Coordination Chemistry Reviews, 69 (1986) 1–55
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

INTRAMOLECULAR FERROMAGNETIC INTERACTIONS IN POLYNUCLEAR METAL COMPLEXES

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(Received 14 May 1985)

CONTENTS

ABBREVIATIONS

bpy	2,2′-bipyridine
tmen	*N*,*N*,*N*′,*N*′-tetramethylethylenediamine
teen	*N*,*N*,*N*′,*N*′-tetraethylethylenediamine
maep	2-(2-methylaminoethyl)pyridine
eaep	2-(2-ethylaminoethyl)pyridine
dmaep	2-(2-dimethylaminoethyl)pyridine
2-NH_2py	2-aminopyridine
t-Bupy	4-tert-butylpyridine

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py-NO	pyridine *N*-oxide
sal	salicylaldehyde
gly	glycinate
mal	malonate
$H_4(fsa)_2en$	*N*,*N′*-bis(2-hydroxy-3-carboxybenzylidene)ethylenediamine
H_2salen	bis(salicylidene)ethylenediamine
$H_2salmen$	bis(salicylidene)1,2-diaminopropane
Im	imidazole
caf	caffeine
DMSO	dimethylsulfoxide
TMSO	tetramethylenesulfoxide
PDA	1,3-propylenediammonium cation
CHAC	cyclohexylammonium cation
CPAC	cyclopentylammonium cation
dx	1,4-dioxane
TPP	tetraphenylporphyrin

A. INTRODUCTION

The quantitative treatment of magnetic interactions between atoms as an exact science goes back almost sixty years to the early work of Heisenberg [1], Dirac, Heitler, and London [2] and their associates on very simple non-metallic systems such as the helium atom and hydrogen molecule. Van Vleck [3] and Kramers [4] were the first theoreticians, in 1934, to publish applications of these models to transition metal systems. In that year also Becquerel, De Haas, and Van den Handel [5] obtained experimental evidence for the occurrence of the so called superexchange interaction in a three-dimensional mineral lattice.

From the chemist's point of view a seminal publication was the appearance in 1950 of a paper by Kambe [6] on intramolecular antiferromagnetic interactions in polynuclear chromium(III) and iron(III) acetate complexes. Two years later a paper by Bleaney and Bowers [7] on the anomalous magnetic properties of copper(II) acetate monohydrate captured rather more attention, as it became clear that the original Heisenberg–Dirac–Van Vleck (HDVV) model could be applied with profit to relatively simple molecular species.

The theoretical framework developed by this time suggested the existence of molecular species containing positive coupling constants in the HDVV Hamiltonian

$$\mathscr{H} = -2J\hat{\mathbf{S}}_1\cdot\hat{\mathbf{S}}_2 \tag{1}$$

The first of these molecules to be positively identified was the linear trimeric nickel(II) chelate $[Ni(acac)_2]_3$ [8], in which both intramolecular ferro- and antiferromagnetic interactions were observed. The eminent success with which the magnetic behavior of this complex could be treated using the HDVV Hamiltonian led to renewed efforts to characterize more complexes of this type. The diversity of transition metal complexes covered in the following review attests to the success of these efforts.

The purpose of this review is to summarize the occurrence of intramolecular ferromagnetic interactions where they have been identified in complexes of the first row transition metal series. Little attempt has been made to list or explain the intricate theories which have been developed to explain the signs and magnitudes of the magnetic interactions in paramagnetic clusters except where those theories provide qualitatively simple pictures relating the structure of the molecule to its resultant magnetism. The orbital models of Hoffmann and Kahn meet, in their simplest incarnations, such a criterion and will therefore be introduced in the appropriate places. This review is designed to be of use to structural chemists and will therefore emphasize those structural features which give rise to the observed intramolecular couplings, hopefully in such a way as to suggest how modifications might give rise to novel systems with expected properties. It will become apparent that the introduction of such novel structural features, and the design of radically original molecular ferromagnets, can involve not only extensive reasoning based on existing acquired knowledge, but also a fair degree of Edisonian research which can only be vindicated by the results obtained.

The classes of complexes of greatest interest will be dealt with individually, with each section including, or being followed by, a discussion of the theoretical models which most successfully correlate structure with observed magnetism. There will be little description or discussion of the battery of experimental techniques used to elucidate magnetic behavior; these various methods, including variable temperature magnetic susceptibility and magnetization methods, specific heat, EPR, and neutron inelastic scattering techniques have been the subject of in depth discussion in several excellent papers [9–12]. The importance of the proper use of these experimental tools, preferably in conjunction, cannot be overemphasized, since even at the lowest available temperatures, magnetic susceptibility data on their own cannot always give a clear picture of the magnetic behavior of the simplest systems.

B. DI-μ-HYDROXO-BRIDGED COPPER(II) DIMERS

The title compounds probably represent the most elegant and completely characterized family of complexes in which a successful correlation has been established between structural parameters and the sign and magnitude of exchange coupling between two metal centers. To date, at least eleven members of this family have been characterized and, with a few exceptions for which plausible explanations are available, a linear relationship has been observed between the isotropic exchange constant J and both the Cu–O–Cu bridging angle (ϕ) and the Cu–Cu distance.

