Coordination Chemistry Reviews
Elsevier Publishing Company, Amsterdam
Printed in The Netherlands

EPR STUDIES OF EXCHANGE COUPLED METAL IONS

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(Received September 9th, 1969)

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A. INTRODUCTION

The study of transition metal ion complexes by magnetic and optical techniques has furnished a considerable body of empirical data, much of which can be understood in terms of the phenomenological ligand field theory. A major portion

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Coordin. Chem. Rev., 5 (1970) 209–244

of these data is primarily concerned with complexes containing a single paramagnetic transition metal ion; relatively little information is available on dimeric or trimeric coordination complexes. In complexes containing two or more paramagnetic transition metal ions, an intramolecular exchange interaction between the unpaired electronic spins may occur.

An important indication of intramolecular exchange coupling in complexes which contain more than one transition metal ion is the characteristic deviation of the magnetic susceptibility of these compounds from the Curie–Weiss Law. When an isotropic interaction occurs between two paramagnetic metal ions with spins $\bar{S}_1$ $(=\frac{1}{2})$ and $\bar{S}_2$ $(=\frac{1}{2})$, the exchange interaction term $J\bar{S}_1 \cdot \bar{S}_2$ is required in the spin Hamiltonian. J is defined such that a positive value corresponds to an antiferromagnetic interaction in which the ground state is a singlet and the triplet state is J energy units above the ground state. If J, expressed in units of temperature, is of the same order of magnitude as the temperature range over which measurements are made, and if J is not a function of temperature, then the temperature dependence of the magnetic susceptibility, as first formulated by Bleaney and Bowers[1], is in accordance with the relation:

$$\frac{1}{T[3+\exp(J/T)]} \tag{1}$$

Numerous copper(II) ion complexes are known which exhibit this behavior, the excellent review by Kato Jonasson and Fanning[2] lists well over one hundred of these complexes. Metal–metal interactions have also been discussed by Lewis[3], Lewis and Nyholm[4], Stone[5], and Cotton[6]. Two recent reviews on the current status of susceptibility studies have been published by Martin[7] and Ball[8].

Concurrently, solid state physicists have been exploring the origins of antiferromagnetism by doping paramagnetic ions into diamagnetic host lattices. Electron paramagnetic resonance, magnetic susceptibility and optical studies are being performed on samples containing a high concentration of the dopant material in order to ascertain the nature of the magnetic interactions in the pairs, triads or larger clusters of metal ions which may be present in such materials.

These studies have been the subject of a number of reviews. Owen has been particularly active in this area and his papers and review are recommended[9–13]. In addition, a number of review articles published in the four volume series entitled *Magnetism* are particularly useful, notably those of Stevens[14], Anderson[15], Moriya[16], Sugano and Tanabe[17], and Smart[18] Goodenough's book[19] and his review paper[20] are also important contributions to the literature in this area, as are some portions of the Proceedings of the Conference on Magnetism and Magnetic Materials, which are published as supplements to the Journal of Applied Physics[21] and the Journal of the Physical Society of Japan[22]. Kokoszka and Gordon[23] have reviewed studies of various aspects of metal–metal exchange interactions performed before the middle of 1967.

In this paper, the discussions are primarily restricted to the more recent investigations of paramagnetic complexes which contain interacting transition metal ions. A number of special topics are also included in this review, such as supertransferred hyperfine fields, biquadratic exchange, antisymmetrical exchange, and one-dimensional antiferromagnetism, a subject which has recently gained the increasing attention of inorganic chemists.

B. THEORETICAL SURVEY

(i) Elementary example

The magnetic behavior of a complex which contains two magnetic ions may often be described by a model which considers the total molecular complex as consisting of two smaller units which are weakly interacting. Ligand field theory generally provides a convenient theoretical framework for a description of the individual units In order to describe the magnetic behavior of the whole molecular complex, a spin Hamiltonian is formulated for each unit and the spin–spin interaction terms are added.

The spin Hamiltonian, a convenient shorthand device for representing the entire data in a concise fashion, can be used to describe the interaction of a single electronic magnetic moment of a paramagnetic monomeric complex with an external magnetic field. With few exceptions, this Hamiltonian is quite sufficient, though a number of very recent studies, both theoretical and experimental, suggest that the original concept of the spin Hamiltonian is too limited[24]. The discussion in this chapter will be limited to cases where the use of the spin Hamiltonian is justified on experimental grounds.

For an octahedral complex which contains a metal atom with a nuclear spin, I and one unpaired electron, the spin Hamiltonian, expressed as a function of an isotropic g and A value, as required by symmetry, is

$$\mathscr{H} = g\beta\bar{H}\cdot\bar{S}+A\bar{S}\cdot\bar{I} \tag{2}$$

In general, g and A will usually be anisotropic for lower symmetry environment. If the ligands contain nuclei with non-zero nuclear magnetic moments, it is also necessary to include terms in the Hamiltonian which reflect the interaction of the magnetic (unpaired) electron or electrons with these nuclear moments.

For S greater than one-half, terms reflecting the electronic spin–spin interaction must also be included in the spin Hamiltonian. The direct interaction of the external magnetic field with the nuclear moments should, for completeness, be included as well.

When two magnetic ions are sufficiently close together to interact, additional effects may be observed. If the spin–spin coupling interaction is isotropic, the most common of these effects may be represented by a cosine coupling expression, the Heisenberg Hamiltonian $J\bar{S}_1 \cdot \bar{S}_2$. The total spin of the coupled spin system may then be represented by a resultant spin vector

$$\bar{S} = \bar{S}_1 + \bar{S}_2 \tag{3}$$

This review is primarily concerned with cases where the magnitude of J is considerably less than typical crystal (ligand) field energies, which are often of the order of 10,000 cm^{-1} for transition metal ion complexes. Specifically, this review will be concerned with cases where $J \sim 1{,}000\ \text{cm}^{-1}$ or less

It is particularly important to note that when the spin Hamiltonian is employed to describe magnetic data, the orbital variables and the crystalline field parameters do not explicitly appear. For this reason, typical energies for the parameters in the spin Hamiltonian of the individual units are of the order of magnitude of 1 cm^{-1}, which is often much smaller than J. In a later section, some of the observed anisotropic spin–spin coupling effects which may be ascribed to the anisotropies of the "individual" metal ion complexes comprising the cluster complex will be discussed.

A simple antiferromagnetic system would be one which consists of two transition metal ions, each possessing one unpaired d electron. Assuming that the orbital angular momentum is completely quenched, that the spin–orbit interaction and the direct dipolar interaction can be neglected, that the axis joining the two ions is the high symmetry axis (*e.g.*, a D_{nh} axis with $n > 3$), that the isotropic Heisenberg Hamiltonian $J\bar{S}_1 \cdot \bar{S}_2$ ($\mathscr{H}_{12}$) describes the spin–spin coupling, and that it is the largest term in the combined spin Hamiltonian, then the total spin Hamiltonian may be expressed as a function of the single ion Hamiltonians $\mathscr{H}_1$ and $\mathscr{H}_2$ and the Heisenberg Hamiltonian $\mathscr{H}_{12}$ as

$$\mathscr{H} = \mathscr{H}_1 + \mathscr{H}_2 + \mathscr{H}_{12}$$

The two $S = \frac{1}{2}$ ions couple to form a singlet ($S = 0$) and a triplet ($S = 1$) state. For positive J, the singlet state is lowest and the energy separation between the singlet and the triplet state is equal to J. Mathematically, the single ion Hamiltonians and the Heisenberg Hamiltonian may be written as

$$\begin{aligned}
\mathscr{H}_{1,2} &= g_{1,2}\beta\bar{S}_{1,2} \cdot \bar{H} + A\bar{S}_{1,2} \cdot \bar{I}_{1,2} \\
\mathscr{H}_{12} &= J\bar{S}_1 \cdot \bar{S}_2 \\
\bar{S} &= \bar{S}_1 + \bar{S}_2 \\
\bar{S}^2 &= (\bar{S}_1 + \bar{S}_2)^2 = \bar{S}_1{}^2 + \bar{S}_2{}^2 + 2\bar{S}_1 \cdot \bar{S}_2 \\
\mathscr{H} &= g_1\beta\bar{S}_1 \cdot \bar{H} + g_2\beta\bar{S}_2 \cdot \bar{H} + J\bar{S}_1 \cdot \bar{S}_2 + A\bar{S}_1 \cdot \bar{I}_1 + A\bar{S}_2 \cdot \bar{I}_2
\end{aligned}$$

The total spin Hamiltonian may be rewritten as follows:

$$\begin{aligned}
\mathscr{H} = {} & (g_1 + g_2)\beta(\bar{S}_1 + \bar{S}_2) \cdot \bar{H} + J/2[S(S+1) - S_1(S_1+1) - S_2(S_2+1)] + \\
& A/2[(\bar{S}_1 + \bar{S}_2) \cdot (\bar{I}_1 + \bar{I}_2)] + A/2[(\bar{S}_1 - S_2)] \cdot [(\bar{I}_1 - \bar{I}_2)]
\end{aligned}$$

or, preferably, as

$$\mathscr{H} = g\beta\bar{S}\cdot\bar{H}+J/2[S(S+1)-{}^3/_2]+A/2(\bar{S})\cdot(\bar{I}_1+\bar{I}_2) \tag{4}$$

S may be either zero or one. The triplet state is at an energy $^1/_4 J$ and the singlet state is at an energy $-3/4J$ when no magnetic field is applied.

If the magnitude of the isotopic cosine coupling term in the spin Hamiltonian of two exchange coupled paramagnetic ions is much larger than any of the other terms, and if the g factors for the individual ions are known and isotropic, or if the principal axes for the individual ions are parallel, then the g factor for the coupled state may be calculated as follows[25].

