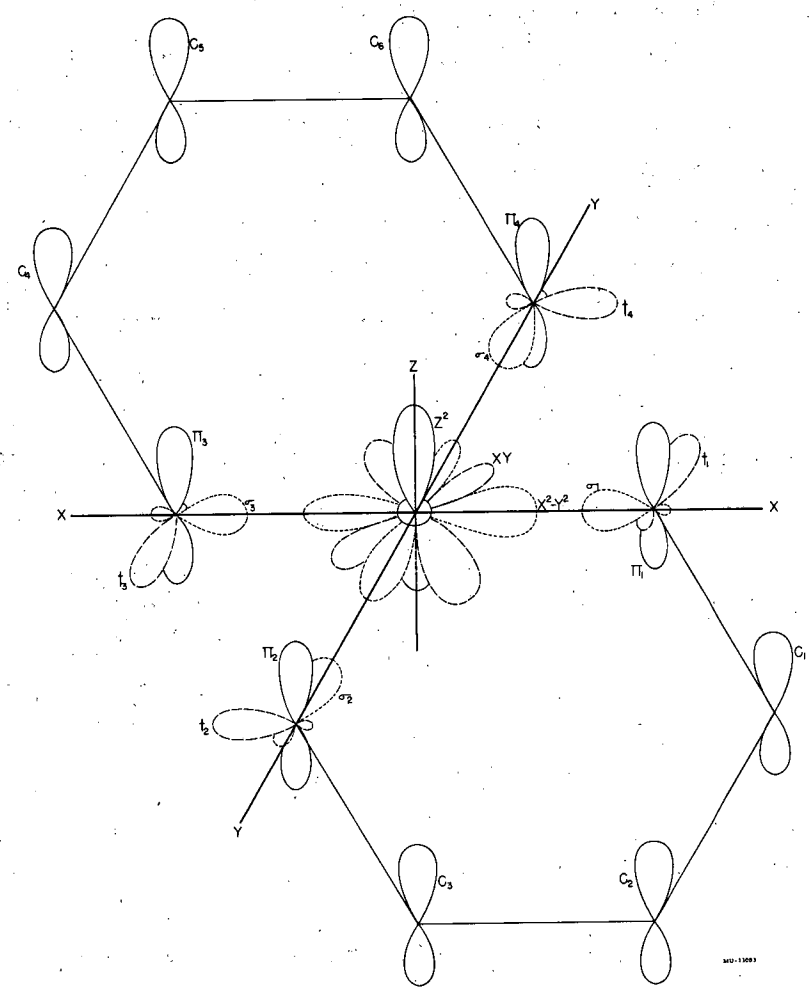


Fig. 2. Diagram of M^{+n} bis acetylacetonate.

the solutions of this secular determinant, the usual assumptions of the LCAO method are made, i.e., neglect of overlap integrals, and assumption that exchange integrals are proportional to the overlap integrals. The only integrals left are of the form $\int \overline{\Psi}^n_{R_i} H \Psi^n_{R_i} \, d\tau \, (Q)$ and $\int \overline{\Psi}^n_{R_i} H \Psi^m_{R_i} \, d\tau \, (\beta)$. Some of the β's are zero, from symmetry considerations, others have been evaluated,[20,21] and still others may be estimated. The interatomic distances assumed are V = O = 1.59 A and V-ligand oxygen = 1.90 A. The only part of the wave function that is not known is the radial part. For evaluation of these integrals, Slater radial wave functions were assumed. These have the form $R_{nl}(r) = N_{nl} r^{n-1} e^{-\mu r/a_H}$, where $\mu_n = Z^*_{a,n}/(n-\sigma_i)$, Z^* is the effective nuclear charge as determined by the methods of Slater.[22] The necessary overlap integrals are given in terms of these parameters.[20,21] This gives:

atom	orbital	Z^*	$n-\sigma_i$	μ	$\frac{\mu_V-\mu_0}{\mu_V+\mu_0}$	$1/2(\mu_V+\mu_0)$
V^{+4}	3d	+5	3	1.667	0.0	1.3646
	4s	+5	3.7	1.446		
	4p	+5	3.7	1.446		
O^{-2}	2p	+3.85	3.0	1.283		

Evaluating the required overlaps (using the published tables[20,21]) or finding them by extrapolation gives the subdeterminants shown in Table V.

Table IV

Symmetry orbitals		
Class		Wave function
A_1		
	d_{z^2}	$1/2\,(c_1 + c_3 + c_4 + c_6) = B_+$
	d_{xy}	$1/\sqrt{2}(c_2 + c_5) = C_+$
	p_{z^2}	$1/2\,(\pi_1 + \pi_2 + \pi_3 + \pi_4) = \pi_+$
		$1/2\,(t_1 + t_2 + t_3 + t_4) = T_+$
		$1/2\,(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4) = \Sigma_+$
A_2	$d_{x^2-y^2}$	$1/2\,(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4) = \Sigma_-$
		$1/2\,(c_1 - c_3 + c_4 - c_6) = B_-$
		$1/2\,(\pi_1 - \pi_2 + \pi_3 - \pi_4) = \pi_-$
		$1/2\,(t_1 - t_2 + t_3 - t_4) = T_-$
B_1	$1/\sqrt{2}(d_{xz}+d_{yz}) = D_+$	$1/2\,(\sigma_1 + \sigma_2 - \sigma_3 - \sigma_4) = \Sigma_1$
		$1/2\,(c_1 + c_3 - c_4 - c_6) = B_1$
	$1/\sqrt{2}(\pi_a + \pi_b) = \pi_a$	$1/2\,(\pi_1 + \pi_2 - \pi_3 - \pi_4) = \pi_1$
	$1/\sqrt{2}(c_2 - c_5) = C_-$	$1/2\,(t_1 + t_2 - t_3 - t_4) = T_1$
B_2	$1/\sqrt{2}(d_{xz}-d_{yz}) = D_-$	$1/2(\sigma_1 - \sigma_2 - \sigma_3 + \sigma_4) = \Sigma_2$
		$1/2\,(c_1 - c_3 - c_4 + c_6) = B_2$
	$1/\sqrt{2}(\pi_a - \pi_b) = \pi_b$	$1/2\,(\pi_1 - \pi_2 - \pi_3 + \pi_4) = \pi_2$
		$1/2\,(t_1 - t_2 - t_3 + t_4) = T_2$

Table V

Factored secular determinant

A_1	p_z	d_z	d_{xy}	C_+	B_+	π_+	T_+	Σ_+
p_z	$Q_{p_z}-E$	$\sim .09\ a_V$	0	0	0	$0.26a_V$	0	$\sim 0.22a_V$
d_{z^2}	$\sim 0.09a_V$	$Q_{d_{z^2}}-E$	0	0	0	0	0	0
d_{xy}	0	0	$Q_{d_{xy}}-E$	0	0	0	$<0.172a_V$	0
C_+	0	0	0	$Q_{C_+}-E$	$2\beta_C$	0	0	0
B_+	0	0	0	$2\beta_C$	$Q_{B_+}-E$	β_0	0	0
π_+	$\sim 0.26a_V$	0	0	0	β_0	$Q_{\pi_+}-E$	0	0
T_+	0	0	$<0.172a_V$	0	0	0	$Q_{T_+}-E$	0
Σ_+	$\sim 0.22a_V$	0	0	0	0	0	0	$Q_{\Sigma_+}-E$

A_2	$d_{x^2-y^2}$	Σ_-	B_-	π_-	T_-
$d_{x^2-y^2}$	$Q_{d_{x^2-y^2}}-E$	$0.50a_V$	0	0	0
Σ_-	$0.50a_V$	$Q_{\Sigma_-}-E$	0	0	0
B_-	0	0	$Q_{B_-}-E$	β_0	0
π_-	0	0	β_0	$Q_{\pi_-}-E$	0
T_-	0	0	0	0	$Q_{T_-}-E$

Table V(cont.)

Factored secular determinant

B_1	π_a	D_+	π_1	B_1	C_-	T_1	Σ_1
π_a	$Q_{\pi_a}-E$	$0.707a_V$*	$0.22a_\ell$	0	0	0	$0.26a_\ell$
D_+	$0.707a_V$	$Q_{D_+}-E$	$1.131a_V$	0	0	0	0
π_1	$0.22a_\ell$	$1.131a_V$	$Q\pi_1-E$	β_0	0	0	0
B_1	0	0	β_0	$Q_{B_1}-E$	$2\beta_C$	0	0
C_-	0	0	0	$2\beta_C$	$Q_{C_-}-E$	0	0
T_1	0	0	0	0	0	$Q_{T_1}-E$	0
Σ_1	$0.26a_\ell$	0	0	0	0	0	$Q\Sigma_1-E$

B_2	π_b	D_-	π_2	B_2	T_2	Σ_2
π_b	$Q_{\pi_b}-E$	$0.707a_V$	$0.22a_\ell$	0	0	$0.26a_\ell$
D_-	$0.707a_V$	$Q_{D_-}-E$	$1.131a_V$	0	0	0
π_2	$0.22a_\ell$	$1.131a_V$	$Q_{\pi_2}-E$	β_0	0	0
B_2	0	0	β_0	$Q_{B_2}-E$	0	0
T_2	0	0	0	0	$Q_{T_2}-E$	0
Σ_2	$0.26a_\ell$	0	0	0	0	$Q_{\Sigma_2}-E$

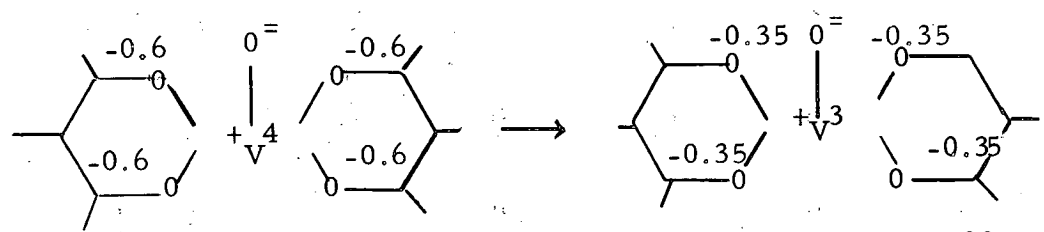
*Bis = $a\,S_{ij}$, and S_{ij} is the overlap integral ($\int \psi_i \psi_j dT$).

Order of Energy Levels

Because the complete secular equation cannot be directly solved or the integrals evaluated, qualitative arguments will be used for the ordering of energy levels. The first assumption is: the larger the overlap, the larger the exchange. The second is: the nearer the value of the Coulomb integrals to each other, the more the interaction between the two orbitals. The third is: the energy of the d orbitals lies in value between the nonbonding ligand orbitals, and the antibonding ligand orbitals. This last assumption is essential in order that molecular orbitals be useful. If the d orbitals were of lower energy than the filled ligand orbitals, then in the complex, the d orbitals would be filled with ligand electrons. If the d orbitals were of higher energy than the lowest excited ligand orbitals, then in the complex some of the ligand orbitals would be filled with d electrons. However, the spectra show the presence of unfilled d orbitals, and of the correct number of d electrons. Therefore, the third assumption is essential.

To get some idea of the relative value of the Coulomb integrals (H_{ii}), one may calculate the energy involved in transferring an electron from ligand to metal, using the following values: the charge on a ligand oxygen of acetylacetone is 0.6 at a distance of 1.9 A, the charge on the vanadium atom is +4, and the charge on the vanadyl oxygen is -2 at a distance of 1.6 A. The energy relationships are as follows:

Reaction	ΔE (kcal)
$V^{+4} + e \longrightarrow V^{+3}$	-1107[23]
$\rangle C{=}\ddot{O}: \longrightarrow \rangle C{=}\ddot{O}\cdot + e$	220[24]
electrostatic	about 967



Total 80

The order found by use of the overlap integrals to estimate the amount of bonding by the various orbitals and by use of the energy for an electron transfer (see above) to estimate the relative Coulomb intergrals is given in Fig. 3. If it is assumed that crystalline-field effects should not be taken into account first, the d_{z^2} orbital would be lowest on the basis of the relative sizes of the various overlap integrals. This is a very surprising result because it might have been expected that this would be the orbital involved in bonding with the vanadyl oxygen, and therefore, would be quite antibonding. The next level is the d_{xy} orbital. The doubly degenerate state d_{xz}, d_{yz} is somewhat antibonding and would be the next highest in energy. The highest energy level from the vanadium d orbitals would be the $d_{x^2-y^2}$ because it would be the most antibonding of the d orbitals.

A somewhat different order is arrived at if the crystalline field is applied first. If the d orbitals are left in the same relative positions with respect to the ligand orbitals, the order of the d orbitals is probably the same as given in the last section. There is the possibility that the d_{xy} could become higher than the d_{z^2} through its greater antibonding character. This probably does not happen because the d_{xy} is a π-type orbital and therefore would exhibit relatively little mixing. The other effect of forming molecular orbitals is either to leave the energy of the $d_{x^2-y^2}$ unchanged or to decrease it slightly and increase the energy of the d_{xz}, d_{yz} pair through π bonding. Any bonding also neutralizes some of the formal charge on the metal ion. Both of these effects act in the same way so far as the crystal-field parameters are concerned, and that is to decrease the separation between the d levels (decrease the effective D_q). This is true only if there is appreciable π bonding.

Is there any other way to test which of these ways of determining the energies of the d levels is correct? One way is to notice that in the crystalline fields a magnetic orbital is lowest, while in the other case an orbital with no angular momentum possible is lowest. This may be confirmed by measuring the g values for these chelates.

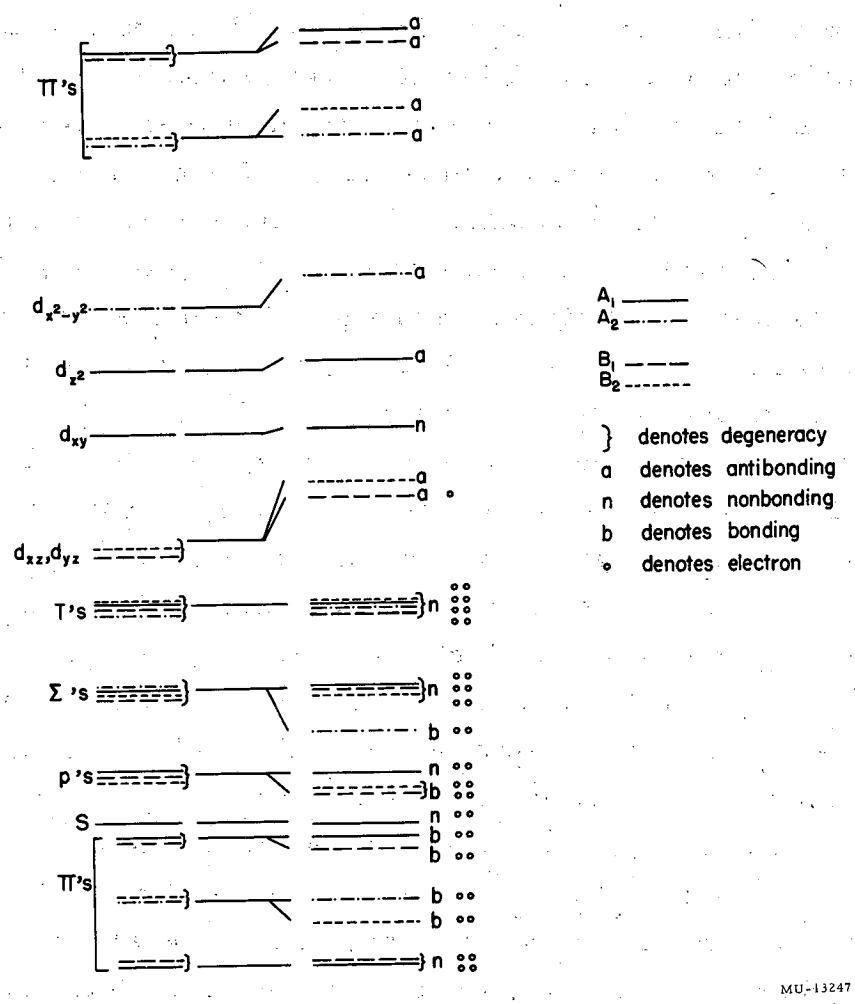


Fig. 3. Energy levels for vanadyl bisacetylacetonate. (The left-hand column is without covalent bonding and the right-hand column is with covalent bonding).

LCAO Molecular Orbitals for Chromium Bisaromatic Complexes

The bonding in "sandwich" molecules has been treated by Moffitt,[25] Dunitz,[26] and others.[27a, 21, 27b] However, none of these authors has treated specifically the chromium dibenzene complexes. In order to simplify this treatment, we consider the complex as two benzene rings and a chromium atom with a molecular symmetry of D_{6h}.

Molecular orbitals for benzene (D_{6h} symmetry) have been thoroughly investigated by many authors.[28, 29] These authors' results will be used for evaluation of the chromium complexes. The order of the molecular orbitals for benzene in order of decreasing energy is b_{2g}, e_{2u}, e_{1g}, and a_{2u}. The six electrons of the benzene π system are placed in the last two orbitals.

Here, again, the closed shells of chromium are left intact, while atomic orbitals whose energy is higher than that of the 4s orbital are considered to have a negligible contribution to the bonding and observed excited electronic states. In the gaseous Cr^{+1} ion, the d and s orbitals are approximately degenerate. On the basis of ionization potentials (9.2 ev for C_6H_6, and 6.76 ev for Cr), the energy of the chromium orbitals is approximately 20,000 cm^{-1} higher than that of the last filled benzene orbital.

The two benzene rings and the chromium are placed together in a configuration as shown in Fig. 4, and are assumed to retain D_{6h} symmetry. If the chromium orbitals are placed just above the last filled orbitals of the two benzene rings, then the way in which the energy of the various orbitals changes can be decided. Two approximately degenerate levels are obtained from each original benzene orbital. Three orbitals are obtained from the chromium, all of which are still doubly degenerate. If the benzene and chromium orbitals are now allowed to interact, then the relative energies of the molecular orbitals in the complex may be tentatively assigned. The e_{1g} and e_{2g} orbitals form bonding and antibonding pairs. Because there is only one orbital of benzene of correct symmetry that combines with the d_{z^2} and 4s orbitals and the energy separation is large, the d_{z^2} and 4s orbitals are nonbonding, and as a first approximation remain at the same energy

as in the free chromium atom. Because the only type of bonds formed by the e_{2g} d orbitals are of the delta variety, it is expected that they will contribute only little to bonding, while the e_{1g} orbitals will be considerably raised in energy through bonding with the benzene orbitals. The energies of the nonbonding a_{1g} levels are a little harder to determine with confidence. However, if the spatial distribution of these orbitals is taken into account, perhaps some better guesses as to their energies can be made. It can be seen that if two benzene rings are placed along the z axis, there will be considerable repulsion between the π-electron clouds of benzene and the d_{z^2} orbital. The same thing is true for the 4s orbital. However, because these two orbitals are degenerate, any linear combination of them may be taken and still have the same average energy. If a linear combination of these orbitals is taken, it can be seen that with benzene rings along the z axis, a_{1g+} will have much less overlap with the π orbitals than a_{1g-} (Fig. 5). Accordingly, this combination has been used rather than the original atomic orbitals. From the above arguments a qualitative energy scheme is obtained as shown in Fig. 6. This is essentially the same scheme as that obtained by Moffitt[25] for ferrocene.

The chromium dibenzene cation has 17 electrons. Placing these electrons into the lowest energy levels, we find that the unpaired electron is in the e_{2g} bonding orbital. If one more electron is added to obtain the chromium dibenzene molecule it is found that this molecule should be diamagnetic, and it is.[12] This is further justification for placing the a_{1g+} orbital lower than the other chromium levels.

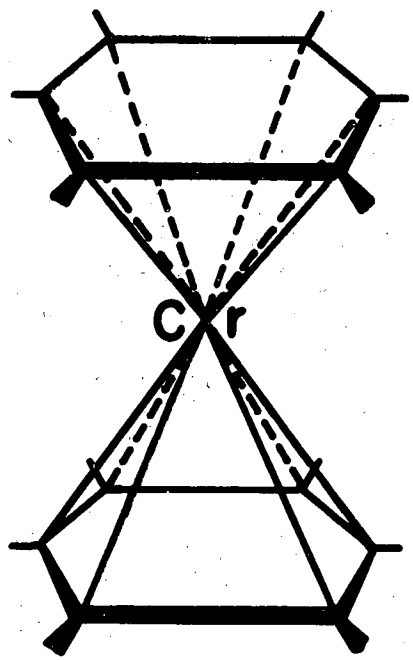


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Fig. 4. Structure of chromium dibenzene.