The systems under discussion have the general formula $[\mathrm{CuL(OH)}]_2^{2+}$, where L is a bidentate ligand such as 2,2′-bipyridine (bpy), *N,N,N′,N′*-tetramethylethylenediamine (tmen), 2-(2-ethylaminoethyl)pyridine (eaep), or 2-(2-dimethylaminoethyl)pyridine (dmaep). Values for the singlet–triplet splitting $2J$ have been measured in the range $-509 < 2J < +172\ \mathrm{cm}^{-1}$, with the corresponding Cu–O–Cu angles in the range $104.1° < \phi < 95.6°$. In all cases the use of complementary EPR studies has verified the presence of a triplet signal. Since the copper(II) ion has only one unpaired electron the singlet–triplet separation is given, in magnetically isolated cases, by the Bleaney–Bowers form of the Van Vleck equation for exchange-coupled pairs of $S = 1/2$ ions.

$$\chi_M = \frac{N\beta^2 g^2}{3kT}\left[1 + \tfrac{1}{3}\exp(-2J/kT)\right]^{-1} + N\alpha \tag{2}$$

In addition, under favorable circumstances, crystal EPR spectroscopy may be used to extract magnetic parameters from the complex under investigation. The formation of binuclear hydroxo-bridged copper(II) complexes had been known for some years before research was initiated with the specific intention of analyzing the magnetic interactions displayed by these compounds [13–17]. Early studies suffered from the limitations of the magnetic susceptibility measurement facilities and provided no indication of profound intramolecular effects. Around 1970 the first definitive evidence appeared for these interactions; in that year Hatfield and co-workers [18] and Casey et al. [19] independently carried out investigations on the binuclear complex $[\mathrm{Cu(bpy)(OH)}]_2\mathrm{SO}_4 \cdot 5\mathrm{H}_2\mathrm{O}$, whose structure is shown in Fig. 1 [19,20]. The

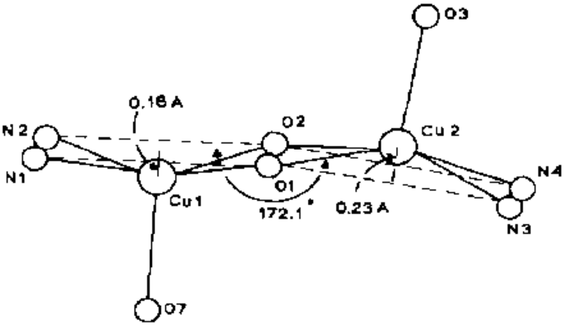
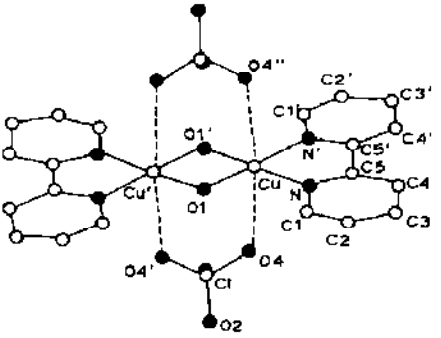


Fig. 1. Environments of the copper(II) ions in $[(\mathrm{H_2O})(\mathrm{bpy})\mathrm{Cu(OH)_2(bpy)(OSO_3)}]\cdot 4\mathrm{H_2O}$.

complex consists of two copper centered distorted square pyramids with a shared basal edge. The axial ligands are a water molecule [0(7)] and sulfate ion [0(3)]. The copper–copper distance is 2.89(3) Å in the range 2.78–3.21 Å found in chain and layer structures having copper bridged to copper by hydroxo groups, but significantly longer than the copper–copper separations (2.63–2.65 Å) found in acetate bridged copper(II) complexes [21–23]. It is therefore assumed that no direct metal–metal interaction occurs in this or any other di-μ-hydroxo-bridged dimeric complex. The Cu–O–Cu bridging angles are ca. 97°. Magnetic susceptibility measurements between 4.2 and 209 K led to an estimate for $2J$, the singlet–triplet energy level separation, of $+48 \pm 10$ cm^{-1}, the range being due to the insensitivity of the Van Vleck equation to small changes in $2J > 0$ cm^{-1}. At worst the results confirm a triplet ground state for this molecule.

Since this initial result, Hatfield and co-workers have extended their structural and magnetic investigations to a variety of complexes of this general structure. Firstly, by varying the counterion in their original complex, a combination of magnetic and EPR studies have shown that the following species also exhibit triplet ground states, in the order $2J(NO_3^-)$ ca. 170 cm^{-1}; $2J(I^-) > 150$ cm^{-1}; $2J(ClO_4^-) > 50$ cm^{-1}; and $2J(Br^-) > 40$ cm^{-1} [24,25]. The observations imply that the complexes under investigation do not have closely similar geometries around the copper(II) centers. In the perchlorate complex, for example, the copper(II) ions are bonded in an essentially square-planar geometry with two perchlorates interacting weakly



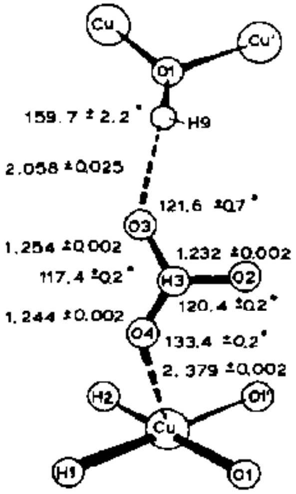


Fig. 2. The structure of $[(bpy)Cu(OH)_2Cu(bpy)](ClO_4)_2$.

Fig. 3. The nitrate group and its environment in $[(bpy)Cu(OH)_2Cu(bpy)](NO_3)_2$.

at axial sites (Fig. 2) [26]. The copper–copper separation in this complex is 2.871 Å and the Cu–O–Cu bridging angle (ϕ) is 96.9°. A structure determination on the nitrate complex shows each half of the dimer to be essentially planar, as in the sulfate and perchlorate salts. The corresponding metal–metal separation and bridging angle are 2.85 Å and 95.6°. A nitrate is weakly bound to each copper ion through one oxygen donor; another oxygen atom of the same counterion is hydrogen-bonded to a bridging hydroxo group of an adjacent dimer, as represented in Fig. 3 [27]. This arrangement can account for the small lattice antiferromagnetic effect indicated by low-temperature magnetic studies [25].

