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THE MAGNETIC PROPERTIES OF POLYNUCLEAR TRANSITION METAL COMPLEXES

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CONTENTS

A. INTRODUCTION

The magnetic properties of a large number of bi-, tri- and tetra-nuclear transition metal complexes have been investigated over the last two decades. In particular a considerable amount of research has been reported on the cryomagnetic properties of binuclear copper(II) complexes. This research was comprehensively reviewed by Kato *et al.*[1] in 1964; their review tabulates much of the magnetic data in a similar manner to that of Foëx[2]. More recently Martin[3] has discussed with

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illustrations, the theoretical interpretations of the cryomagnetic properties of isolated clusters of transition metal complexes.

A brief introductory description of the theory used to interpret the observed exchange interactions, arising from the spin dependence of the energy states of the molecule, and a number of the different theoretical approaches to the mechanism of these interactions, is given in section B. The calculation of the exchange integral from the cryomagnetic data has previously been given[4]. In the subsequent three sections the magnetic data of a large number of isolated clusters is reviewed. In this review no data on lattice antiferromagnets are given, thereby avoiding the complexities associated with cooperative phenonema.

B. EXCHANGE INTERACTIONS

Most transition metal compounds are magnetically dilute. In such compounds the paramagnetic ions act independently of each other. There are, however, cases where the paramagnetic ions influence each other; these spin–spin interaction phenomena are referred to as magnetic exchange interactions, and may arise because the distance between the paramagnetic ions is small (direct exchange), or because the intervening atoms, which are diamagnetic in their ground state, are capable of transmitting the magnetic exchange interaction (super exchange).

(i) The exchange integral (the Heisenberg–Dirac–Van Vleck model)

The magnetic susceptibility for a polynuclear transition metal complex for which the orbital angular momentum is quenched (A, B and cubic field E ground terms are non-magnetic) is calculated by assuming that the spin–spin interaction can be accounted for by including the term $\mathscr{H}_x = -2\Sigma J_{ij}\vec{S}_i \cdot \vec{S}_j$ in the perturbing Hamiltonian for the system, where J_{ij} is the exchange integral between the ith and jth ions. This spin–spin interaction between paramagnetic centres has been considered by Van Vleck[5].

If J is positive the lowest state is that for which the spin vectors tend to align themselves parallel (ferromagnetic coupling), whereas if the exchange integral is negative the lowest energy state is that for which the spin vectors are paired (antiferromagnetic coupling). (The exchange interaction only resembles a spin–spin coupling because the Pauli exclusion principle demands that the total wavefunctions must be antisymmetrical in every pair of electrons[6].) Ferromagnetic spin alignment of the spin angular momenta produces susceptibilities in excess of those for normal paramagnetic materials, whereas antiferromagnetic spin alignment produces susceptibilities which are less than those for normal paramagnetics. Where the antiferromagnetic interaction is direct, it results in covalent bonding which in the limit gives complete spin pairing between the metal ions, and diamagnetism is observed (*e.g.*, $Fe_2(CO)_9$).

For two ions with spin angular momenta specified by the quantum numbers S_1 and S_2 the perturbing Hamiltonian will be $-2J\vec{S}_1 \cdot \vec{S}_2$*, and since it can be shown that

$$\vec{S}_1 \cdot \vec{S}_2 = \tfrac{1}{2}[S'(S'+1) - S_1(S_1+1) - S_2(S_2+1)]$$

where S' is the quantum number specifing the spin angular momentum of the dimer, the energy levels under the perturbing Hamiltonian will be

$$E(S') = -J[S'(S'+1) - S_1(S_1+1) - S_2(S_2+1)]:$$

and if $S_1 = S_2 = S$, then

$$E(S') = -J[S'(S'+1) - 2S(S+1)], \tag{1}$$

where $E(S')$ is the energy of the dimer in the absence of the magnetic field. (The quantum numbers S' can have $2S+1$ values, each corresponding to a particular energy level. The separation between a level specified by S' and the ground level is given by $J\{S'(S'+1)\}$. Frequently the value of J is defined as twice that given here.)

The effect of an external homogeneous magnetic field on the energy levels specified by $E(S')$ is to split them into $2S'+1$ levels separated by $g\beta H$, where H is the field strength, g the Lande splitting factor and β, the Bohr magneton, is a constant relating orbital angular momentum, in atomic units, to magnetic moment in c.g.s. units. (In other words the perturbing Hamiltonian is the sum of the first order Zeeman term and the exchange interaction *i.e.* $\mathscr{H} = g\beta\vec{H} \cdot \vec{M}_{s'}, +2\vec{S}J_1 \cdot \vec{S}_2$, where $M_{s'}$ takes values $S', S'-1, \ldots -S'$). The magnetic susceptibility for an ion of the ion-pair is calculated from a modified form of the familiar Van Vleck equation[5], from

$$\chi_m = \frac{N}{2} \cdot \frac{g^2 \cdot \beta^2}{kT} \cdot \frac{\sum\limits_{Ms'} (M_{s'})^2 e^{-E(S')/kT}}{\sum\limits_{Ms'} e^{-E(S')/kT}} \tag{2}$$

Note that instead of N, $N/2$ has been written because the susceptibility is that per ion, for which there are $N/2$ pairs.

For tri- and tetra-nuclear systems, the energies of the spin levels can be estimated in a similar manner to those for binuclear systems[3]. The general expression for the paramagnetic susceptibility for three interacting ions (triangular cluster) has been given by Kambe[7]; the expression for three nickel(II) ions (linear cluster) has been given by Ginsberg, Martin and Sherwood[10]; that for four chromium(III)

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* Strictly speaking $\vec{S}$ represents a vector of magnitude $\hbar\sqrt{S(S+1)}$ *i.e.* the exchange term in the Hamiltonian should be written $-2J/\hbar^2 \cdot \vec{S}_1 \cdot \vec{S}_2$.

ions (tetrahedral cluster) by Wentworth and Saillant[8]; that for four chromium(III) ions (trigonal pyramidal cluster) by Barraclough, Gray and Dubicki[9]; and that for four nickel(II) ions (tetrahedral cluster) by Andrew and Blake[11]. (Wentworth and Salliant in attempting to calculate the susceptibility expression for four chromium(III) ions with a trigonal arrangement, calculated that for a tetrahedral cluster[10].)

(ii) Theories of the origin of the exchange term

While the spin Hamiltonian $\mathscr{H}_x = -2\Sigma J_{ij} \vec{S}_i \cdot \vec{S}_j$ provides an accurate description of exchange interactions, it provides no information regarding their origin. Unfortunately, in only a few of the papers concerned with intramolecular exchange interactions have attempts been made to describe the way in which the spins interact.