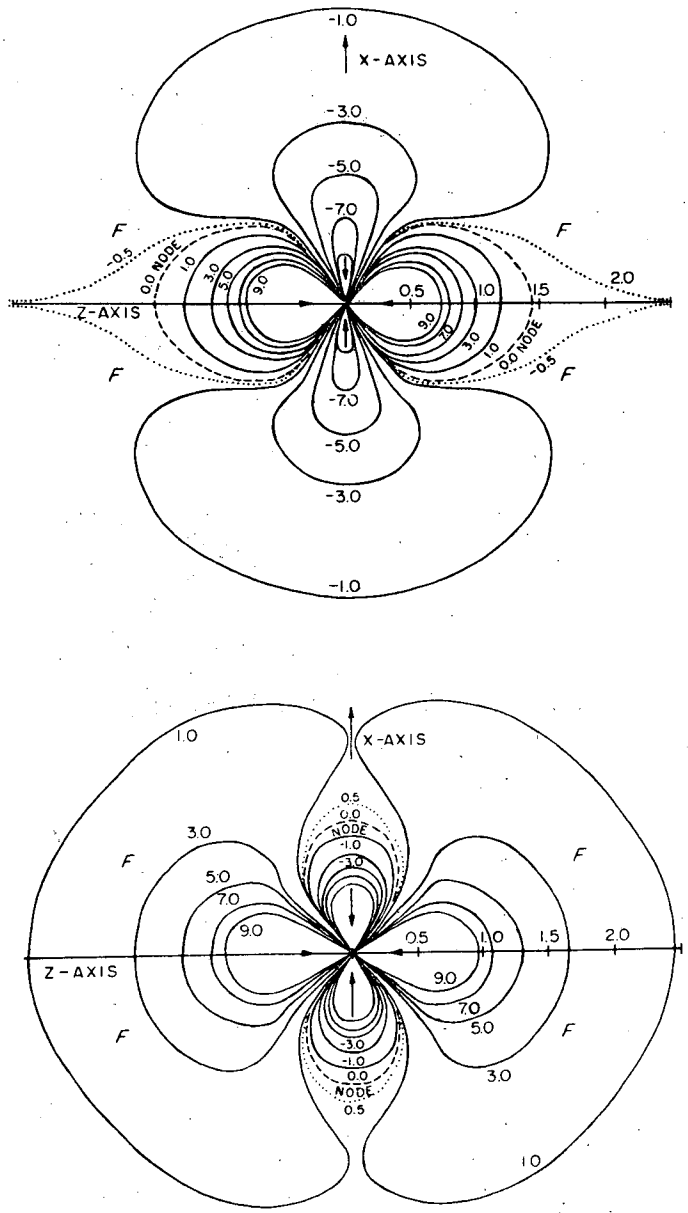

Fig. 5. Hybrid orbitals of symmetry A_{1g}. Top, 4s - d_{z^2}; bottom, 4s + d_{z^2}. (after Moffitt.[25])

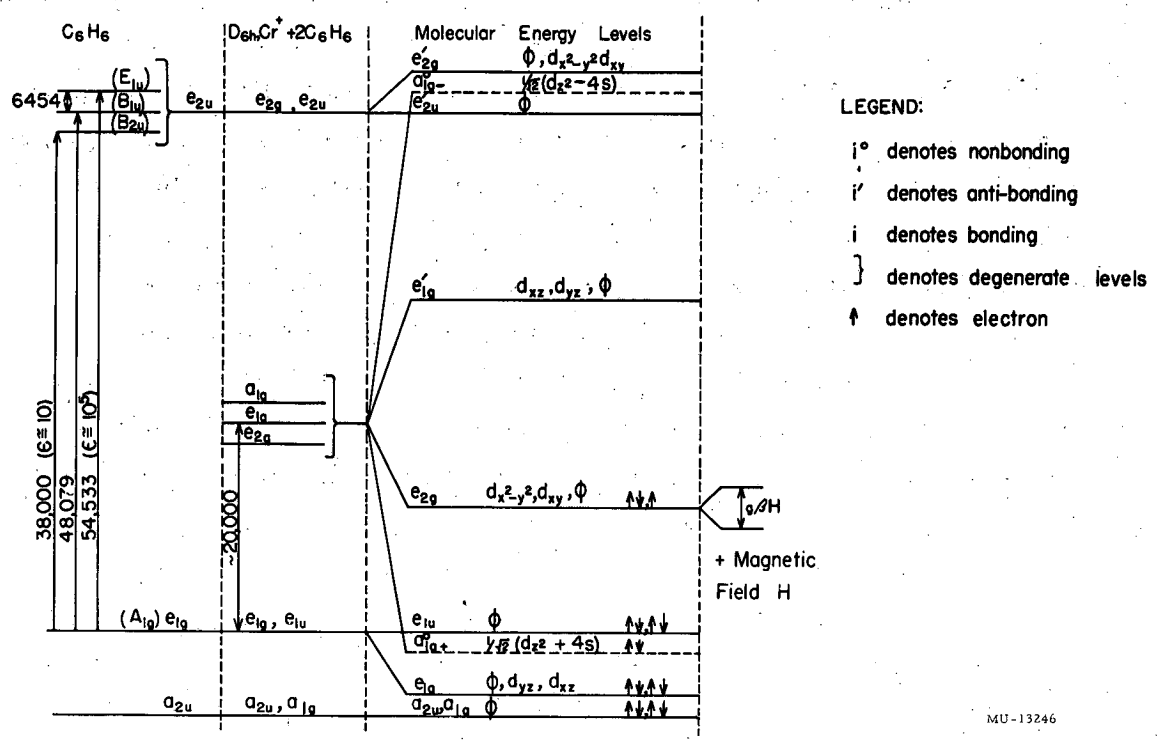

Fig. 6. Energy levels for chromium dibenzene.

LCAO Molecular Orbitals for Copper Chelates

The molecular orbitals for copper acetylacetonates are essentially the same as those for the vanadyl chelates. The differences between themare due mainly to the presence of the extra oxygen in the vanadyl chelates. The effect of the absence of this oxygen will be to lower the energy of the d_{xz} and d_{yz} orbitals by decreasing their antibonding character. Another important energy factor is the energy separation between the d orbitals and the σ, π, and t orbitals of the ligand. This can be estimated only in a very approximate way as already described for the vanadium acetylacetonate. A qualitative picture of the differences between vanadyl and copper chelates can be obtained by use of these arguments. The center of gravity of the copper orbitals will be lower than that of the vanadyl orbitals, but the odd electron in each case will have approximately the same energy, because the effect of the crystal field will be to lower the energy of the electron in the vanadyl chelates and to raise the energy of the odd electron in the copper chelates.

IV. EXPERIMENTAL PROCEDURE

Molecular-Weight Determinations

The molecular weights were determined by the freezing-point lowering of solutions of the chelate in dioxane. The dioxane used was Eastman "white label." The dioxane was placed in polyethylene bottles and was frozen until it was needed. The freezing point was reproducible to 0.24%. The approximate lowering was 2%, and the approximate error in the change in freezing point was 10 to 20%.

Copper Bisacetylacetonate

First, 5 milliliters of dioxane was added to the cryostate and the freezing point was determined. Then 0.0262 gram of the copper compound was added, and the new freezing point determined. The finding was $\Delta t = 0.107^{o}$, with a value of 4.67 for K_f;[30] the observed molality is 2.29×10^{-2}. The molality calculated, on the basis of a monomer, from the measured weights of solute and solvent is 2.19×10^{-2}.

Copper Bisacetate Monohydrate

The crystal structure shows this compound to exist as a dimer.[31] It was therefore necessary to determine whether or not it existed as such in weakly coordinating solvents. After the freezing point of the pure dioxane was determined, 0.0200 of the cooper compound was added to 5ml of dioxane. The value of Δt is 0.117^{o}. The observed molality is 2.51×10^{-2}. Using the measured weights of materials, and assuming two moles of water and one mole of dimer to be liberated in solution, we calculated th molality as 2.92×10^{-2}.

Vanadyl Bisacetylacetonate

By the same procedure as outlined above the observed molality is determined as 2.56×10^{-2}. The molality calculated on the basis of monomer is 1.96×10^{-2}. Analysis of this compound shows that there may be some water of hydration present.

Visible and Ultraviolet Spectra

Introduction

The transitions in the region from approximately 10,000 to 2000 A are attributed to electronic transitions of the molecules in question. The transitions whose molar extinction coefficients (ϵ), as measured at the position of maximum absorption, are between approximately 10 and 1000, are interpreted as transitions between the d levels of the gaseous ion whose degeneracy is removed by the presence of the electrostatic field of the ligand. These transitions are weak because they are simultaneous electronic and vibrational transitions, with the electronic transitions having no chance of the vibrational state's being forbidden. The transitions with ϵ equal to 10,000 or greater, which are usually in the uv are the "charge-transfer" bands and ligand transitions. Though the region of the spectrum usually identifies the type of transition involved, this is not a sufficient criterion, and the intensities, shapes, and solvent effects must also be considered.

The spectra of these chelates were obtained for several different solvents for several reasons. There were no problems of solubility, as the compounds were soluble to at least 0.01 molar in all the solvents used except cyclohexane. The positions of the visible bands and some of the uv bands, however, show a marked dependence upon the basicity of the solvent used. This behavior is attributed to coordination of the metal ion of the complex with solvent molecules. This coordination affects the symmetry and strength of the electrostatic field, and in turn the spacings of the d levels and positions of the transitions involved.

Material and Apparatus

All solvents were of spectral grade, except pyridine and dioxane, which were redistilled Baker's cp analyzed reagent grade. The dioxane probably still contained some peroxides and was used as little as possible.

All spectra in these regions were obtained by using a Cary Model 14 recording spectrophotometer. In all cases, unless otherwise specified, the wave-length scan was 10 A per second. The chart drive was 60 or 120

inches per hour, and the slit width was $\leq$ 0.1 mm. The resolution of the absorption bands was in no way changed by use of scanning speeds up to 50 A per second. The above conditions were used simply because they were the most convenient set for the particular absorptions involved.

The solid spectra were obtained by use of techniques developed by Shibata.[32] A thin film of the compound whose absorption spectra was desired was deposited on a quartz plate by evaporation of a solution of the compounds. Because such a film scatters light entering the sample, an appropriate blank must be used. Shibata's technique makes use of either opal glass or oil-impregnated filter paper in both the blank and reference. This material scatters the light so that when the sample is added the only change in absorption is due to the presence of excited states of that compound.

Vanadyl Spectra

The characteristic spectrum for VO^{++} complexes has three absorption bands in the visible or near-ultraviolet region. Depending on the type of compound that serves as ligand, these absorptions may occur almost anywhere in the visible region. In order to help identify which energy levels are involved in these absorptions, the spectra of several vanadium complexes with substituted acetylacetone were obtained, as shown in Figs. 7, 8, 9, and 10. Figure 11 shows the effect on the visible spectra of substituting fluorines for hydrogens in acetylacetone. The three weak transitions in the visible move to the red with the addition of fluorines. This behavior can be seen to parallel the acidity of the ligand. The addition of fluorines increases the acidity of the acetylacetone, and shifts the whole visible spectrum to the red.

The positions of the visible absorptions may also be changed by changing the solvent used to dissolve the compound. As more basic solvents are used, the positions of the absorptions vary in a regular manner. The uv absorption at approximately 4000 A (u_1) shifts to lower energies. The next absorption encountered on moving to the visible is u_2, which moves to higher energies with increasing solvent basicity. The last absorption (u_3) moves to lower energies with increasing solvent basicity. It is apparent that pyridine and methanol do not exactly

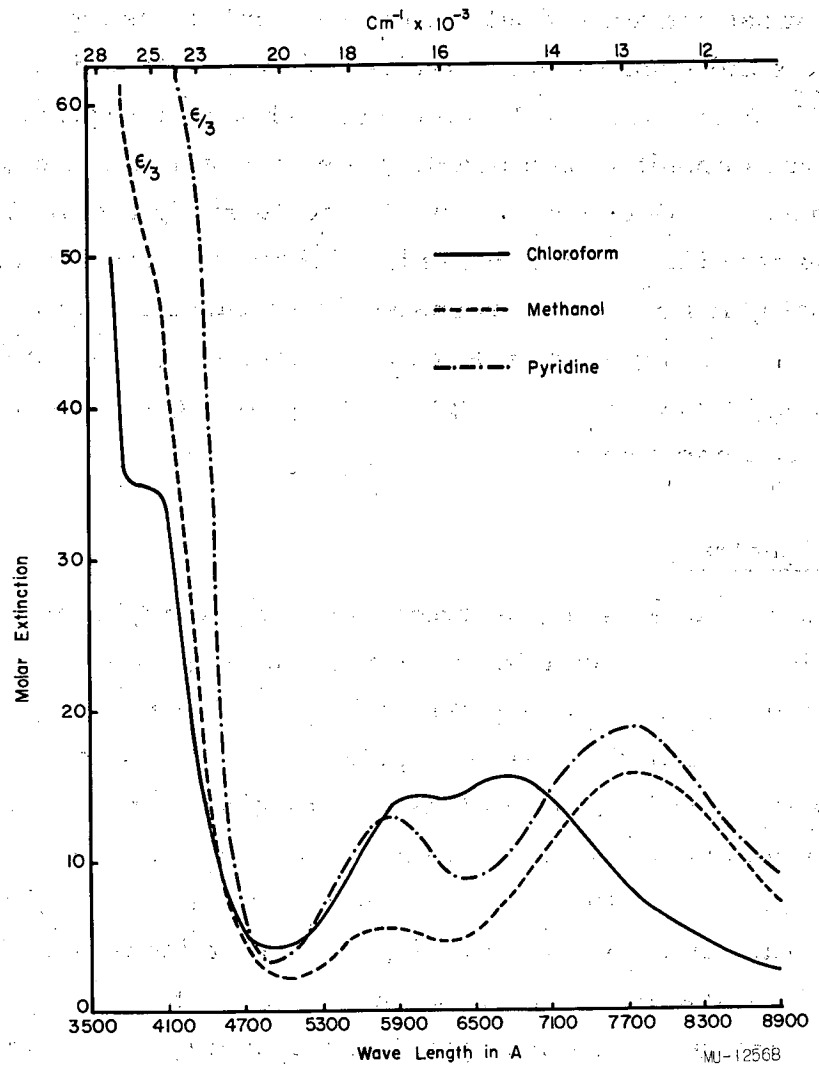

Fig. 7. Effect of solvent on vanadyl bisacetylacetonate.

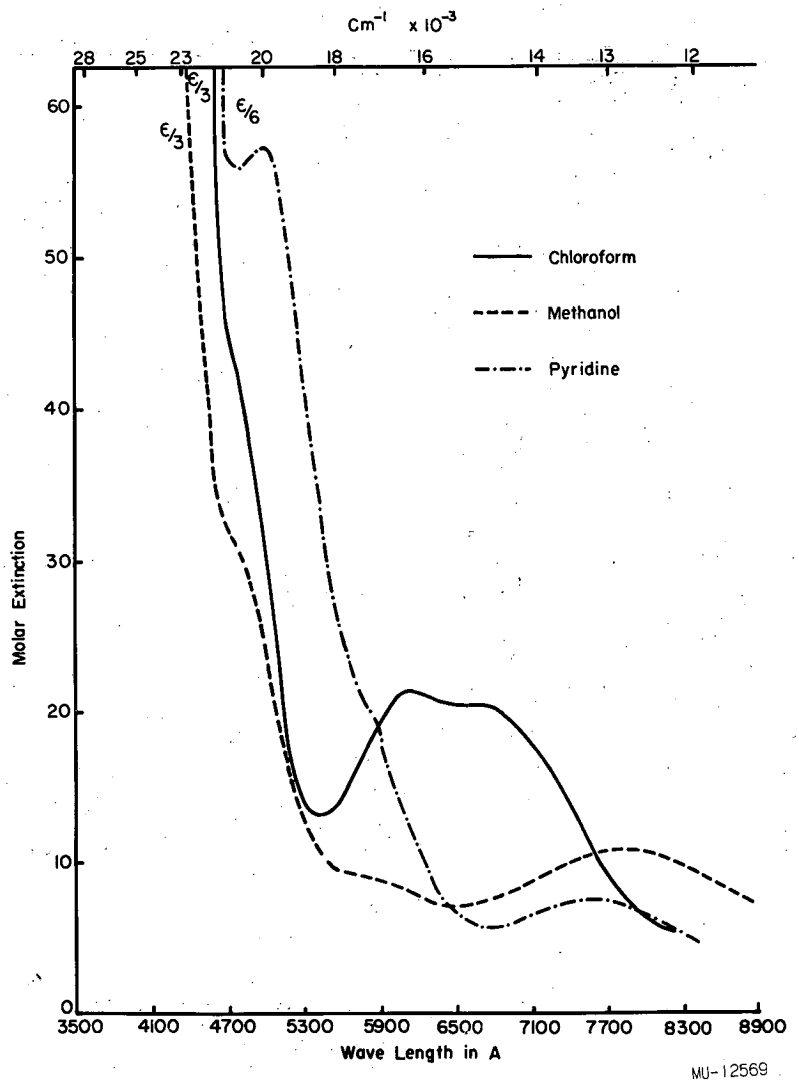

Fig. 8. Effect of solvent on vanadyl bisdibenzoylmethanate.

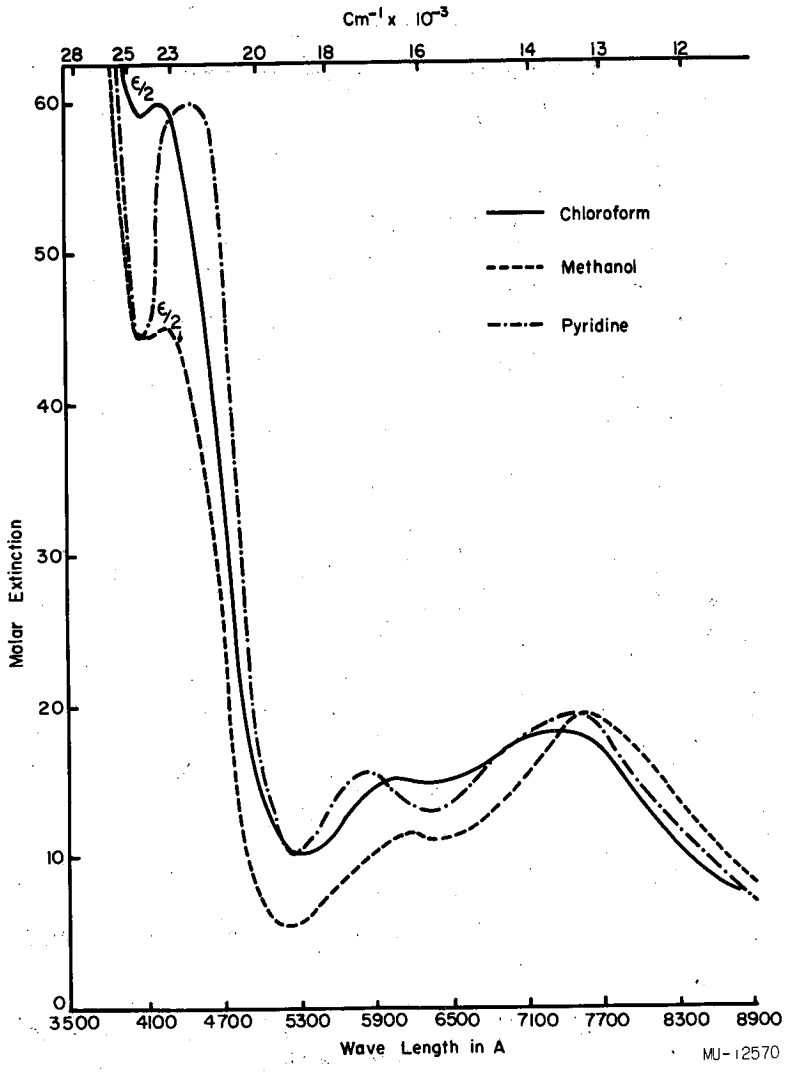

Fig. 9. Effect of solvent on vanadyl bistrifluoroacetylacetonate.