In addition to these hydroxo-bridged dimers, other related species have been synthesized and subjected to intensive structural, spectroscopic, and magnetic studies. These have been found to exhibit, without exception, large stabilizations of the singlet spin state. For example, salts of general formula $[Cu(amine)(OH)]_2(ClO_4)_2$, where the amine is a N,N,N',N'-tetrasubstituted chelate, have been prepared and studied [28,29]. These complexes have been found to exhibit large antiferromagnetic interactions. In the case of the tetraethylsubstituted perchlorate salt $2J = -410$ cm^{-1} [30]. Interestingly, an X-ray analysis showed a similar situation to that already observed in the bipyridyl nitrate complex, with a perchlorate anion (not coordinated in this case) forming a hydrogen bond to a neighboring hydroxo bridge. In this complex the metal–metal separation is 2.98 Å and $\phi = 103.0°$. In the tetramethyl analog $2J = -360$ cm^{-1} [29]. No structural data were presented, although infrared spectra indicated a weak interaction between the dimeric cation and a perchlorate counterion. Structural and magnetic studies on copper(II) dimers of the chelating ligands dmaep and eaep have given similar structure–magnetism correlations; the large antiferromagnetic interactions observed have been equated with the large bridging angles [31,32].

TABLE 1

Structural and magnetic properties of di-μ-hydroxo-bridged copper(II) dimers

Complex	R_{Cu-Cu} (Å)	R_{Cu-O} (Å)	$\phi_{Cu-O-Cu}$ (°)	$2J$ (cm^{-1})	g	Ref.
$[Cu(bpy)OH]_2(NO_3)_2$	2.847	1.920–1.923	95.6	+172	2.10	25, 27
$[Cu(bpy)OH]_2(ClO_4)_2$	2.870	1.92	96.6(2)	+93	2.22	26
$[Cu(bpy)OH]_2SO_4 \cdot 5H_2O$	2.893	1.92–1.95	97.0(2)	+49	2.20	18, 19 24, 62
$[Cu(eaep)OH]_2(ClO_4)_2$	2.917	1.895–1.930	99.8–99.5(3)	−130	2.04	31
β-$[Cu(dmaep)OH]_2(ClO_4)_2$	2.935	1.900–1.919	100.4(1)	−200	2.03	32
$[Cu(tmen)OH]_2(ClO_4)_2$	2.966	1.897–1.931	102.3(4)	−360	2.09	33
$[Cu(teen)OH]_2(ClO_4)_2$	2.978	1.899–1.907	103.0(3)	−410	2.05	25, 28
$[Cu(tmen)OH]_2Br_2$	3.000	1.902	104.1(2)	−509	2.0	34

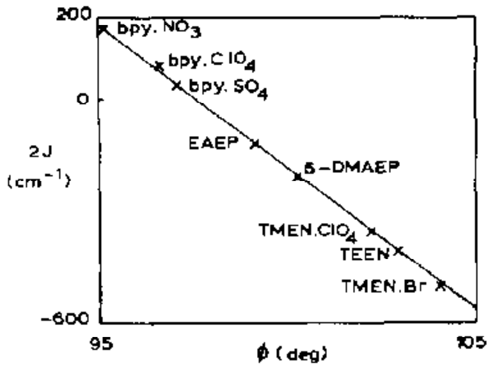


Fig. 4. Plot of $2J$ vs. ϕ for a series of structurally characterized di-μ-hydroxo-bridged copper(II) dimers.

The magnetic coupling constants for the eight copper(II) dimers whose structures have been fully characterized [29] are listed in Table 1, along with pertinent structural information. The apparent correlation between $2J$ and ϕ is brought out more clearly in the plot of Fig. 4 in which it can be seen that at a bridging angle of ca. 97.5° a switch over in the sign of the net magnetic interaction may be expected.

C. MOLECULAR ORBITAL APPROACH TO EXCHANGE COUPLING BETWEEN METAL IONS

At this point it becomes highly desirable to account for the measured intramolecular magnetic interactions in the molecules described in the previous section. It has been generally recognized that the easiest way to develop a concise and reasonable model of these types of interactions is to start with the simplest case, in which only two unpaired electrons, one on each metal center, interact with each other. This is the situation which exists in the copper(II)–copper(II) binuclear complexes. The most recent approach to magnetic coupling, based on the concepts of orthogonal magnetic orbitals, will be described.

It was Anderson [35,36] who first developed a reasonably successful model with which he could calculate the energy level ordering of coupled metal pairs. This superexchange model was developed using a valence bond formalism. Schematically, for a d^1–d^1 (or d^9–d^9) system, the unpaired electron on each metal center is assigned to an orbital, called a magnetic orbital. In the absence of an interaction the unpaired electron around metal A is centered on the metal but partially delocalized towards any bridging and/or terminal ligands surrounding it. The same situation pertains to the unpaired electron around metal B. The interaction between the two metals leads to two molecular states; a spin singlet and triplet separated by energy J. If relatively few assumptions are made then this singlet–triplet gap can be expressed as the sum of two components; a negative antiferromagnetic term J_{AF} and a positive ferromagnetic contribution J_F. Thus

$$J = J_{AF} + J_F \tag{3}$$

This basic equation, which is that used by Kahn in his treatment of this orbital interaction problem [37–42] can be expressed as follows. It has been determined that for a non-symmetrical d^1–d^1 (or d^9–d^9) system

$$J_{AF} = -2S(\Delta^2 - \delta^2)^{1/2} \tag{4}$$

$$J_F = 2j \tag{5}$$

where S is the overlap integral between the two magnetic orbitals and j is the two-electron exchange integral. Defining the overlap density between the two orbitals as

$$\rho(i) = \phi_A(i)\phi_B(i) \tag{6}$$

then S and j are given by

$$S = \int_{\text{space}} \rho(i)\,\mathrm{d}\tau_i \tag{7}$$

$$j = \int_{\text{space}} \frac{\rho(i)\rho(j)}{r_{ij}}\,\mathrm{d}\tau_i\,\mathrm{d}\tau_j \tag{8}$$

Δ is the energy gap between the two molecular orbitals Ψ_A and Ψ_B constructed from the magnetic orbitals, for the $S = 1$ state. δ is the energy gap between the ϕ_A and ϕ_B magnetic orbitals, as represented qualitatively below. Obviously if metals A and B are the same then $\delta = 0$ and $J_{AF} = -2\Delta S$ (Fig. 5).

