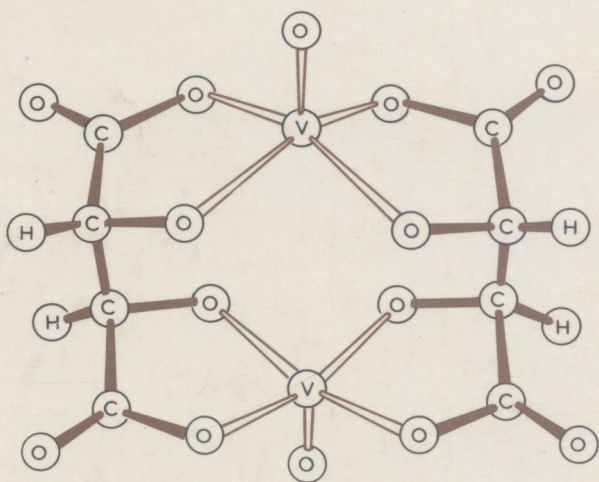


TRANSITION METAL CHEMISTRY

Edited by
Gordon A. Melson
Brian N. Figgis



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TRANSITION METAL CHEMISTRY

A SERIES OF ADVANCES

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TRANSITION METAL CHEMISTRY

Preface

Since the publication of *Transition Metal Chemistry* was suspended with Volume 7, the subject has shown considerable changes in emphasis. Many workers, old and new alike, have turned from the traditional fields of physical inorganic chemistry toward metal organic chemistry and biological inorganic chemistry. Each of these areas is serviced by a review series of its own. However, the editors and the publishers feel that there is a need to bring some features of these fields together with the longer established subject matter under a cohesive heading of Transition Metal Chemistry. It is with that aim the series has been restarted with Volume 8.

The series will continue to include comprehensive reviews and monographs at the research level. These reviews will be authored by scientists active in their individual research areas and will seek to cover transition metal chemistry widely and in-depth.

GORDON A. MELSON
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ESR Spectra of Metal Complexes of the First Transition Series in Low-Symmetry Environments

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I. INTRODUCTION

Electron spin resonance (ESR) spectroscopy has become increasingly popular in recent years for the characterization of the electronic structure of transition metal complexes. Its field of application is now extremely broad, ranging from the study of metalloenzymes and metalloproteins to minerals, polymers, and metallozeolites. This wide variety of applications demands a thorough knowledge of the ESR spectra of simple model complexes in order to compare them with the complicated patterns observed, for instance, in the study of naturally occurring molecules.

In the initial development of the technique, simple complexes of relatively high symmetry were studied, and the results are now covered by many excellent textbooks [1-14] and review articles [15-20]. References to the current literature can be found in the *Chemical Society (London) Specialist Periodical Reports on Electron Spin Resonance*, and more concise reports are also published in *Analytical Chemistry* [21].

We wish to review here the ESR spectra of transition metal complexes in low-symmetry environments, with the aim of showing how it

is possible to obtain a considerable insight into their electronic properties by collecting accurate ESR data, and using sophisticated spin Hamiltonian, ligand field, and molecular orbital calculations. In order to keep the matter as tractable as possible, we shall limit our interest to metals of the first transition series. We shall consider in general only studies on solids, either single-crystal or polycrystalline powders, since only in these cases can one meaningfully relate the spin Hamiltonian parameters to structure.

We shall consider only simple mononuclear complexes and shall ignore the expanding field of spin-spin coupled systems [22-26]. In general, we shall mention only "true" discrete complexes, mostly with organic ligands, and shall ignore the subject of paramagnetic impurities in ionic lattices. Also, we shall not mention the ESR spectra of metalloenzymes and metalloproteins, which are covered by some excellent reviews [27-33], and which would require a book by themselves.

Of the possible oxidation states of a metal ion, only the most important will be considered. Of course the expression "most important" is vague; by it we mean the oxidation states that are most commonly encountered in classic transition metal chemistry, not considering organometallic complexes in general.