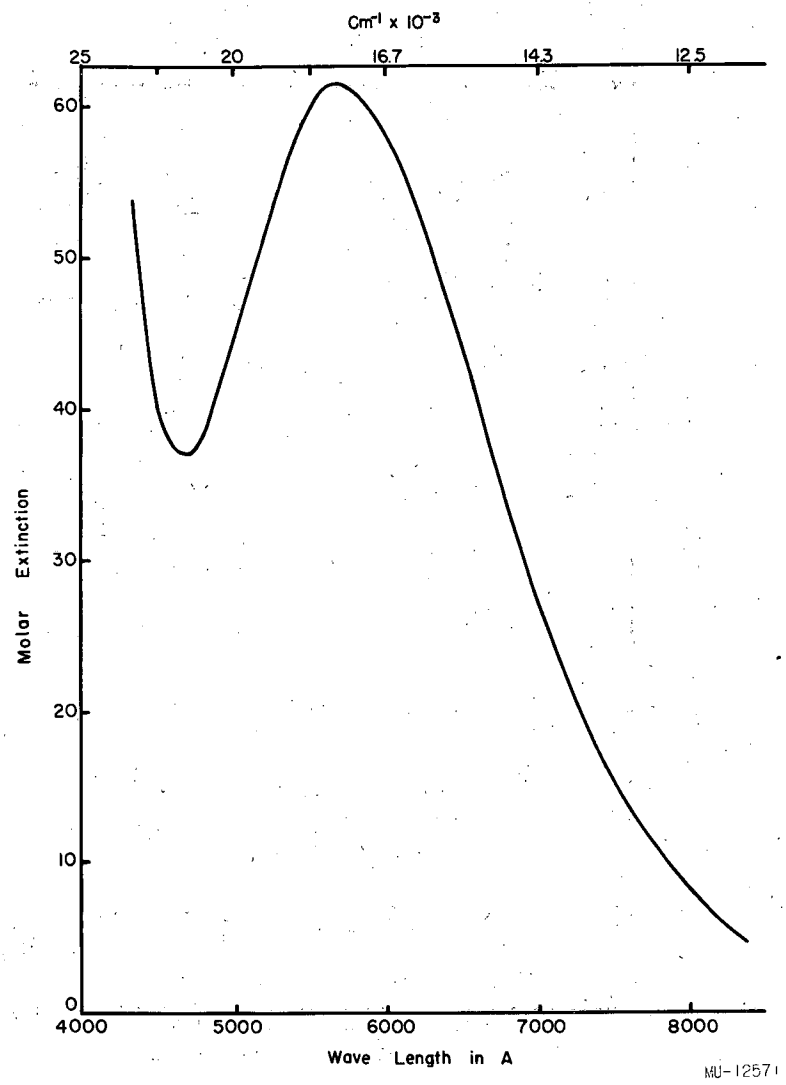

Fig. 10. Spectrum of vanadium bissalicylaldehydeethylenediiminate diacetate.

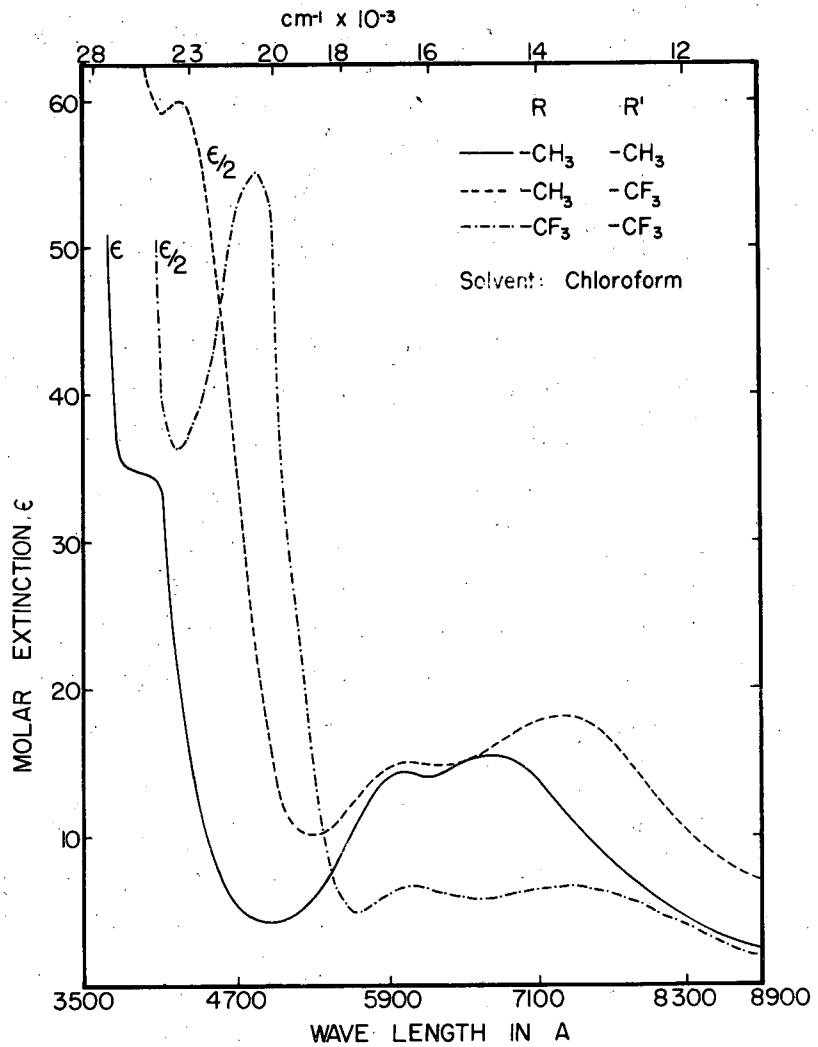

Fig. 11. Effect of fluorine substitution on the visible spectrum of vanadyl bisacetylacetonates.

follow this scheme. All the solvents used may be more complicated than at first assumed because not only is the basicity changing, but the π systems of the solvents are also being considerably changed. Table IV lists the visible absorptions along with their intensities for several vanadyl complexes.

The effect of fluorine substitution on the ultraviolet absorptions is shown in Fig. 12. It may be seen that there is a shift of the absorptions toward the red and an increased resolution of the first ultraviolet band. The first intense absorption in the chelates with 3d electrons is further to the red than the ligand absorptions. However, in a chelate such as lithium acetylacetonate the first absorption is little affected (Fig. 13).

The lone uv absorption is not shifted very much in comparison with that of the free ligand. It also maintains approximately the same shape as that of the absorption of the free ligand. However, the shape and number of the absorptions of the copper and vanadium chelates are quite different from those in the free ligand. In Fig. 14 it can be seen that there is also a solvent effect on the ultraviolet absorptions in the vanadyl chelates. The ultraviolet spectra of acetylacetone and trifluoroacetylacetone are shown in Figs. 15 and 16. It may be seen that there is little or no solvent effect on the free ligand except perhaps as to intensity. The scale for the ligand absorptions is left in terms of optical density because there is a keto-enol equilibrium in these ligands and the exact amount of enol is not known. Table VII gives the ultraviolet absorptions of the vanadyl chelates along with their molar extinction coefficients.

Table VI

Summary of spectra of some vanadyl chelates

Compound	Solvent	u_1 (A)	ϵ	u_2 (A)	ϵ	u_3 (A)	ϵ
Vanadyl bis-acetylacetonate	Chloroform	4000	40	5950	34	6750	38
	Methanol	4000	80	5750	10	7550	32
	Pyridine	4200	100	5800	37	7700	56
Vanadyl bis-benzoylacetonate	Chloroform	4550	30	6075	48	6700	48
	Methanol	4500	50	5850	19	7800	40
	Pyridine	----	--	5725	36	7625	43
Vanadyl bis-dibenzoylmethanate	Chloroform	4750	75	6150	64	6650	60
	Methanol	4800	60	5700	26	7820	32
	Pyridine	5000	340	5800	50	7600	47
Vanadyl bis-trifluoroacetylacetonate	Chloroform	4250	60	6250	30	7300	36
	Methanol	4300	70	6100	24	7550	40
	Pyridine	4550	100	5850	32	7400	39
Vanadyl bis-hexafluoroacetylacetonate	Chloroform	4850	112	6150	28	7350	29
	Methanol	4825	120	6000	21	7200	29
	Pyridine	4800	70	6200	47	7300	47
Vanadyl bis-salicylaldehyde-ethylenediiminate	Chloroform	4700	10	6000	24	2100	10
	Methanol	4600	40	5700	58	7600	75
	Pyridine	4800	50	5950	140	7600	50
$Vanadyl^{+2}$ solvate	Water	2800	240	6300	6	7675	15
	Pyridine	(3525)	300	5900	34	7750	52
$Vanadium^{+4}$ salicylaldehyde-ethylenediimine diacetate	Acetic anhydride	One band only at 4700 A, ϵ = 61					

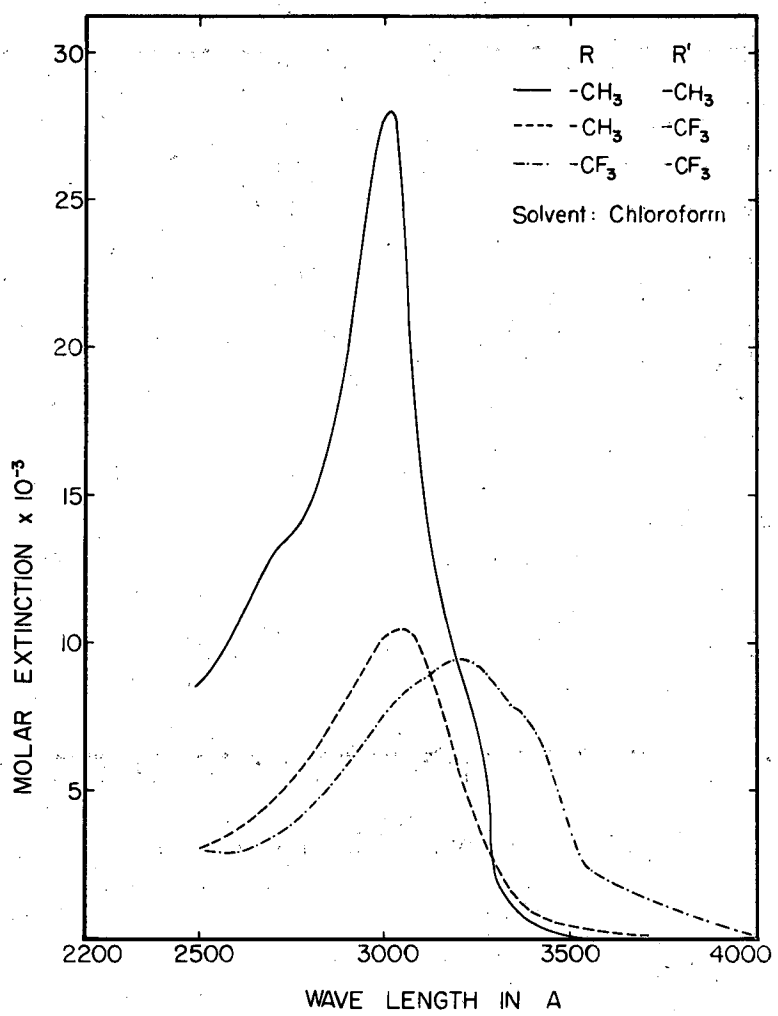

Fig. 12. Effect of fluorine substitution on the ultraviolet spectrum of vanadyl bisacetylacetonates.

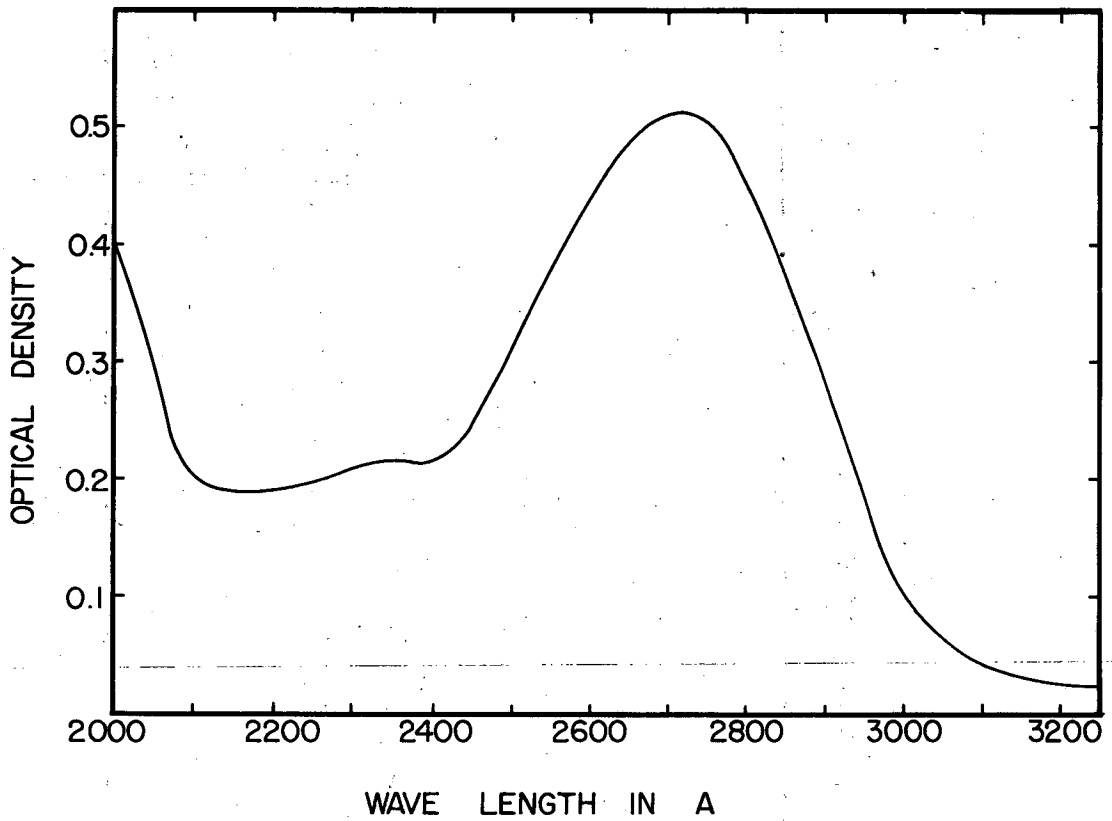

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Fig. 13. Ultraviolet spectrum of lithium acetylacetonate.

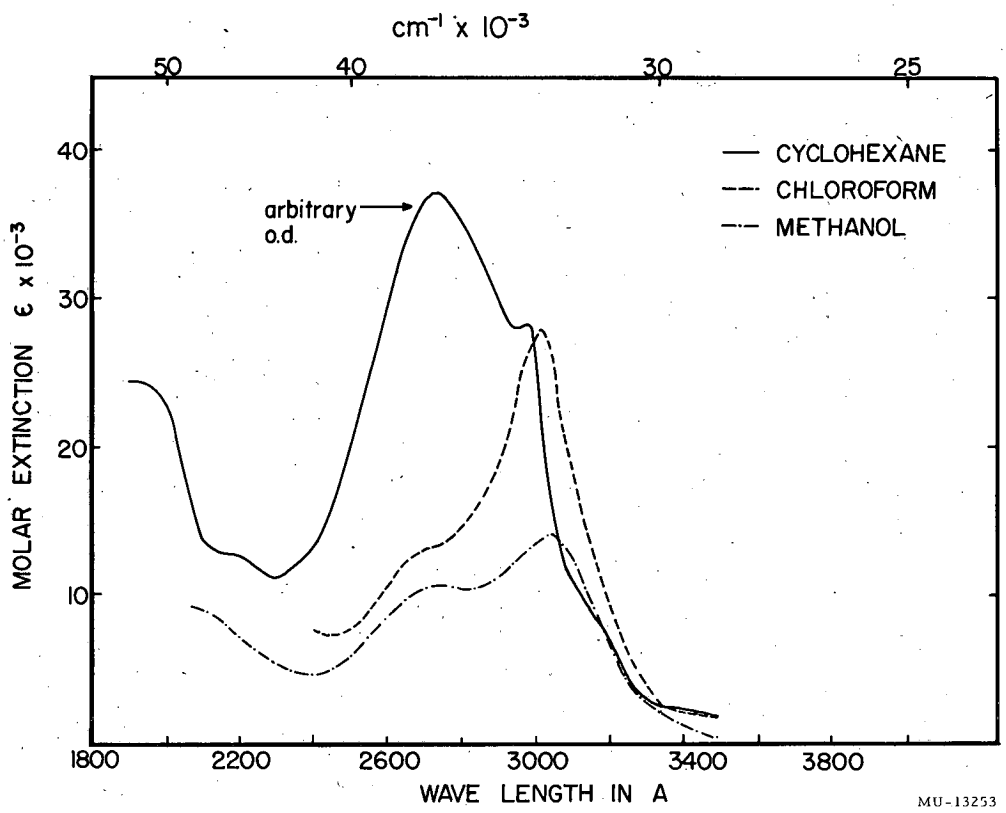

Fig. 14. Effect of solvent on the ultraviolet spectrum of vanadyl bisacetylacetonate.

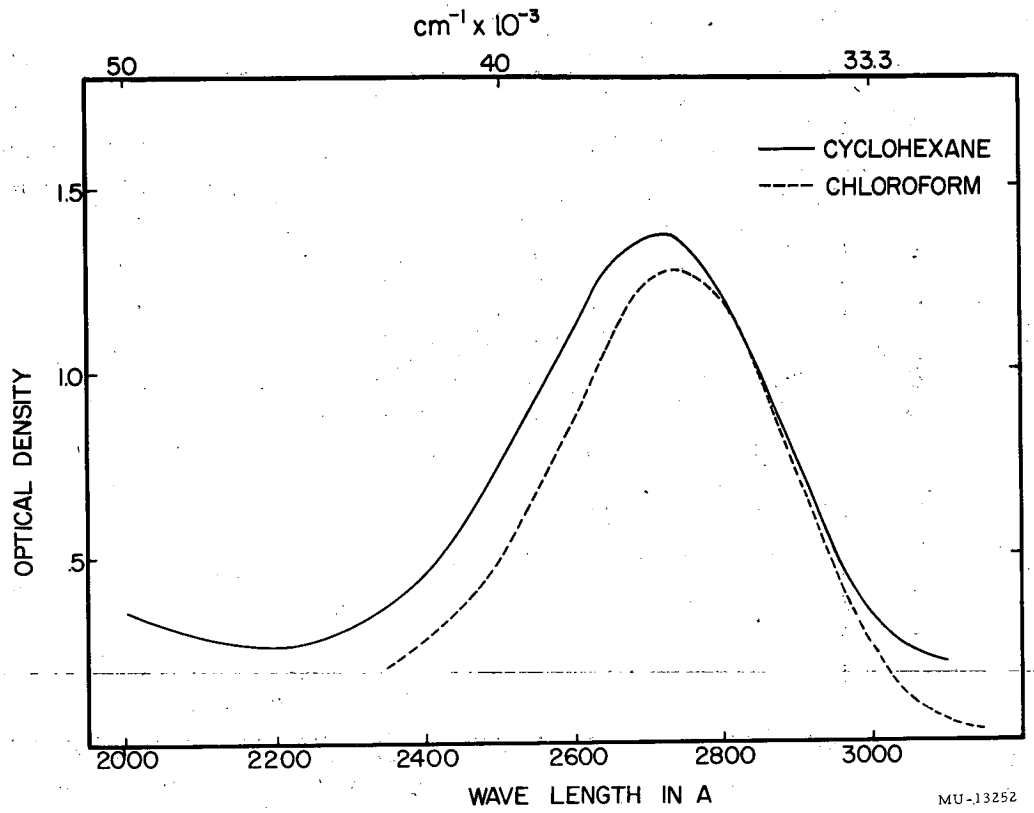

Fig. 15. Ultraviolet spectra of acetylacetone.