Metal-to-metal interactions in which the separation between the paramagnetic ions is approximately the sum of their covalent radii are traditionally referred to as direct exchange interactions. (The extent of exchange, measured by the so-called transfer integrals, b_{ij}, between the pair of orbitals i and j, is proportional to the orbital overlap.) More frequently, interactions are observed between paramagnetic centres which are separated by distances which are much greater than the sum of their covalent radii; these interactions are widely referred to as superexchange interactions. Any mechanism which describes this superexchange must describe the delocalisation of the spin(s) of the bridging ligand orbitals into the half-filled or empty cation orbitals, so that the overall result is the same as a direct spin–spin alignment. In all the mechanisms postulated to describe the superexchange interactions, it has been customary and convenient to distinguish between two limiting cases; (a) exchange interactions between octahedrally co-ordinated cations with corner sharing of the octahedra: so called the 180° case; and (b) exchange interactions between octahedrally co-ordinated cations with edge sharing of the octahedra: so called the 90° case. The main advantage of the mechanisms postulated by Kramers[12] (which Anderson reformulated[13]), Slater[14], Goodenough[15,16] and Anderson and Hasegawa[17] is that they are pictorially simple. For example, Goodenough's mechanism takes into account the partial bond formation of the ligand orbitals with the non-orthogonal cation orbitals, by electron transfer from the filled ligand orbitals to the half-filled or empty cation orbitals.

Kanamori[18] has shown that the sign of the superexchange interaction is so closely connected with the symmetry relationships between the cation and ligand orbitals that it does not depend on any specific mechanism. For orbitals that have finite overlap a negative (antiferromagnetic) superexchange is predicted, while for orbitals which are orthogonal the effect will be small and positive (ferromagnetic). (It is convenient, at this point, to indicate that for a monatomic ligand the $p_\pi - t_{2g}$ $[\pi]$ exchange is smaller, energetically less favourable, than the $p_\sigma - e_g$ $[\sigma]$ exchange owing to the smaller orbital overlap in the former. However for polyatomic bridges for which there is a π-electron delocalisation in the ligand bridge, then the π-exchange becomes more important and in some cases is considered to be more favourable than the σ-exchange.) Ligand s orbitals can also participate in superexchange interactions (ligand s and cation t_{2g} orbitals are orthogonal).

More recently Anderson[19] has made an entirely new approach to the problem of the mechanism of the exchange interaction, which[20] he refers to as Anderson's "second paper". In this new approach there is no difference between what has been considered above as direct and superexchange. Anderson considers the exchange to result from both the "incipient" chemical bond formation *via* the diamagnetic ligands (because of the Pauli exclusion principle this is always antiferromagnetic), and from the two-electron exchange between the paramagnetic ions (because of the repulsive interelectronic potential energy effects this is always ferromagnetic). The former effect is referred to as 'super' exchange and the latter effect, which is considered to be very small indeed except when between two orthogonal orbitals, as 'direct' exchange. This more mathematical theory appears to provide a formally more correct interpretation of the experimental results.

C. BINUCLEAR SPECIES

(i) Carboxylate bridged dimers

More results have been reported in the literature concerning the magnetic and spectral properties of binuclear carboxylate bridged complexes of copper(II) than for all the other magnetically interesting bi-, tri- and tetra-nuclear species.

The most widely studied, and one of the simplest paramagnetic species, is copper(II) acetate monohydrate. Van Niekerk and Schoening's[21,22] investigation of the crystal structure of copper(II) acetate monohydrate has shown that the copper(II) ions occur in isolated pairs in the crystal. The copper(II) ions are very close together, their separation is 2.64 Å as compared with the copper-to-copper separation of 2.56 Å in the metal. A low molar susceptibility was recorded for this compound as early[23] as 1915. Bleaney and Bowers[24,25] have shown that the electron spin resonance spectrum corresponds to spin $S = 1$, rather than spin $S = \frac{1}{2}$ as might be expected for copper(II). More recently[26-28], especially pure samples have been prepared and the susceptibility measured over a temperature range. From equation (2), using $S = \frac{1}{2}$ and $S' = 0$ or 1 we have

$$\chi = \frac{g^2N/\beta^2}{3\,kT}\cdot\frac{3}{3+e^{-2J/kT}} + N\alpha \tag{3}$$

The cryomagnetic results for copper(II) acetate monohydrate are well interpreted using equation (3), with a J value of $-151\,\mathrm{cm}^{-1}$ ($J/k = -216°$). The value of

J/k estimated from the θ value is $-216°$ ($\theta = -108°$), and the value estimated from the Curie temperature T_c is also $-216°$ ($T_c = 270$ °K). Figgis and Martin[28] have also studied anhydrous copper(II) acetate, and they report a value of J for this compound of -143 cm^{-1}. Figgis and Martin[28], using arguments based on a theoretical treatment by Craig *et al.*[29], have proposed that the physical origin of the exchange interaction arises from the lateral overlap of the $3d_{x^2-y^2}$ orbital functions (δ bond). More recent calculations by Ross[30] and by Boudreaux[31] have supported this δ-bond model. (The postulation of a strong σ-bond ($3d_{z^2} - 3d_{z^2}$ orbital overlap)[32] between the two copper ions has now been discarded.) It is important at this point to note that when the hypothesis of the δ-bond model was put forward, it was emphasised that, "the bond is so weak that the configuration of the binuclear molecule can only be maintained by the four bridging acetate groups." Dubicki and Martin[33] have proposed that the band at about 28,000 cm^{-1} observed in the visible spectrum of copper(II) acetate is characteristic of this bridging system rather than of the copper-to-copper linkage as was first thought[34,35]. The intimate relationship of this band with the binuclear structure has been confirmed by cryoscopic molecular weight[36] and magnetic measurements[36,37].

The same sort of exchange coupling may be expected in other compounds with the same crystal structure. Figgis and Martin[28] have suggested that the family of copper(II) salts of straight chain fatty acids having the general formula

$$Cu_2(C_nH_{2n+1}CO_2)_4 \cdot x(H_2O)$$

where $x = 0$ or 2 would exhibit exchange interactions. Gilmour and Pink [38], Abe[39] and especially Martin and Waterman[40] have found experimental evidence for exchange with J ranging from -170 to -139 cm^{-1} ($J/k = -245°$ to $-200°$). Apparently neither the length of the alkyl chain nor the absence or presence of water molecules has much effect on the extent of exchange.

The expectation that the extent of the magnetic exchange interaction increases as the bridging carboxylates supply more electron density to the copper(II) ions, thereby increasing the orbital overlap, is realised for a large number of acids[41-45], except when other factors, such as steric effects or structural changes, become important. The electron donating power of the acid can be measured by its pK value. Further, Martin[46] has shown that the same promotion effect in the exchange interaction can be brought about by the terminal molecules.

Chromium(II) acetate monohydrate has been shown to be isostructural with copper(II) acetate monohydrate[47], having an identical metal to metal separation of 2.64 Å. Its diamagnetism[48] would seem to be most readily explained by assuming a strong antiferromagnetic coupling *via* a π-mechanism which so separates the $S' = 0$ and $S' = 1$ levels that the chromium(II) compound is diamagnetic at room temperature. The t_{2g} subshell for copper(II) is fully occupied whereas the t_{2g} subshell is only half-filled for chromium(II). The anhydrous benzoate of chromium(II) is nearly diamagnetic, and a similar binuclear structure seems likely[49]. A cryomagnetic investigation of chromium(II) oxalate monohydrate and of the anhydrous oxalate indicate that there is a weaker exchange interaction than for the acetate (μ_{eff} decreasing from 4.5 B.M. at 340 °K to 4.0 B.M. at 100 °K). The structures of these compounds are not known.