Finally, we shall not touch upon electron spin relaxation phenomena.

We shall treat in Sec. II the spin Hamiltonian formalism, showing all the subtleties that are required to extend it to the interpretation of the low-symmetry transition metal complexes. The restraints on the spin Hamiltonian parameters imposed by crystal symmetry will be covered in Sec. III. Section IV will provide general solutions to the spin Hamiltonian, whereas in Sec. V the solutions for different S values will be given. Section VI will be devoted to an outline of the computer analysis of single-crystal and polycrystalline powder spectra. Sections VII and VIII will review recent achievements in the molecular orbital and ligand field analyses of the spin Hamiltonian parameters. In Sec. IX a survey of the

experimental results of various metal ions in different oxidation states will be provided.

II. THE SPIN HAMILTONIAN

The simplest approach to the interpretation of ESR spectra is that of the spin Hamiltonian [34,35] formalism, which, as Griffith puts it, "is a convenient resting place during the long trek from fundamental theory to the squiggles of an oscilloscope" [9]. Essentially, the spin Hamiltonian is an operator equivalent that is designed to act on spin coordinates only, giving the same results as the true Hamiltonian, which may be difficult to handle, with respect to the energies of the electronic and nuclear systems. The spin coordinates that are used are not necessarily the true spin coordinates, but rather may be fictitious ones. Although essentially the same as the true coordinates for systems with $S = 1/2$, they can be completely different in the case of $S > 1/2$ [1,9]. The choice of the spin multiplicity to be used for interpreting the ESR spectra within the spin Hamiltonian formalism is determined a posteriori by the nature of the ESR spectra themselves.

Another advantage of the spin Hamiltonian formalism is that many different interactions can easily be taken into consideration by adding the appropriate terms to the Hamiltonian. A rather complete form of spin Hamiltonian, which can be used for the interpretation of the spectra of magnetically diluted complexes, neglecting interactions involving the ligand nuclei, is

$$\begin{aligned} \underline{H} = & \mu_B \underline{B} \cdot \underline{g} \cdot \underline{S} + \underline{I} \cdot \underline{A} \cdot \underline{S} + \underline{S} \cdot \underline{D} \cdot \underline{S} + \sum_{k=4}^{2S} \sum_{q=0}^k B_k^q O_k^q + \\ & \underline{I} \cdot \underline{P} \cdot \underline{I} - \mu_N \underline{B} \cdot \underline{g}_N \cdot \underline{I} \quad (k \text{ even}) \end{aligned} \quad (1)$$

where μ_B and μ_N are the Bohr and nuclear magnetons, respectively; \underline{B} is the magnetic flux density vector relative to the static magnetic field; \underline{S} and \underline{I} are the electron and nuclear spin vector operators, respectively; \underline{g} , \underline{A} , \underline{D} , \underline{P} , and \underline{g}_N are matrices; O_k^q are combinations of spin operators equivalent to combinations of spherical harmonics,

and B_k^q are parameters. Although \underline{g} , \underline{A} , \underline{D} , \underline{P} , and \underline{g}_N are often referred to as second-rank tensors, only \underline{D} and \underline{P} are true tensors; \underline{g} , \underline{A} , and \underline{g}_N are not [1], since their behavior under a rotation of the reference frame cannot be represented in general by Eq. (2),

$$\underline{Y}' = \underline{X} \cdot \underline{Y} \cdot \underline{X}^{-1} \quad (2)$$

In Eq. (2), \underline{X} is a rotation matrix, and \underline{Y} and \underline{Y}' stand for general tensors. In general, therefore, \underline{g} , \underline{A} , and \underline{g}_N are not represented by symmetric matrices. This can present several difficulties in the use of the spin Hamiltonian, but these are easily overcome if one considers the $\underline{g}^2 = \underline{\tilde{g}}\underline{\tilde{g}}$ and $\underline{A}^2 = \underline{\tilde{A}}\underline{\tilde{A}}$ matrices, which are real symmetric and represent true second-rank tensors. The principal values and directions of these tensors are obtained by ESR experiment, yielding the moduli of \underline{g} and \underline{A} .