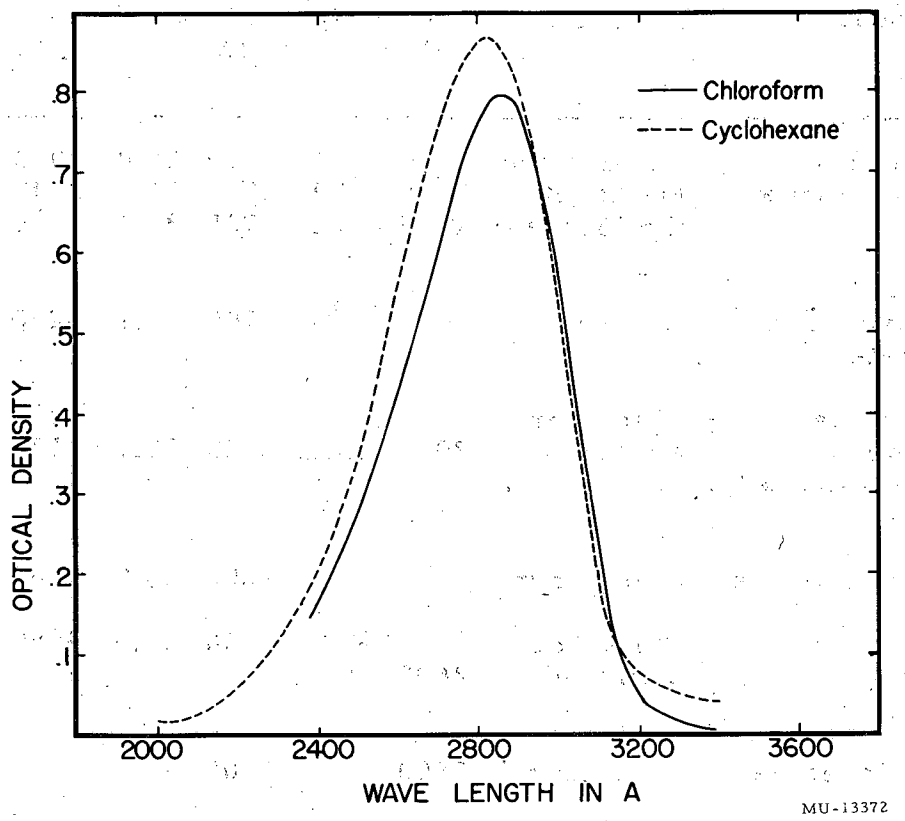

Fig. 16. Ultraviolet spectra of trifluoroacetylacetone.

Table VII

Ultraviolet absorptions of vanadyl chelates

Compound	Solvent	λ (A)	ε x10^{-3}	λ (A)	ε x10^{-3}	λ (A)	ε x10^{-3}	λ (A)	ε x10^{-3}
Vanadyl bis-acetylacetonate	Chloroform			2720	15.0	3010	28.0	~3350	--
	Methanol	2060	13.1	2740	15.3	3040	10.4		
	Cyclohexane	1975	~28.0	2725	37.1	2975	28.0	3150	9.8
Vanadyl bis-trifluoroacetyl-acetonate	Chloroform			3100	8.2	3200	9.4	3350	8.4
Vanadyl bis-hexafluoro-acetylacetonate	Chloroform					3060	10.5		
	Methanol	2025	15.15	3050	13.7	3125	12.9	(3250)[a]	(4.5)
Vanadyl bis-benzoylacetonate	Chloroform			2600	30.0	3200	47.0	3300	52.0
Vanadyl bis-dibenzoyl-methanate	Chloroform			3500	38.0	3650	28.0		
	Methanol	2600	20			3550	37.0		
Benzoylacetone	Chloroform	2500	--	3100	---				
Dibenzoylmethane	Chloroform	2500	--	3000	---	3450	---	3700	--

[a] ( ) represents shoulder

Copper Spectra

In order that there might be some confidence in the theoretical interpretation of the spectra of VO^{++} chelates that are complicated by the presence of the fifth oxygen, it seemed desirable that there be a re-investigation of the assignment of copper chelate spectra as made by Belford[15] and Balhausen.[33] In the course of checking the copper spectra, it was found advisable to get some additional information on several more copper chelates. Figure 17 shows the visible absorption spectra of copper acetate in various solvents. The striking feature of this spectrum is the presence of the weak absorption in the near uv. This corresponds quite well to a near-uv transition in the copper bisacetylacetonate. There is one intense uv absorption in the copper acetate, as shown in Fig. 18. The position of this band corresponds quite closely to that of one of the uv absorptions in copper bisacetylacetonate. The powder spectrum of copper acetate was also obtained and is essentially the same as that in dioxane. To determine whether or not this uv absorption was characteristic of the acetate anion, the spectrum of potassium acetate (Fig. 18) was obtained with dioxane as solvent. No uv absorption was detected up to wave lengths of less than 2000 A.

Figure 19 shows the ultraviolet absorption spectrum of copper bisacetylacetonate in various solvents. It can be seen that there is at least one absorption that is not present in either the free ligand or the vanadyl bisacetylacetonate. This corresponds in shape and position to that of the lone uv band in copper bisacetate.

The polarized spectra of a single crystal of copper bisacetate monohydrate have been obtained.[34] They show that the band at 3700 A is z polarized, while the two bands in the visible are x, y polarized. Because of the similarity of the spectra of the acetate to the acetylacetonate, it might be expected that the polarization of the absorptions would also be the same. Table VIII gives the visible and ultraviolet absorptions for several copper chelates.

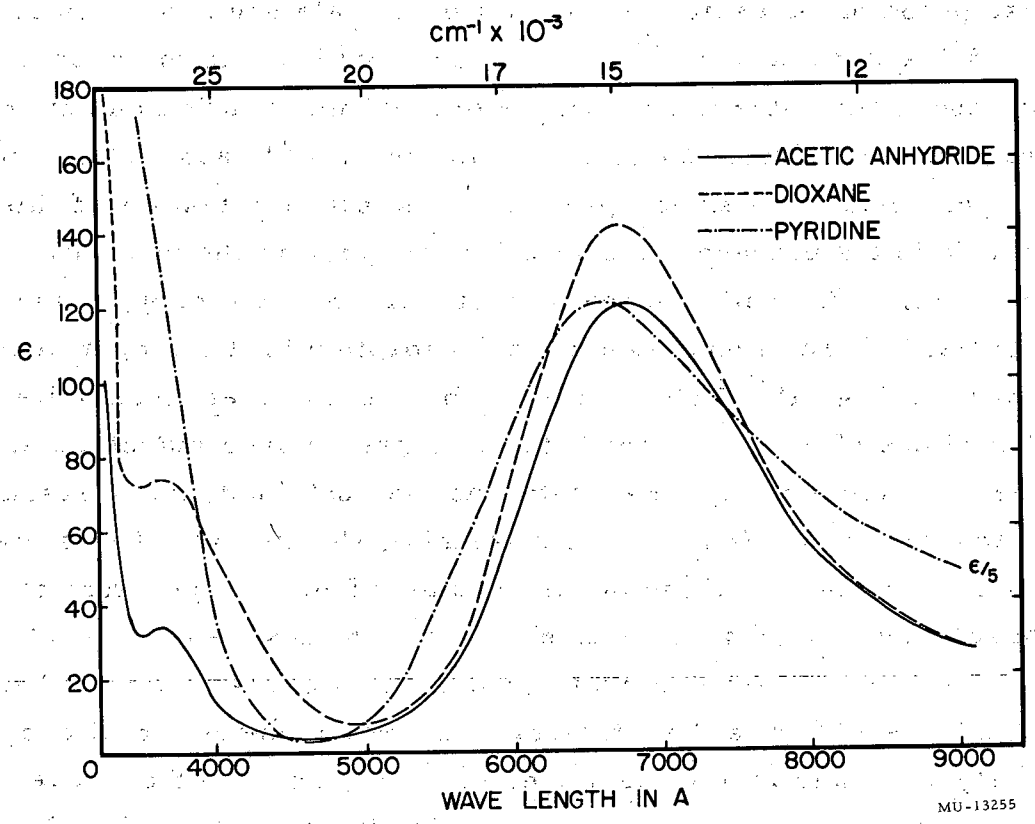

Fig. 17. Effect of solvent on spectrum of copper bisacetate monohydrate.

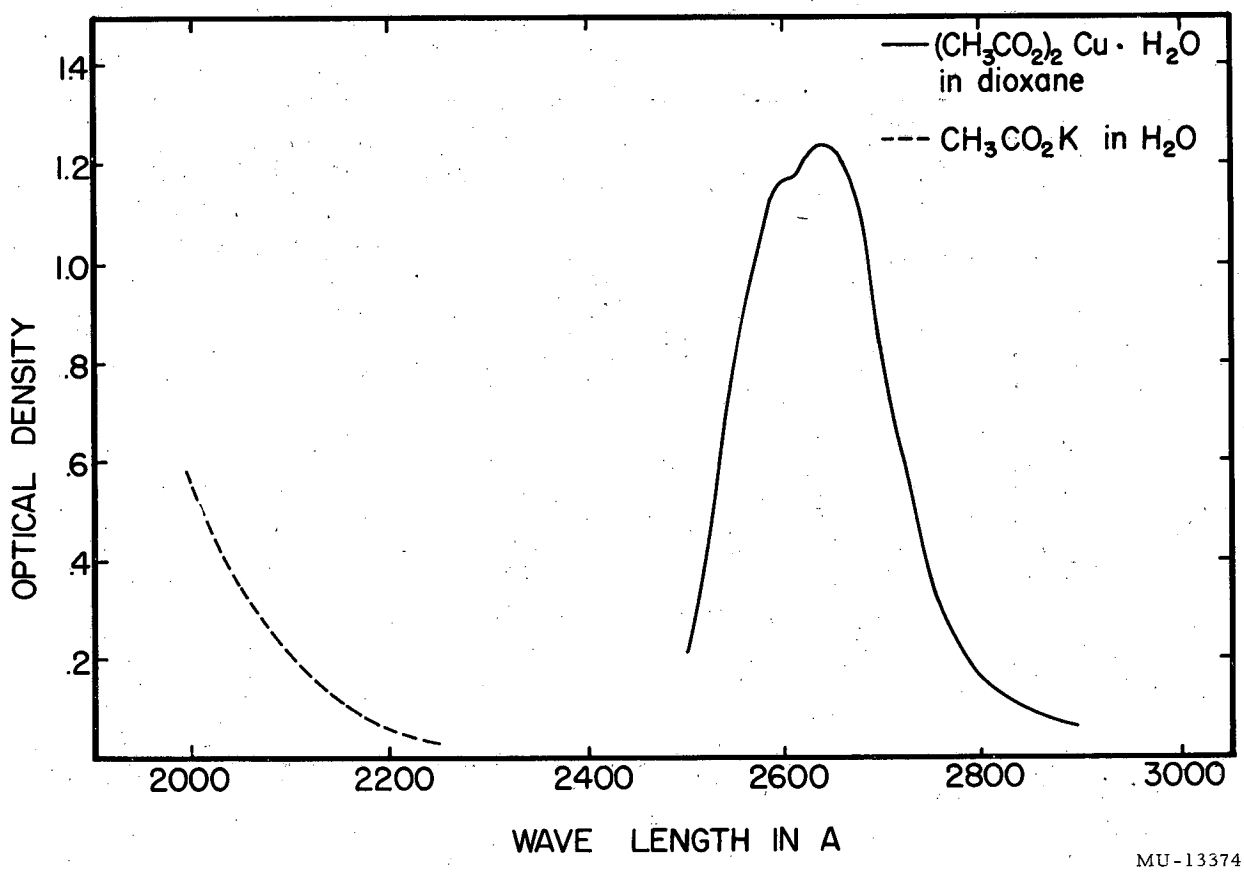

Fig. 18. Ultraviolet spectra of copper bisacetate monohydrate and potassium acetate.

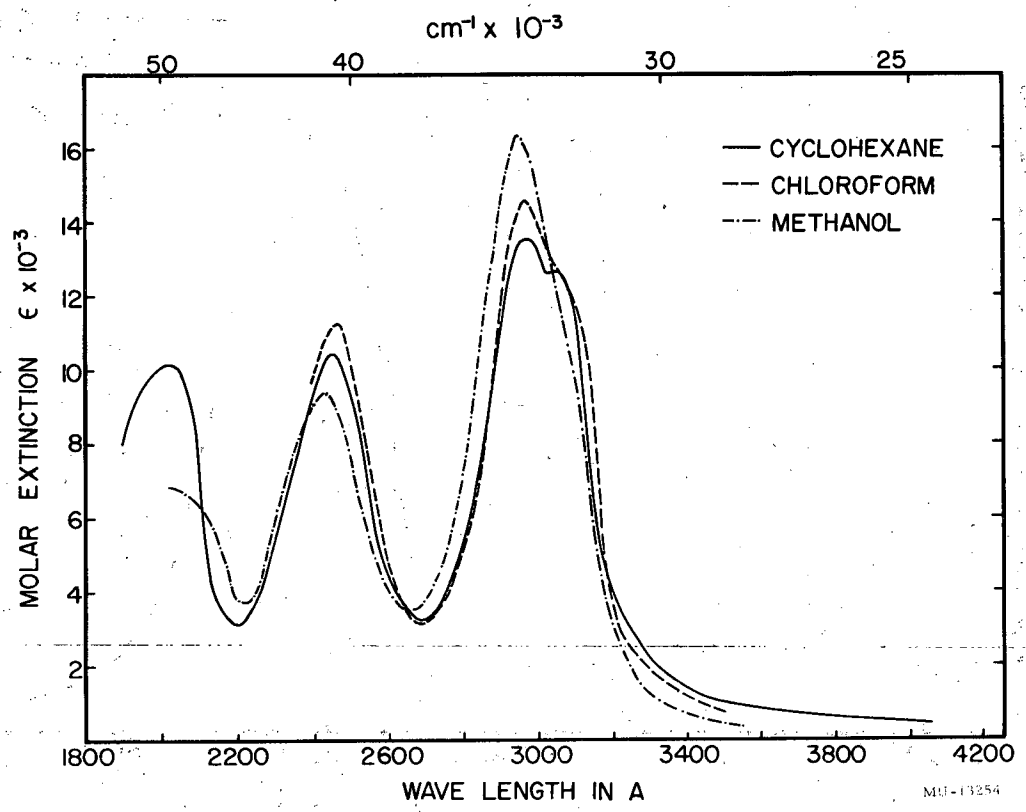

Fig. 19. Effect of solvent on ultraviolet spectrum of copper bisacetylacetonate.

Table VIII

Ultraviolet and visible absorptions of copper chelates

Compound	Solvent	λ (A)	ε x10^{-3}	λ (A)	ε x10^{-3}	λ (A)	ε x10^{-3}	λ (A)	ε x10^{-3}	λ (A)	Σ	λ (A)	Σ	λ (A)	Σ
Copper bis-acetylacetonate	Chloroform			2460	11.3	2970	14.5	(3050)[a]	(12.5)	3750	~200	5510	29.0	6500	33.0
	Methanol	(2050)	>20	2475		2945		(3050)		3850		6350		~6800	
	Pyridine					2990	10.6	(3075)	(9.5)	3900	~110	6250	60.0		
	Cyclohexane	2015	~20	2450		2960		3040							
	Solid Powder							3750		4050		5550		6500	
Copper bis-benzoylacetonate	Chloroform											5600		6600	
Copper bis-dibenzoylmethanate	Chloroform											5300		6500	
Copper bis-acetylacetonethylenediiminate	Chloroform			2425	12.1	2760	11.0	3100	21.5	3700	400	5250	160	(6200)	(60.0)
Copper bis-acetate	Dioxane	(2610)	>20	2640						3700	75			6700	142.0
	Methanol			2450										7050	
	Acetic Anhydride			2825						3700				6750	122.0
	Pyridine										34			6550	60

[a] ( ) represents shoulder

Chromium Dibenzene Spectra

Of all the metal-organic compounds investigated in this paper, these have chemical properties that are the most unlike the uncomplexed materials. They may, therefore, be expected to be quite "covalent." That is, the properties such as spectra, solubility, etc. should be quite distinctive from all other compounds. The chromium dibenzene used in obtaining the spectra was resublimed in vacuo and dissolved in cyclohexane that had been saturated with dry nitrogen. Figure 20 shows the uv spectra of chromium dibenzene and chromium dibenzene cation. The major difference between the two spectra is the disappearance of one of the lower-energy uz bands. Figure 21 gives the visible spectrum of the chromium dibenzene molecule. There is only one weak absorption in the visible region. This is a shoulder and may be either a spin-forbidden or symmetry-forbidden transition. Figure 22 shows the near-infrared absorption in chromium dibenzene cation.

The ultraviolet spectra of some substituted chromium dibenzene cations are compared in Fig. 23. There is little or no effect on the positions of the low-lying uv absorptions. The major effect is to decrease the resolution of these uv bands. Because the change in these molecules is the addition of a phenyl group, and benzene has an absorption at approximately 2500 A, the increase in absorption in this area is thought to be due to this benzene absorption.

Infrared Spectra

Apparatus and Materials

All the infrared spectra were obtained with a Baird infrared spectrometer. The solution spectra were measured in a NaCl cell with a light path of approximately 0.1 mm. The concentrations were between 0.1 and 1 molar. The solid spectra were obtained by use of KBr discs. In all cases except for the vanadyl bishexafluoroacetylacetonate it was possible to obtain the spectra by grinding KBr and the samples together into a fine powder and pressing together at approximately 14,000 psi.

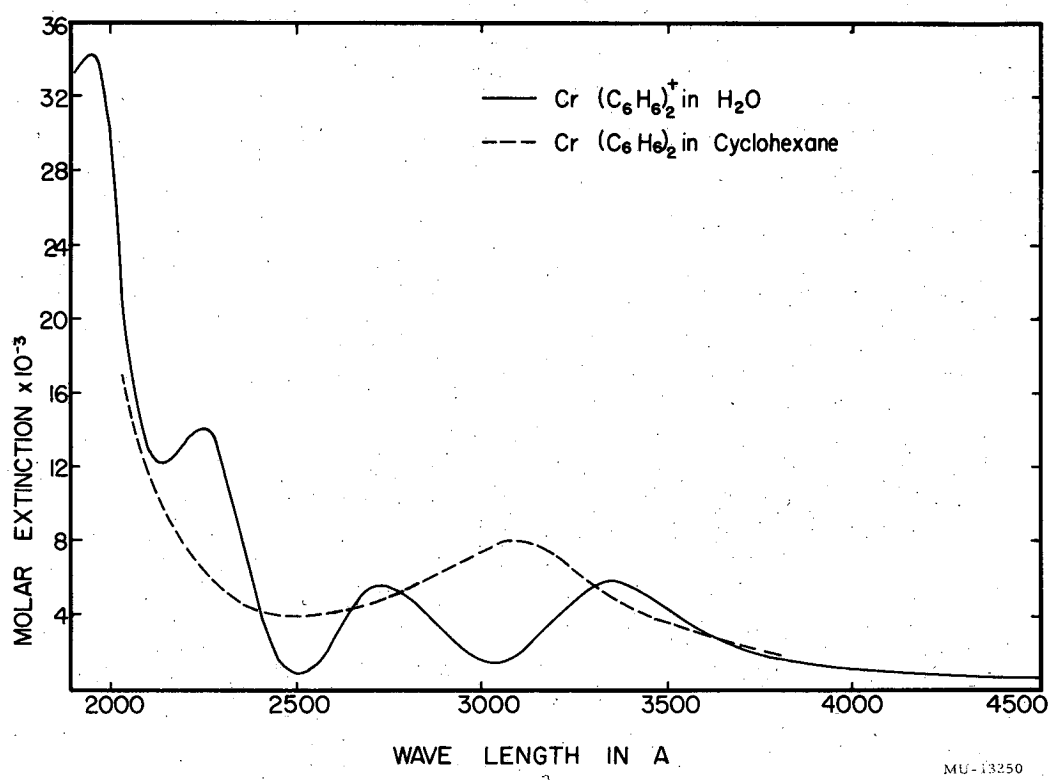

Fig. 20. Ultraviolet spectrum of chromium dibenzene and chromium dibenzene cation.