An X-ray investigation of rhodium(II) acetate monohydrate[50] has shown that the compound has the same dimeric structure as the hydrated copper(II) and chromium(II) acetates. Further, from spectrophotometric measurements[51] the dimeric anhydrous rhodium(II) acetate appears to be more stable in aqueous solutions and in a variety of organic solvents than the corresponding copper(II) and chromium(II) salts. A diamagnetic binuclear acetate-bridged complex of rhenium-(III), $[ReCl(OCOCH_3)_2]_2$, had also been prepared[52]. Related species $[ReOCl(OCOCH_3)]_2$ and $[ReO_2(OCOCH_3)]_2$ which are believed to have carboxylato and oxo bridges have also been prepared by Wilkinson[52]. A π-allyl-palladium acetate has been shown to have a structure similar to copper(II) acetate with a palladium–palladium bond length[53] of 2.94 Å. Molybdenum(II) acetate has also been shown to have a binuclear structure similar to copper(II) acetate, except that the molybdenym–molybdenum distance[54] is very short (2.11 Å) and indeed less than that (2.80 Å) in molybdenum metal. A whole range of yellow diamagnetic molybdenum(II) carhoxylates have been shown by osmometric methods to be dimeric[55, 56, 57]. The diamagnetism of the molybdenum(II), rhodium(II) and rhenium(II) acetates most probably arises from a strong covalent metal-to-metal bond system[58, 59].

Molecular weight, infrared and proton n.m.r. spectra show that vanadium-(III) acetate and benzoate are dimeric and probably have a structure with four bridging and two terminal carboxylate groups[60]. Their magnetic behaviour is complicated and a detailed interpretation has not been given. A large number of vanadyl complexes have been reported[61] for which there is an indication from cryomagnetic studies that there is magnetic exchange, most likely *via* the carboxylate groups. There is evidence from the electron spin resonance and optical spectra that the tartrate groups bridge two equivalent vanadyl (VO^{2+}) ions in a number of oxovanadium(IV) tartrates. Cryomagnetic results indicate a small exchange ($J \leq -50\,\mathrm{cm}^{-1}$ or $J/k = -72°$)[62]. An X-ray crystal structure of the complex $(NH_4)_4(VO)_2(\text{tartrate}) \cdot xH_2O$ has proved the dimeric structure with a vanadium to vanadium distance[63] of 4.35 Å.

Copper(II) formate yields a wide range of complexes, several anhydrous forms, and many solvated compounds. A large variation in magnetic properties is shown by this group of complexes; some are normal, whereas others have subnormal moments. In the latter group, both direct exchange and superexchange interactions are postulated. Martin[64] has suggested that the subnormal moment of copper(II) formate tetrahydrate, the structure of which has been completely elucidated[65] (Cu–Cu = 5.80 Å) is primarily due to super-exchange through a π-pathway set up by using the $3d_{yz}$ and $3d_{xz}$ orbitals of the copper(II) ion and the

$2p_\pi$ orbitals of the bridging formate ions. Chromium(II) forms two anhydrous formates[49], a blue form which is probably mononuclear and a red form which from its magnetic properties is probably binuclear.

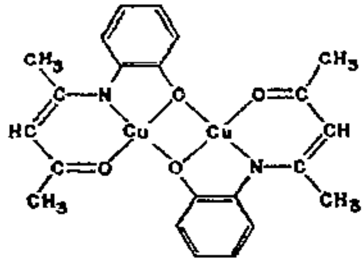
Walton *et al.*[66] have reported that the magnetic moment for silver(II) nicotinate ($\mu_{eff} = 1.67$ B.M.) shows a marked temperature dependence ($\theta = -52°$). (The diffuse reflectance spectrum indicates a planar environment.) They conclude that their cryomagnetic data are probably a consequence of an antiferromagnetic exchange interaction. (Indeed a reasonable fit with equation 3 can be obtained for their cryomagnetic results with $J = -40\ \text{cm}^{-1}$ ($J/k = -57°$), $g = 2.10$ and $N\alpha = 0$ or $100{\cdot}10^{-6}$ c.g.s.)

A review describing the properties of complexes of simple carboxylic acids has recently appeared[67].

(ii) *Schiff-base dimers*

In 1937 Pfeiffer prepared salicylal-*o*-hydroxy-anil copper(II)[68]; the room temperature magnetic moment of this compound was reported to have a value of 1.53 B.M. This low moment was considered to result from the presence of impurities. Yamaguchi[70], Muto[71,73] and Kishita[74–77] have synthesised and recorded the magnetic susceptibilities of a large number of similar complexes. It was found that most of these complexes had subnormal moments whereas their monopyridine adducts have normal magnetic moments. Kishita attributed the subnormal moments to the occurence of tri-co-ordinated copper(II) and possible direct copper(II) to copper(II) interaction in the solid state due to dimerisation. Kubo[78] has suggested a new binuclear structure in which the magnetic interaction takes place *via* the oxygen atoms, see Fig. 1. An X-ray analysis by Barclay[79] of the copper(II) complex formed with *N*-(2-hydroxy-phenyl)-2-acetyl-1-methyl ethylideneimine has shown that this complex contains an essentially square co-ordinate arrangement around the copper(II) atoms which are linked by oxygen bridges (Cu–Cu = 3.00 Å)

More recently Ginsberg *et al.*[80] and Hatfield[81] have prepared a number of complexes of tridentate Schiff-bases derived from the condensation of substituted



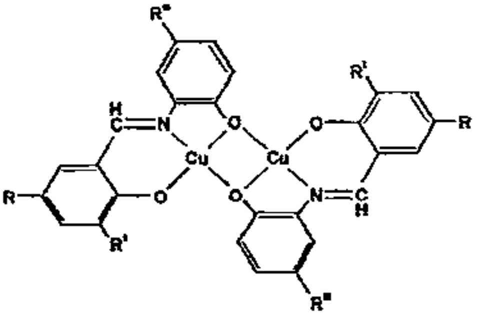


Fig. 1. Acetylacetone-mono(*o*-hydroxyanil)copper(II).

Fig. 2. 3,5-Substituted *N*-(2-hydroxyphenyl)salicylideneimine complexes of copper(II).

and unsubstituted salicylaldehyde and substituted and unsubstituted *o*-aminophenol, see Fig. 2. Although there is disagreement between certain sets of results reported by the two authors, most of the complexes exhibit exchange interactions, and in most cases the variation of the susceptibility with temperature is given by equation (3). Depending on the substituents, J varies between -170 cm^{-1} and -20 cm^{-1} ($J/k = -245°$ to $-29°$). The superexchange interaction has been postulated to take place *via* a mechanism similar to that for copper(II) formate tetrahydrate[1]. Qualitatively speaking, Anderson's "second paper" predicts that the greater the overlap between the metal orbitals and the orbitals of the bridging ligand atoms, the greater will be the magnitude of the exchange. Making reasonable assumptions about the electronic effects on the bridging and non-bridging ligand atoms, Ginsberg was able to show that, in general, the qualitative variation of J from compound to compound can be predicted from the extent of the overlap of the ligand and metal orbitals. Lewis and Walton[82] have reinvestigated the cryomagnetic properties of several of the copper(II) Schiff-base complexes previously reported by Calvin and Barkelew[68] to have "low moments", and have shown that they are magnetically dilute ($\theta = -5°$). Similar behaviour for several Schiff-base alkylamines has been reported by Sacconi[83,84].