If spin S_1 with g value g_1 is coupled to spin S_2 with g value g_2, then the total spin angular momentum of the system is $\bar{S} = \bar{S}_1+\bar{S}_2$, characterized by the quantum numbers S, M, S_1 and S_2; the mean value of g in the expression

$$g\beta\bar{S} = g_1\bar{S}_1+g_2\bar{S}_2$$

is given by

$$g = \tfrac{1}{2}(g_1+g_2)+\tfrac{1}{2}(g_1-g_2)\,\frac{S_1(S_1+1)-S_2(S_2+1)}{S(S+1)} \tag{5}$$

Gibson, Hall, Thornley and Whatley[26] incorporate this expression in their analysis of the EPR spectrum of reduced spinach ferredoxin. In this study, it was proposed that the reduced complex contains exchange coupled iron ions, one ferric and the other ferrous, with bridging sulfur ligands. The complex, schematically represented as

$$\mathrm{Fe}^{3+}\ (d^5,\ S = 5/2) - \text{Sulfur ligand(s)} - \mathrm{Fe}^{2+}\ (d^6,\ S = 2)$$

will have a total spin of $\tfrac{1}{2}$ in the ground state if the exchange interaction is antiferromagnetic. With $S_1 = 5/2$, $S_2 = 2$ and $S = \tfrac{1}{2}$, the experimental g value should be

$$g = (7g_1-4g_2)/3 \tag{6}$$

These workers chose $g_1 = 2.019$ (isotropic). The experimental values $g_x = 1.88$, $g_y = 1.94$, and $g_z = 2.04$ were used to calculate g_2 in the three principal directions. A satisfactory fit of the data was obtained with a simple model for the ferrous ion. In addition, this model is consistent with a strongly temperature-dependent relaxation mechanism, which operates by a two phonon process involving the other low-lying states, $S = 3/2$, $S = 5/2$, *etc.*

For exchange coupled copper(II)–nickel(II) pairs, the g values for the copper(II) ion have been assumed to be equal to those measured for the Cu$^{\mathrm{II}}$–M$^{\mathrm{II}}$ pairs, where M$^{\mathrm{II}}$ may be one of the diamagnetic metal ions Zn$^{\mathrm{II}}$, Cd$^{\mathrm{II}}$ or Pd$^{\mathrm{II}}$[27]. The g-values for the copper(II) ion are $g_z = 2.32$, $g_x = 2.06$ and $g_y = 2.08$

With the measured value for the pairs $g_z = 2.14$, $g_x = 2.54$ and $g_y = 2.49$, and the equation

$$g = (4/3)g_{\mathrm{Ni}} - (1/3)g_{\mathrm{Cu}} \tag{7}$$

the calculated values of g for the nickel ion are $g_z = 2.19$, $g_x = 2.42$ and $g_y = 2.39$. The interpretation of this large anisotropy in the g factor for a nickel(II) ion suggests that the nickel ion is in a five-coordinated square pyramidal environment. This implies that the nickel(II) ion enters the host lattice substitutionally, an observation consistent with other experimental results.

When the ions are identical, the second term in the general expression given above is zero and the g factor for the pair is identical to the g factor for an individual ion. On the other hand, extremely strong exchange interactions involving extensive metal–metal covalency or large orbital effects would necessitate certain modifications in this theory.

The electron paramagnetic resonance observed in the triplet state consists of $2I+1$ lines with a hyperfine splitting of $A/2$; A is the hyperfine splitting for the individual ions. Usually more than one set of $2I+1$ lines is observed in a triplet state since an anisotropic spin–spin interaction gives rise to a zero field splitting. For example, a dipole–dipole interaction will remove the three-fold degeneracy in the triplet state so that even in the absence of a magnetic field, the $M_s = 0$ and the $M_s = \pm 1$ levels will have different energies. The application of a magnetic field will cause the energy levels to separate as shown in Fig. 1; the two allowed

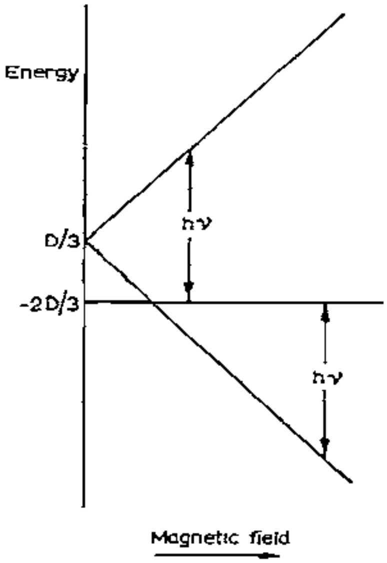


Fig 1. The energy level diagram for a triplet state ($S = 1$) The two allowed transitions are represented by arrows of length h.

transitions $\Delta M_s = \pm 1$ are also shown. The energy of the spin–spin interaction is usually small compared to J and is often comparable to typical microwave energies.

The position of the resonance lines will be a function of the angle between the magnetic field and the high symmetry axis joining the two metal ions; such resonances are expected to follow the usual dipolar expression $(3\cos^2\theta - 1)$. Whether or not the two resonances can be observed in all orientations will be a function of the relative magnitudes of the microwave energy and of the dipole–dipole interaction. If the latter term is sufficiently large, the low field resonance may not be observed in certain orientations. The intensity of the resonance line may also become quite weak at low fields, as observed for copper acetate monohydrate[28].

The analysis of the EPR spectrum of an antiferromagnetic polycrystalline substance with $S = 1$ and with the direction of largest zero field splitting parallel to a principal axis of the g tensor, is only slightly more complicated[29] than that for the case of an $S = \frac{1}{2}$ species, discussed previously by many authors. Kokoszka and Gordon[24], for example, analyze a simple example and include an extensive list of references.

In a sample of randomly oriented axially symmetric crystallites, the probability that the axially symmetric axis is perpendicular to the direction of a magnetic field is highest. Conversely, the probability that this axis of symmetry lies in a direction parallel to that given field direction is the lowest for random orientation. Therefore, the "perpendicular" portion of the spectrum from a polycrystalline sample is considerably stronger than the "parallel" portion.

A schematic illustration of the spectrum obtained from a polycrystalline sample of copper propionate monohydrate and zinc-doped copper propionate monohydrate is shown[29] in Fig. 2. The former species has a spin of 1, and the spectral components associated with it are labeled T. The latter species has a spin of $\frac{1}{2}$ and the salient EPR features are labeled D. The two components, $D_{\parallel}$ and $D_{\perp}$ correspond to the "parallel" and "perpendicular" portions of the $S = \frac{1}{2}$ spectrum

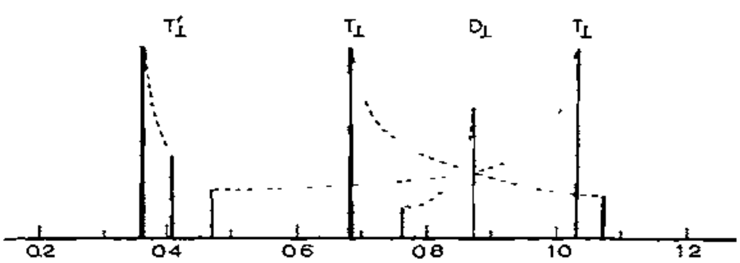


Fig 2 Schematic representation of the polycrystalline EPR spectrum obtained from copper propionate monohydrate (labelled with D's) and zinc-doped copper propionate monohydrate (labelled with D's).

with an anisotropic g tensor ($g_{\parallel} > g_{\perp}$). For an $S = 1$ species with a large zero field splitting, there will be two "parallel" and two "perpendicular" sets of lines. The two lines labeled $T_{\perp}$ are the perpendicular components of the $S = 1$ spectrum; it is assumed that the g tensor for the $S = 1$ species has the same values as for the $S = \frac{1}{2}$ species. Similarly, the two lines labeled $T_{\parallel}$ are the parallel components of the $S = 1$ polycrystalline spectrum. The resonances labeled with primes are associated with the $\Delta M = 2$ transitions. As a first approximation, the g value for the parallel portion of the spectrum may be related to Planck's constant h, the Klystron frequency ν, the Bohr magneton β and the average value of the parallel field components, H_A, by the expression:

$$h\nu = g\beta H_A$$

Experimentally, the derivative of the absorption line is usually recorded. The perpendicular portion of the copper propionate spectrum which occurs at about 0.1 Tesla (10^5 gauss) is shown in Fig. 3.

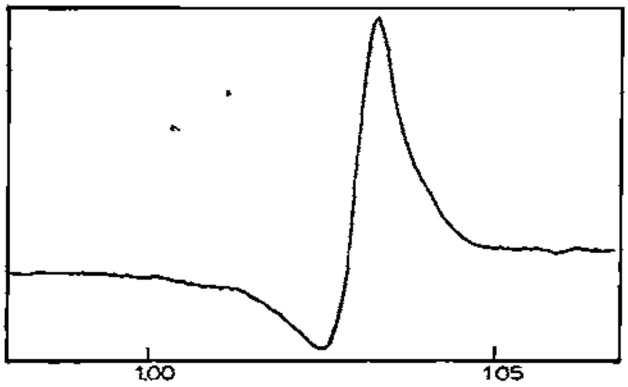
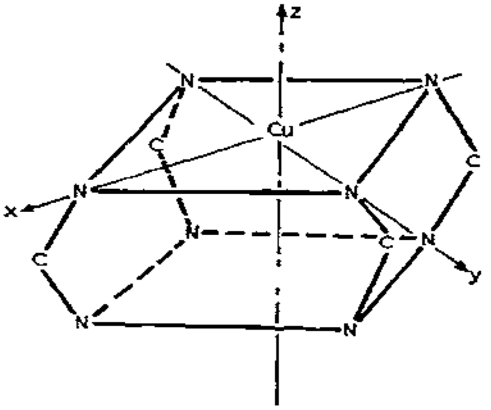


Fig 3. Experimental EPR spectrum of the perpendicular component of copper propionate which occurs at about 1 Tesla.

A number of complexes are known to have structures similar to that of copper acetate[27]. These include not only the other copper alkanoates, the chromium[30], and molybdenum acetate complexes[31], but also dimeric copper adenine complexes[32]. A schematic representation of the latter complex is shown in Fig. 4 and its polycrystalline EPR spectrum[33] is shown in Fig. 5. The dominate spectral features include the two perpendicular components (0.37 and 0.25 Teslas) and the $\Delta M = 2$ spectral region (0.3 Teslas)[29]. The parallel portions are of much lower intensity and the high field parallel portion is shown in Fig. 6. Magnetic parameters obtained from such spectra furnish data with a precision comparable to that for single crystal data.

Empirical deviations from the aforementioned elementary equations are often observed and their sources are manifold. If the magnetic data are not ade-



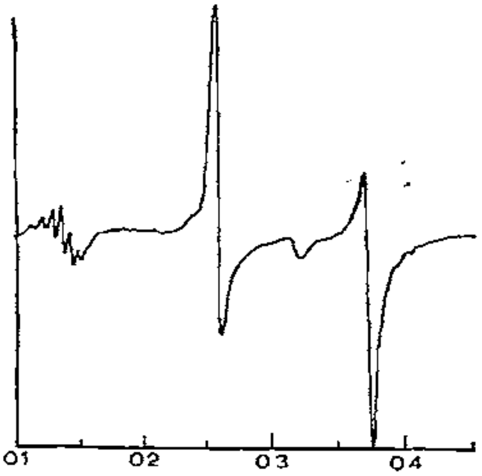


Fig 4. A schematic representation of a dimeric copper adenine complex.