Thus in this model the singlet–triplet splitting J arises from the competition between two driving forces, one of which favors the singlet state and

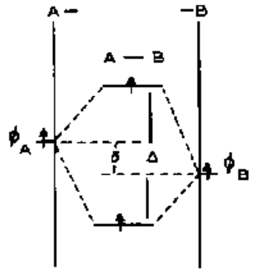


Fig. 5. Definition of Δ and δ.

one the triplet state. To a first order approximation $S\alpha(\Delta^2 - \delta^2)^{1/2}$, and so J_{AF} in absolute value, varies approximately as $-S^2$, or $-(\Delta^2 - \delta^2)$. Interestingly, Hoffman et al. derived the same dependence of J_{AF} on Δ^2 for a homobinuclear complex by a different route. Girerd et al. [40] have extended this theoretical analysis to the general case of n unpaired electrons on N paramagnetic centers, where N is large; i.e., one-dimensional linear chain paramagnets, but the analysis is beyond the scope of this review.

The simplest, if least interesting, situation to which the analysis of the two electron case (d^1–d^1 or d^9–d^9) can be applied is that in which the relative orientation of the magnetic orbitals on metals A and B is unfavorable towards any interaction; i.e., ρ is negligible and J_{AF} and J_F are both zero. In this case the magnetic properties of the dimer will simply be those of the separate mononuclear fragments.

Another relatively simple situation, from the theoretical viewpoint, occurs when $\rho \neq 0$, but in spite of this $S = 0$. From eqn. (4), $J_{AF} = 0$ and the experimentally observed J is composed entirely of J_F, the ferromagnetic component. This situation corresponds to orthogonality of the interacting magnetic orbitals. Orthogonality of the magnetic orbitals leads to $\Delta = 0$. As we shall see, there are two types of situations in which this orthogonality may arise.

(i) Strict orthogonality, imposed by the symmetry of the system.

(ii) Accidental orthogonality, an occurrence not directly related to the symmetry of the complex.

The most common situation arises when the J_{AF} component predominates. In fact when the antiferromagnetic interaction is very strong one of the simplifying assumptions made in developing this theory, that the low lying $S = 0$ and $S = 1$ states can be accurately described by Heitler–London wave functions [42,44], is no longer strictly true. In less extreme cases, where the above wave functions are still adequate, the singlet–triplet splitting becomes Δ rather than $2\Delta S$. This molecular orbital framework will now be used to provide semi-quantitative explanations for the magnetic properties of the di-μ-hydroxo-bridged copper(II) complexes that were introduced in the previous section. It will be seen that this treatment is flexible enough to deal with a wide range of bridging situations, not necessarily only those involving hydroxo bridges.

The Cu–X_2–Cu planar framework ($X = OH^-$, F^-, Cl^-, N_3^-, or OR^-, where R = alkyl or aryl) has the necessary elements to allow for accidental orthogonality [29,41,43]. The two magnetic orbitals are based on the $d_{x^2-y^2}$ metal orbitals and transform as the b_1 irreducible representation of the C_{2v} point group, which describes the local symmetry around each copper(II) site to a good approximation if the terminal ligands are ignored. From these two magnetic orbitals with b_1 local symmetry two molecular orbitals can be

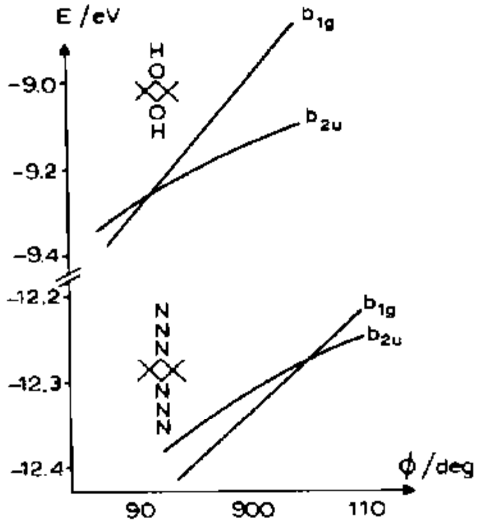
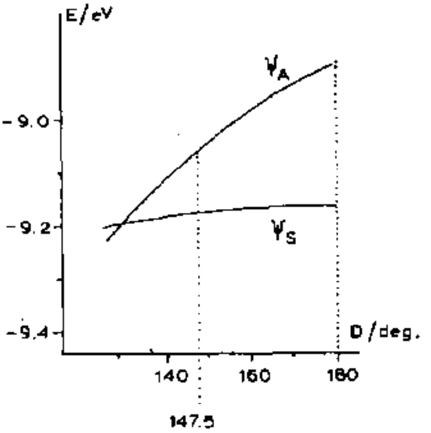


Fig. 6. Variations of the energies of the b_{1g} and b_{2u} molecular orbitals with ϕ in planar di-μ-hydroxo- and azido-bridged copper(II) dimers.