The complex, *N,N'*-disalicylidene-ethylenediamine copper(II) is interesting in so far as the X-ray crystal structure[85,86] has shown that the complex is dimeric, with copper to oxygen bridges joining the two units of the dimer, in which the copper atoms are in an essentially square pyramidal environment, whereas the molar susceptibility measurements of Lewis and Walton[82] clearly indicate that there is no significant exchange interaction between the two copper(II) ions. The absence of exchange interactions is possibly associated with the long copper-to-oxygen bonds (2.41 Å) but it is also considered that it may be related with the copper–oxygen–copper bond angle. (Magnetic exchange is usually only considerable in systems where there is a linear metal–oxygen–metal arrangement, as is found[87], for example, in $K_4(Ru_2OCl_{10})H_2O$.)

Ginsberg *et al.*[88] have prepared several complexes of 5-substituted *N*-(2-

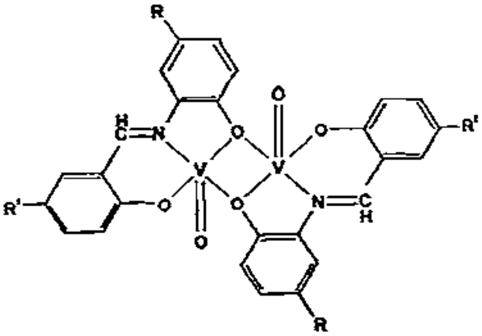


Fig. 3. 5-Substituted *N*-(2-hydroxyphenyl)-salicylideneimine complexes of vanadium(IV).

hydroxyphenyl) salicylideneimines with the vanadyl ion, the general structure being shown in Fig. 3. Several of these complexes have been previously reported[89,90]. The temperature dependence of the susceptibility is characteristic of magnetic exchange interactions; indeed the complexes are presumed to be dimeric with a structure similar to the analogous copper(II) compound discussed above. J values have been obtained by fitting the experimental results with equation (3). (J varies from -125 to -90 cm^{-1} or $J/k = -182$ to $-130°$.) However, in direct contrast to the superexchange mechanism postulated for the formally similar copper(II) complexes, the exchange interaction in the d^1-d^1 case is considered to result from a direct metal interaction between the unpaired spins on the two vanadium(IV) ions.

Earnshaw *et al.*[91] have prepared a binuclear manganese(II) complex, *N,N'*-ethylenebis(salicylideneiminato)manganese(II), and interpreted their cryomagnetic data using equation (4);

$$\chi_M = \frac{g^2N\beta^2}{3kT}\cdot\frac{55+30e^{-10J/kT}+14e^{-18J/kT}+5e^{-24J/kT}+e^{-28J/kT}}{11+9e^{-10J/kT}+7e^{-18J/kT}+5e^{-24J/kT}+e^{-28J/kT}+e^{-30J/kT}}+N\alpha \tag{4}$$

(Equation 4 is obtained from equation 2 with $S = 5/2$ and $S' = 5,4,3,2,1,0$) with $J = -6.5$ cm^{-1} ($J/k = -4.5°$), $g = 1.96$ and $N\alpha = 0$. Several other manganese(II) compounds which are formed with ligands similar to *N,N'*-ethylenebis(salicylideneiminate) are reported to have low room temperature moments[92].

(iii) Oxo- and hydroxo-bridged species

Lewis and Earnshaw[93] have investigated a series of binuclear chromium(III) complexes which had previously been shown to have hydroxo- and oxo-bridging groups[94]. These complexes, which contain a single bridging group, are the so-called erythro- and rhodo-series of ammines. The acid erythro-series have the general formula $[(NH_3)_5CrOHCr(NH_3)_4H_2O]X_5$ and the acid rhodo-salts $[(NH_3)_5CrOHCr(NH_3)_5]X_5$, the basic salts being formed by loss of a proton from the bridging hydroxyl group in the case of the rhodo-salts and from the aquo-group in the erythro-series. Thus the acid and basic erythro-salts and the acid rhodo-salts contain a hydroxyl bridging group, whereas the basic rhodo-salts contain an oxo-bridging group. The cryomagnetic results for the hydroxo-bridged species can be interpreted from equation (5). (Equation (5) is obtained from equation (2) with $S = 3/2$ and $S' = 3,2,1,0$.)

$$\chi_M = \frac{g^2N\beta^2}{kT}\cdot\frac{42+15e^{-6J/kT}+3e^{-10J/kT}}{7+5e^{-6J/kT}+3e^{-10J/kT}+e^{-12J/kT}}+N\alpha \tag{5}$$

The exchange integrals for these ammines are small (J is about -14 cm^{-1} or $J/k = -20°$). For the basic rhodo-salts[93-95] the recorded room temperature moment of 1.3 B.M. per metal atom is much less than mononuclear chromium(III) species, and decreases with decreasing temperature to about 0.6 B.M. at 80 °K. There is evidence, from the ultra-violet spectra[94,95] and from the infrared spectra[93] of the basic rhodo complexes, for π-bonding between the bridging oxygen and the chromium(III) ions; this π-bonding is assumed by Wilmarth[94] to account for the large reduction in the magnetic moment. A similar molecular-orbital explanation was given by Dunitz and Orgel[87] to account for the diamagnetism of the chloro-ruthenium complex $K_4(Ru_2OCl_{10}) \cdot H_2O$. Some binuclear oxybridged complexes of rhenium(IV) containing the ion $(Re_2OCl_{10})^{4-}$ have also been shown to be diamagnetic[96]. As Lewis points out, application of the Dunitz–Orgel molecular-orbital approach to these rhenium(IV) complexes and to the basic rhodo-salts should give a moment corresponding to two unpaired spins per molecule (*i.e.* μ about 2.0 B.M. per metal atom), and consequently there must be an additional interaction reducing the moment.

A simpler interpretation of these results would seem to be in terms of the mechanisms mentioned earlier; for example, in terms of the mechanism developed by Goodenough[15,16] according to which, if the spins of the two chromium(III) ions are antiparallel, there will be an exchange interaction. There will be both a π-mechanism and a second order σ-mechanism, which Goodenough believes is more important than the π-mechanism, because of the greater overlap. The $p_\sigma - e_g$ partial bond formation involves the transfer of the p_σ electron, say, with ↑ spin to a vacant e_g orbital on the chromium(III) ion, for which the 3 unpaired spins are ↑ (Hund's rule of maximum spin multiplicity). Similarly the p_σ electron with ↓ spin will be transferred to the neighbouring chromium(III) ion for which the t_{2g} electrons have ↓ spin (Pauli's exclusion principle), and the p_π electron with its ↓ to the other chromium(III) ion for which the t_{2g} electrons have ↑. Both the π- and σ-mechanisms favour antiparallel spin alignment and hence give antiferromagnetic exchange, which reduces the effective magnetic moment of the chromium(III) ions below the spin only value.