Fig. 5. The polycrystalline EPR spectrum of a dimeric copper adenine complex

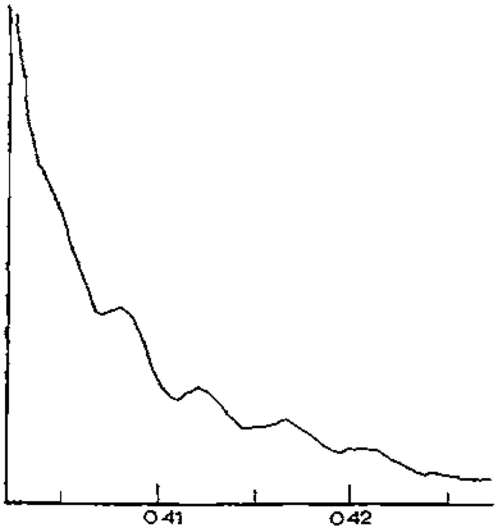


Fig 6. The high field parallel portion of the polycrystalline EPR spectrum of a dimeric copper adenine complex.

quately described by the inclusion of the isotropic Heisenberg interaction and by an anisotropic g tensor in the spin Hamiltonian, then an additional term, the anisotropic spin–spin coupling expression, may be required. The direct dipolar interaction must often be included[34–36] as well as orbital effects which are quite important in many systems[37–40].

Furthermore, for two ions, each with a spin greater than one-half, or for cases with more than two ions in the cluster, it is necessary to include other spin–spin interaction terms in the Hamiltonian[14,41–44]. Vibronic effects can also be important in some cases[45]. For some complexes, J is not very large with respect to the other terms in the dimeric spin Hamiltonian[46]; and a somewhat different analysis must be employed. The magnetic electrons centered primarily in the orbitals of one metal ion may be transferred into the orbitals of a neighboring second metal ion. This supertransferred hyperfine field (STHF) has been observed in a number of cases[47–49].

All of these effects must be considered in order to present a plausible and reasonable interpretation of the empirical results of dimeric complexes, and in order to elucidate the nature of the metal–metal, metal–ligand, and metal–ligand–metal bonding in these complexes. A more-detailed discussion of several of these effects is now in order.

(ii) Zero field splitting

In a complex which possesses an odd number of electrons, Kramer's theorem dictates that the ground state has at least a two-fold degeneracy[24]. However, when the total number of magnetic electrons is even, then the degeneracy of the ground state may be removed in accordance with the Jahn–Teller effect. The terms in the spin Hamiltonian which analytically represent this phenomenon are usually defined as D and E. As an example, consider the spin Hamiltonian for an $S = 1$ species with $E = 0$

$$\mathscr{H} = g\beta\bar{H}\cdot\bar{S}+DS^2$$

If the magnetic field is along the z axis, then the energies of the three spin states $\bar{S} = 1$, $M_s = 1$ ($|1, 1\rangle$); $\bar{S} = 1$, $M_s = 0$ ($|1, 0\rangle$), and $\bar{S} = 1$, $M_s = -1$ ($|1,-1\rangle$) are

$|1, 1\rangle$ $g\beta H+D$
$|1, 0\rangle$ 0
$|1,-1\rangle$ $-g\beta H+D$

The two transitions from the $|1,-1\rangle$ state to the $|1, 0\rangle$ state and from the $|1, 0\rangle$ state to the $|1, 1\rangle$ state are described by the selection rule $\Delta M = 1$. These transitions occur at energies $h\nu_1 = g\beta H_1-D$ and $h\nu_2 = g\beta H_2+D$ respectively. In typical experiments, the microwave frequency is held constant, $\nu_1 = \nu_2$, and the value for D is furnished by the expression

$$D = \frac{g\beta(H_1-H_2)}{2} \tag{8}$$

For systems in which $E \neq 0$, the term $E(S_x{}^2+S_y{}^2)$ must also be included in the spin Hamiltonian. The magnitude of E may be associated with the degree to which the zero field splitting has deviated from axial symmetry. Normally, D is much larger than E.

The origin of the observed zero field splitting may be attributed to the following interactions: (1) the dipolar interaction[1,14,18,34,49] (2) the antisymmetrical spin–spin interaction[50,51], (3) the single ion zero field splitting[12], and (4) the isotropic exchange interaction itself[12,18,52].

The magnitude of the dipolar interaction term, determined primarily by the coulomb (or exchange) and spin–orbit interactions, is $(\lambda/\Delta)^2 J$; λ is the spin–orbit coupling constant, Δ is the energy separation from the ground state to an appropriate excited state and J is the isotropic exchange parameter. As a first approximation, this contributing term is expected to increase with atomic number within any of the transition periods, since the spin–orbit coupling increases in that fashion.

The magnitude of the dipolar term is also determined by the dipole–dipole interaction, but to a lesser extent. This interaction between the electronic spins will give rise to a splitting in the triplet state. The magnitude of this interaction, expressed as a function of the magnitudes of the magnetic moments μ_1 and μ_2 and as a function of the separation between these spins may be estimated on the basis of a classical expression $\mu_1\mu_2/r^3$. For two ions separated by about 2.5Å, as in the case of the copper alkanoate system, the direct dipole–dipole interaction energy is about 0.2 cm^{-1}.

Terms have been introduced which represent combinations of these interactions. Van Vleck[14,49], for example, introduced the term "pseudodipolar" interaction, which is the sum of an isotropic exchange interaction together with a dipolar interaction. The most general biquadratic form of this interaction for pairs of identical and isotropic g values is

$$-J\bar{S}_1 \cdot \bar{S}_2 + C\left[\bar{S}_1 \cdot \bar{S}_2 - \frac{3(\bar{S}_1 \cdot \bar{r})(\bar{S}_2 \cdot \bar{r})}{r^2}\right] \tag{9}$$

Also, Bleaney and Bowers[1] derived an expression which represents the combined effect of the crystalline field and the exchange interactions. Their expression for the copper alkanoate system, takes the form

$$D = \tfrac{1}{2}[4J_1(\lambda/\Delta E_1)^2 - J_2(\lambda/\Delta E_2)^2] \tag{10}$$

ΔE_1 and ΔE_2 are of the order of 10 Dq, and J_1 and J_2, the exchange integrals in excited configurations, are believed to be of the same order of magnitude as the J value in the ground state[1,29].

The second term in (9), the antisymmetrical spin–spin interaction term, can also produce a zero field splitting. Because the antisymmetrical part of the general binuclear spin–spin coupling term is the cross product of two spins[16], the contribution of this term to the on-diagonal elements of the energy matrix is zero. Thus, the antisymmetrical term will add no first order contribution to the Hamiltonian.

A more complete discussion of antisymmetrical exchange interactions follows in a later section; only the special case where d_x and d_y are equal to zero will be considered here. Note that $\vec{d} \cdot \vec{S}_1 \times \vec{S}_2$ connects $|0, 0\rangle$ and $|1, 0\rangle$[25]. The presence of d_z in the energy matrix accounts for an interaction between these levels which possesses an energy of approximately d^2/J. Since $|d| \simeq \lambda/\Delta J$, the term d^2/J equals $(\lambda/\Delta)^2 J$.

The usual second order crystal field terms are required in the spin Hamiltonian if one or both of the two ions contains more than a single unpaired electron, namely, if one of the ions is in a triplet or higher state. This interaction, which is also represented by a bilinear spin–spin coupling term, can also contribute to the observed zero field splitting for the exchange-coupled ions. Similar considerations apply to cases where there are triads or larger clusters[11,12].

Since the antisymmetrical spin–spin interaction term may be either positive or negative, the contribution of this term may either increase or decrease the zero field splitting[50–51]. The measured zero field splitting will be a combination of all of the previously mentioned effects. Also, the separation of the antisymmetrical exchange contribution from the other contributing terms may not be possible. It should be noted, however, that the antisymmetrical part contributes to the zero field splitting only if the ions are not related by a center of symmetry.

(iii) Supertransferred hyperfine fields (STHF)

In a recent series of papers, Owen, Taylor, Simanek, Huang and Orbach[47,48] have discussed a mechanism by which the hyperfine field at the nucleus of a paramagnetic metal ion is altered due to the presence of a neighboring metal ion. An elementary description of this phenomenon can be discussed without recourse to excessive mathematical details.

Consider a linear chain of three ions: a paramagnetic metal ion M, an intervening diamagnetic ligand L, and a diamagnetic metal ion M′. Through covalency and overlap mechanisms, the metal ion M transfers a portion of its unpaired spin density to L and thence to M′. If M′ is replaced by another paramagnetic ion M, identical to the first, then the hyperfine field at the nucleus of each of the metal ions will be the original hyperfine field A plus the supertransferred hyperfine field (STHF) A', which is the original hyperfine field at M′.

This process is schematically illustrated in Fig. 7, where the length of the arrows represents the electronic spin density in the outer orbitals of the atoms in question. For simplicity, the measured value of A is assumed to be due to the isotropic Fermi contact interaction and is proportional to the electronic spin density at the nucleus.

Thus, the net electronic spin density at the metal ions M in the lower portion of the figure is greater than that in the upper portion of the figure. If the electronic spin of each of the metal ions M is $\frac{1}{2}$, then the measured value of the hyperfine

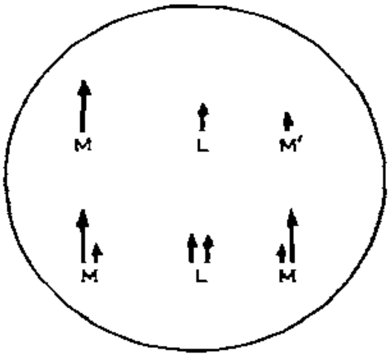


Fig 7. A schematic representation of the origin of the STHF.

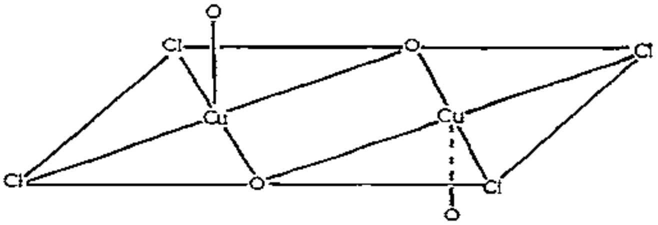


Fig 8 A schematic representation of $Cu(pno)_2Cl_2$

field in the triplet state of the dimeric complex with a STHF is $\frac{1}{4}(A+A')$ rather than $\frac{1}{2}A$.