constructed having b_{2u} (Ψ_S) and b_{1g} (Ψ_A) symmetry with respect to the mirror plane perpendicular to the CuN_2O_2 framework. The energies of these orbitals are shown in Fig. 6, as they vary with the Cu–X–Cu bridging angle —this plot was obtained from extended Huckel calculations. For a certain angle ϕ_0 these molecular orbitals are accidentally degenerate, and the energy gap in the relationship $J_{AF} = -2\Delta S$ is zero. Notice that this model, like that developed by Hoffmann et al., implicitly assumes that J_F does not vary significantly with minor structural changes in the molecule. For $\phi < \phi_0$ the b_{2u} orbital lies higher in energy, whereas for angles greater than ϕ_0 the opposite situation occurs. In theory this value of ϕ_0 is 90°; experimentally when $X = OH^-$ it has been found to be ca. 97.5°. For $\phi > 97.5°$ the J_{AF} component predominates, and for ϕ less than this angle a ferromagnetic interaction is observed. It should not be assumed from this discussion that as the Cu–X–Cu bridging angle becomes continually smaller the ferromagnetic interaction steadily increases. At angles much below 90° the metal–metal direct interaction becomes important, leading to a singlet ground spin state. Thus for this bridged geometry only a relatively narrow range of ϕ will be expected to give a net positive exchange coupling constant.

It appears, then, that this molecular orbital theory can adequately account for the linear relationship between $2J$ and ϕ for di-μ-hydroxo-bridged copper(II) complexes. The linear relationship between $2J$ and the metal–metal separation follows, since this distance will depend closely on the bridging angle. In addition this theory can explain the apparent exceptions to this experimental trend, shown by the complexes in which the



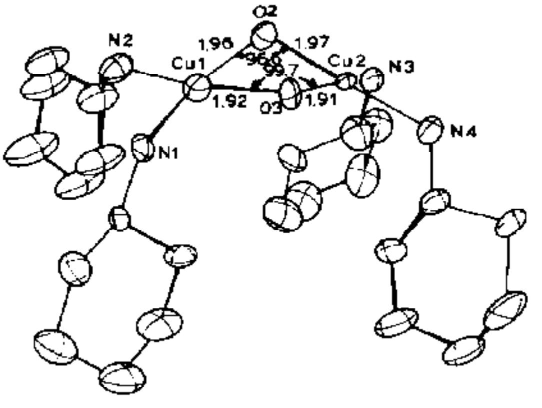
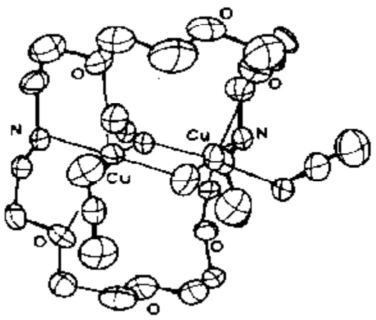


Fig. 7. Variation of energies of the ψ_S and ψ_A molecular orbitals vs. dihedral angle D for roof-shaped di-μ-hydroxo-bridged copper(II) dimers.

Fig. 8. Structure of tetrakis(cyclohexylamine)di-μ-hydroxo-dicopper(II) perchlorate.

terminal ligands are cyclohexylamine [45] and methylamine [46,47]. The rationalization runs as follows. Start with a planar $[Cu(OH)]_2$ network with a large ϕ of, say, 105°. From Fig. 6, Δ and J_{AF} will be large for this situation. Now bend the molecule along the O–O axis, without changing the Cu–O or O–O distances; as Kahn elegantly describes it, this is like bending a book along its spine. The mirror plane in the molecule remains, and therefore the Ψ_S and Ψ_A designations for the two molecular orbitals remain appropriate, indicating that the orbitals are symmetric (b_{2u}) or antisymmetric (b_{1g}) with respect to this plane. Figure 7 shows what happens to the relative energies of these molecular orbitals as the bending proceeds. The above analysis is valid for each set of parameters used in the extended Huckel calculation—these parameters are the Cu–O and O–O distances and the Cu–O–Cu and O–Cu–O angles. It can be seen that as the dihedral angle D, originally 180° decreases, so does the copper–oxygen antibonding overlap, whereas the bonding overlap does not vary to nearly the same extent. In short, Ψ_A becomes more stabilized relative to Ψ_S, and at an angle D ca. 130° the molecular orbitals become degenerate, allowing the possibility of a net ferromagnetic interaction between the metal centers at a smaller value. This reasoning appears to be valid, judging by the structural and magnetic data obtained from the two di-μ-hydroxo-bridged complexes in question. Figure 8 shows the structure of the complex cation of the cyclohexylamine complex. In this complex $D = 147.5°$ and the observed singlet–triplet splitting corresponds to a value of $2J = -256$ cm^{-1} [45]. Using the computed correlation of Hatfield and co-workers [29] with $D = 180°$ one would expect a value of $2J =$ ca. -600 cm^{-1}, so bending the molecule in this manner clearly has decreased the antiferromagnetic interaction between the copper centers. In the similar methylamine complex one copper(II) ion is coordinated weakly by an axial water and the other even more tenuously bound to a bridging hydroxo group from a neighboring dimer in the crystal lattice. These interactions combine to give a dihedral angle $D = 123.9°$ (the copper(II) ions are displaced slightly from their respective N_2O_2 planes towards the axial sites, so the dihedral angle in this case is best defined as the angle between the two CuO_2 planes). The singlet spin state is stabilized by only 7.9 ± 0.5 cm^{-1} [47] It appears, then, that only a slightly greater distortion would be required to achieve a net ferromagnetic ground state. A similar conclusion has been reached by other researchers from studies on the binuclear copper(II) complex $Cu(apaca)(CH_3COO)$ [48] (apaca is the Schiff base ligand derived from condensation of one equivalent of 2-hydroxy-1,3-diaminopropane with two equivalents of 2,4-pentanedione). This complex contains one endogenous alkoxo bridge from the Schiff base ligand and an additional acetate bridge. The dihedral angle is 119.2° and a net ferromagnetic interaction of $J = +18.9$ cm^{-1} is observed. These results, although taken from a rather different system than the di-μ-hydroxo-bridged dimers that have been discussed so far, suggest that this picture of non-coplanarity of coordination spheres can be applied widely to an analysis of the magnetic properties of binuclear systems. As well as describing the magnetic properties of the di-μ-hydroxo-bridged copper(II) dimers studied by Hatfield, Hodgson, and others, this theory has the ability not only to explain the observed magnetism in other bridged systems but also to suggest how new binucleating systems with predetermined properties might be designed ("molecular engineering") [42]. This possibility can best be considered by a description of two other bridging systems where an intramolecular ferromagnetic effect has been observed.