The smaller interaction observed in the erythro- and acid rhodo-salts as compared with the basic rhodo-salts may be associated with a metal–oxygen–metal bond angle of the order of 120° in the former as compared with the 180° that may occur in the basic rhodo-salts.

Earnshaw and Lewis[93] have investigated the cryomagnetic properties of three chromium(III) complexes which have two hydroxyl bridging groups,

$[(o\text{-phenanthroline})_2Cr^{III}(OH)_2Cr^{III}(o\text{-phenanthroline})_2]I_4 \cdot 4H_2O$,

$[(\text{glycine})_2Cr^{III}(OH)_2Cr^{III}(\text{glycine})_2] \cdot H_2O$ and

$[(\text{phenylalanine})_2Cr^{III}(OH)_2Cr^{III}(\text{phenylalanine})_2]$. Their results are well interpreted by equation (5) with J values of less than -7 cm^{-1} or J/k about $-10°$.

A more complicated system is the corresponding iron(III) phenanthroline complex. This complex was originally formulated[97] as

$[(o\text{-phenanthroline})_2Fe^{III}(OH)_2Fe^{III}(o\text{-phenanthroline})_2]Cl_4$. Elliott[98] was able to interpret his cryomagnetic results by using equation (3), *i.e.*, by assuming that the iron(III) ions are in low spin states. He obtained a "best" fit with the theoretical curve for $g = 2.22$, $N\alpha = 360\cdot10^{-6}$ c.g.s. and $J = -172\ \text{cm}^{-1}$ ($J/k = -249°$). Earnshaw and Lewis[93,99] have also studied the same complex and by similarly assuming a spin-paired complex the general characteristics of the reciprocal molar susceptibility–temperature curve are reproduced with $g = 1.97$, $N\alpha = 628\cdot10^{-6}$ c.g.s. and $J = -139\ \text{cm}^{-1}$ or $J/k = -200°$. There is infrared and chemical evidence [93] that this complex is more accurately formulated as $[(o\text{-phenanthroline})_2\text{Cl}\,(\text{H}_2\text{O})\text{Fe}^{\text{III}}\text{O}\ \text{Fe}^{\text{III}}\text{Cl}(o\text{-phenanthroline})_2]\text{Cl}_2$, and indeed more recently Lewis *et al.*[100] have prepared a series of "oxygen-bridged iron(III) phenanthroline complexes", including $[(o\text{-phenanthroline})_2\text{Cl}\ \text{Fe–O–Fe}\ \text{Cl}\ (o\text{-phenanthroline})_2]^{2+}2\text{X}^-\cdot n\text{H}_2\text{O}$ where X^- is Cl^- or $\text{ClO}_4{}^-$, and interpreted their cryomagnetic results using a binuclear spin-free model, *i.e.*, using equation (4) ($S = 5/2$). The values of J obtained are about $-100\ \text{cm}^{-1}$, much the same as those for the $[\text{Fe}^{\text{III}}(\text{salen})_2]\text{O}$ complexes discussed below. More reasonable values of g (2.00), and $N\alpha$ (0) have been used in this latter interpretation.

A recent investigation[101] of the cryomagnetic properties of some iron(III) binuclear oxy-bridged Schiff base complexes of N,N'-ethylenebis(salicylideneimine) (salen) has shown that the cryomagnetic properties are well interpreted by equation (4) ($S = 5/2$) or equation (5) ($S = 3/2$), with $J = -100\ \text{cm}^{-1}$ or $J/k = -144°$ ($g = 2.00$, $N\alpha = 0$). (The reason why both equations give a reasonable interpretation of the cryomagnetic results is that in the case of $S = 5/2$ with $J = -100\ \text{cm}^{-1}$, contributions to the susceptibility from states with S' greater than 3 are negligible over the temperature range 300 °K to 80 °K.) The exchange integral appears to be independent of the substituents on the Schiff base ligands and thus primarily dominated by the iron–oxygen–iron bridge. The bridge is supposed to be linear, and consequently one would expect a large antiferromagnetic interaction. Both a π-mechanism and a σ-mechanism should give rise to antiferromagnetic coupling in the d^5 case. (The weaker interaction in the double bridged dimeric $(\text{Fe}^{\text{III}}\ \text{salen}\ \text{Cl})_2$ (ref. 102) $J = -7.5\ \text{cm}^{-1}$ ($J/k = -11°$) is associated with iron–oxygen–iron angles of 105° and the availability of only one p_π-orbital per bridging oxygen.)

Hatfield *et al.*[103] have measured the variation of the magnetic susceptibility with temperature for $\text{Cu}^{\text{II}}[(\text{C}_2\text{H}_5)_2\text{NCH}_2\text{CH}_2\text{NHCH}_3]\text{OHClO}_4$ and $\text{Cu}^{\text{II}}[(\text{C}_2\text{H}_5)_2\text{NCH}_2\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2]\text{OHClO}_4$. The room temperature magnetic moments for the two ammines are 1.69 B.M. and 1.38 B.M., respectively. Their cryomagnetic data are considered to support Pfeiffer and Glaser's formulation as binuclear hydroxy-bridged complexes[104].

(iv) Halogen bridged dimers

The ions $(\text{Mo}_2\text{Cl}_9)^{3-}$, $(\text{Cr}_2\text{Cl}_9)^{3-}$ and $(\text{W}_2\text{Cl}_9)^{3-}$ have similar structures in which the two $\text{MCl}_6{}^{3-}$ octahedra are fused together by a common face[105–107].

The short metal-to-metal bond (W–W = 2.41 Å) and the small paramagnetism (μ_{eff} = 0.47 B.M. at 300°)[108] for the tungsten compound can be understood by assuming that there is a triple bond between the metal ions. The molybdenum complex anion is also effectively diamagnetic[109]. The chromium(III) anion is very different; it has a larger metal-to-metal separation (Cr–Cr = 3.12 Å) and its room temperature moment (μ_{eff} = 3.71 B.M. per metal atom) is only slightly less than the expected spin-only value; in fact the cryomagnetic results are typical of a dimer with weak antiferromagnetic coupling (J is about -21 cm^{-1} or $J/k = -30°$. Martin[3] suggests that this difference in properties is due to the increasing radial extension of the metal d orbitals down the iso-electronic triad. The chromium(III) results are themselves interesting as they provide an example of the 90° interaction between two d^3 ions. Referring to the two p orbitals in the chromium(III)–chlorine–chlorine–chromium(III) plane as the $p_{\sigma x}$ and $p_{\sigma y}$ orbitals, and attaching primes to the orbitals of one of the cations, there will be a third-order ferromagnetic coupling arising from the e_g–$p_{\sigma x}$–$p_{\sigma y}$–e_g' interaction, and further ferromagnetic interactions from the e_g–$p_{\sigma x}$–t_{2g}' and e_g'–$p_{\sigma y}$–t_{2g} interactions. There will be antiferromagnetic coupling arising from both the t_{2g}–p_π–t_{2g}' interaction and any direct $t_{2g}-t_{2g}'$ interaction. (The p_π orbital is the p orbital on the chlorine which points out of the chromium(III)–chlorine–chromium(III) plane.) The experimental results can only be explained if the antiferromagnetic interaction is greater than the ferromagnetic interaction.