Although this simple example serves to illustrate a mechanism for the origin of the STHF, it is not complete since other mechanisms are possible whereby the supertransferred field occurs with a sign opposite to that of the original field[48]. Similarly, orbital effects can influence the hyperfine field[37-40].

The STHF has been observed in dimeric coordination complexes by Duerst and Kokoszka[49]. The dimeric copper(II) complex dichlorobispyridine-*N*-oxide copper(II), $[Cu(pno)_2Cl_2]$ has been doped with nickel(II), zinc(II) cadmium(II), lead(II) and barium(II) ions. A schematic representation of this molecule is shown in Fig. 8. In this complex, the hyperfine field measured at the copper nucleus for the Cu^{II}–M^{II} pairs, where M = Zn^{II}, Cd^{II}, and Pb^{II}, was identical. This result indicates little effect due to size, electronegativity, *etc.*, of the dopant ion. For Cu^{II}–Ni^{II} pairs, with the nickel ion in a paramagnetic state, a value of $A/3$ is anticipated; A is the value obtained in the Cu^{II}–M^{II} pairs. Experimentally, a value of about 15% lower than $A/3$ is observed. For Cu^{II}–Ba^{II} pairs, the hyperfine field is about 10% higher than A. These results have been rationalized in terms of the STHF mechanism and the availability of open orbitals on the dopant metal ion[49]. Such data can provide considerable insight into the electronic distribution in dimeric species and concomitantly may be useful in discussing their physical properties. It might be mentioned that no unambiguous STHF has been found in the dimeric alkanoate complexes[29].

(iv) Antisymmetrical exchange

An examination of the effects of the antisymmetrical exchange interaction $d\cdot(S_1\times S_2)$ on the magnitude of the magnetic parameters is worthwhile. For illustrative purposes, the case of two $S=\frac{1}{2}$ ions with different isotropic g factors will be considered[51,27]. The spin Hamiltonian for this system is

$$g_1\beta\bar{H}\cdot\bar{S}+g_2\beta\bar{H}\cdot\bar{S}+\bar{d}\cdot(\bar{S}_1\times\bar{S}_2)+J\bar{S}_1\cdot\bar{S}_2 \tag{11}$$

If the magnetic field is defined along the z direction, then the energy matrix is

$$\begin{array}{c|cccc} & |0,0\rangle & |1,1\rangle & |1,0\rangle & |1,-1\rangle \\ \hline |0,0\rangle & -(3/4)J & \dfrac{d_y-id_x}{2\sqrt{2}} & \dfrac{(g_1-g_2)\beta H}{2}+\dfrac{id_z}{2} & \dfrac{d_y+id_x}{2\sqrt{2}} \\ |1,1\rangle & \dfrac{d_y+id_x}{2\sqrt{2}} & \dfrac{J}{4}+\dfrac{(g_1+g_2)\beta H}{2} & 0 & 0 \\ |1,0\rangle & \dfrac{(g_1-g_2)\beta H}{2}-\dfrac{id_z}{2} & 0 & \dfrac{J}{4} & 0 \\ |1,-1\rangle & \dfrac{d_y-id_x}{2\sqrt{2}} & 0 & 0 & \dfrac{J}{4}-\dfrac{(g_1+g_2)\beta H}{2} \end{array} \tag{12}$$

The contributions from the three components of the antisymmetric coupling tensor appear only in the off-diagonal elements of this matrix. This term describes the coupling between the three levels of the triplet state and the singlet ground state.

Wagner, Schumacker and Friedberg[50] have found evidence for this type of exchange interaction between copper(II) pairs in $Zn(HCOO)_2\cdot 2H_2O$. Also, Seehra and Castner[53] have found an unusual linear dependence of the linewidth in $Cu(HCOO)_2\cdot 4H_2O$ in the temperature range 70 to 270 °K, and attribute this behavior to a phonon modulation of the antisymmetrical exchange term.

Recently, Duerst and Kokoszka[27] have observed a deviation of the principal axes of the g tensor of copper(II)–nickel(II) exchange coupled pairs from that of copper(II)–M^{II} pairs, where M is a diamagnetic ion such as zinc, cadmium or lead. This deviation may be attributed to interactions which occur only in systems which lack a center of symmetry. A simple semi-classical argument is proposed by these authors which may account for the experimental data

The isotropic term $J(\bar{S}_1\cdot\bar{S}_2)$, which represents the tendency of the spins to align parallel or antiparallel to each other, is usually assumed to be the largest term in the spin Hamiltonian The antisymmetrical term $\bar{d}\cdot(\bar{S}_1\times S_2)$ has its lowest energy value when the spins are perpendicular to each other. The $J\bar{S}_1\cdot\bar{S}_2$ term varies as $\cos\theta$, whereas the $\bar{d}\cdot(\bar{S}_1\times\bar{S}_2)$ term varies as $\sin\theta$ (θ is the angle between the two spin directions) If, (d is the magnitude of $\bar{d}$) the energy of the spin system may be crudely approximated as

$$E \sim J\cos\theta + d\sin\theta$$

the minimum energy is

$$\frac{\delta E}{\delta\theta} = 0 = -J\sin\theta + d\cos\theta \tag{13}$$

or, $\tan\theta = d/J$.

Since d is of the order of magnitude[16] of $(\lambda/\Delta)J$, $\tan\theta \approx \lambda/\Delta$. For first row transition metal ions, the spin–orbit coupling constant λ is typically of the order of 100 cm^{-1}, and the central field splitting of the ion Δ is of the order of 10,000 cm^{-1} θ is thus approximately one degree.

(v) Higher order exchange interactions

Generally, the assumption of a simple cosine coupling between spins is sufficient to account for the empirical results. Harris and Owen[41] were the first workers to report a case where this description is inadequate and they proposed a modification in the simple theory to account for their experimental data.

The coupled system of $\mathrm{Mn^{II}}$ ions doped into MgO can be described by the spin states $S = 1, 2, 3, 4$ and 5; Harris and Owen[41] observed resonance in the $S = 1, 2, 3$ and 4 levels. The simple coupling scheme predicts that the spacing between adjacent levels is given by

$$\Delta E = JS$$

Since the energy level separations can be obtained by examining the intensity of the spectral lines as a function of temperature, it is possible to obtain four values for the exchange integral J that should be identical in the absence of additional interactions. However, the observed exchange integral values are not equivalent.

Thus, a modified interval rule which correctly correlates the experimental data with the calculated values, based on an exchange Hamiltonian of the form

$$\mathscr{H}_{\mathrm{ex}} = J(\bar{S}^{\mathrm{a}} \cdot \bar{S}^{\mathrm{b}}) - j(\bar{S}^{\mathrm{a}} \cdot \bar{S}^{\mathrm{b}})^2$$

was proposed. The ratio of the magnitudes of the two exchange parameters $j/J \approx 0.05$ is consistent with Anderson's[15] theory of superexchange. That the agreement of the calculated J and j values with the experimental results is quite satisfactory suggests that the contribution from higher order exchange terms must be very small.

The study of the magnetic and thermal behavior of $\mathrm{Cr(CH_3COO)_6OCl \cdot 5H_2O}$ is another example of a system in which the introduction of a higher order exchange coupling term into the spin Hamiltonian may be used to represent the data[54,59]. In this substance, the three chromium atoms are located at the corners of an equilateral triangle and the total exchange Hamiltonian should reflect this symmetry. Uryû and Friedberg[42] have accounted for the low temperature specific heat and susceptibility behavior of this material including the biquadratic term

$$J[(\bar{S}_1 \cdot \bar{S}_2)(\bar{S}_2 \cdot \bar{S}_3)+(\bar{S}_2 \cdot \bar{S}_3)(\bar{S}_3 \cdot \bar{S}_1)+(\bar{S}_3 \cdot \bar{S}_1)(\bar{S}_1 \cdot \bar{S}_2)] \tag{14}$$

in the spin Hamiltonian.

Ikeda, Kimura and Uryû[44] have found evidence for magnetic susceptibility biquadratic exchange in binuclear chromium complexes, and Kobayashi, Tsujikawa and Kimura[43] have obtained susceptibility data from a quadrinuclear complex of chromium which require the inclusion of a similar term in the spin Hamiltonian in order to account for the empirical results.

C EMPIRICAL REPORTS

(i) Direct spectroscopic determinations of J

Direct observation of transitions between the various multiplets in exchange coupled pairs of ions is of considerable interest, such transitions would be of the order of magnitude of J and, therefore, would be observed in the infrared region for some systems

In a system of two $S = \frac{1}{2}$ ions which are exchange coupled, these transitions would not be expected, since one energy level is symmetrical ($S = 0$) and the other levels are antisymmetrical ($S = 1$). Singlet–triplet transitions are usually forbidden. However, three recent studies on diamagnetic complexes containing a high concentration of paramagnetic ions do, indeed, report a direct observation of the J value in the far infrared region.

In 1967, Moser, Zingg, Steffen and Kneubuhl[55] reported a number of transitions in Cr^{3+}, V^{3+}, and Ti^{3+}-doped Al_2O_3. In a comprehensive paper, Baltes, Moser and Kneubuhl[56] discuss the symmetry properties of exchange coupled pairs and the relationship between these symmetry properties and the selection rules for pair spectra in ruby. For pairs of high symmetry (D_{3h} or D_{2h}) the selection rules are $\Delta S = 0, \pm 2$; thus, only a few lines are predicted for these pairs. However, for pairs with low symmetry (C_2 or C_i), there are no restrictions on ΔS, so a larger number of transitions are predicted and all have been observed[57].

Platt and Martin[58] have studied pairs and triads of Ir^{4+} ions in $(NH_4)(Ir, Pt)Cl_6$. The magnetic parameters had previously been determined by Griffiths, Owen, Park and Partridge in an earlier study[9]. Platt and Martin's value for J of 5.34 ± 0.08 cm^{-1}, determined by a direct spectroscopic method, is considerably more accurate than a value for J of 5.2 ± 0.8 cm^{-1}, determined from the EPR measurements. However, the parameters D and E, determined by EPR, are the preferred values. The samples were sufficiently concentrated so that the ratio of triads to isolated pairs is one to seven, assuming a random distribution of doped ions. The isotropic Hamiltonian

$$\mathscr{H} = J(\bar{S}_1 \cdot \bar{S}_2 + \bar{S}_2 \cdot \bar{S}_3 + \alpha \bar{S}_1 \cdot \bar{S}_3)$$

describes the open triad structure for α much smaller than unity; the closed configuration is an equilateral triangle for $\alpha = 1$. Each of these two types of triads has an energy level at 3/2 J. With $J = 5.34\ \text{cm}^{-1}$, transitions in triads might be expected at about $8\ \text{cm}^{-1}$; a band centered in this region was indeed observed and tentatively assigned to the triads. Harris and Owen[10] have also studied triads of Ir^{4+} in $K_2(Ir, Pt)Cl_6$ and in $NH_4(Ir, Pt)Cl_6$ by electron paramagnetic resonance.