With reference to Fig. 7 and the preceding discussion, it can be shown that if the bridging groups X are highly electronegative the *s* valence orbitals on X will be too low in energy to interact with the appropriate magnetic orbitals centered on the metals, and ϕ_0 will be close to 90°. For a less electronegative ligand the *d*–*s* separation will be smaller. This interaction stabilizes the b_{2u} molecular orbital relative to the b_{1g} orbital, and hence shifts ϕ_0 to a larger value. Extended Huckel calculations have demonstrated that if $X = N_3^-$, ϕ_0 will be ca. 103° rather than the value of ca. 92° for a hydroxo bridge [42,49]. (N in nitrogen end-on bridging azide is less electronegative than O in bridging OH^-.) Such a situation has been realized experimentally with the synthesis of the cryptate complex shown in Fig. 9 [49]. In this complex each copper(II) ion is bound to one terminal and two end-on (1,1-) bridging azido groups, as well as one chelating diethanolamine unit from the macrocycle, to give an overall tetragonally distorted octahedral



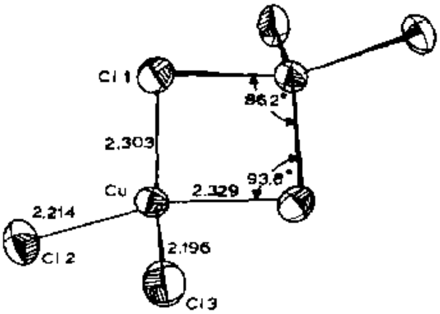


Fig. 9. Structure of the complex molecule $[Cu_2(N_3)]_4(C_{16}H_{34}N_2O_6)]$.

Fig. 10. Geometry of the $Cu_2Cl_6^{2-}$ anion in tetraphenylarsonium trichlorocuprate(II).

environment around each metal center. The bridging Cu–N–Cu angle is 103.6° and the observed magnetic interaction represents a stabilization of the triplet ground state by 70 ± 20 cm^{-1}. Another interesting example of this bridging mode in a copper(II) complex is given by $[Cu(acac)N_3]_2$, where magnetic susceptibility studies down to 90 K suggest a ferromagnetic interaction between the metal ions with $2J = +21$ cm^{-1} [50]. Infrared spectroscopy showed the presence of a di-μ-azido end-on structure in this complex. It seems reasonable to expect that replacement of the terminal chelate by its higher homologs would preserve the essential geometry of this system and so lead to the observation of triplet ground spin states in these new species also.

Bridging chloride is more electronegative than bridging hydroxide. Hence, in the $Cu_2Cl_6^{2-}$ anion, one would expect that the application of the foregoing analysis would yield a value of ϕ_0 somewhat less than 92°. Experimental results suggest that the crossover point actually occurs at ca. 94°; the disagreement with theory is not great in view of the many simplifying assumptions involved. Several dimers containing this complex anion have been synthesized, however few have been structurally characterized, so the correlation of $2J$ with ϕ cannot be confirmed. One complex that has been demonstrated to exhibit a triplet ground state is $[Ph_4As]_2Cu_2Cl_6$, in which $2J = +46$ cm^{-1} [51–53]. Figure 10 shows the pertinent structural parameters obtained through the results of an X-ray structural determination. The bridging angle of 93.6° is slightly smaller than in nearly all of the other structurally characterized members of this family. Where they have been measured these other complexes exhibit antiferromagnetic interactions, although the situation in this system is complicated by the presence of an extra deformation; the bridging chlorides are twisted out of the molecular plane so that the overall geometry at each copper is intermediate between planar and tetrahedral. Hoffmann et al. have analyzed the effect of this distortion on the relative stabilities of the appropriate molecular orbitals and have shown [43] that a ferromagnetic interaction may arise when the twist angle exceeds ca. 35°. Experimental results bear this out: in $[Ph_4As]_2Cu_2Cl_6$ the twist angle is 48° and a triplet ground state is indeed observed. It is interesting to compare this behavior with that expected for two other complexes containing the same dimeric anion. One of these, tetraphenylphosphonium trichlorocuprate(II), has been structurally characterized [54]. Its structure is very similar to the analogous tetraphenylarsonium complex, with $\phi = 93.3°$ and a twist angle of 50°. The local geometry is close to D_{2d}. The other complex, $[(C_4H_9)_4N]_2Cu_2Cl_6$, has been studied by spectroscopic techniques [55]. Given the results of the theoretical analysis and its successful application to a member of this class of complexes one would expect that both of these complexes would have triplet ground states with $2J > +50$ cm^{-1}. It is also not unreasonable to expect that other members of this family should be accessible simply by a variation in the countercation. The main restriction on this counterion is that of size, as an insufficiently large one would probably allow three dimensional antiferromagnetic ordering as is found in $KCuCl_3$ [56] and $(CH_3)_2NH_2CuCl_3$ [57]. Lastly, the observation of triplet ground states in $Cu_2Br_6^{2-}$ and $Cu_2Br_2Cl_4^{2-}$ dimers [53] indicates a further logical expansion in the search for additional intramolecular ferromagnets of this type.