Recently the cryomagnetism of $Cs_3Cr_2X_9$ where X = Cl, Br or I has been studied[110] and it was found that the Weiss constants decreased according to $Cl^- > I^- > Br^-$, which is difficult to understand if the iodide has the same structure as the chloride and bromide. Wentworth[110] has also found that the formally similar $Cs_3V_2Cl_9$ is magnetically simple, *i.e.* obeys the Curie–Weiss law, but that the magnetic properties of $Cs_3Ti_2Cl_9$ are not simple: there is a minimum in the molar susceptibility curve at 165° and the magnetic moment decreases smoothly from 1.3 B.M. at 300 °K to 0.7 B.M. at 80° K.

Copper(II) compounds with halogen bridges may have normal or subnormal moments. Recently the presence of isolated planar $Cu_2Cl_6^{2-}$ ions in $LiCuCl_3 \cdot 2H_2O$ (ref. 111) and $KCuCl_3$ (ref. 112) has been confirmed by X-ray analysis. The cryomagnetic results for $LiCuCl_3 \cdot 2H_2O$ indicate that there is a ferromagnetic interaction between the copper(II) ions *via* the chlorine bridge. The copper–chlorine–copper angle in $KCuCl_3$ is 93°, and consequently one would also expect a ferromagnetic interaction within the $Cu_2Cl_6^{2-}$ unit in this compound. However the cyromagnetic results for $KCuCl_3$ indicate an antiferromagnetic interaction. It is difficult to understand the magnetic results reported for these two compounds. Kubo *et al.*[113] have investigated the temperature variation of the magnetic susceptibility of $KCuBr_3$, which is isomorphous with $KCuCl_3$, and found that the results are well interpreted by a modified form of equation (3), namely

$$\chi_M = \frac{g^2N\beta^2}{3k(T-\theta)} \cdot \frac{1}{1+3e^{-2J/kT}} + N\alpha$$

(where θ is considered to allow for the spin–spin interaction between the dimers).

It is usually found that the exchange coupling between metal ions bridged by bromide anions (*e.g.* the linear antiferromagnetic $CuBr_2$ for which $\mu_{\mathrm{eff}} = 1.31$ B.M. at 300 °K.)[114] is greater than for the corresponding chloride (*e.g.* $CuCl_2$ for which $\mu_{\mathrm{eff}} = 1.15$ B.M. at 300 °K). This is in agreement with the mechanisms mentioned above, because the transfer integral, b_{ij} and hence the coupling should become larger as the electronegativity of the anion decreases.

(v) "Quadridentate bridging ligands"

Recently a number of binuclear complexes of nickel(II) and cobalt(II) have been prepared[116] with 1,4-dihydrazino-phthalazine (dhph), of the type [dhph $MX_2 \cdot nH_2O]_2$ (M = Ni or Co; X = Cl, Br or I; $n = 0.5$ to 3); with 3,6-bis-(2′-pyridyl) pyridazine (dppn), of the type [dppn $MX_2 \cdot nH_2O]_2$ (M = Co or Ni; Y = ClO_4 or NO_3; $n = 2$ or 1) or dppn $M_2(SO_4)_4 \cdot 5H_2O$ (M = Co or Ni); and with 3,6-bis(6′-methyl-2′-pyridyl) pyridazine (Me_2 dppn), of the type Me dppn $M_2(NO_3)_4 \cdot nH_2O \cdot m$MeOH (M = Co or Ni; $n = 0$ and $y = 2$ for M = Co, $n = 1$ or 2 and $m = 1$ or 0 for M = Ni). These "quadridentate bridging" ligands (dhph, dppn and Me_2dppn) are capable of behaving as bidentate chelates to two metal ions simultaneously, so that it is possible for the spins of the cations to interact *via* an $-\mathrm{N}\overline{\cdots\cdots}\mathrm{N}-$ bridge. The electronic spectra for the compounds given above suggest binuclear structures. (dhph Ni $Cl_2 \cdot 3H_2O]_2$ has been shown to be binuclear[116,117]. The structure consists of two nickel ions bridged by the phthalazine nitrogen atoms of the ligand molecules, with two water molecules completing a distorted octahedral arrangement about each metal ion. The Ni–Ni distance is 3.79 Å. The magnetic properties of these compounds are consistent with a structure containing isolated pairs of M^{2+} ions with a weak antiferromagnetic exchange interaction. The variation in the computed exchange integrals from complex to complex and the larger J value for the nickel(II) complexes as compared with the structurally similar cobalt(II) complexes, are best interpreted in terms of the postulates[19] of Anderson's "second paper" in which, part of the "super" exchange for the nickel(II) as well as the cobalt(II) complexes is described by a π-type orbital interaction. (This π-type interaction for the nickel(II) complexes requires an excitation of a t_{2g} electron to an e_g orbital prior to the exchange interaction.) The computed J values for the nickel(II) complexes are about $-21\ \mathrm{cm}^{-1}$ ($J/k = -30°$).

(vi) Metal complexes as ligands

Harris, Gruber and Sinn[118–121] have prepared a series of oxygen-bridged bi- and tri-nuclear complexes by using metal salicylaldimine complexes as bidentate chelating ligands. This invokes the well established ability of the two-co-ordinate oxygen atoms in such compounds to raise their co-ordination number to three[122]. In this way it is possible to bring almost any two metals, similar and dissimilar, into combination with two bridging phenolic oxygen atoms. By forming a complex of metal M with a tetradentate Schiff base L and then using this complex ligand ML to complex with a metal halide $M'X_2$ or perchlorate $M'Y_2$, complexes of the general type $[(ML)M'X_2]$ and $[M'(ML)_2]Y_2$ can be formed. Particular emphasis has been placed on homonuclear copper(II) complexes[118-121] of the type $[(CuL)CuX_2]$, all of which display antiferromagnetic interactions; the cryomagnetic results are well interpreted by equation (3) with J values varying from -49 to -236 cm^{-1} ($J/k = -71°$ to $-340°$). The variation of the extent of exchange probably depends considerably on the stereochemistry about the oxygen bridges.