Belorsky, Ng, and Phillips[60] observed the far infrared spectrum of Co^{2+} ion pairs in MgF_2, and measured the magnetic field dependence of these lines. The isotropic component of the exchange splitting was found to be about $9.8\ \text{cm}^{-1}$, while the anisotropic contribution was almost $0.2\ \text{cm}^{-1}$. In addition, transitions attributed to clusters of exchange coupled triads were also observed.

(ii) Small J values

When the level of doping of a paramagnetic ion into a diamagnetic host lattice is sufficiently high, satellite lines may be observed about a primary monomeric resonance signal One recent study of the EPR spectra of weakly coupled transition metal ions has appeared in which several satellite lines are observed.

Meredith and Gill[46] have studied the EPR spectra of nearest-neighbor exchange coupled Cu^{2+} ions doped into a potassium zinc sulfate lattice; the copper(II) to zinc(II) ratio is in the range 0.01 : 0.05. The term

$$\bar{S}_1 \cdot A \cdot \bar{I}_1 + \bar{S}_2 \cdot A \cdot \bar{I}_2$$

which is not invariant with respect to exchange of S_1 and S_2, describes the coupling between the singlet and triplet states. The position of the satellite resonance lines depends on J, and may be used to evaluate J at a single temperature[35]

The Hamiltonian which describes the Cu^{2+}–Cu^{2+} pair spectrum is

$$\mathscr{H} = E_1 S_{1z} + E_2 S_{2z} + (J+D) S_{1z} S_{2z} + \tfrac{1}{2}(J - \tfrac{1}{2}D)(S_{1+}S_{2-} + S_{1-}S_{2+}) \qquad (15)$$

E_1 and E_2 are the energies of two single ion transitions, the spectrum consists of "strong" and two "weak" transitions in the pair spectrum at energies

$$\tfrac{1}{2}(E_1 + E_2) \pm \tfrac{1}{2}\{(J+D) - \alpha(J - \tfrac{1}{2}D)\}$$

In this equation, α is equal to $\pm\,[1 + \{(E_1 - E_2)/(J - \tfrac{1}{2}D)\}^2]^{\frac{1}{2}}$. The addition or subtraction of the square root term corresponds to the strong or weak transitions respectively. Meredith and Gill found that the exchange interaction is ferromagnetic with a magnitude of $0.034\ \text{cm}^{-1}$, a value which is somewhat smaller than 0.045 cm^{-1}, observed in a temperature study of the EPR line intensity[60] and also by a specific heat study[61].

(iii) Recent EPR studies

Consideration of the symmetry properties of coordination complexes has been extremely helpful in understanding their physical behavior. Baltes, Moser and Kneubühl[56] also discuss the point groups for exchange coupled pairs of metal ions. While the discussion in this paper focuses primarily on identical exchange coupled ions artifically doped into diamagnetic host lattices, the treatment applies equally as well to many of the naturally occurring complexes, particularly since many of these complexes contain identical ions. An analysis such as this based on symmetry relations is especially significant in that it indicates a minimum number of parameters which must be specified. Baltes, Moser and Kneubühl[56] discuss the theory of exchange coupled pairs grouped into two major divisions: (1) metal ions interchanged by the symmetry operations and (2) those which are not. The antisymmetrical exchange interaction is also discussed and for identical spins the antisymmetrical component of the spin–spin interaction is demonstrated to be zero through the use of two coordinate systems, each with its origin located at the position of one of the metal ions.

Lohr[45] has discussed the static and dynamic aspects of the Jahn–Teller effect in binuclear copper (II) complexes, in which the copper atoms are six-fold coordinated and share one or more ligands. Electron paramagnetic resonance data obtained by Borcherts, Kanzaki and Abe[62] on the binuclear species formulated as $Cu_2Cl_{11}{}^{7-}$ forms the basis for Lohr's discussion. This complex is formed by the replacement of two Na^{I} ions by two Cu^{II} ions along the (100) direction in NaCl. A detailed analysis is presented for thirteen types of structures consisting of joining, elongated and/or compressed octahedra, which may be formed when a pair of $CuCl_6{}^{4-}$ units share a vertex. The g values for all thirteen types of pairs are approximated by averaging the g values of each of the two monomers with proper regard to the relative position of the axis of elongation.

The electron paramagnetic resonance of Cr^{3+} ions in ruby has received considerable attention over the years and the recent work of Shelekhin, Voinov and Berkovskii[63] is another valuable addition to the literature. These workers have identified spectral lines which may be attributed to exchange coupled pairs of metal ions. A zero field splitting parameter of about 0.09 cm^{-1} was measured and J was estimated to be about 350 cm^{-1}. Only rough estimates of the line intensities were possible because overlapping lines precluded accurate intensity measurements. The role of relaxation processes in intensity determinations is also discussed.

Imbush and Graifman[64] have observed electron paramagnetic resonance in the excited optical state of exchange coupled chromium pairs in ruby. In their optical detection technique, the fluorescence of the species in question was monitored while the microwave power changed the electronic population in the excited state. The authors found evidence that when an ion of the pair is excited, it is coupled antiferromagnetically to the fourth nearest neighbor, while both ions are ferromagnetically coupled in the ground state.

Saunders, Standley and Wilson[65] have observed no significant differences in the zero field splitting, linewidths, or intensities of the Cr–Cr pair lines in the spectra of vapor-phase, Verneuil or fluxed-melt ruby samples.

The EPR of chromia alumina mixtures calcined between 500 and 1400 °C were studied by Poole and Itzel[66] in the temperature range 125 to 550 °K. Though ruby samples, which have a low chromium content, are paramagnetic, bulk chromia is antiferromagnetic. With larger concentrations of Cr_2O_3 in the sample (>50 mole %) these workers found that the Neel point of the 1400 °C series is fairly sharp, indicating that all of the Cr^{3+} spins are essentially coupled together. Indeed, the authors suggest that the Cr^{3+}–O–Cr^{3+} species are superexchanged coupled throughout the sample. As the chromium content decreases, the sharpness of T_N decreases, which are attributed to the replacement of Cr^{3+} ions by Al^{3+} ions, which perturb the uniformity of the magnetic coupling Below a certain critical concentration of chromium, the Cr^{3+} spins form clusters of Cr^{3+} ions strongly coupled to each other and weakly coupled to the other clusters.

Parrot and Roget[67] have attempted to assess the influence of an electric field on the EPR spectra of pairs of Cr^{3+} ions in ruby and have devised a method which permits the characterization of the observed transitions and facilitates their identification. The majority of the peaks observed when the crystal is subjected to a strong electric field may be associated with the 4th, 6th and 7th nearest neighbors pairs, assuming that $J \gg D$; no resonance signal is found due to 1st, 2nd or 3rd nearest neighbor pairs.

A precise determination of the hyperfine structure of synthetic ruby crystals with a chromium content less than one percent was carried out by Gunser, Hille and Knappwost[68]. The majority of the approximately fifty transitions observed in the field strength interval between 6 and 10 kOe were accounted for by involking the assumption of exchange coupled chromium pairs. Lack of transitions ascribed to nearest and next-nearest neighbor pairs validates the assumption of a coupling of chromium ions through an indirect superexchange mechanism by way of bridging oxygens.

Bené and White[69] have studied the EPR spectrum of chromium doped into single crystals of BiL_3 in concentrations ranging from 0.25% to 20%. Cr^{2+} single ion, Cr^{3+} ions and Cr^{3+}–Cr^{3+} pairs transitions were observed. The ionic interaction of Cr^{3+} pairs is believed to be intraplanar.

More recently, Trapp, Smith and Shyr[70] have reported the EPR spectrum of pairs of Mn^{2+}, Co^{2+} and Ni^{2+} in $CdCl_2$. The intralayer interactions were found to be of the order of 10 cm^{-1} and ferromagnetic, whereas the interlayer interaction is of the order of 1 cm^{-1} and is antiferromagnetic. The crystal structure consists of triangular net layers of cations separated by two triangular net layers of anions.

Ryabchenko[71] examined the paramagnetic resonance of Cu^{2+} ions in $CdCl_2$ and concluded that the exchange interaction which occurs between the nearest Cu^{2+} neighbors is isotropic.

Zaripov, Kropotov, Livanovna, and Stepanov[72] have identified transitions in the spectrum of titanium-doped CaF_2 which may be described by a spin Hamiltonian with g values of 1.909 and 1.975 for $g_{\parallel}$ and $g_{\perp}$ respectively. The observed transitions represent exchange coupled pairs of Ti^{2+} ions whose ground state is characterized by the maximum multiplicity $S = 2$.

In a series of papers, Kask and co-workers[73–75] have investigated the nature of the interaction of Nd^{3+} ions doped into CaF_2 and SrF_2. In the Nd^{3+}-doped CaF_2 system, the non-dipole nature of the interaction may involve magnetic and exchange interactions of multipoles of higher order than a dipole. An additional contribution to the interaction energy of coupled Nd^{3+} ions, which is dependent on the magnitude of the external field, is a phonon exchange mechanism[74]. Kask and Kornienko's[75] analysis of Nd^{3+}-doped SrF_2 included an angular dependence study and a comparison of their results with the similar spectral results obtained from the CaF_2 lattice. The orthorhombic spectra of the Nd^{3+}-doped SrF_2 crystal consisted of twelve absorption lines corresponding to six different orientations of an Nd^{3+}–Nd^{3+} pair; the doubling of the number of lines is due to the spin–spin interaction between the ions in a pair. That the non-dipole interaction of the two crystals CaF_2 and SrF_2 differs not only in magnitude but also in nature, is indicated by the change in the sign of the magnetic parameters[75]. The predominant interaction between Nd^{3+} ions in CaF_2 is almost non-existent in SrF_2 because of the increase in the distance between the ion pairs

Reid, Perkins and Sienko[76] have examined the magnetic, susceptibility, X-ray, EPR, optical absorption and Mössbauer spectra of the isomorphous series $NaSc_{1-x}Fe_xTiO_4$ as a function of progressive replacence of Fe^{3+} for Sc^{3+}. When the Fe^{3+} concentration is low, a strong band at 28,600 cm^{-1} is observed in the optical reflectance spectrum As the concentration increases, this band becomes weaker and a new band at 24,000 cm^{1} is observed. With increasing concentration the sharp EPR line at $g = 4.27$ is replaced by a broad line at $g = 2.00$. The data are interpreted in terms of isolated Fe^{3+} ions at low concentrations and super-exchange coupled oxygen bridged Fe^{3+} pairs in distorted octahedral sites at higher concentrations. Mulay and Hofmann[77] studied the EPR spectra of a number of Fe^{3+} 1:10-phenanthroline complexes prepared with various iron salts, many of which are binuclear.