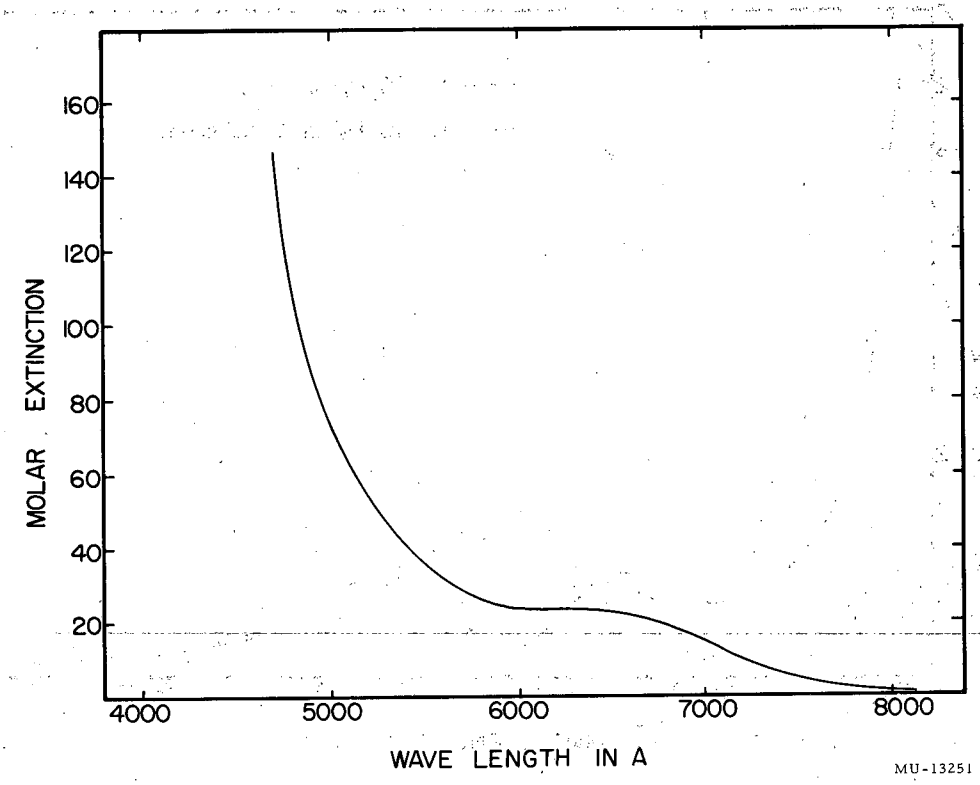

Fig. 21. Visible spectrum of chromium dibenzene.

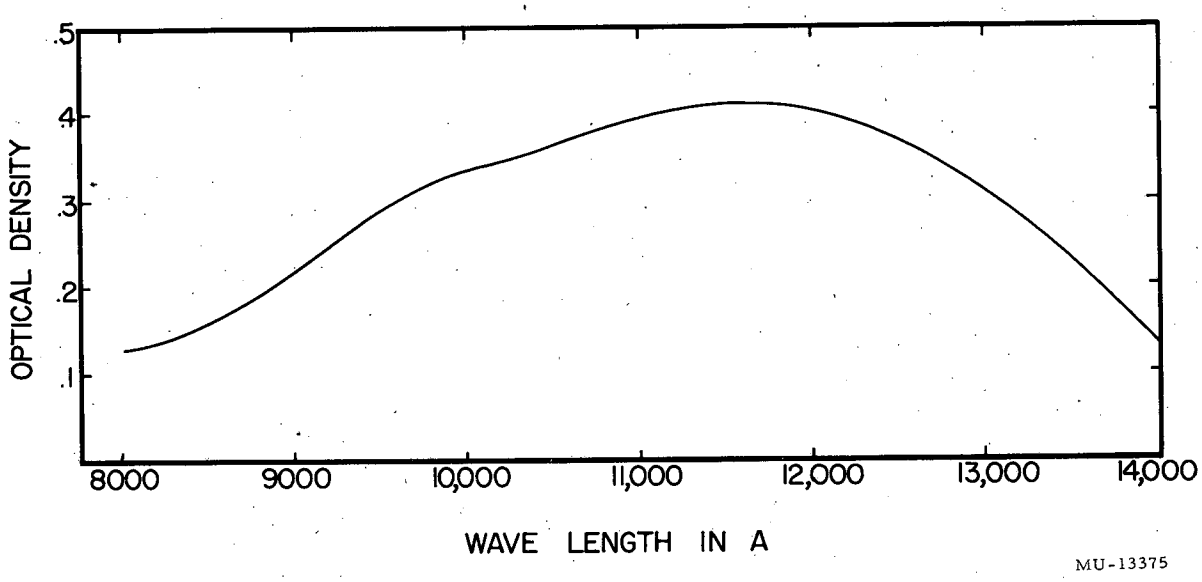

Fig. 22. Near-infrared spectrum of chromium dibenzene cation.

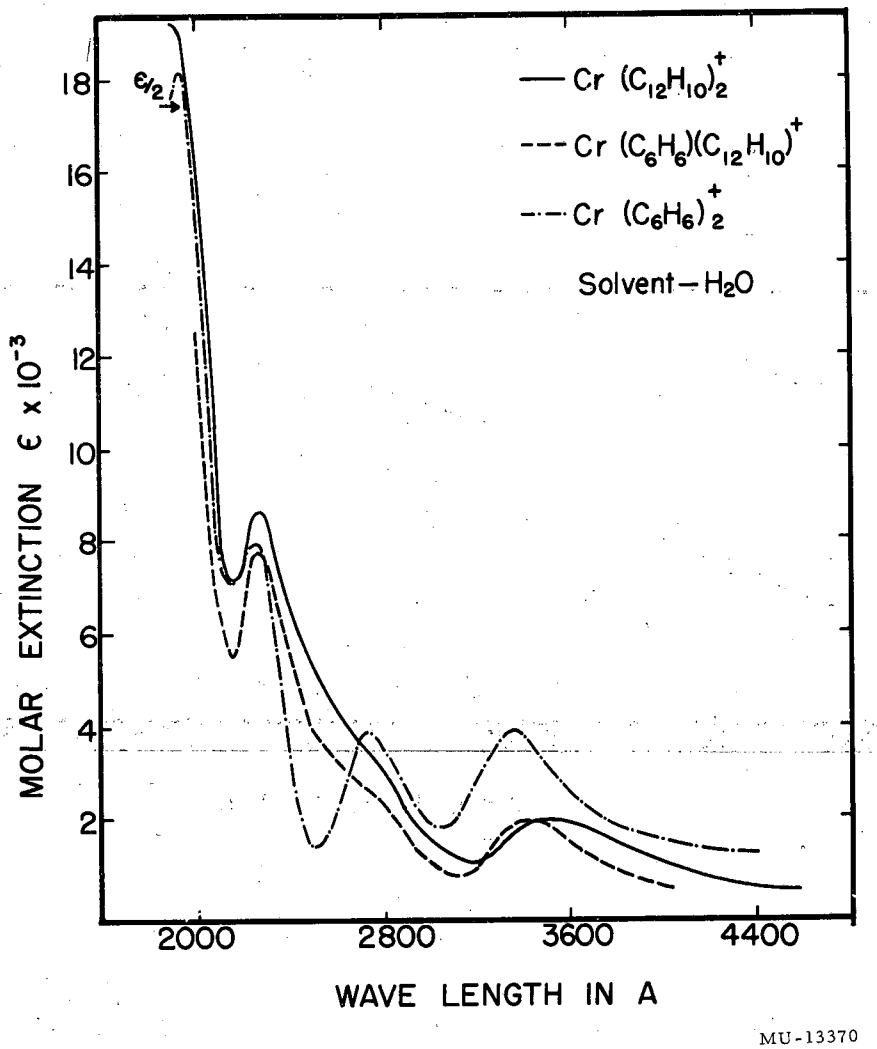

Fig. 23. Ultraviolet spectra of substituted chromium dibenzene cations.

When this procedure was applied to the hexofluoro chelate a cloudy brown disc always resulted. Apparently there was a reaction between the vanadyl chelate and the KBr. Solvents other than chloroform, such as CS_2, were tried in order to study the C-H and O-H stretching area. However, the solubility of the chelates in solvents was not sufficient to yield an infrared spectrum.

In Table IX the principal infrared absorptions are summarized. The absorption frequencies are estimated to be accurate to approximately 20 cm^{-1}. The general areas for a given type of absorption are tentatively identified in the left-hand column. The relative intensities of the absorptions are indicated by s (strong), m (medium), and w (weak). A frequency with brackets around it indicates a shoulder or unresolved lines.

Discussion

As pointed out earlier by Lecompte, the area of approximately 700 cm^{-1} and lower has a varying number of absorption bands for various acetylacetone chelates.[35] In the vanadyl chelates there is also a new absorption in the area around 1000 cm^{-1}. This was identified as the V-O stretching mode. An identical conclusion was reached by Erdman for vanadyl porphyrin complexes.[36]

The other areas are harder to identify with much certainty. According to the discussion of β-diketones by Rasmussen, the effect of chelation of hydrogen by this type of compound is to produce a shift of the C=O stretching to lower frequencies.[37] It may be observed that the effect of Cu and V on the carbonyl frequencies is to shift them to even lower frequencies. This may represent conjugation over and above that corresponding to the structure

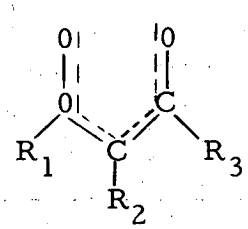

Table IX

Infrared absorption frequencies						
	Solvent[a]					
Region	1	1a	2	2a	3	3a
OH str.	3550		3360m		3400	
			3120w			
CH str.	2960m	3100m	2980m	3100	3150m	3100m
	2620w	2950w			(3080)m	
	2350w	2530w		2450	1980w	
		2340w	2350w		1940w	
		2180w			1910w	
		2000w				
C=O	1725		1775s		1820w	1605ms
and	(1708)m		1745s		1620vs	(1570)s
C=C str.		1580s	(1713)s		(1595)s	1545s
	1550s		1680m			1501ms
				1630s		
				1510s	(1510)m	1460m
CH_2 and	1448ms	1448ms	1475w	(1450)ms	(1480)m	1373s
CH_3 defm.	1425m		1455m		1440m	1320ms
C-C str.	1365s	1380s	1430	1369ms	1370m	(1305)m
	1295s	1375	1315vs	1325m		
	1252m	1233m	1350		(1310)m	
		1032s	1282		1285s	
			1230	1230ms	1205m	
{VO str}[b]		{1005}s	1200	1205s	1188m	1185m
			1160	1165s		1115m
		940s	1095	1145s	1105m	1074w
		801m	1030	1118m	(1088)m	1035m
		794m	990	1048w	(1070)m	{1001}s
	780m		900	1022w	1033ms	965m
		682m	822	930m	993ms	893w
		658w	730	870m	945m	853s
			700	795m	838m	809w
			665	759w	768s	780m
				738m	698s	(773)m
				ca.625m	(683)m	718ms
						(711)ms
						693 ms
						(686)ms
						<625 m

[a]Key: 1. acetylacetone; 1a. vanadyl bisacetylacetonate; 2. trifluoroacetylacetone; 2a. vanadyl bistrifluoroacetylacetonate; 3. benzoylacetone; 3a. vanadyl bisbenzoylacetonate.

[b]( ) denotes shoulder or unresolved bands.

[c] { }denotes V=0 stretch.

Table IX (cont.)

Infrared Absorption Frequencies*						
Region	4	4a	5	6	7	7a
OH	3400					
					3650m	3550s
CH str	3100m	3080m	3100m	3100m		(3220)s b
			2900m	3000m		
	1980w			2420m	1640m	1650m
	1920w					
	1830w		1670s			1970w
C=O	1780w	1610s	1660m	(1650)ms		
C=C	1630vs	(1601)s	1630s	1640s		
	1580vs	1540s	1610m	(1620)ms	1170s	1165s
	1508s		1595m		(1110)s	(1110)s
	(1490)s	1495s	1550ms	1550s	1010m	1028m
	1440m	1465m	1500m	(1540)ms		{1008} ms c
CH_2 and	1312s	1448m	1445m	1490ms		
CH_3 defm	(1293)s	1375s	1400w	1460s	672m	700 to 800m very broad
C-C str	1233m	1333s	1330w	1400ms	658m	
	1188m	1315m	1290s	1340m		
	1165mw	1230m	1230s	1310ms		
	1108mw	1185mw	1210s	1230s		
	1068m	1165w	1160s	1210s		
{VO st}	1028m	1134w	1135w	1155m		
	1005m	1078m		1135m		
	928w	1030m		990 m		
	850w	(1005)s		925m		
	(843)w	{1000} s	{998} m	908m		
	813w	983m	908m	793s		
	788m	(946)m	887s	663s		
	758s	842w				
	704m	817m				
	658s	792m				
		766s				
		723s				
		(693)s				
		686s				
		667m				
		648m				

*Key: 4. dibenzoylmethane; 4a. vanadyl bisdibenzoylmethanate; 5. vanadyl bissalicylaldehyde; 6. vanadyl bissalicylaldehydeethlenediiminate; 7. calcium sulfate; 7a. vanadyl sufate; denotes V=O stretch;

( ) denotes shoulder or unresolved bands.

According to Bellamy, there is little effect on the C-O frequency in a compound of the type C-O-R as the weight of the attached R group is increased, so long as there is no possibility for π bonding by the R groups (about $\lesssim$ 100 cm^{-1}).[38] The shifts in these cases are in the opposite direction, even, from those observed for the metal chelates (if R = H, 1050 cm^{-1}; if R = CH_2, 1060 cm^{-1}).

In trying to identify the absorptions in the area from 600 to 700 cm^{-1} it seemed advantageous to find if any simple complexes of copper or vanadium had been well characterized. The Reman spectrum of $CuCl_2 \cdot 2H_2O$ was reported by Mathieu.[39] The infrared spectrum of this compound has been discussed by Rundle.[40] The authors seem to be in agreement that the absorptions around 400 cm^{-1} are due to Cu-O stretching. If the Cu-O bonds are much stronger in the acetylacetonate chelates, which seems entirely plausible, then the "new" bands in the area of 600 cm^{-1} may be due to the metal-oxygen stretching modes. They also may be combination bands. A definite assignment cannot be made at this time. It does seem however that a study of this area as well as of lower-energy infrared absorptions might help clarify ideas on the bonding in transition metal chelates.

Electron Spin Resonance Spectra

Introduction

One of the newest techniques in electronic spectroscopy is electron spin resonance. There have been several excellent review articles on this subject.[41,42,43] The spectra that are observed are due to transitions between the Zeeman levels of an odd electron in a magnetic field. Because the energy separations of these spin levels is only about 0.3 cm^{-1}, many experimental difficulties are encountered. First, the levels at room temperature are almost equally populated. This means that there are few electrons that can be excited from the ground state to upper states. Secondly, the energies involved lie in the microwave region of the spectrum, which is the main reason that these techniques were developed only recently. One further difficulty, due to the small

differences in energy of the electronic states, is the problem of saturation, that is, equal population of the states involved. If too much radiation is applied to the system per unit time, equal population of the levels results, and no further absorption occurs.

As in all spectra, there are three characteristics of the absorption that are of interest--the width, intensity, and shape. These factors are quite well discussed in the recent book by Ingram.[44] With these limitations, the ultimate sensitivity of this type of absorption spectra is the detection of approximately 10^9 free radicals. The instrument used detects an estimated 10^{12} free radicals with signal-to-noise ratio of 10 to 1.

The orbital state of the electron remains essentially unchanged when absorptions in this region of the spectrum occur, and direct information about this orbital may be obtained from electron spin resonance. Because we know the excited electronic states from the visible and ultraviolet spectrum, and the ground state from the electron spin resonance spectrum, the theoretical explanations for these states may be developed and checked as to the accuracy of their description of the molecule in question.

Apparatus and Techniques

The spectra were obtained by use of a differentiating transmission-cavity spectrometer operating at a frequency of 9.3 kMc/sec. This instrument was built by Dr. Power B. Sogo of the Bio-Organic Chemistry group. A block diagram of the apparatus is shown in Fig. 24. The sample is placed in the center of the resonant cavity, which is in a magnetic field, the strength of which is continuously varied by a variac driven by a synchronous clock motor. The klystron is the source of the microwave radiation. The frequency of the klystron is "locked into" the resonant frequency of the davity to provide stability for the radiation source. On passing through the cavity, the radiation is detected by means of a bolometer suitably placed in the wave guide. This radiation gives an average dc current from the bolometer, which is balanced out by means of a Wheatstone-bridge arrangement. Mounted on the magnet

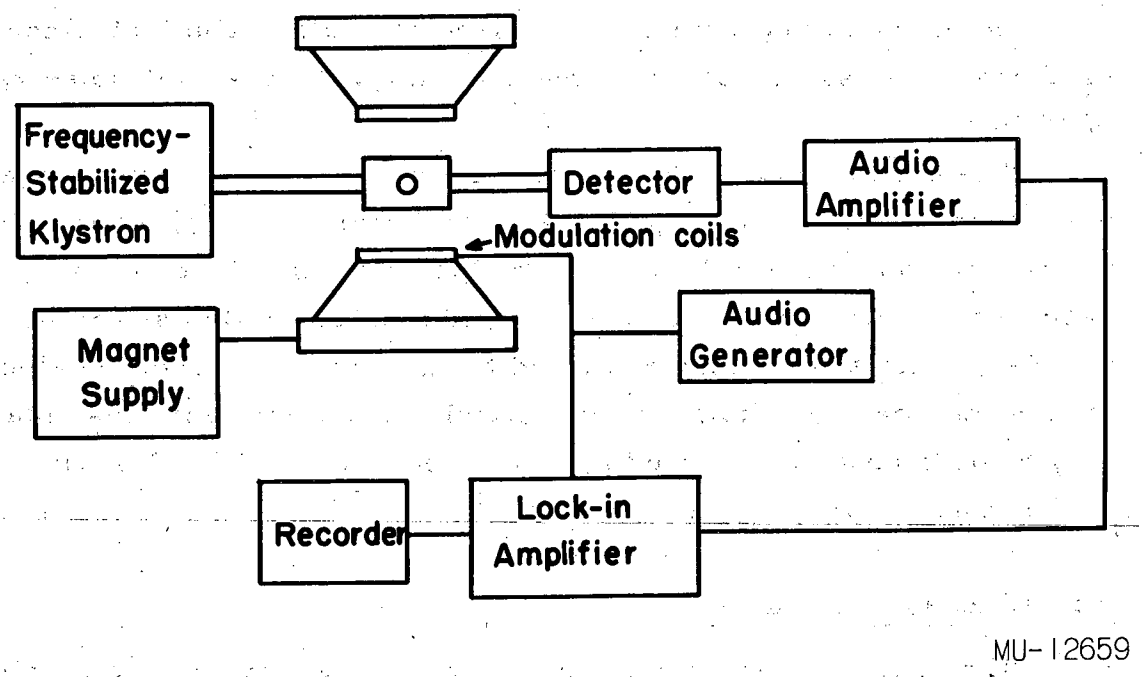

Fig. 24. Block diagram of electron spin resonance spectrometer.

are modulating coils that sweep a short range of magnetic field at a frequency of between 100 and 250 cycles per second. The modulating magnetic field is constantly sweeping at a given frequency, and the magnitude of magnetic field swept is controlled by the amplitude of the modulating signal. When there is a change in absorption by the sample, an alternating signal of the same frequency as the modulating field is detected by the bolometer, and amplified by means of an audio amplifier. The output of this amplifier is then put into a lock-in amplifier, and only signals of the same frequency as the modulation are detected at this stage. The dc output from this stage is then put into a recorder. The dc signal recorded is the derivative of the absorption curve. All spectra in this paper are reported in the form of the derivative. The relation of signal to field for resonance absorption detection is shown in Fig. 25.

With the aid of a microscope, a single crystal of vanadyl bisacetylacetonate was attached to the flattened end of a glass rod by means of paper cement. The rod was attached to a pointer, and a crystal face was aligned with the pointer. The angle between this pointer and the magnetic field was measured by means of a calibrated dial. In all cases for which g values are reported, a small particle of 1, 1-diphenyl-2 picrylhydrazyl was attached to the sample tube and was in or near the center of the cavity during the measurement. The electron spin resonance spectra of solutions were obtained by placing approximately 0.1 ml of the solution in a sealed capillary tube, and placing this tube inside the cavity.

In order to be certain that the measured line widths, g values, and other properties of the spectra were due to inherent properties of the sample, and not instrumental artifacts, the instrumental variables were changed over wide ranges.

Vanadyl Complexes

A spectrum typical of all chelates with formulas corresponding the VO^{++} unit and four other donor atoms is shown in Fig. 26. This is the spectrum of vanadyl bisacetylacetonate. There are eight resolved lines of varying width (maximum to minimum approximate measure of the width).