The terms that have been included in the spin Hamiltonian (1) represent the Zeeman interaction of electrons ($\mu_B \underline{B} \cdot \underline{g} \cdot \underline{S}$); the electron spin-nuclear spin interaction ($\underline{I} \cdot \underline{A} \cdot \underline{S}$), often referred to as hyperfine interaction; the electron spin-electron spin interaction ($\underline{S} \cdot \underline{D} \cdot \underline{S} + \sum_{k=4}^{2S} \sum_{q=0}^k B_k^q O_k^q$), often referred to as fine interaction; the nuclear quadrupole interaction ($\underline{I} \cdot \underline{P} \cdot \underline{I}$); and the nuclear Zeeman interaction ($\mu_N \underline{B} \cdot \underline{g}_N \cdot \underline{I}$). Since in the spin Hamiltonian formalism there is no place for the electron orbital momentum, the electron spin-electron spin term will contain the contributions from electron spin-spin, spin-orbit, and orbit-orbit interactions. In the case of transition metal complexes, it is the spin-orbit interaction that essentially determines the fine structure term in the spin Hamiltonian. The most important O_k^q operators have been tabulated by Abragam and Bleaney [1] and are shown in Table 1. The same reference also gives the matrix elements of the O_k^q operators in the spin manifolds from $S = 1$ to $S = 8$.

The terms $\sum_{k=4}^{2S} \sum_{q=0}^{2S} B_k^q O_k^q$ have a different form compared to the others included in Eq. (1). They have their origin in a more general formalism by which in principle it is possible to express all

Table 1 The O_k^q Equivalent Operators Needed for 3d Ions

$O_2^0 = 3S_{\underline{z}}^2 - S(S+1)$
$O_2^2 = (1/2)(S_{\underline{+}}^2 + S_{\underline{-}}^2)$
$O_4^0 = 35S_{\underline{z}}^4 - 30S(S+1)S_{\underline{z}}^2 + 35S_{\underline{z}}^2 - 6S(S+1) + 3S^2(S+1)^2$
$O_4^2 = (1/4)\{[7S_{\underline{z}}^2 - S(S+1) - 5](S_{\underline{+}}^2 + S_{\underline{-}}^2) + [7S_{\underline{z}}^2 - S(S+1) - 5]\}$
$O_4^3 = (1/4)[S_{\underline{z}}(S_{\underline{+}}^3 + S_{\underline{-}}^3) + (S_{\underline{+}}^3 + S_{\underline{-}}^3)S_{\underline{z}}]$
$O_4^4 = (1/2)(S_{\underline{+}}^4 + S_{\underline{-}}^4)$

the terms of (1). As a matter of fact, the spin Hamiltonian can be expressed as a sum of terms having the dimensions $B^\ell S^s I^i$ with $s \leq 2s$ and $i \leq 2l$ in order to have nonzero representative matrix elements in the spin basis set and $\ell + s + i = 2n$ in order to be invariant under the Kramers operator. The terms with $\ell = i = 0$ are the fine structure terms, $s = 2$ corresponding to

$$B_2^0 O_2^0 + B_2^2 O_2^2 \quad (3)$$

The terms with $\ell = 0, s = 1, i = 1$, and $\ell = 0, s = 0, i = 2$ are equivalent to the terms $\underline{S} \cdot \underline{A} \cdot \underline{I}$ and $\underline{I} \cdot \underline{P} \cdot \underline{I}$ of Eq. (1). Higher-order terms involving the \underline{I} operators will not be discussed here. In general terms, with $i = 0, \ell = 1$ and $s \neq 1$ may be required. For $S = 3/2$ spin systems, terms in BS^3 have been used frequently [36,37]. It has to be noted that the latter terms are required for ions having appreciable "unquenched" orbital momentum. However, it has been shown [1] that for an orbitally nondegenerate state, the spin Hamiltonian (1) is correct to first order in perturbation theory up to $S = 5/2$ spin systems.