D. TRIMERIC SPECIES

Welo[123], in his extensive study on the magnetic susceptibilities of various salts, showed that a number of polynuclear salts of chromium(III) and iron(III) obeyed the Curie–Weiss law, the iron(III) complexes having larger θ values than the corresponding chromium(III) complexes; for example, for $[Fe_3(CH_3COO)_6(OH)_2]NO_3 \cdot 6H_2O$, θ is approximately $-600°$ and for $[Cr_3(CH_3COO)_6(OH)_2]Cl \cdot 8H_2O$, θ is approximately $-100°$. Kambe[7] has interpreted a number of Welo's results assuming that the cations form an equilateral triangle, so that the spin Hamiltonian used to describe the system is

$$\mathscr{H}_x = -J[S'(S'+1)-3S(S+1)] \text{ where } S' = 3S, 3S-1, \ldots, \tfrac{1}{2}.$$

The cryomagnetic results are reasonably well interpreted by assuming $J = -28$ cm^{-1} or $J/k = -40°$ for the iron(III) salts and $J = -13$ cm^{-1} or $J/k = -18°$ for the chromium(III) salts. Lewis *et al.*[124] have investigated the cryomagnetic properties of 5 basic carboxylate complexes of chromium(III) and 7 basic carboxylate complexes of iron(III). The basic chromium(III) carboxylates have been shown by X-ray crystal structure analysis[125] to be correctly formulated as $[Cr_3O(RCO_2)_6(H_2O)_3]^+$ rather than $[Cr_3(RCO_2)_6(OH)_2]^+$. Each chromium(III) ion is nearly octahedrally co-ordinated by oxygen, and the three cations form an equilateral triangle about a central oxide anion. The interpretation of the cryomagnetic results for $[Cr_3O(CH_3COO)_6(H_2O)_3]Cl \cdot 6H_2O$ is slightly improved [126] by assuming that the three cations are at the corners of an isosceles triangle rather than at the corners of an equilateral triangle as assumed by Kambe[7] in his calculations. However acceptable agreement has been obtained assuming an equilateral triangle. The J value of -7 cm^{-1} ($J/k = -10.4°$) reported by Lewis[124] is in excellent agreement with the values reported by Wucher and Gijsman[127] and Schriempf and Friedberg[126]. The cryomagnetic results for the other chromium(III) complexes reported by Lewis[124] are well interpreted with the same model, using similar J values. The cryomagnetic properties of most of the iron(III) complexes reported by Lewis[124] are also well interpreted on the same model with J values of about -21 cm^{-1} ($J/k = -30°$). The J values for the isomorphous iron(III) compounds are larger than for the chromium(III) complexes. The σ- and π-systems of both the trigonal oxide anions and the bridging carboxylate groups provide suitable pathways for the superexchange interactions.

The cryomagnetic results for three trimeric iron(III) n-alkoxides $[\mathrm{Fe_3(OR)_9}]$ have been interpreted[128] in terms of an intramolecular exchange interaction between the three iron(III) ions at the corners of an equilateral triangle, with an isotropic J value of -10 cm^{-1} ($J/k = -15°$). The fact that the room temperature magnetic moments in benzene solution are the same as those of the solid (4.2 to 4.4 B.M.) and are independent of solute concentration is good evidence for intramolecular rather than intermolecular interactions.

Recently[129,10] a cryomagnetic investigation of the linear trimeric $\mathrm{Ni_3(acac)_6}$ has shown that there is a ferromagnetic exchange between nearest neighbour metal ions (J is about 26 cm^{-1} or J/k is 37°) as would be expected for a superexchange mechanism operating *via* a 90° nickel–oxygen–nickel pathway. The terminal atoms appear to be coupled antiferromagnetically and more weakly (J is about -7 cm^{-1} or $J/k = -10°$).

The complex bis[*N*,*N*′-1,3-propylene bis(salicylaldiminato) copper(II)] nickel(II) perchlorate is of particular interest because it is the first compound with a copper–nickel–copper combination[118,121]. (A preliminary X-ray structure determination indicates that the metal ions lie at the corner of an isosceles triangle $[\mathrm{Cu}\diagup^{\mathrm{Ni}}\diagdown\mathrm{Cu}]$. The computed exchange integrals are reported as $J_{\mathrm{Cu-Ni}} = -61$ cm^{-1} ($J/k = -88°$) and $J_{\mathrm{Cu-Cu}} = -5$ cm^{-1} ($J/k = -7°$). It is to be noted that when either the central or the two outer metal ions in the cluster are diamagnetic, appreciable intramolecular exchange interactions are not observed[121]. In the trinuclear clusters bis[bis(*N*-ethylsalicylaldiminato) nickel(II)] nickel(II) nitrate and bis [bis(*N*-isopropylsalicylaldimino) nickel(II)] nickel(II) perchlorate monohydrate, all three nickel(II) ions are paramagnetic[120]. The respective increases in the magnetic moments per nickel(II) ion from 3.31 and 3.28 B.M. at 300 °K, to 3.54 and 3.35 B.M. at 80 °K seem to be indicative of ferromagnetism but no detailed interpretation has yet been made. More recently this method of using metal complexes as ligands has been extended to form a number of trinuclear complexes of the form $\mathrm{(CuL)_2\,M(ClO_4)_2 \cdot \mathit{n}H_2O}$, where[130] M is copper(II), nickel(II), cobalt(II), iron(II) and manganese(II). The complexes are considered to contain the unit $\mathrm{Cu}\diagup^{\mathrm{M}}\diagdown\mathrm{Cu}$ and $J_{\mathrm{Cu-Cu}}$ has been assumed to be zero. The exchange integrals, $J_{\mathrm{M-Cu}}$ for the five complexes in which M = Cu, vary from -40 to -240 cm^{-1} ($J/k = -58$ to $-346°$). As M changes from Cu to Ni, $J_{\mathrm{M-Cu}}$ decreases appreciably, $J_{\mathrm{Ni-Cu}}$ being larger than $J_{\mathrm{Co-Cu}}$, $J_{\mathrm{Fe-Cu}}$ and $J_{\mathrm{Mn-Cu}}$ for the corresponding complexes.

E. TETRAMERIC SPECIES

On the basis of molecular weight measurements, and spectral and magnetic evidence for six-fold co-ordination of the nickel(II) ions, Schrauzer and Kohnle[131] concluded that $Ni^{II}(O \cdot C_6H_4 \cdot CHO)(OCH_3) \cdot CH_3OH$ has a cubane-type structure, with nickel(II) ions and methoxy groups at alternate corners of a distorted cube. Bertrand and Caine[132] simultaneously reported the preparation of the analogous cobalt(II) compound. The cryomagnetic results for the methanol and a similar ethanol solvate are well interpreted for the nickel(II) compounds assuming that the nickel(II) ions are at the corners of a tetrahedron, and using J values of 4 cm^{-1} ($J/k = 6°$) and 7 cm^{-1} ($J/k = 10°$) respectively[11]. This ferromagnetic effect is predicted by the mechanisms mentioned earlier, for d^8 ions with 90° metal–oxygen–metal angles. The reciprocal susceptibility–temperature curve for the cobalt complexes suggests a similar ferromagnetic interaction for the cobalt(II) ions. No detailed theoretical interpretation of the cobalt(II) results has yet been possible although theory would predict a smaller exchange integral.

A tetranuclear oxopivalate of cobalt(II), $Co_4O[(CH_3)_3C \cdot CO_2]_6$, has been prepared[133]. It is assumed to have a structure similar to the well known beryllium and zinc oxoacetates[134], consisting of a central oxygen atom surrounded tetrahedrally by four metal atoms. There is evidence from the electronic spectrum that the cobalt(II) ions are in tetrahedral fields. This compound has a low magnetic moment and although the reciprocal susceptibility–temperature curve is not simple there is evidence for a weak antiferromagnetic interaction with J about -6 cm^{-1} ($J/k = -9°$).

Wentworth and Saillant[8] have measured the variation of the magnetic susceptibility with temperature of the tetranuclear ion $[Cr_4(OH)_6(en)_6]^{6+}$, first reported by Pfeiffer[135]. Their results were interpreted on an inaccurate theoretical model[9]. More recently[10], the variation of the magnetic susceptibility with temperature, over the temperature range 300–77 °K, agrees well with that expected for four chromium(III) ions in a tetrahedral cluster with $J/k = -3.57°$.