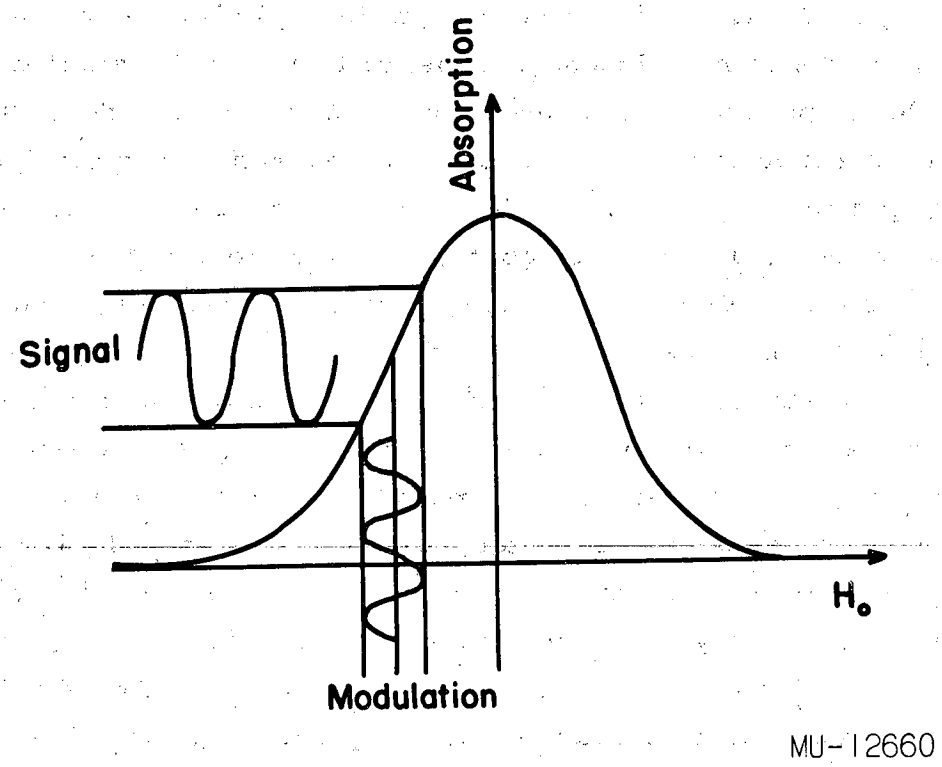

Fig. 25. Relation of signal to field for resonance-absorption detection.

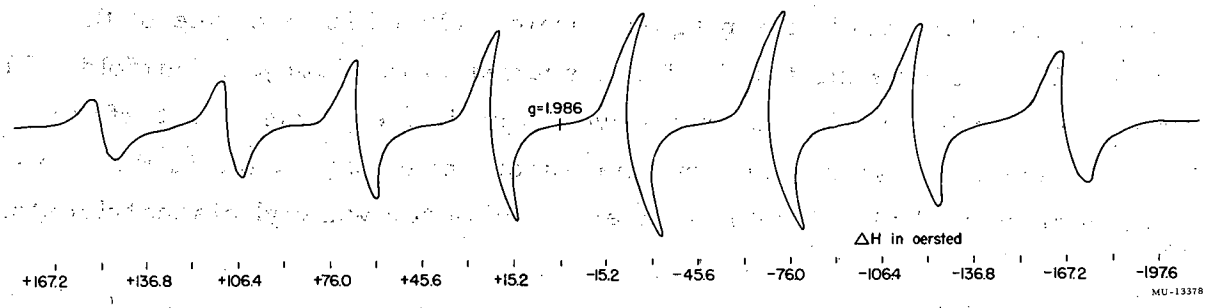

Fig. 26. Electron spin resonance spectrum of vanadyl bisacetylacetonate.

The naturally occuring isotope of vanadium (approximately 100%) is V^{51}. This isotope has a nuclear spin (I) of 7/2. It would be expected to give a hyperfine structure of eight lines (2I+1). It was therefore concluded that this is the cause of the eight lines in the spectra. Figure 27 is the spectrum of a solution of vanadyl sulfate in water. It may be seen that the spectra are essentially identical. Figure 28 shows the spectrum of VCl_4. It may be seen that this spectrum is quite different from the other spectra.

The single-crystal spectra of vanadyl bisacetylacetonate were obtained for several orientations of the crystal with respect to the magnetic field. Figure 29 shows a plot of the square of the measured g value as a function of the angle the magnetic field makes with one face of the crystal. The reasons for the large scatter in the data are fourfold. The lines are quite broad, the crystal was small, there was an interfering resonance in the glass, and the measurement of the magnetic field was not too accurate. Table X summarizes the data for vanadyl bisacetylacetonate.

Copper Complexes

The spectra of copper complexes characteristically have four broad lines in solution. There are two copper isotopes with spins of 3/2, which partially accounts for the poor resolution. Figure 30 shows a typical complex of copper (the acetylacetonate) with oxygens as ligands. Figure 31 shows the analogous acetylacetoneethylenediimine complex of copper. It may be seen that in this case the spectrum is more complex. The narrowest line is seen to be split into at least five components. The next line is also split, but because these lines are broader, the resolution is not so good. Line broadening is the only observable effect on the last two lines. Figure 32 shows another copper nitrogen complex (copper bisglycinate). The copper tetraammonia complex also shows no nitrogen hyperfine splitting.[41] This spectrum can be seen to exhibit no resolvable structure other than that from the magnetic copper nuclei.

The g values for copper bisacetylacetonate are $g_{\parallel} = 2.2661$, and $g_{\perp} = 2.0538$.[45] These values are to be compared with those of copper

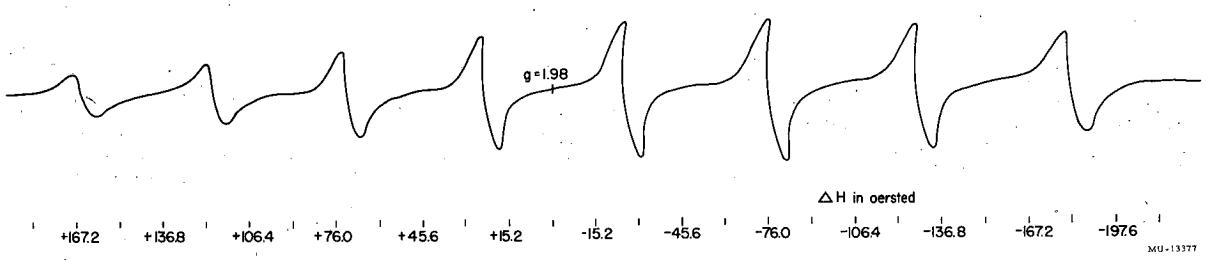

Fig. 27. Electron spin resonance of an aqueous solution of vanadyl sulfate.

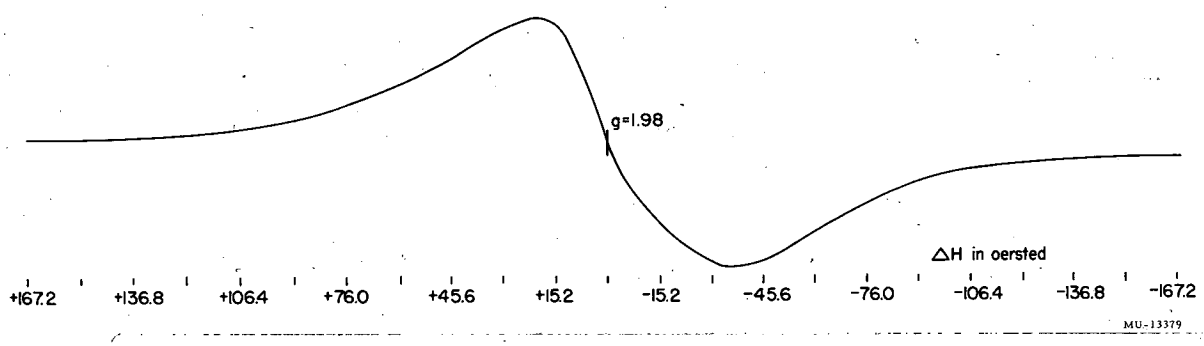

Fig. 28. Electron spin resonance spectrum of VCl_4.

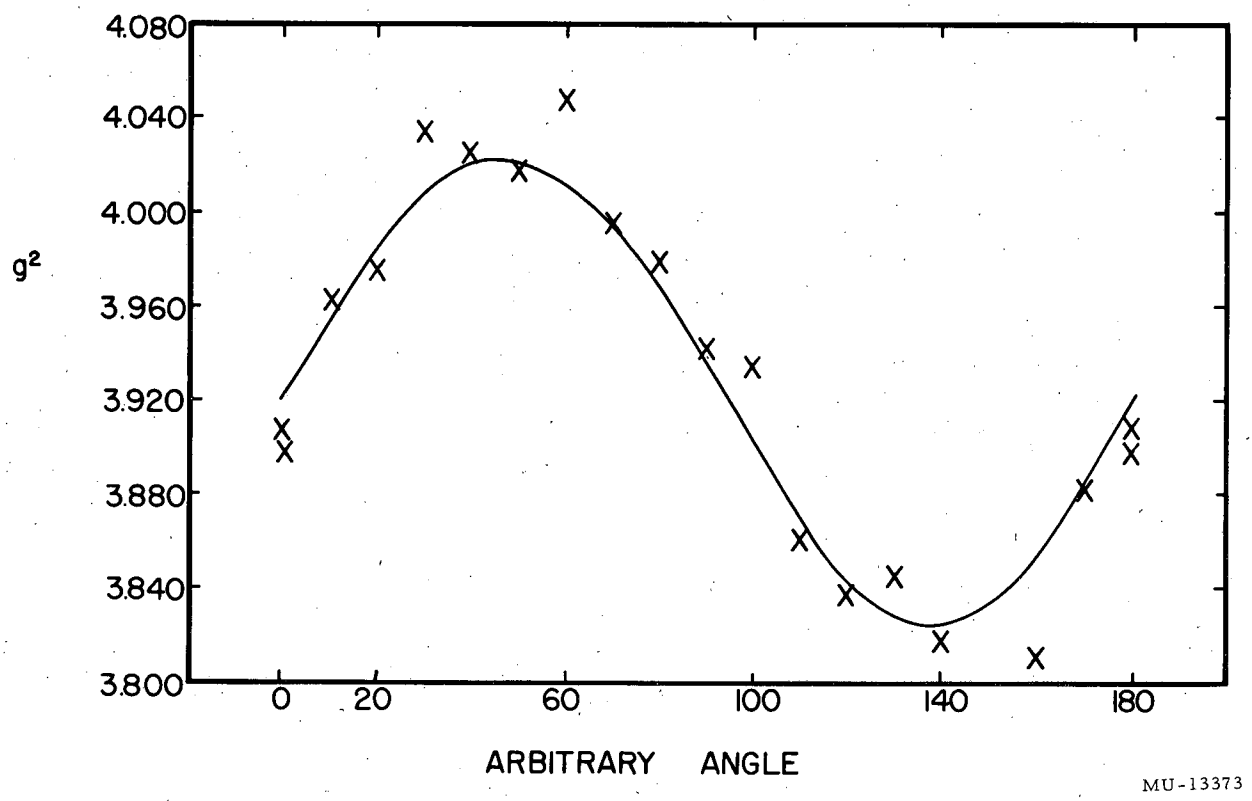

Fig. 29. Angular dependence of g^2.

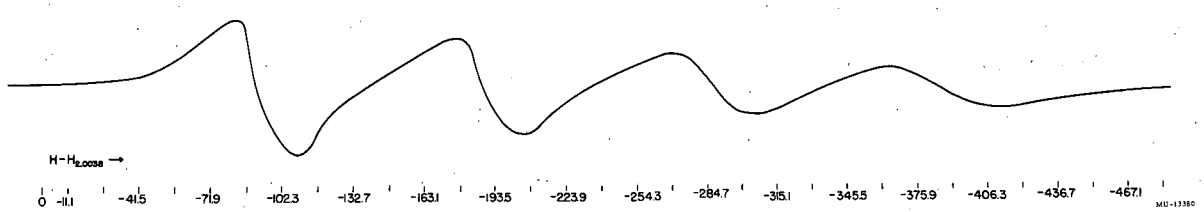

Fig. 30. Electron spin resonance spectrum of copper bisacetylacetonate in chloroform.

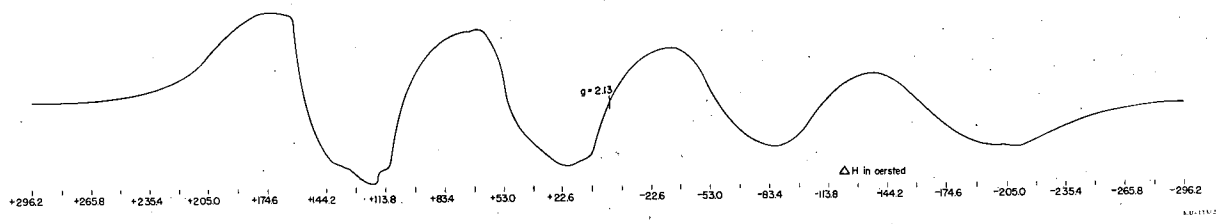

Fig. 31. Electron spin resonance spectrum of copper bisacetylacetoneethylenediimine complex, in carbon tetrachloride.

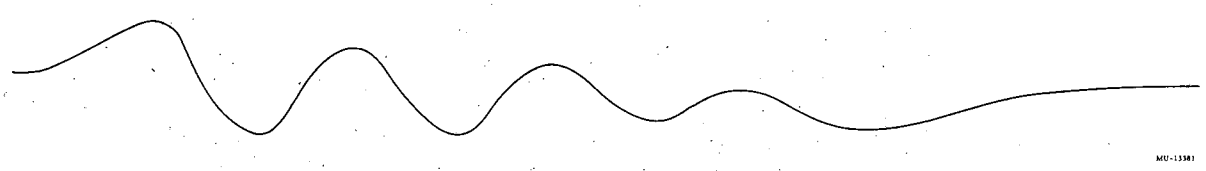

Fig. 32. Electron spin resonance spectrum of copper bisglycinate in water.

Table X

Observed and calculated g values for vanadyl bisacetylacetonate

	g average	g	g	Estimated error
Solution	1.9859	------	(1.9772)	±0.0005
Single crystal	1.990	2.02	1.950	±0.03
Theoretical	1.9845	2.0023	1.9756	------

bisacetate monohydrate, which are $g_{\parallel} = 2.34$, and $g_{\perp} = 2.05\text{-}0.09$.[46] These values are also consistent with the results from the visible spectra, which show that the electronic structure of the two compounds are quite similar.

Chromium Bisaromatic Complexes

The monopositively charged chromium dibenzenes are paramagnetic. It was therefore of interest to determine what the behavior of an odd electron would be in a complex that involves a transition metal and that is considered to be quite covalent. According to the previous theoretical treatment, the electron should be in a slightly bonding Δ-type molecular orbital. Figure 33 is the spectrum of $Cr(C_6H_6)_2^+$ in an aqueous solution. It consists of approximately eleven barely resolved lines with a spacing of about 3.5 gauss. The g value for the center of the pattern is 1.983 ± 0.001, as determined on the basis of g = 2.0038 for 1, 1-diphenyl-2-picrylhydrazyl. Further dilution together with degassing of the sample, failed to decrease the line width, while more concentrated solutions exhibited poorer resolution.

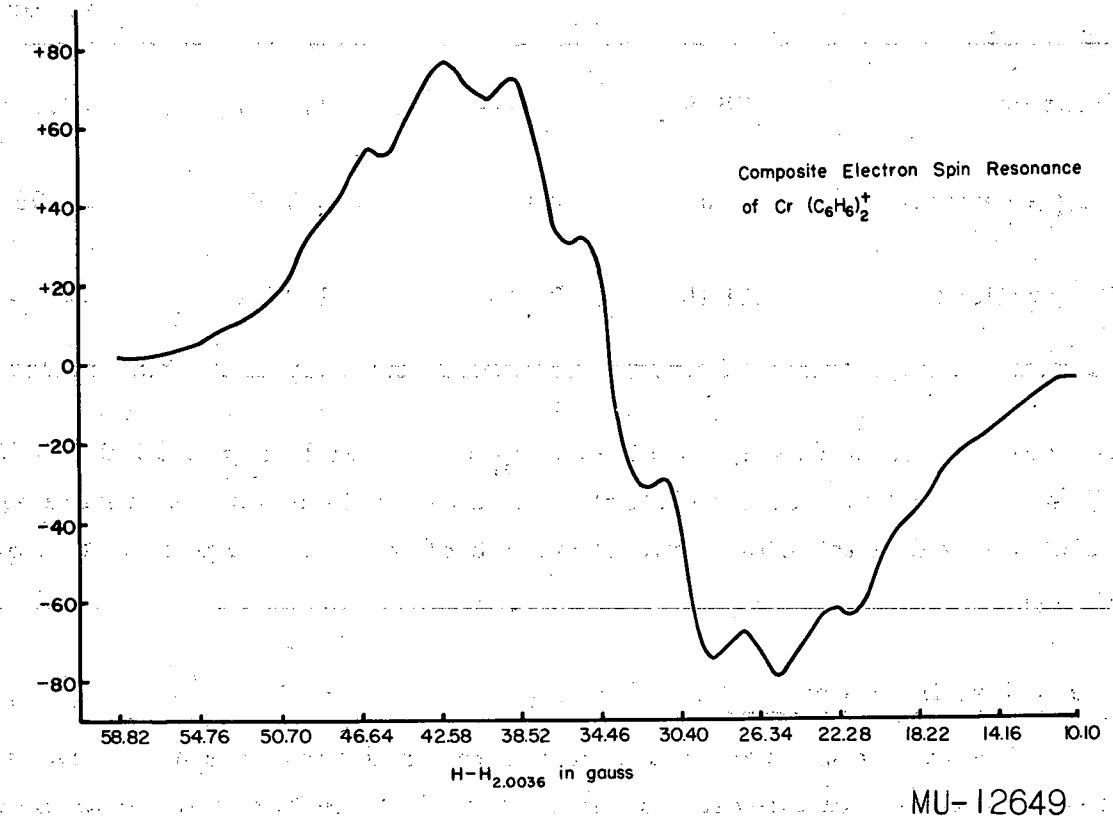

Fig. 33. Electron spin resonance spectrum of chromium dibenzene cation.

Figure 34 gives the resonance spectrum of chromium dideuterobenzene cation in an aqueous solution. The general characteristics are the same as those of the undeuterated complex. The main differences are: first, the resolution is slightly better in the deuterated complex; second, the total spread is less; and third, the relative heights of the unresolved components are different. The same spectrum resulted when the deuterated complex was dissolved in D_2O, and therefore one concludes that the deuterium present is not exchangeable.

Figures 35 and 36 give the spectra of chromium benzene diphenyl and chromium bisdiphenyl cations respectively. In these cases the spectra are much better resolved, and the individual hyperfine components may be readily observed. The chromium benzene diphenyl complex is the only one of the complexes observed to have a pattern characteristic for an even number of lines. In the attempt to resolve the theoretical number of lines (12) for the chromium benzene diphenyl cation, a number (12 or 14) of satellites of weaker intensity were found. The separations between these weaker lines are the same as the separations between the lines of the more intense spectrum. These lines cannot be a part of the intense spectrum because their position as calculated from the positions of the major components is not correct. As a matter of fact, the weaker lines may be seen to overlap the major lines somewhat (Fig. 37). The only other abundant magnetic isotope is Cr^{53} (9.5%), which has a nuclear spin of 3/2 and a small magnetic moment. This would give rise to four lines, with the same pattern for each of them as exhibited by the chromium isotopes with no nuclear spin. The intensity ratio of the center of the major pattern to the center of the minor pattern is 40 to 1. Because Cr^{53} is only 10% abundant, the intensity should be down by a factor of 9.5, and a spin of 3/2 giving rise to four lines would reduce the intensity by another factor of four, giving a ratio of 38 to 1. Accordingly, there should be similar satellites present in all the complexes. Figure 38 gives the spectrum of chromium dideuterobenzene. This spectrum was obtained at a faster field sweep in order to bring out these two satellites. The presence of the two satellites has been demonstrated in chromium bisdiphenyl also (Fig. 39). The other two lines from Cr^{53} are obscured by the major resonance.