In general the spin Hamiltonian is expressed in the form of Eq. (1), the only $B_k^q O_k^q$ terms used being those with $k = 4$.

Since \underline{Q} and \underline{P} are traceless tensors, it is customary to reformulate the spin Hamiltonian terms that contain them in such a way as to reduce by one the number of parameters. The relations required are

$$\underline{D}_{xx} + \underline{D}_{yy} + \underline{D}_{zz} = 0$$

$$\underline{P}_{xx} + \underline{P}_{yy} + \underline{P}_{zz} = 0 \quad (4)$$

In the case of orthorhombic symmetry, the spin Hamiltonian (1) takes the explicit form:

$$\begin{aligned} \underline{H} = & \mu_B \left(\underline{g}_x \underline{B}_x \underline{S}_{-x} + \underline{g}_y \underline{B}_y \underline{S}_{-y} + \underline{g}_z \underline{B}_z \underline{S}_{-z} \right) + \left(\underline{A}_{-x-x} \underline{S}_x \underline{I}_x \right. \\ & + \underline{A}_{-y-y} \underline{S}_y \underline{I}_y + \underline{A}_{-z-z} \underline{S}_z \underline{I}_z \left. \right) + D \left[\underline{S}_z^2 - \frac{S(S+1)}{3} \right] + E \left[\underline{S}_x^2 - \underline{S}_y^2 \right] \\ & + P_{\parallel} \left[\underline{I}_z^2 - \frac{I(I+1)}{3} \right] + \eta \left[\underline{I}_x^2 - \underline{I}_y^2 \right] + B_4^0 \underline{O}_4^0 \\ & + B_4^4 \underline{O}_4^4 + B_4^2 \underline{O}_4^2 + \text{nuclear Zeeman terms} \end{aligned} \quad (5)$$

where $D = (3\underline{D}_z/2)$, $E = (\underline{D}_x - \underline{D}_y)/2$, $P_{\parallel} = (3\underline{P}_z/2)$, and $\eta = (\underline{P}_x - \underline{P}_y)/\underline{P}_z$.

Sometimes the $B_4^2 \underline{O}_4^2$ term in Eq. (5) is assumed to be negligible and the quartic fine structure terms of (5) are written as

$$B_4 \left(\underline{O}_4^0 + 5 \underline{O}_4^4 \right) + B_4^0 \underline{O}_4^0 \quad (6)$$

Strictly, this represents a cubic field plus a tetragonal distortion. A commonly used equivalent form of Eq. (6) is

$$\begin{aligned} & \frac{a}{6} \left[\underline{S}_x^4 + \underline{S}_y^4 + \underline{S}_z^4 - \frac{S(S+1)(3S^2 + 3S - 1)}{5} \right] \\ & + \frac{F}{180} \left[35 \underline{S}_z^4 - 30S(S+1) \underline{S}_z^2 + 25 \underline{S}_z^2 + 6S(S+1) \right] \end{aligned} \quad (7)$$

with

$$F = 180 B_4^0 \quad a = 120 B_4 = 24 B_4^4 \quad (8)$$

When the $\underline{S} \cdot \underline{D} \cdot \underline{S}$ term is expressed according to the equivalent formalism as in Eq. (3), relations

$$D = 3 B_2^0 \quad E = B_2^2 \quad (9)$$

hold.

In both the Hamiltonians (1) and (5), we have neglected terms relative to the interactions between the electron spin and the nuclear spins of ligands. Where these are present, the hyperfine term in the Hamiltonian (1) becomes

$$\sum_{i=1}^N \vec{S} \cdot \vec{A}_i \cdot \vec{I}_i \quad (10)$$

where N is the number of nuclei that interact with the unpaired electrons.