Finally, this theory can be appplied to possibly the most unusual example of a dimer exhibiting an intramolecular ferromagnetic effect yet characterized, a μ-azido-μ-hydroxo-bridged copper(II) complex. Only one example has been made to date, and that apparently by accident [58]. Figure 11 shows the important structural parameters for the complex, $[Cu_2(tmen)_2(N_3)(OH)](ClO_4)_2$. At first glance the Cu–O–Cu and Cu–N–Cu bridging angles of 102.5° and 95.7° respectively would not suggest a net ferromagnetic coupling in this complex, whereas Kahn and co-workers have in fact measured a triplet ground state stabilization in excess of 200 cm^{-1}. Only a lower limit could be placed on the magnitude of this splitting, as it turns out that for the copper(II) dimers the theoretical variation in the magnetic

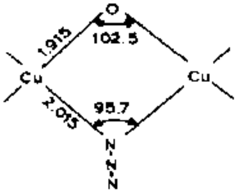


Fig. 11. Structural parameters for $[Cu_2(tmen)_2(N_3)(OH)]^{2+}$, ignoring the disorder on the bridges.

susceptibility is much more sensitive to small changes in $-J$ than in $+J$. This is particularly true when J is so large that the excited singlet state is virtually depopulated at room temperature, as in the present case.

Why does the end-on azido bridge have such a large stabilizing influence on the triplet spin state in this type of structure? A pertinent observation was made in an earlier paper concerned with this type of bridging mode, namely that when ϕ varies between 90° and 110° the splitting, Δ, between the two molecular orbitals constructed from the appropriate $d_{x^2-y^2}$ based magnetic orbitals remains weak for $X = N_3^-$, according to extended Huckel calculations [49]. This is not the case when $X = OH^-$, as has already been noted. If this is true then J_{AF} is close to zero regardless of the bridging angle, and the ferromagnetic contribution to the overall measured J will predominate. This explanation, then, seems to rationalize the results. The problem of how to explain the magnitude of the splitting has been overcome by the introduction of the concept of spin polarization. A brief qualitative description of this phenomenon in the two types of azido-bridging follows.

Ab initio calculations on the electronic structure of the azide ion show that in the ${}^1\Sigma_g^+$ ground state the highest occupied molecular orbital (HOMO) is a $(\pi_g)^4$ level well separated (by ca. 54000 cm^{-1}) from the next highest level. Thus this molecular orbital, which lies in the plane of the bridging network, will play a crucial role in determining the nature and strength of the interactions between the metal ions. At any given instant, in the π_g^x molecular orbital an electron with, say, α spin will be located at one of the terminal nitrogens, while one of opposing β spin will then be localized at the other, non-bridging, terminus. When bridging in the 1,1- mode the electron on the bridging nitrogen will be partially delocalized towards the metal $d_{x^2-y^2}$ orbital (or d_{xy}, using the axes defined in Kahn's treatment of this effect) [58]. This situation is shown schematically in Fig. 12. The delocalization is a function of the overlap $\langle (d_{xy})_{Cu} | (p_x)_N \rangle$ and of the d-π_g energy gap. It leads to an instantaneous α spin in both metal orbitals, and as a result each unpaired electron localized in its magnetic orbital will have a probability of β spin greater than 0.5, favoring a triplet spin ground state. In a similar vein for the end-to-end azido bridge (Fig. 12b), if an α electron is partially delocalized toward the magnetic d orbital centered on metal A, a β electron will be similarly delocalized toward the corresponding magnetic orbital on metal B. Hence the unpaired electron around metal A will have a probability of β spin greater than 0.5 while that around metal B will have a greater than 0.5 probability of having α spin. This coupling of opposing, antiparallel spin probabilities will favor a ground singlet state.

The concept of spin polarization is not a new model for the spin interaction, but is a factor which should be added to the J_F and J_{AF} components already defined. Recent support for the hypothesis has come

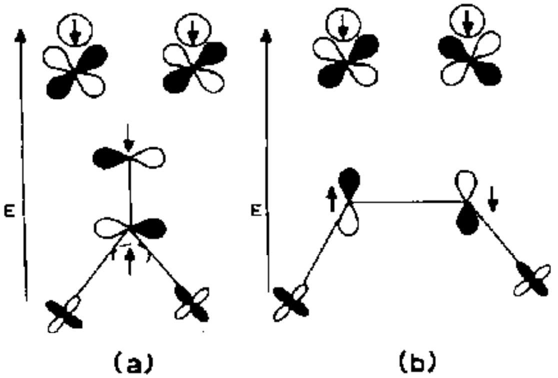


Fig. 12. The molecular orbitals resulting from spin polarization from (a) end-on bridging azides and (b) end-to-end bridging azides toward the magnetic orbitals in a mixed bridge copper(II) dimer. The electrons in the bonding MO's with mainly ligand character are denoted by ↑ and ↓, while those in the magnetic orbitals are circled.

from studies on another di-μ-azido-bridged copper(II) dimer, $[Cu(t\text{-}Bupy)_2(N_3)]_2(ClO_4)_2$, in which the less common 1,1-bridging mode has again been confirmed. Low-temperature magnetic susceptibility studies, in tandem with EPR measurements, have shown a triplet ground state 105 ± 20 cm^{-1} below the excited singlet. Since $\phi = 100.5°$ it appears, as suggested, that this structural feature is not crucial to defining the magnitude of the intramolecular magnetic coupling, as it so obviously is in the case of the chloro- and hydroxo-bridged copper(II) dimers.