The studies of Tapscott and Belford[78] demonstrate quite effectively the use of electron paramagnetic resonance in coordination chemistry. Two anionic acid complexes of VO^{2+} in aqueous solution were examined, one active and the other racemic. The two complexes are dimeric and the racemic complex exhibits a hyperfine splitting due to two equivalent vanadium nuclei. The relative intensities of the fifteen lines of the spectrum, follow the 1:2:3:4:5:6:7:8:7:6:5:4:3:2:1 pattern and the splitting is about one-half that found in monomeric vanadium complexes. The exchange coupling is believed to be less than 50 cm^{-1}. The authors propose structures for the two complexes and a comparison of the magnetic and optical behavior of these two substances is presented. Dunhill and Smith[79], who analyzed the EPR spectra of vanadyl citrate and tartrate chelates, have expressed some doubt concerning the detailed analysis of Tapscott and Belford[78]. While it seems clear that under certain conditions dimers do form, the hyperfine patterns are somwhat more complicated than a simple analysis based on a dimeric model would indicate. Dunhill and Symons[80] covering this work somewhat further here found additional relatively weak lines in the EPR spectrum which are consistent with the dimeric model. These studies were carried out at low pH. On the other hand, Belford, Chasteen, So and Tapscott[81] have investigated the EPR of a number of vanadyl–hydroxycarboxylate complexes in neutral liquid as well as in frozen solutions. In addition a single crystal study of vanadyl *d,l*-tartrate was completed. The data for the latter sample are: $g_{\parallel} = 1.953$, $g_{\perp} = 1.982$, $A_{\parallel} = 72.3 \times 10^{-4}$ cm^{-1}, $A_{\perp} = 21.3 \times 10^{-4}$ cm^{-1} and $D = 338 \times 10^{-4}$ cm^{-1}. Virtually identical data were obtained from the frozen solutions Further the half field "forbidden" transitions were also observed. A simple dipolar interaction satisfactorally accounts for the zero-field splitting[81].

Dall'Olio, Dascola and Varacca[82] have examined the EPR spectra of a number of polycrystalline chloro-substituted copper acetate complexes In the anhydrous tri- and dichloro-substituted complex, only isolated ions appear to be present, while the hydrated copper acetate and monochloroacetate complexes exhibit characteristics typical of both types of spectra. It seems likely that in such complexes there exists a mixture of both $S = \frac{1}{2}$ and $S = 1$ species with nearly the same chemical composition.

A detailed analysis of *X*-band spectra of $S = 1$ species in polycrystalline complexes has been presented by Wasson, Sbry and Trapp[83]; these investigators studied the copper(II) cyanoacetate and copper(II) acetate monohydrate complexes and derived their corresponding magnetic parameters. A general method for obtaining the magnetic parameters of dimeric copper compounds from EPR powder spectra is presented. Since the magnitude of the zero field splittings is somewhat larger than the microwave energy, all of the spectral components were not observed. In addition, some doubt exists as to the viability of assigning the low field component as the z component. In single crystal studies at *X*-band frequencies the intensity of the observed low field z component is not comparable to the high field peak. Additional studies must be undertaken on polycrystalline complexes before this problem is resolved.

A more complete analysis of the spectra of $S = 1$ ions in polycrystalline complexes has been presented by Kokoszka, Linzer and Gordon[84], who analyzed the spectrum of copper propionate monohydrate at *X*-band and *K*-band frequencies. In these studies all of the spectral components were observed and the magnetic parameters were overdetermined.

Goodgame and Price[85] first reported the EPR spectrum of a copper(II) adenine complex; in this case the zero field splitting was sufficiently small so that the entire spectrum could be observed at *X*-band frequencies. However, because of signal-to-noise problems, the z components were not observed. Duerst, Baum and Kokoszka[30] have resolved all of the spectral components for the same complex as well as that for the copper adenine perchlorate complex. An example of the hyperfine pattern is shown in Fig. 6: some of the hyperfine components of the parallel spectrum that are shown overlap with the perpendicular spectrum

Lewis, Mabbs, Royston and Smail[86] have studied the magnetic properties of several copper carboxylate complexes by magnetic susceptibility and EPR methods. The g values were determined from the EPR data while the J values were derived from the susceptibility studies. Several interesting observations concerning substituent effects are discussed. The observed low field absorption is assigned as a parallel peak; an assignment which is open to some question for reasons outlined above. In many cases, complexes which were apparently analytically pure produced EPR spectra which contained evidence of monomeric impurities. The stereochemistry of these monomers could not be inferred from the EPR data but their magnetic parameters differed from the dimeric complexes. Hyde and coworkers[87] have noted similar effects.

An electron paramagnetic resonance investigation of polycrystalline copper(II) benzoate was undertaken by Herring, Thompson and Schwertfeger[88] at 9.1 and 12.0 GHz, yielding a $2J$ value of 333 cm^{-1}. Most of the magnetic parameters determined for the benzoate are similar to those obtained for the copper acetate homologue; however, the E value is twice as large as that for the acetate, which suggests that the benzoate exhibits a greater deviation from tetragonal symmetry.

Yablokov *et al.*[89] have studied copper(II) benzoate complexes of the type $(XC_6H_4CO_2)_2Cu$ and $(XC_6H_4CO_2)_2CuY$ by electron spin resonance, where X may be *p*-Br, *m*-NO_2, *o*-NO_2 or *m*-I and Y may be pyridine, quinoline, benzoic acid or t-butylalcohol. Variations in the magnetic parameters were attributed to differences in the charge distribution on the copper atom.

Yablokov *et al.*[90] have also studied the polycrystalline ESR spectra of copper succinate and copper orthophthalate and surmised that these systems consist of exchange coupled pairs of copper atoms. However, copper maleate and copper terephthalate exhibit no exchange coupling. The authors suggest that in these carboxylic acid copper complexes, in which the carboxyl groups are located in a conjugated bond system, the absence of dimers is probably not accidental.

Goodgame *et al.*[91] determined the g values for $(Me_4N)_2[Cu(RCO_2)_2$-

(NCS)]$_2$ (R = H or Me) by ESR and the J values by magnetic susceptibility. The conclusions formed from this study as well as structural investigations of these systems, which furnish evidence that these complexes are analogous to copper(II) acetate dimers, suggest that the direct metal–metal bond plays an insignificant role in their antiferromagnetism.

Suntsov and co-workers[92] prepared a series of copper salicylate adducts and examined their EPR spectrum, which was observed to be typical for compounds in which the copper ions combine in pairs by the exchange reactions. These investigators reported g and D values but no J values.

Recently, Matsuura and Kawamori[93] have studied the temperature variation of the EPR linewidth of copper acetate monohydrate between the temperatures 55 and 355 °K. The agreement between the experimental values and the calculated values, assuming that only the dipole interaction between the molecules is important, is satisfactory only at low temperatures with the magnetic field parallel to the x-axis of the system. These authors suggest that the discrepancy may be explained by an intermolecular exchange interaction. More detailed calculations concerning the temperature variation of linewidth will be published later[161].

Bose, Bagchi and Sen-Gupta[94] have suggested a refinement in the interpretation of the bonding in copper acetate monohydrate. They assume C_{2v} symmetry for the electronic state of each half of the complex rather than C_{4v} and an overall symmetry of D_{2h} for the dimeric complex. Jotham and Kettle[95] have re-examined the metal–metal interaction in copper acetate and suggest that the spin coupling between copper atoms is ferromagnetic, although the overall energy level diagram is that of an antiferromagnetic system. In this interesting approach, the authors suggest that the basis set should include the configuration which represents two electrons, both located on a single copper(II) ion, and calculate the energy level diagram, which consists of three singlets and a triplet state.

In an important series of papers, T. D. Smith and his co-workers at Monash University[96–101] have included the direct dipole–dipole terms in the spin Hamiltonian and hence calculated distances between copper(II) ion by computer simulation of the EPR line shape. In their study of a variety of copper(II) peptide complexes for example, the metal–metal distances are consistent with X-ray results[97]. In addition the metal–metal distance was estimated in copper(II) protoporphyrin IX and several amino acids[99] as well as copper(II) in haemocyanin and copper(II) in diethyldithiocarbonates[101].

Moores and Belford[102] studied the EPR spectrum of the planar chelate bis(*N*-methylsalicylaldiminato) copper(II) in the isomorphous nickel(II) lattice; when the doping level was almost 5% satellite lines were observed which corresponded to exchange coupled pairs. D was found to be 0.046 cm^{-1}. Since the dipolar interaction is expected to be 0.014 cm^{-1}, it is likely that other terms are involved in the anistropic spin–spin interaction. The J value was estimated to be about 40 cm^{-1}.

For many copper-containing enzymes and proteins, an EPR signal is either not observed or is somewhat less intense than that predicted on the basis of the concentration of the metal ions[103,104]. It appears that exchange interactions can be important in many of these cases. The proceedings of the Second International Conference on Magnetic Resonance in Biological Systems[105] contain many excellent papers discussing the role of monomeric and dimeric metal ion complexes of biological significance. A very good volume on the biochemistry of copper edited by Peisach, Blumberg and Aisen is also available[106].

Blumberg and Peisach[107] studied the EPR spectrum of a pair of interacting copper(II) ions in copper uroporphyrin(III) and reported the conditions necessary for dimer formation. They have also studied the EPR and optical properties of several complexes of copper(II), in which the ligands are two nitrogen and two nitrogen and two sulfur atoms[108]. Evidence for dimerization formation promoted by protonation is observed Their interpretation of the temperature dependence of the EPR spectrum of the red crystalline complex of copper(II) bis(dicarbonyl)-bis(thiosemicarbazone) established the existence of a triplet state approximately 23 °K above the singlet ground state.

Sigwart, Hemmerich and Spence[109] investigated a binuclear mixed-valence copper acetate complex as a model for copper–copper interactions in enzymes. This study is the first reported spectrum of a mixed valence $\mathrm{Cu^{I}}$–$\mathrm{Cu^{II}}$ complex showing electron delocalization. The results suggest, as a possible structure, a binuclear complex with oxygen bridges, similar to the structure proposed by Hemmerich *et al.*[110] for the $\mathrm{CuS_2Cu}$ complex.