The form of the Hamiltonian (5) is fairly general. However, lower-symmetry environments often can be found for transition metal ions, and a more detailed analysis of the symmetry properties of the tensors that appear in the spin Hamiltonian (1) is appropriate. Abragam and Bleaney [1] showed, using Kramers doublet and time-reversal symmetry, that D_2 symmetry the principal axes of \vec{g} and \vec{A} tensors had to be coincident, whereas this is not the case in C_3 symmetry. These relations were generalized [38] to show that whenever the complex has a two (or higher)-fold axis and either a perpendicular binary axis C'_2 or σ_v symmetry elements, \vec{g} and \vec{A} are necessarily collinear. Without the C'_2 or σ_v symmetry elements, \vec{g} and \vec{A} have off-diagonal elements, resulting generally in noncollinear principal axes. The noncollinearity of \vec{g} and \vec{A} tensors in this case will cause \vec{B} and \vec{I} to be referred to different axis systems, and this will be observable if the nuclear Zeeman effect is measured together with the hyperfine terms. That can be achieved through electron nuclear double resonance (ENDOR) experiments.

In Table 2 the relations imposed by crystal symmetry on \vec{g} and \vec{A} are shown.

At the end of this section we want to mention, for the sake of completeness, an equivalent formulation of the spin Hamiltonian that can be obtained using tensor operators [36,39,40]. In this formalism the generalized spin Hamiltonian is

$$\underline{H} = \sum_{\ell, m} a_{\ell m} T_{\ell m} (B_{\ell}^{m_1} S_{\ell}^{m_2} I_{\ell}^{m_3}) \quad (11)$$

In Eq. (11) the summation over m goes from $-\ell$ to $+\ell$, where ℓ is an even integer. $T_{\ell m}(B_{\ell_1}^{m_1} S_{\ell_2}^{m_2} I_{\ell_3}^{m_3})$ is concise notation for the tensor product of the tensor operators $T_{\ell_1 m_1}(B)$, $T_{\ell_2 m_2}(S)$, and $T_{\ell_3 m_3}(I)$, which are the Racah tensor operators constructed with the components of B , S , and I , respectively.

The values of ℓ_1 , ℓ_2 , and ℓ_3 are restricted so that they sum up to give ℓ even, and the maximum possible values for ℓ_2 and ℓ_3 are $2S$ and $2I$, respectively. There are no general restrictions on ℓ_1 except those from parity considerations; usually, however, power terms greater than quadratic in B are neglected.

In this formalism the linear Zeeman term is obtained by putting $\ell_1 = 1$, $\ell_2 = 1$, and $\ell_3 = 0$ in Eq. (11):

$$\underline{H}_Z = \sum_{q=-1}^1 \sum_{k=-1}^1 \mu_B g_k T_{1q}(B) T_{1k}(S) \quad (12)$$

and the zero field term taking $\ell_1 = \ell_3 = 0$, $\ell_2 = 2S$ in (11) is

$$\underline{H}_{Zfs} = \sum_{\ell=0}^{2S} \sum_{m=-\ell}^{\ell} B_{\ell m} T_{\ell m}(S) \quad (13)$$

Buckmaster, Chatterjee, and Shing [41] have written a review article on the use of the tensor operator formalism in the analysis of ESR and ENDOR spectra and have reported several tables that are useful in computations.

III. ESR SPECTRA AND CRYSTAL SYMMETRY

In order to obtain the most complete experimental information from an ESR experiment, it is necessary to record single-crystal spectra. The appearance of single-crystal spectra depends on the site symmetry of the metal ion and the point symmetry of the space group of the lattice. Although often the ESR spectra of a low-symmetry complex may appear to be of higher symmetry than is allowed by the site symmetry, it must be understood that it can be true only to some level of approximation, and if the experimental data were obtained