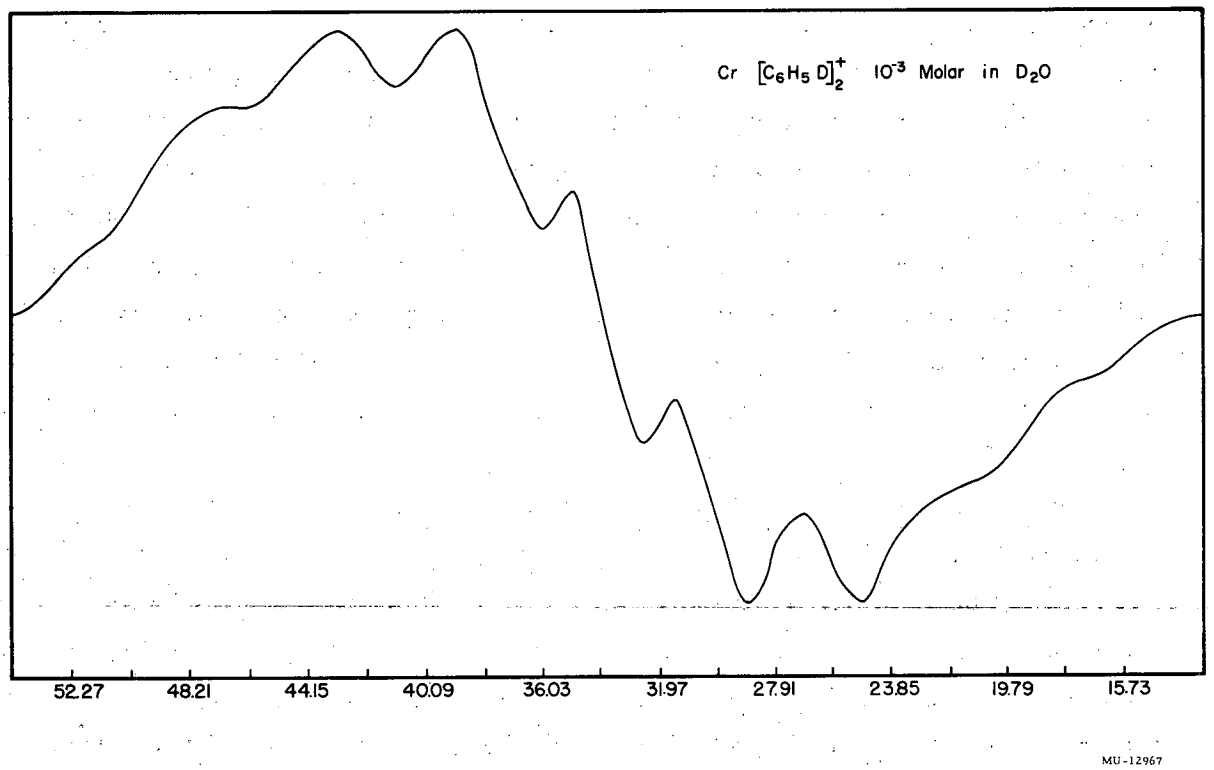

Fig. 34. Electron spin resonance spectrum of chromium dideuterobenzene cation.

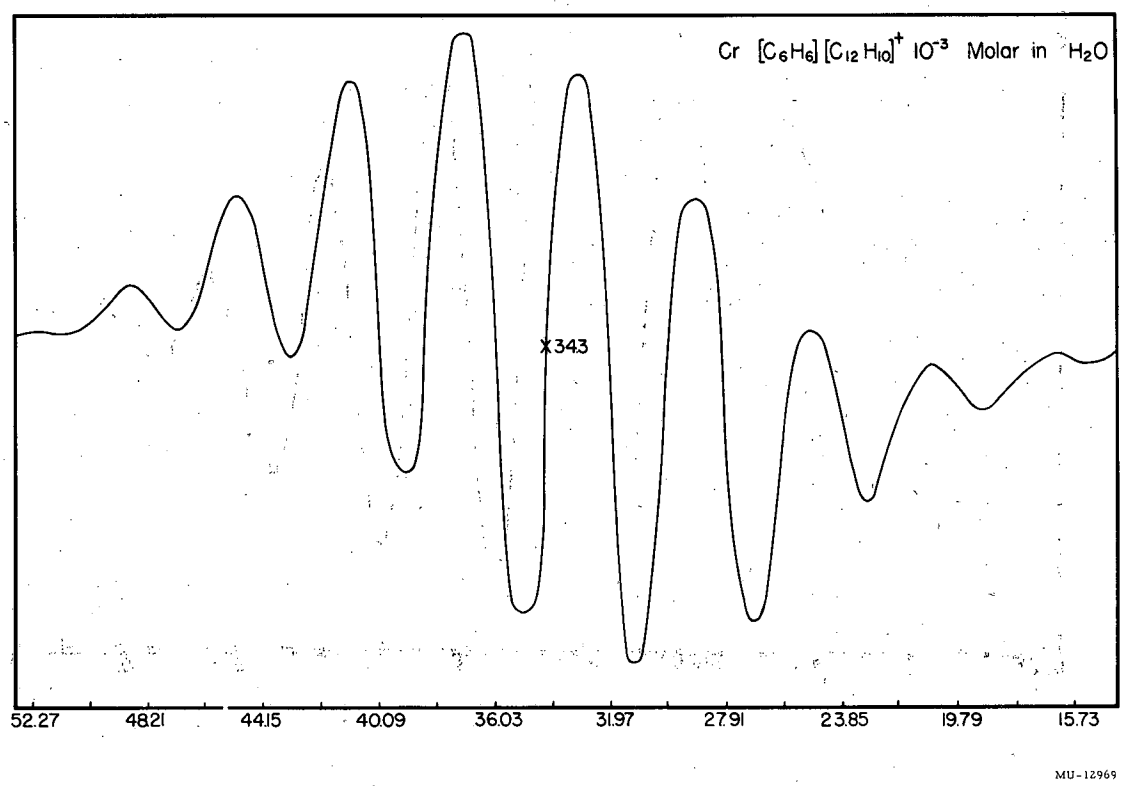

Fig. 35. Electron spin resonance spectrum of chromium benzene diphenyl cation.

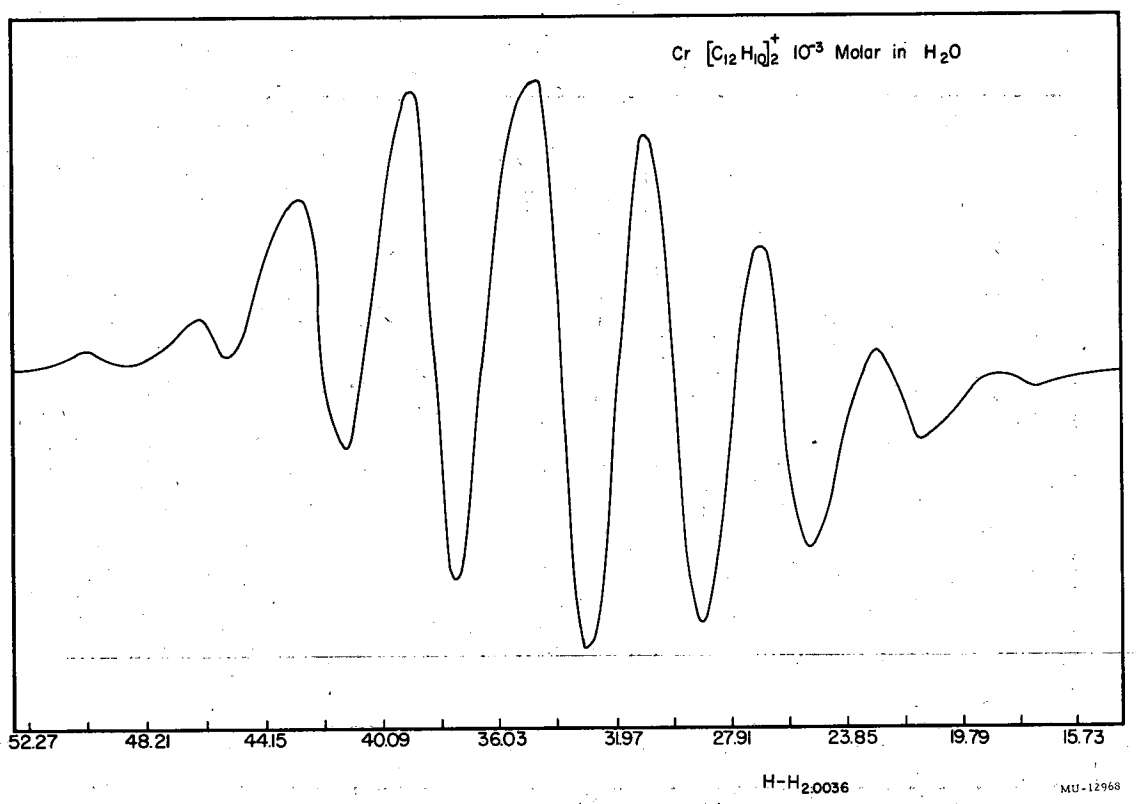

Fig. 36. Electron spin resonance spectrum of chromium bisdiphenyl cation.

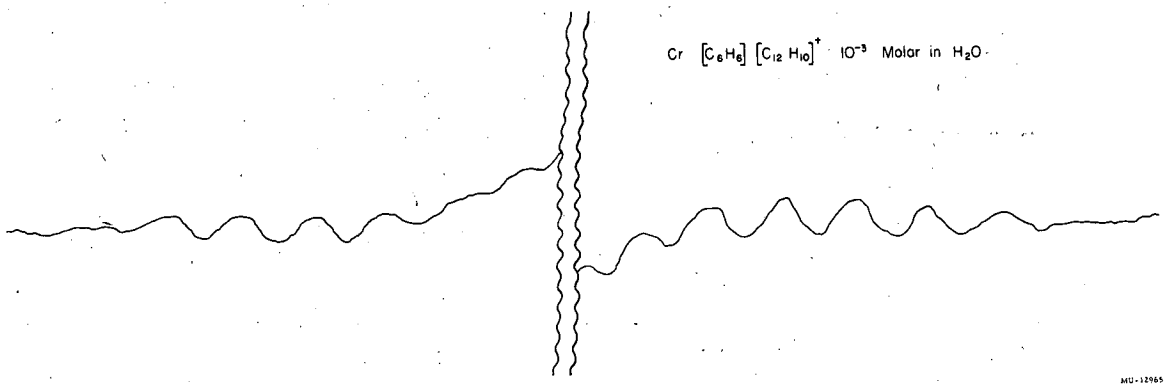

Fig. 37. Satellites in the electron spin resonance spectrum of chromium benzene diphenyl cation.

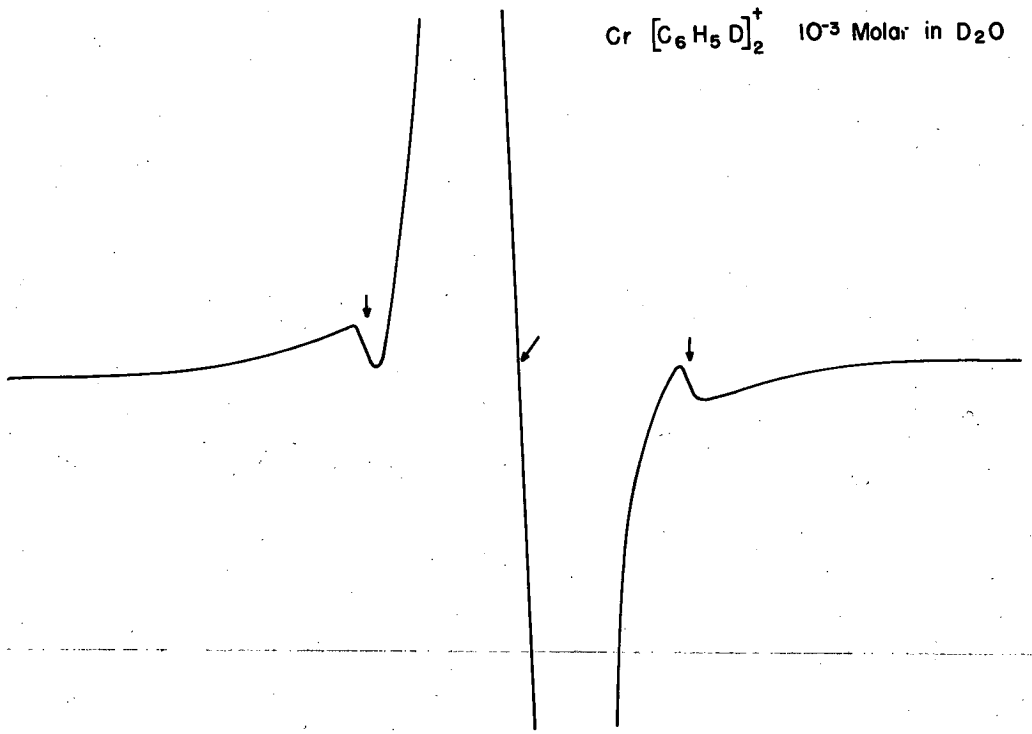

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Fig. 38. Satellites in the electron spin resonance spectrum of chromium dideuterobenzene cation.

Fig. 39. Satellites in the electron spin resonance spectrum of chromium bisdiphenyl cation.

The g values for all the chromium complexes that were measured are ~1.98. There are no other known Cr^{+} complexes with which to compare this g value, but Cr^{+3} has been observed by Low, and has g values of approximately 1.97.[47] Low also observed the Cr^{53} isotope. The ratio of the intensities of Cr^{53} lines to the lines of the even isotopes of chromium is approximately 1/40.

V. DISCUSSION

Chromium Bisaromatic Complexes

The unusual geometry of these compounds has attracted much attention. These compounds are reasonably stable, and have reactions that are somewhat characteristic of the usual "aromatic" molecules. They represent the most recently discovered types of compounds, the so-called π complexes of transition-metal ions. Various organic molecules with π orbitals available for additional bonding often form complexes with transition-metal ions.

Molecular-orbital formation is assumed to be the determining factor in the bonding of the chromium with the benzene ring. The richness of the electron spin resonance and optical spectra allows a detailed investigation of the electronic states of this system. With a detailed knowledge of the structure of the energy levels, the details of the bonding may be more easily inferred.

First consider the chromium dibenzene cation. According to the bonding scheme, there should be one unpaired electron in an antibonding orbital. If the electron finds its way onto the π orbitals of the benzene ring, then it may be expected to behave similarly to the odd electron in benzene negative ion. Weissman found that the spin resonance spectrum of benzene negative ion consists of seven lines with a total spread of 22.5 oersteds.[48] The spectrum of $Cr(C_6H_6)_2^+$ consists of thirteen lines with a total spread of approximately 46 oersteds. Although there are twice as many protons, there is still only one electron, and it would spend half of its time on each ring. If there were no other change in the molecule then the total spread would be expected to remain the same.[49] The presence of the chromium with its high nuclear charge would also be expected to remove the electron from the protons. The reverse is true, however. The spin density on each proton is the same in benzene negative ion and $Cr(C_6H_6)_2^+$, and therefore the total spin density on the proton is twice that in $C_6H_6^-$.

The increase in the hyperfine interaction by the protons in $Cr(C_6H_6)_2^+$ over that in $C_6H_6^-$ may be explained by the change in the hybridization of the carbon atom. In benzene it has a p_z and three sp^2 orbitals. In the chromium dibenzene the best hybrids would be those of a mixture of p_z or sp^2 with sp^3. This would increase the coupling with the carbon and, indirectly, with the proton on that carbon.

It is interesting to note the effect of substituting a phenyl group for a proton in the chromium dibenzene cation. There are several possibilities for the type of changes introduced by this substitution. The electron could be free to wander over every atom in the molecule. Secondly, it could remain only on the original twelve carbons and chromium atom, but now the protons would not necessarily still be equivalent. Thirdly, the only major change would be to decrease the number of interacting protons by one. The latter proposal is apparently close to fact.

The $Cr(C_{12}H_{10})_2^+$ has a spectrum consisting of only eleven lines. This shows conclusively that the odd electron has an appreciable probability only on the protons that are on the carbons directly adjacent to the chromium atom. The probability on the other two rings not directly attached to the chromium atom is apparently of a much smaller magnitude. This would be expected if the only interaction that would place an electron on these two outer rings was of the sigma-sigma type. If there were appreciable π- Σ interaction by the chromium and (or) the directly attached carbons with the other two benzene rings present, then a much larger interaction would be expected. It must therefore be concluded that there is little or no π interaction by the chromium or the carbons attached directly to the chromium with the two attached benzene rings.

The $Cr(C_6H_6)(C_{12}H_{10})^+$ has a spectrum consisting of twelve lines. The hyperfine splitting is a little larger than in $Cr(C_6H_6)_2^+$. In order to try to decide whether the protons were equivalent or whether the benzene protons were different from the diphenyl protons, a spectrum was synthesized using the splittings from $Cr(C_6H_6)_2^+$, and $Cr(C_{12}H_{10})_2^+$. This is found to consist of approximately seven major lines and is not at all similar to the observed spectrum, which consists of twelve lines.

The interaction of the electrons with the chromium nucleus deserves some comment. There are no known Cr^{+} complexes, and therefore, no other observed hyperfine splittings for this species. An estimate of the value may be made by using the observed hyperfine term for Cr^{+3}. The observed hyperfine splittings for Cr^{+3} are approximately 17 oersteds. The hyperfine interaction would be expected to be about the same for Cr^{+}. The observed splitting is approximately 20 oersteds. The g value shows the electron to be in an orbital with some angular momentum. All these factors show the molecular-orbital scheme to be at least qualitatively correct.

The excited electronic states should also be explainable by use of this scheme. There should be one low-lying symmetry-forbidden transition. There is one at approximately 10,000 A, which is similar to the usual d-d transitions. There should be two allowed transitions from the e_{1u} ligand π orbitals to the two d orbitals with vacancies (Fig. 6). In the chromium dibenzene cation, there is just such a doublet. The chromium dibenzene molecule should have an optical spectrum that is almost identical to that of the cation, except for minor differences in positions, and the presence of only one transition from the e_{1u} ligand orbitals to the chromium d orbitals, because the e_{2g} d orbital is now filled. It is found that the doublet in the uv in the cation is replaced by a single absorption band in this region in the chromium dibenzene molecule. There should also be transitions that are quite similar to those in benzene, except that they are from the e_{2g} d orbitals to the e'_{2u} ligand π orbitals. There are just such bands in the same region as in benzene. Except for quantitative calculations, this scheme seems to account for the spectral properties completely.

Copper Chelates

Copper Bisacetate Monohydrate

Copper bisacetate monohydrate will be used as a model for the other copper chelates since more is known about the physical properties of this compound. As pointed out earlier, the electron spin resonance (except for a small Cu-Cu interaction) and visible spectra of the copper bisacetylacetonate are almost identical to those of the acetate. The symmetry around the copper acetate should be almost exactly D_{4h}, except possibly for some very slight distortions.

Van Vleck first suggested that the visible absorption spectra were electric-dipole transitions and that the absorptions took place by means of vibrational interaction.[50] The intensity of the absorption is proportional to $\int \overline{\psi}_E^0 \, \overline{\psi}_V^0 \; e.r \rightarrow \psi_E^i \, \psi_V^1 \, dT$, if the transition is allowed by simultaneous electronic and vibrational excitation. $\overline{\psi}_E^0$ refers to the ground-state electronic wave function, $\overline{\psi}_V^0$ to the zero or ground-state vibrational mode, ψ_V^1 to the first excited vibrational mode, and ψ_E^i to the particular excited electronic state involved in the transition. In order that the integral not vanish the product under the integral must have A_{1g} symmetry.[19] The orbital ground state is B_{2g} $(d_{x^2-y^2})$, and the excited orbital state for u_1 is E_g (d_{xz}, d_{yz}). The vibrational ground state is A_{1g}. The symmetry of the product of wave functions under the integral sign is $B_{2g} \times E_g = E_g$. Since we have $E_g \times E_u(x, y) = A_{1u} + A_{2u} + B_{1u} + B_{2u}$, and $E_g \times A_{2u}(z) = E_u$, there must be a vibrational mode with either some or all of these symmetries in order that this integral not vanish. It may easily be shown that of these symmetries, only E_u contains a stretching mode. If it is assumed that stretching modes have the most interaction and are most effective in allowing the transition, then this absorption must be z polarized. Similarly, for the transitions to the d_{z^2} (u_2) and $d_{xy}(u_3)$ orbitals, we have

$B_{2g} \times A_{1g} = B_{2g}$, $B_{2g} \times B_{1g} = A_{2g}$,

$B_{2g} \times E_u(x, y) = E_u$, $A_{2g} \times E_u(x, y) = E_u$,

$B_{2g} \times A_{1u}(z) = B_{1u}$, and $A_{2g} \times A_{2u}(z) = A_{1u}$.