Heitner-Wirguin and Selbin[111] find evidence for exchange coupling in a new mixed valency complex of vanadium dissolved in acetonitrile. This is an important area of study because many dimeric coordination complexes are found to exist in solution but have not been isolated in the solid state.

Kawamori and Miyagawa[112] have examined the EPR spectrum of X-irradiated single crystals of copper acetate monohydrate. Though relatively similar to the studies on zinc doped copper acetate, a number of differences were noted in the magnetic parameters. This suggests that an electronic rearrangement was caused by irradiation. Ewald and Sinn[113] have investigated the effects of high pressure (1–3000 atm) on the magnetic properties of the binuclear carboxylate complexes of copper(II). They indicate that their results are consistent with a weak metal–metal interaction.

EPR measurements of $\mathrm{Gd^{3+}}$ pairs in the host lattices $\mathrm{LaCl_3}$ and $\mathrm{EuCl_3}$ as reported by Birgenau, Hutchings and Wolf[114–117] have been interpreted as an indication of isotropic exchange between both nearest neighbor and next-nearest neighbor pairs. Since the exchange interactions in the case of $\mathrm{Gd^{3+}}$ doped into $\mathrm{LaCl_3}$ were relatively small and roughly comparable in magnitude to the dipolar interactions, the exchange constants were determined precisely from the pair line positions alone, though all the lines were not unambigously assigned in their earliest studies[114–116]. The most recent refinements in the data[117] include more accurate J_{nn} and J_{nn} values and separation dependences of $\sim r^{13}$ and $\sim r^{22}$, respectively, which are appreciably more rapid than the recently proposed tenth-power law for superexchange[118]. Interaction constants measured for Gd^{3+} pairs in $EuCl_3$, which has a lattice spacing similar to that of $LaCl_3$, have been utilized by the same authors to make quantitative predictions of the magnetic bulk properties of $GdCl_3$[116].

Results of EPR data for Ce^{3+} in $LaCl_3$ and susceptibility and specific heat measurements on single crystals of $CeCl_3$ were combined by Landau, Birgeneau, Hutchings, Rogers and Wolf[119–120] to obtain estimates for the eight parameters which characterize the nearest and next-nearest neigbbor Ce^{3+} interactions. Most of the interactions were accounted for by magnetic dipole–dipole and second order electric quadrupole–quadrupole-coupling, but evidence for anisotropic exchange and higher order coupling electric multipole interaction was also observed.

From the EPR spectra of pairs of Ce^{3+} and Nd^{3+} ions in $LaCl_3$ and $LaBr_3$, Baker, Birgeneau, Hutchings and Riley[121] have determined the contributions due to the high-degree anisotropic superexchange interactions of the form $J_+{}^5$ (1) $J_-{}^5$ (2) and $J_z{}^1$ (1) $J_\pm{}^5$ (2).

Culvahouse *et al.*[122] measured and discussed tbe hyperfine structure of pairs of Pr^{3+} in the $La_2(C_2H_5SO_4)_6 \cdot 9H_2O$ and $LaCl_3$ and Co^{2+} pairs in $La_2Mg_3(NO_3) \cdot 24H_2O$ and interpreted the results in terms of a spin Hamiltonian which included the spin–spin interaction terms of the form $K_0\, \bar{S}_1 \cdot \bar{S}_2 + K_z S^z{}_1 \cdot S^z{}_2$.

Kachalov and Kreines[123] have studied the temperature dependence of the magnetic susceptibility and the paramagnetic resonance of monoclinic $Na_2Mn_2Si_2O_7$. The susceptibility behavior is in qualitative agreement with the Bleaney–Bowers expression.

Ordering within groups may be responsible for the anomalous anisotropic temperature dependence of tbe EPR linewidth. No temperature dependence of the EPR line position was found over the entire temperature range 27 to 300 °K.

The EPR spectra of solid samples of two monomeric imidiphosphenato-copper(II) chelates reported by Keller and Schmidpeter[124] show the resolved copper hyperfine structure tbat is otherwise found only for magnetically dilute copper complexes. Their J value for the exchange interaction of Cu^{II} ions in $Cu[N(Ph_2PO)_2]_2$, defined by the relation

$$H = -2J \sum_{i<j} (S_i S_j)$$

was given as $1 \cdot 10^{-3} < J < 5 \cdot 10^{-3}$ cm^{-1}.

That this value is quite small compared to the dipole–dipole interaction substantiates the calculated large distance of ~ 10 Å between the paramagnetic centers in the lattice.

In their EPR and magnetic susceptibility study of five polycrystalline copper compounds of *d*-tartaric acid, Ablov, Popovich and Suntsov[125] found evidence for exchange interaction between copper ions in a complex precipitated at a pH of seven.

Free oxy radicals of 2,2,6,6-tetramethylpyridine-*N*-oxide and its 4-hydroxy derivative were studied by Karimov[126] in the temperature range 0.1 to 100 °K. The results show that organic paramagnetic substances can be used in the study of magnetic behavior in linear structures.

Zvyagin, Moiseev and Pshisukha[127] have reported the concentration and temperature dependence of the EPR spectrum of an Mn^{2+} impurity in zinc tungstate. They observed that as the Mn^{2+} concentration is increased, the line first broadens due to an anistropic dipole–dipole interaction and then with a further increase in concentration, the linewidth decreases due to exchange. More recently, the same authors[128] extended the measurements to the 1.5 °K to 300 °K range and have observed that a reduction of the temperature results in line broadening. The results are qualitatively explained by an exchange interaction between the *d* electron of Mn^{2+} ions.

Fused mixtures of $MnCl_2$ and alkali chlorides have been studied by Owston[129] using both the ESR and magnetic susceptibility techniques. Two types of spectra were observed, that due to $MnCl_2$ and that due to the species $XMnCl_3$, where X is the alkali ion. Evidence for antiferromagnetic coupling in $KMnCl_3$ and $RbMnCl_3$ was found.

Eisenberger and Pershan[130] ascribed a portion of the ESR spectrum of a semiconducting CdF_2 single crystal doped with Gd^{3+} to an exchange interaction between a "conduction" electron and the electron of the paramagnetic trivalent rare-earth ion. Such a "conduction" electron is attracted to the rare-earth ion and held near it, but not so near, so that a divalent rare-earth ion is not formed. They postulated that although all of these electrons are trapped, in the sense that these electrons could not contribute to the d.c.-conductivity, some of them could move over sufficiently large distances to interact with more than one rare-earth ion. Since the concentrations of the rare-earth ions is low, the ions could not be randomly distributed throughout the crystal, but must tend to form local regions of higher than average concentration in order to facilitate an interaction with more than one rare-earth ion.

A recent international conference on semi-conducting compounds presented reports of ESR data evidencing the existence of Mn^{2+}–Mn^{2+} pairs in ZnS[131] and Cu^{+}–Fe^{3+} ion pairs in ZnSe[132].

(iv) One dimensional antiferromagnetism

The magnetic properties of coordination compounds in which the individual structural units form linear chains is a topic of increasing interest[133–139]. In dichloro (1,2,4-triazole) copper(II), for example, each copper atom has four chlorine and two nitrogen atoms as nearest neighbors. The electronic spins of the copper(II) ions can interact by way of the bridging chlorine atoms, an arrangement which forms infinite linear chains. Interchain copper(II) interactions may also occur through the 1,2,4-triazole group. This complex as well as copper(II) benzoate trihydrate has been investigated by Inoue, Emori and Kubo[136] by magnetic susceptibility methods in the temperature range 4.2 to 300 °K. They conclude that the superexchange interaction is predominant rather than the interaction of a direct nature and that although novel magnetic moments have been observed for these compounds at room temperature, the spins are not free from one another, and antiferromagnetic interaction occurs between neighboring spins in a chain. The susceptibility behavior of the former complex may be associated with either magnetically isolated ions, end effects, or the odd or even number effect of spins in a chain[140–141].

The two most common mathematical expressions used to describe the pairwise interaction of the electronic spins of the metal ions in a linear chain complex are (1) the Ising model, $J\bar{S}_{1z}\cdot\bar{S}_{2z}$, and (2) the isotropic Heisenberg model, $J\bar{S}_1\cdot\bar{S}_2$. In keeping with the convention adopted in this review, a positive J value corresponds to an antiferromagnetic interaction. While both of these models are useful, the more general form of the spin Hamiltonian

$$\mathscr{H} = J\sum_{i=1}^{N}\left[S_{iz}S(i+1)_z+\alpha(S_{ix}S(i+1)_x+S_{iy}S(i+1)_y)\right] \tag{16}$$

is preferred. For $\alpha = 0$, this equation reduces to the Ising form, while for $\alpha = 1$, the Heisenberg form is obtained.

Bonner and Fisher[142] have discussed the magnetic and thermal behavior of one-dimensional ferro- and antiferro-magnetic materials in considerable detail in terms of this more general intermediate equation. The authors suggest that for all $\alpha < 1$, namely for anisotropic coupling, the ground state splitting ΔE decreases more rapidly than $1/N$, so that in the limit as N approaches infinity the limiting ground state may be said to be (two-fold) degenerate. In the isotropic limit, however, ΔE decreases only as $1/N$ and the antiferromagnetic ground state should be regarded as non-degenerate. For an Ising chain, the first excited states lie at an energy $\Delta E = (J)$ above the ground states, but at the Heisenberg limit the ground state is the limit of a continuum and there is no anistropy gap.

Among the materials which exhibit linear chain antiferromagnetism are anhydrous $CuCl_2$ and $CuBr_2$. Barraclough and Ng[143] presented a quantitative theory to account for the magnetic behavior of these two compounds, which is in good agreement with the experimental data. A number of copper(II) methoxides were investigated by Adams, Barraclough, Martin and Winter[144] who fit the data with the equations derived by Fisher[145] and Katsura[146] from the Ising model. A similar treatment was employed by Dubicki, Harris, Kokot and Martin[147] for copper(II) oxalate and by Hyde, Kokoszka and Gordon[138] for a number of copper(II) chloride bidentate heterocyclic amine addition complexes.

In some cases it has been possible to differentiate between the two extreme models. In their critical review, Domb and Miedema[148] point out that studies of the thermal and magnetic properties of copper(II) salts have provided good examples of the Heisenberg model of spin $\frac{1}{2}$. The experimental studies of $Cu(NH_3)_4SO_4 \cdot H_2O$ by Griffiths and of $KCuF_3$ by Kodata and co-workers[140], for example, are quite unambiguous in demonstrating that the Heisenberg model is preferable.