The crystal structure[136] of cobalt(II) acetylacetonate shows that the unit cell contains a centrosymmetric tetramer. The structure of the tetrameric anhydrous cobalt(II) acetylacetonate (Co_4acac_8) is, in some respects, similar to that for the trimeric nickel(II) acetylacetonate. Both compounds achieve six-co-ordination through the sharing of oxygen atoms. The crystal structure[137] of the copper(II) compound $Cu_4OCl_6(OPPh_3)_4$ shows that the four copper ions tetrahedrally surround an oxygen atom; chlorine atoms bridge adjacent copper(II) ions, and each is thus bonded to three chlorine atoms. The oxygen of phosphine oxide completes the slightly distorted trigonal bipyramid around each copper(II) ion. In both of these tetrameric species the cryomagnetic results, in the temperature range 1.5 to 300 °K, indicate that at low temperatures (below 60 °K for the copper complex and below 75 °K for the cobalt complex) antiferromagnetic coupling dominates the ferromagnetic interaction which appears to be larger at room temperature. The room temperature magnetic moment for the cobalt(II) tetramer is now reported to be 5.11 B.M.[138] as compared with the earlier value of 4.87 B.M.[137]; and that of the copper(II) tetramer is reported to be 1.87 B.M.[138] as compared with the earlier value of 2.2 B.M.[139]

F. CONCLUSIONS

(i) The present status of the interpretations

So far nobody has succeeded in calculating a susceptibility expression for two or more interacting ions, which have T ground terms. [Recently the behaviour of the magnetic properties of the $^2T_2$[140], $^5T_2$[141], $^3T_1$[142], and $^4T_1$[143] terms under simultaneous perturbations by spin–orbit coupling and axial crystal fields have been presented. The magnetic perturbation calculations were performed using the operator in which k, Stevens's orbital reduction factor[144], may be related to the proportion of ligand character in the basis molecular orbitals $\{\mu = \beta\,(k\,L+2S)\}$. This three parameter model, involving distortion, spin–orbit coupling and "covalence", provides good agreement between theoretical and experimental susceptibilities observed over a temperature range. However for a number of "octahedral" cobalt(II) complexes the interpretation of the experimental data does not lead to an unambiguous choice of the set of parameters k (amount of t_{2g} orbital reduction), λ (spin–orbit coupling constant for the term) and Δ (the axial field splitting of the cubic-field term). The magnitude of the effect of the low symmetry ligand field component is expressed as the ratio of the splitting of the T orbital wave functions to the spin–orbit coupling constant, $v = \Delta/\lambda$.]

However the Heisenberg–Dirac–Van Vleck model has provided a sound basis for evaluating the exchange integral from the experimental cryomagnetic results for a wide variety of clusters, for which the paramagnetic ions have A,B or cubic field E ground terms. For a complex of known crystal structure containing a discrete cluster it would seem possible to make very reasonable qualitative predictions concerning both the sign and the extent of the exchange. (For example the exchange interactions for iron(III) complexes are larger than those for the analogous chromium(III) complexes for 180° exchange, because only for the iron(III) complexes is there a first-order σ-mechanism.) As Kanomori[18] has predicted, M-X-M angles and M-X and M-M distances are critical in determining the extents of exchange.

The first four mechanisms[12–15] given, provide a useful pictorial representation of the exchange interaction, and, for example, they accurately predict an antiferromagnetic exchange for 180° interactions between two d^8 ions while predicting a ferromagnetic exchange for 90° interactions between two such ions. However they cannot always explain the different extents of exchange observed between similar compounds with different metal ions (for example, the different Néel temperatures[145] for MnO, FeO, CoO and NiO). The postulates[19] of Anderson's "second paper" would seem to be capable of giving a more accurate interpretation of the exchange integrals, and furthermore these postulates can explain the differences in the extents of exchange between similar compounds with different metal ions.

At this point it is again worth emphasising the importance which has been attached to π-pathways for exchange interactions *via* polyatomic ligands, particularly for the copper(II) complexes which exhibit exchange.

(ii) *Prospects for the future*

Theoretical predictions about the signs and magnitudes of exchange interactions are difficult to test on solids with cooperative lattice magnetism: there are complications due to multiple interactions and sublattices. In general, ferromagnetic interactions can only be indirectly inferred because there is usually an antiferromagnetic interaction tending to couple the ferromagnetic sublattices together. However, the study of clusters of known structure offers the prospect of resolving these uncertainties. (An example is the 90° Ni−O−Ni interaction, confirmed as ferromagnetic in $[Ni(acac)_2]_3$[129,10] and $[Ni(O \cdot C_6H_4 \cdot CHO)(OCH_3)(ROH)_4]$[11].) Other theoretical predictions, such as the dependence of exchange on electron configuration and ligand basicity, conjugation and geometry, can also be more conveniently tested on clusters. The use of bridging chelating ligands[116,116a] and of mononuclear complexes as ligands[118−121] provides a promising way of getting the desired clusters.

Many interactions in materials that are of practical importance (or potentially so), such as ferrimagnets, are between ions of different types. A more extensive study of mixed metal bi- and poly-nuclear clusters could give useful insight into these systems. An example might be the so far unconfirmed prediction of ferromagnetic exchange in the linear cluster d^3-O-d^5. Again, the possibility of obtaining suitable clusters is increased by the use of specialized ligands, especially mononuclear complexes.

It is becoming evident that intercluster interactions can sometimes be far from negligible (*e.g.* in the series $M_3Ti_2Cl_9$, $M_3V_2Cl_9$, $M_3Cr_2Cl_9$, with M^+ varying in size[146−148]. One should be cautious in interpreting magnetic behavior in terms of intramolecular exchange unless one can be satisfied that the clusters are magnetically dilute.

Further refinements in the theoretical interpretation of the magnetic data are necessary; for example, (a) an investigation of the effects of vibrational motion on exchange (the separations of vibrational and spin levels are often comparable); (b) further investigations of the effect of incompletely quenched orbital magnetism on the properties of polynuclear complexes; (c) more detailed molecular orbital treatments of simple systems, with the interelectronic repulsion effects included[149].

Ferromagnetic exchange may be more common than has previously been believed, and several compounds formerly dismissed as "magnetically normal" on the basis of their room temperature magnetic moments being slightly higher than usual may be worth reinvestigating. For example, the cryomagnetic results for $Cu_4OBr_6py_4$[150] are indicative of an intramolecular ferromagnetic interaction, and the more recent investigations of the magnetic and structural properties of the violet cobalt acetylacetonate have shown that it is tetrameric[3].

The extension of the lower temperature limit from 80 °K down to 1.5 °K is becoming more common. These low temperature measurements provide a more critical test of the theoretical interpretations involving fairly weak exchange than do the 80–300 °K data.

Consequently it would seem that a more detailed understanding of magnetic exchange phenomena will be found, not only as the theory is refined, but with more extensive cryomagnetic investigations of isolated clusters, particularly where specialized ligands are employed.

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