Because there are no stretching modes of A_{1u} or B_{1u} symmetry, only the x or y component of the dipole moment allows these transitions if only stretching modes are allowed to interact. These results agree with the experimental results of Tsuchida.[34]

The assumptions involved in the above analysis are: first, that only electric-dipole transitions are involved; second, that the only important vibrational interactions in these transitions are the stretching modes; and third, that the copper-copper interaction is small. The 3700 A band should be split by spin-orbit coupling ($2\lambda' = 1328$ cm^{-1}), giving rise to a band at 3891 or 3528 A. This band has not been observed.

The g values as measured by electron spin resonance also compare quite well with the calculated values.

	Calculated	Measured[51]
$\Delta g_{\parallel}$	0.4426	0.34
$\Delta g_{\perp}$	0.0631	0.05-0.09

On the basis of these results the theoretical approach is assumed to be valid, and the other copper and vanadium chelates are discussed on the same basis.

Copper Bisacetylacetonate

The electronic spectra of these complexes are essentially identical to those of the acetate. The band at 3900 A must therefore be identified as u_1 ($d_{x^2-y^2}$ to d_{xz}, d_{yz}). If this identification is used, there is no need to attempt to account for all three transitions by means of the doublet in the visible.

The solvent effect shows that the 6600 A band, which does not change position is the transition to the d_{xy} orbital , whereas the 5800 band, which moves to the red, is the transition to the d_{z^2} orbital. On the basis of this assignment and the g values as measured by Maki,[45] the mixing parameters

of the d orbitals with the ligand orbitals may be calculated. The effect on Δg because of mixing of the ligand orbitals may be calculated from the following basis wave functions:

$$\psi_{0\alpha} = (a\, d_{x^2-y^2} - \sqrt{1 - a^2}\, \Sigma_-)\alpha$$
$$\psi_{0\beta} = (a\, d_{x^2-y^2} - \sqrt{1 - a^2}\, \Sigma_-)\beta$$
$$\psi_{1\alpha} = (b\, d_{xz} - \sqrt{1 - b^2}\, \pi_1)\alpha$$
$$\psi_{1\beta} = (b\, d_{xz} - \sqrt{1 - b^2}\, \pi_1)\beta$$
$$\psi'_{1\alpha} = (b\, d_{yz} - \sqrt{1 - b^2}\, \pi_2)\alpha$$
$$\psi'_{1\beta} = (b\, d_{yz} - \sqrt{1 - b^2}\, \pi_2)\beta$$
$$\psi_{2\alpha} = (c\, d_{xy} - \sqrt{1 - c^2}\, T_-)\alpha$$
$$\psi_{2\beta} = (c\, d_{xy} - \sqrt{1 - c^2}\, T_-)\beta\ .$$

If the assumption is valid that there is no contribution by the ligand orbitals to the angular momentum, the expressions for the g values of copper bisacetylacetonate are:

	Theoretical	Calculated	Experimental	
$\Delta g_{\parallel}$	$\frac{8\lambda a^2 c^2}{u_3}$	0.4366	0.2638	$a^2c^2=0.604$
$\Delta g_{\perp}$	$\frac{2\lambda a^2 b^2}{u_1}$	0.0645	0.0515	$a^2b^2=0.798$
				$c^2/b^2=0.757$

If b^2 is set equal to 0.9, then the values of the other coefficients are $c^2 = 0.841$ and $a^2 = 0.886$. The value of these parameters would be expected to be $a^2(d_{x^2-y^2}) \geq c^2\,(d_{xy})$, because the ligands are directly along the $d_{x^2-y^2}$ extensions. The relative values of c^2 and b^2 are much harder to guess, but would be expected to be near 1 because these are the less bonding π orbitals. The values of these parameters could deviate for other reasons, and thus this deviation does not prove mixing of ligand and d orbitals. The spin resonance of the copper bisacetylacetone-ethylenediiminate shows conclusively that the odd electron does spend

some time on the ligands. Because there are four ligands for each d orbital, the values of these coefficients represent little contribution to the molecular orbital by each donor atom.

Valence-bond theory would predict that the electron would occupy a 4p orbital. This would give rise to quite different values for g and g. Pure d orbitals would not allow the electron to have a large probability at the ligand nuclei. However, the modified ligand field and LCAO MO's account for these facts quite easily.

The experimental data are not limited to these spectra, but abound with weak and intense ultraviolet absorptions. These spectra should be susceptible of explanation in these same terms. The absorptions in the area of 3000 A are not present in the enol or the lithium salt. There are also no absorptions in this region in the copper acetate. These absorptions exhibit a solvent effect. Neither of the unchelated acetylacetonates (acetylacetone or trifluoroacetylacetone) has much solvent effect. On the basis of solvent effect, these are identified as involving d orbitals. In copper acetate there is a new doublet at approximately 2600 A. This is directly between the two major areas of uv absorption in the copper bisacetylacetonate. The acetate ion is also a conjugate system, and though the excited states are quite high (as evidenced by the potassium salt), this absorption could still be between a copper d orbital and an unfilled π orbital. Accordingly the spectra of several copper salts in ethylene glycol were obtained (not shown). All these salts (chloride, nitrate, and sulfate) have an absorption at 2550 A. Even aqueous solutions have some absorption in the region of 2400 A, though the peak of maximum absorptions is at approximately 2100 A. The ethylene glycol would approach the symmetry of the acetylacetonate much more closely than the hydrate. Accordingly, the transition in the region of 2500 to 2600 A is assigned to transition from the nonbonding orbitals of the ligand to the $d_{x^2-y^2}$. The area around 3000 A is assigned to the transition from the copper to the first excited state of the ligand π system. The only other area to be accounted for is that at approximately 2000 A. There is no absorption in this region in the free ligand. This is attributed to the ligand-ligand transition, which occurs at 28-- A in the free ligand. These assignments are summarized in Fig. 40. The accompanying configurations are as follows:

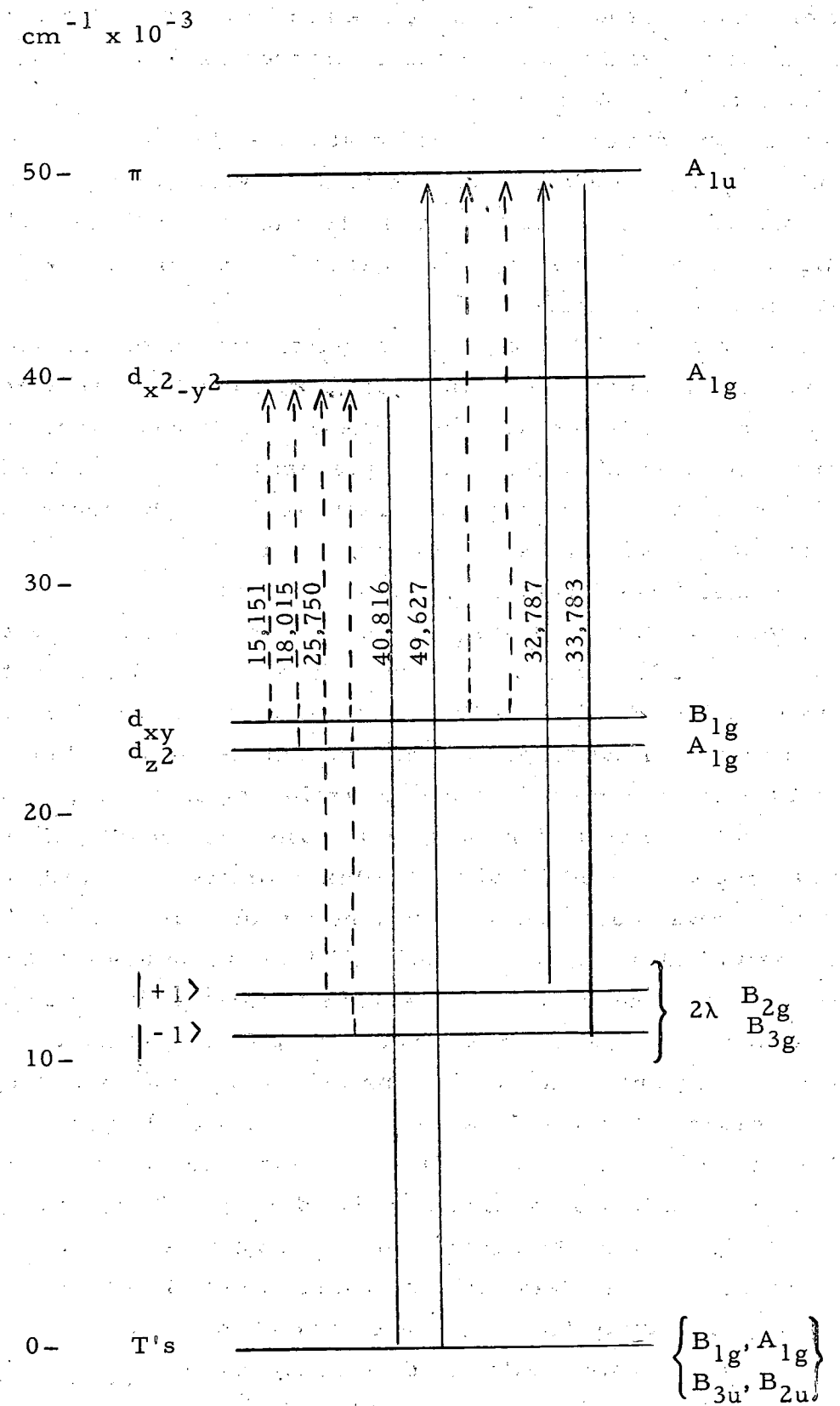


Fig. 40. Assignments for copper bisacetylacetonate. A broken line indicates a weak or forbidden transition.

$$\psi_8 = (T)^7 (\quad - 1\rangle)^2 (\quad + 1\rangle)^2 (d_{x^2})^2 (d_{xy})^2 (d_{x^2-y^2})(\pi)$$
$$\psi_7 = (T)^7 (\quad - 1\rangle)^2 (\quad + 1\rangle)^2 (d_{z^2})^2 (d_{xy})^2 (d_{x^2-y^2})^2$$
$$\psi_6 = (T)^8 (\quad - 1\rangle)^2 (\quad + 1\rangle)^2 (d_{z^2})^2 (d_{xy})^2 (d_{x^2-y^2})(\pi)$$
$$\psi_5 = (T)^8 (\quad - 1\rangle)^2 (\quad + 1\rangle) (d_{z^2})^2 (d_{xy})^2 (d_{x^2-y^2})(\pi)$$
$$\psi_4 = (T)^8 (\quad - 1\rangle) (\quad + 1\rangle)^2 (d_{z^2})^2 (d_{xy})^2 (d_{x^2-y^2})^2$$
$$\psi_3 = (T)^8 (\quad - 1\rangle)^2 (\quad + 1\rangle) (d_{z^2})^2 (d_{xy})^2 (d_{x^2-y^2})^2$$
$$\psi_2 = (T)^8 (\quad - 1\rangle)^2 (\quad + 1\rangle)^2 (d_{z^2})(d_{xy})^2 (d_{x^2-y^2})^2$$
$$\psi_1 = (T)^8 (\quad - 1\rangle)^2 (\quad + 1\rangle)^2 (d_{z^2})^2 (d_{xy})(d_{x^2-y^2})^2$$
$$\psi_0 = (T)^8 (\quad - 1\rangle)^2 (\quad + 1\rangle)^2 (d_{z^2})^2 (d_{xy})^2 (d_{x^2-y^2})$$

Having gained some confidence in the model, we may extend it to the more complicated case of VO^{++} chelates. These are discussed in the next section.

Vanadyl Complexes

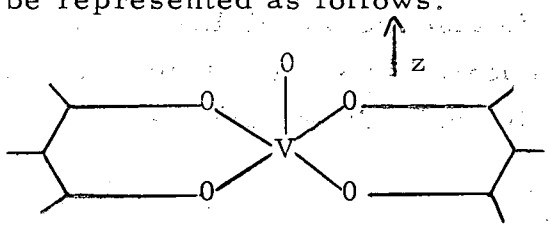
Vanadyl Bisacetylacetonate

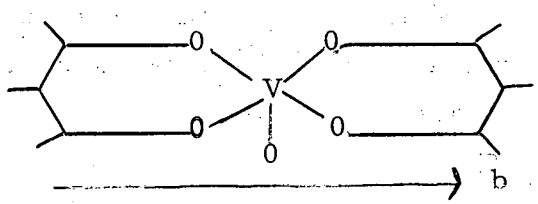
According to the energy-level scheme on page 27 there should be no transitions in this range of energies that would be due to transfer from vanadium to oxygen, or from oxygen to vanadium. The spectra should be essentially identical to that of the copper chelates except for exact positions of the absorptions. The odd electrons, both in copper and in vanadium, were predicted to have about the same energy, and consequently, the first uv transition should come at about the same position for both copper and vanadium. There are empty d orbitals in the vanadium to which an electron from the ligand nonbonding orbitals may be more easily transferred than for copper, where the only orbital available is half filled ($d_{x^2-y^2}$). There is also the possibility for four absorptions, instead of only one as in copper. This area is much more poorly resolved for vanadium chelates, but at least one more absorption is present in the uv.

The visible region for vanadyl chelates shows three weak transitions. The recent report on vanadyl complexes reports four in the visible region.[52] This is impossible if the ground state is the doubly degenerate d_{xz}, d_{yz} state. The electron spin resonance spectrum was taken and showed that under the conditions for which the visible spectrum shows four absorptions, there were at least two different species present in solution. The ground state is d_{xz}, d_{yz}, the first transition in the visible is to the d_{xy} orbital, the second to the d_{z^2} orbital, and the third to the $d_{x^2-y^2}$ orbital. Using these assignments, we may calculate the theoretical g values (Table X). It may be seen that within experimental error there is good agreement between theory and experiment. If the $d_{x^2-y^2}$ or d_{xy} was the ground state, then $g_{\parallel} < g_{\perp}$, and $g_{\parallel} \pm 2.0023$. It cannot be determined with these data whether or not we have $g_{\parallel} = 2.00023$, but $g_{\parallel}$ can be seen to be $> g_{\perp}$.

The electron spin resonance of single crystals gives some indication of the crystal structure of the vanadyl bisacetylacetonate. The V-O bond is approximately perpendicular to the b (needle) axis. If the molecule has a tetragonal pyramid structure, the x and y axes of the molecule must be parallel to the b axis. The angle made by $g_{\perp}$ and the c axis is approximately 50°.

A preliminary x-ray examination of the crystal structure shows it to be triclinic, with two molecules per unit cell.[53] The V-V vector makes an angle of 38° with the c axis, when a section is viewed perpendicular to the b axis. This roughly agrees with the position of $g_{\parallel}$ (45°). For this particular system Dodge concluded that there probably is a center of symmetry between the two molecules in the unit cell. The observations listed above seem to eliminate a trigonal bipyrimidal structure. Accordingly, the structure of the molecules in the unit cell may tentatively be represented as follows.





Vanadyl Hydrate

There has been some controversy in the literature about whether the structure of the dipositive ion of vanadium (IV) was $V{=}O^{++}$ or $V(OH)_2^{++}$. The electron spin resonance spectra give some clues. The more symmetric compounds VCl_4 and the six-coordinated chelates give one broad resonance. The visible spectra of these compounds also are quite similar, with only one absorption in the visible region. The five coordinated vanadyl chelates give a well-resolved eight-line electron spin resonance spectrum, and have two or more absorptions in the visible region. The V(IV) ion in aqueous solution is quite similar to the five coordinated vanadyl chelates in its visible and electron spin resonance spectra. It is concluded, therefore, that it must exist in aqueous solution as $V{=}O^{++} \cdot n\,H_2O$.

Applications

The discussion here should be capable of being extended without change to all the metal acetylacetonates of the first transition group. If the metal ion has a $3d^2$ configuration, then the only change that needs to be made in the discussion comes when these one-electron molecular orbitals contain more than one electron. If the energy separation between these d antibonding orbitals is of the same order of magnitude as the repulsion between the two electrons in the same orbital, then there may be a triplet ground state instead of a singlet. Therefore, the multiplicity of the ground state is not necessarily determined by the type of bonding in which the metal ion is involved. In general, however, the greater the mixing of ligand and metal orbitals, the greater the separation of the antibonding orbitals (d). This would lead to some correlation between bonding and multiplicity of the ground state. The visible spectra of these compounds ($3d^n$) may be approached in exactly the same way, and does give some clues to the symmetry and bonding in these chelates.[54]

The stability of the 3d transition metal chelates may be explained by the modified crystal-field approach. In the series from Ti^{++} to Cu^{++} complexes it is found that the stability of these complexes increased in the order indicated below.[55]

Configuration	M^{++} ion	log K_1[a] (acetylacetone)	log K_1 (ethylenediamine)	I (ev) II
$3d^2$	Ti	---	---	13.6
$3d^3$	V	---	---	14.2
$3d^4$	Cr	---	---	16.6
$3d^5$	Mn	5.51	2.73	15.6
$3d^6$	Fe	6.99	4.28	16.5
$3d^7$	Co	7.02	5.89	17.4
$3d^8$	Ni	(7.14)[b]	7.66	18.2
$3d^9$	Cu	9.73	10.72	20.2
$3d^{10}$	Zn	5.59	5.92	17.9
	H^+	8.94	10.0	13.60

[a] $K = (M^{++}\ \text{chelate})/[(M^{++})\ (\text{chelate})]$

[b] This compound in the solid state has been shown to have three nickel nuclei at very close distances (2.8A).[57]

The first trend that is obvious is the correlation of the stability constants with the second ionization potential, as first noted by Calvin and Melchior.[56]

A reason for this behavior is easily seen in terms of molecular orbitals. The increase in ionization potentials in this series represents a lowering of the energy of the d orbitals in going from Ti^{++} to Cu^{++}. To a first approximation the energy of the ligand will be the same no matter which of the M^{++} ions is combined with the ligand. Therefore the d orbitals of Cu^{++} are nearer in energy to those of the ligand than the d

orbitals of Ti^{++}. The closer the energy of metal ion and ligand orbitals, the more they interact, and the better the bond that is formed. This would clearly make the Cu^{++}-ligand bond stronger than Ti^{++}-ligand bond.

If the only interaction between metal ion and any ligand is the formation of Σ bonds, then the order of stabilities of a series of ligands with a given metal ion should be the same regardless of the metal ion involved. That is, if the order of stabilities of acetylacetone and ethylenediamine with Cu^{++} is: acac $<$ en, then the order with Mn^{++} should also be acac. $<$ en. This is certainly not the case, therefore there must be some other effect or effects in operation. The assumption of π bonding may be used to account for this behavior in the following way. The acetylacetone molecule has π orbitals available for π bonding, whereas the ethylenediamine molecule does not have such orbitals. In D_{4h} or octahedral symmetry, the $d\pi$ orbitals lie lowest (d_{xz}, d_{yz}, d_{xy}). There are some vacancies in these $d\pi$ orbitals from Ti^{++} through Mn^{++}. The acetylacetone chelates of these metal ions should be stabilized with respect to the ethylenediamine chelates, if π bonding is important. The chelates of Fe^{++} through Cu^{++} should either lack this extra stabilization in the acetylacetone chelates or be somewhat destabilized by the repulsion of the nonbonding π orbitals of the metal ion and the nonbonding π orbitals of the ligand.

There also are other effects that were not considered. There are certainly differences in the ligand-field stabilizations from ligand to ligand and from metal ion to metal ion, and there are probably changes in the energies of the ligands. However, it is felt that these are of minor importance in the total binding energies, though still of importance in the energies of the low-lying excited electronic states. Because the heats of hydration also follow this same general trend, the same explanation may be extended to account for this trend as well.

VI. CONCLUSIONS

The electronic spectra of metal chelate compounds may be successfully interpreted in terms of a ligand electrostatic field theory, modified by the formation of molecular orbitals between the metal and ligand. Many of the parameters that are introduced by this theory may be experimentally determined. When enough of these paramters have been evaluated, it may be possible to correlate these with quantities of interest to chemists such as bond energies, force constants, rates of reactions, reaction mechanisms, etc. The extension of the theory to qualitative interpretations of the relative stabilities of the metal complexes is seen to be successful. So far as the theory has been applied here, it has been quite successful in interpreting the known data.

For a very general approach to molecular bonding, it seems apparent that only the most general schemes will be adequate to describe any given system, and LCAO seems to be one of the most useful of these models. It quite successfully explains the magnetism of all the known "sandwich" molecules. It also explains the electronic spectra of chromium dibenzene and chromium dibenzene cation, as well as the electron spin resonance spectra of $Cr(C_6H_6)_2^+$ The models described here must be considered as reasonably accurate.

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