Favorable representations of the Ising model have been obtained from cobalt and rare earth salts at low temperatures[148]. Inoue, Emori and Kubo[134] have indicated that the sharp rise in the magnetic susceptibility at low temperatures is inconsistent with the Heisenberg model. They found that a calculation of J/k and g, based upon the linear Ising model, furnished values of -19.0 and 2.13 °K respectively, which are good in agreement with the values evaluated from the data at lower temperatures, -17.9 and 2.07 °K.

In a recent interesting analysis of the thermal and magnetic properties of $CsCuCl_3$, Rioux and Gerstein[150] demonstrated that the experimental data are consistent with a linear antiferromagnetic exchange interaction above 10.4 °K. Below this temperature, three-dimensional interactions are believed to dominate.

R. N. Rogers and co-workers[152–154] have extended the work of Abe *et al.*[155] on linear chain antiferromagnetism in the systems $Cu(NH_3)_4SO_4 \cdot H_2O$, $K_2CuCl_4 \cdot 2H_2O$, $(NH_4)_2CuCl_4 \cdot 2H_2O$ and $Cu(NH_3)_4 \cdot (NO_3)_2$, where J is very small. Particularly interesting are their studies of the electron paramagnetic resonance of these salts as a function of microwave frequency. A distinct change in the linewidth occurs in the region where the exchange integral J is of the same order of magnitude as the energy associated with the microwave frequency. This type of study should be useful for J values below about 2 cm^{-1}. Saito[155], who investigated the EPR of $Cu(NH_3)SO_4 \cdot H_2O$, has reported unusual linewidth effects when the temperature of a simple of $Cu(NH_3)SO_4 \cdot H_2O$ is below 2 °K. He also reports an anisotropy in T_1, which is attributed to a strong exchange interaction along the –O–Cu–O– chain.

(v) Relaxation rate studies

Harris and Yngvesson[156] have measured the spin–lattice relaxation rates of isolated $(IrCl_6)^{2-}$ complexes in $(NH_4)_2PtCl_6$ and K_2PtCl_6, and have found evidence for several factors which contribute to the relaxation rate, namely, a direct process, a Raman process, and a concentration dependent process. The concentration dependence of the relaxation rate was found to vary according to the expression:

$$\frac{1}{T_{1c}} \propto f(c) \exp\left(\frac{-\Delta}{kT}\right)$$

The concentration function $f(c)$ is of the form c^2 for concentrations below 3%. The experimental value for Δ is very close to the value found for nearest neighbor exchange interactions. However, Harris and Yngvesson[156] indicate that the dominant relaxation mechanism occurs by way of cross relaxation to exchange-coupled clusters of three or more complexes. They observed that exchange coupled pairs do not significantly contribute to the relaxation of single ions in materials studied.

Harris and Yngvesson[157] have also measured the spin–lattice relaxation rate for pairs and found that such rates are much too slow to explain the rapid relaxation of single ions. Furthermore, there are no energy intervals in the energy level diagram for the system which correspond exactly to the energy interval for pairs or single ions. A relaxation mechanism involving pairs would thus be expected to be slow and anisotropic; however, no anisotropy was observed. Several relaxation mechanisms are considered which involve triads and single ions. The authors suggest that the triad, consisting of a nearest neighbor pair and a third ion which is a next nearest neighbor to one member of the pair, is one of the more likely types of triads which can be effective in relaxing single ions It is important to note that the high symmetry of the chloroiridate ion does not allow an antisymmetric interaction of the form $\bar{d} \cdot (\bar{S}_1 \times \bar{S}_2)$, which is probably important in ruby[158].

Tenglbad and Yngvesson[159] have examined the spin relaxation in Cr^{3+} doped crystals of $K_3Co(CN)_6$. These data furnish further proof of the existence of relaxation processes involving triads.

(vi) *Related studies*

While the primary purpose of this review is to discuss the recent EPR studies of exchange coupled metal ions, a number of recently published related studies should also be included. The magnetic susceptibility measurement technique is perhaps the most common method employed in the study of cluster complexes. The investigations of Kato, Martin, Jonassen, Lewis, Figgis, Hatfield, Harris, Kubo, Sinn and Baker and their co-workers are especially important in this area of endeavor and have been discussed in the review literature previously cited. In view of the unique features of a number of recent investigations, a brief comment on some of items seems appropriate here.

Pfeiffer's cation $[Cr_4(en)_6(OH)_6]^{6+}$ has been the subject of three recent papers[162–165]. The magnetic properties of this complex at temperatures as low as 80 °K have been discussed in terms of both a trigonal arrangement of metal atoms[149] with a central Cr^{III} atom[162] as well as a tetrahedral cluster[163] consistent with magnetic measurements at a temperature of 4.2 °K as well as a crystal structure determination revealed that the four chromium ions form a planar rhomboid array held together by bridging hydroxo groups. Flood, Barraclough and Gray[165] are able to account for the observed susceptibility behavior of this complex over the entire temperature range studied.

Jonassen, Muto, Kato and co-workers have had some success in correlating the magnetic properties of dimeric copper complexes with other physiochemical properties[166–169]. In the dimeric complexes of copper(II) halides with substituted pyridine-*N*-oxides, relationship between the spectral frequencies and the effective value of the magnetic moment at 25 °C is observed. On the other hand, the substituted *N*-*n*-propano-salicylaldiminato copper(II) complex do not exhibit the parallelism between these parameters, because the substituent on the benzene ring does not strongly affect the superexchange pathway which is postulated to proceed through alcohol bridges[163].

Kubo and co-workers[170] have studied various *N*-[2-(2-hydroxyethylthio)-phenyl] arenesulfonamidatocopper(II) chelates and addition compounds thereof with methanol and ethanol and have obtained evidence for the formation of dimeric aggregates in the bis-alcohols of these compounds as well as evidence for trimeric species in the alcohol-free copper(II) complexes. Such complexes most probably possess equivalent electron spins.

Gruber, Harris and Sinn[171] have studied trimeric complexes of the type Cu–M–Cu where M may be copper(II), nickel(II), cobalt(II), iron(II), or manganese(II); the metal ions are bridged by oxygen atoms. The complexes were prepared from tetradentate Schiff bases. While interactions between the terminal copper atoms are exceedingly small, the antiferromagnetic interactions between the central metal atom M and the adjacent copper(II) atoms are quite significant.

Andrew, Ball and Blake[172] have investigated binuclear cobalt(II) and nickel(II) complexes of dihydrazinophthalazine and dipyridylpyridizine in order to assess the magnitude of the exchange interactions between clusters of metal ions in an invariant magnetic environment. They find that the ratio of J values for the nickel and the cobalt complexes is about 2.8. The ratio would be 2.25 if the efficiency of the exchange interaction process is the same for the two different metal ion clusters and if the only relevant variable is the number of unpaired electrons. The observed ratio suggests that exchange is somewhat more efficient in the case of nickel; and the result is attributed to ferromagnetic effects due to the t_{2g} spin of the Co^{2+} ions.

Several binuclear oxygen-bridged complexes of iron(III) were investigated by Reiff, Baker and Erickson[173]. The spin multiplicity of the ground state of the individual iron atoms is discussed. In many cases it is not possible to distinguish two interacting $S = 3/2$ ions from two $S = 5/2$ ions on the basis of susceptibility studies alone over the temperature range normally studied. This conclusion has also been reached by Bancroft, Maddock and Randl[174], who suggest that measurement of the Mössbauer chemical shift, the quadrupole splitting and linewidths may provide a better method for the determination of valency. Duncan, Kareheer and Mok[175] have studied several trinuclear iron(III) complexes by both magnetic and Mössbauer methods; their data suggest that the iron ions in such complexes are not equivalent.

In an earlier study, Mulay and Hofmann[176] examined the magnetic susceptibility and the electron paramagnetic resonance of *o*-phenanthroline complexes of iron(III), formed from aqueous solutions of various ferric compounds. These authors point out that under conditions of rapid precipitation, monomeric and dimeric species are produced which yield non-reproducible susceptibility data. The EPR data were particularly important in revealing the source of this discrepancy.

In an important series of theoretical papers, Wojciechowski[177] investigated the magnetic susceptibility behavior of several general classes of dimeric species with similar and dissimilar exchange coupled ions and with negative and positive values of J.

Hynes, Garrett and Moulton[178] have analyzed the nuclear quadrupole resonance spectrum of $KCuCl_3$, and have observed an unusually large temperature shift which could not be accounted for by the unmodified Bayer theory. The inclusion of an excited state about 40 °K above the ground state provided an excellent fit of the data. The 40 °K separation is in reasonable agreement with the value obtained from magnetic susceptibility data[179].

Owen and Taylor[180] have studied the metal-to-metal hyperfine interactions by the ENDOR technique. The ^{27}Al hyperfine structure was observed in the structures Fe^{3+}–O^{2-}–Al^{3+} and Cr^{3+}–O^{2-}–Al^{3+}. This interaction is closely related to the super-transferred hyperfine interaction discussed earlier, and this paper discusses the origin of the interaction.

Several examples are considered in detail. Of related chemical importance are the studies of several soluble organometallic catalysts by Angelescu, Nicolau and Simon[181]. The relatively large aluminum hyperfine structures observed in these cases are an indication of the strength of metal–metal interaction which occurs in these catalysts. Tkac[182] has also studied the magnetic properties of several similar catalytic systems by electron paramagnetic resonance.

Henrici-Olive and Olive[183] have observed that gallium-69 and -71 hyperfine structures in a dimeric cyclopentadienyl complex. The metal ions are joined by bridging groups, and, in this case, a large metal-to-metal hyperfine interaction is readily observed. They also report ESR results for ^{27}Al in $Cp_2TiCl_2AlCl_2$ and ^{11}B in $Cp_2TiCl_2BCl_2$[184]. Marov *et al.*[185] report the superhyperfine structure due to ^{31}P nuclei in a Mo^V phosphate dimer; one of the few observations of hyperfine interaction of a central ion in an inorganic complex with a nucleus not directly bonded to it.

Exchange interactions between unpaired electrons in biradicals is an area of study which is closely related to that of electronic interactions in metal–metal pairs. Brauer *et al.*[186] report an ENDOR study of Tschitschibabit's hydrocarbon and discuss the scalar spin–spin coupling between unpaired electrons in this compound.

D. CONCLUSIONS

The experimental evidence presently available suggests that exchange interactions proceed through bridging ligands rather than by means of a direct metal–metal bond. The number of studies which require the inclusion of the $d \cdot (\bar{S}_1 \times \bar{S}_2)$ and $(\bar{S}_1 \cdot \bar{S}_2)^2$ terms in the spin Hamiltonian is small and this area requires intense study, preferably on single crystals Electron paramagnetic resonance, optical and magnetic susceptibility measurements will remain important techniques for the study of magnetic interactions in materials containing groups of exchange coupled metal ions.

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