A recent communication [60] has expanded this area by describing the synthesis, and structural and magnetic attributes, of binuclear copper(II) complexes in which a 1,1-azide bridge, as well as an acetate and endogenous phenolate bridge link the metal centers. The overall magnetic properties of the complex are best described by a weak antiferromagnetic interaction with $J = -17.4$ cm^{-1}. Thus, as might be expected, the antiferromagnetic contribution from the phenolato bridge overwhelms the intrinsic ferromagnetic contribution from the end-on azido linkage. The magnetic properties of a complex contaning the isoelectronic 1,1-cyanato bridge ($J = -6.3$ cm^{-1}) suggest that this latter group also possesses the electronic properties necessary to transmit a ferromagnetic contribution to the overall observed magnetic properties of a molecular species.

The description of the structurally characterized binuclear systems known to stabilize a triplet spin ground state, together with a semi-quantitative description of the molecular orbital theory which has been developed to rationalize these observations, has enabled the identification of the structural features which appear to be crucial to a ferromagnetic interaction, and as a consequence suggest ways in which to design new complexes with the same desirable features. These features can be summarized as follows.

(i) The bridging angle (ϕ). As already noted (Fig. 4), in most of the copper(II) dimers that have been characterized this parameter represents the single most important structural feature in determining the sign and magnitude of the intramolecular exchange interaction. It is apparent that prototypical new intramolecular ferromagnets should incorporate a favorable value of this parameter. The existing literature gives no hint on how this might be accomplished, but does at least suggest that when some members of a family of chelating terminal ligands lead to the required structural features it may be worthwhile to extend studies along these paths. Three possibilities can be given as examples.

(a) 2,2′-Bipyridyl chelates. All of the examples of ferromagnetic di-μ-hydroxo-bridged copper(II) dimers to date contain this terminal chelate. It would be interesting to continue work in this field using substituted bipyridyl ligands which, in addition to imposing a constant N–Cu–N angle, could control the amount of electron density on the bridging groups.

(b) 1,10-Phenanthroline chelates. Little work has been carried out on these dimers, which should be structurally similar to the 2,2′-bipyridyl complexes. These compounds were originally made by Sinn and co-workers [61]; somewhat inconclusive magnetic susceptibility studies were initiated by Casey [62], but it appears that no thorough study has been carried out.

(c) 2,4-Pentanedione chelates. Given the wide variation possible in complexes of this type, and the results on the di-μ-azido-bridged complex reported by Martin et al. [50], a more extensive investigation of this type of dimeric system might well yield new examples of intramolecular ferromagnetism in copper(II) dimers.

(ii) The extent of planarity of the binuclear bridging network. It has been shown how either a decrease in the dihedral angle or increase in the torsion angle can, at least in the identified cases, lower the net antiferromagnetic interaction in these complexes. Again it is not easy to see how such a feature could be built into a new ligand system, especially as solid state crystal packing forces are undoubtedly responsible for at least part of these distortions.

(iii) Electron density on the bridging group. As the amount of *s* character on the bridge increases so does the magnitude of the antiferromagnetic interaction. McWhinnie has shown [16] that in a series of alkoxo-bridged complexes of general formula $[(2\text{-NH}_2\text{py})_2\text{Cu(OR)}]_2(\text{NO}_3)_2$, where R = H, CH_3, or C_2H_5, the room temperature magnetic moment fell in the order

(R = H) > (R = CH_3) > (R = C_2H_5). This implies that as more electron density is supplied to the bridge the antiferromagnetic contribution increases. When the bridge is involved in hydrogen bonding the same effect is observed. The molecular orbital picture of this situation can be explained as a stabilization of the b_{2u} molecular orbital relative to the b_{1g} orbital with an increase in the electronegativity of the bridge (Fig. 7) [42]. Changing the counterion in the complex may change the electron density on the bridge, either directly via a hydrogen bonding interaction, or indirectly by interacting weakly with the copper(II) ion, thus removing it from the plane of the bridging system.

(iv) From the results of work carried out primarily by Kahn and coworkers [58,59] it appears that the azide and cyanate groups possess some intrinsically favorable electronic properties which make them the bridging ligands of choice if a large ferromagnetic interaction is desired. The synthesis of new complexes containing these 1,1-bridges will involve the synthesis of ligand systems satisfying several requirements.

(a) The ligand must hold the metal centers sufficiently close to prevent intramolecular 1,3-bridging, but not so close that direct metal–metal interactions occur.

(b) The ligand should prevent interdimer association via 1,3-bridges.

(c) The ligand should preserve a planar framework of metal and donor atoms. Macrocyclic ligands may offer the best design features in this respect, and it may be possible to find existing macrocycles, whether two-dimensional or cryptates, which possess these features.

D. COMPARTMENTAL COMPLEXES: THE ORTHOGONALITY PRINCIPLE AS APPLIED TO BINUCLEAR COMPLEXES OF *N,N′*-BIS(2-HYDROXY-3-CARBOXYBENZYLIDENE)ETHYLENEDIAMINE

The following section concerns complexes of so-called "compartmental" ligands, a name coined by Fenton to describe one particular type of binucleating ligand but generally applicable to the families of ligands to be introduced in the following sections. These ligands contain donor sites which encapsulate two or more metal ions in a fixed geometric arrangement such that they are bound sufficiently close to allow magnetic interactions between the metal centers. The ligands are planar and bind metal ions in a side-by-side arrangement, with two donor atoms from the ligand acting as bridges. In most cases these bridging atoms are phenolate or ketonate oxygens. This definition is intended to differentiate these ligands from those such as cryptates, cofacial diporphyrins, and other binucleating ligands containing isolated donor sets.

While many of the compartmental complexes characterized to date ex-

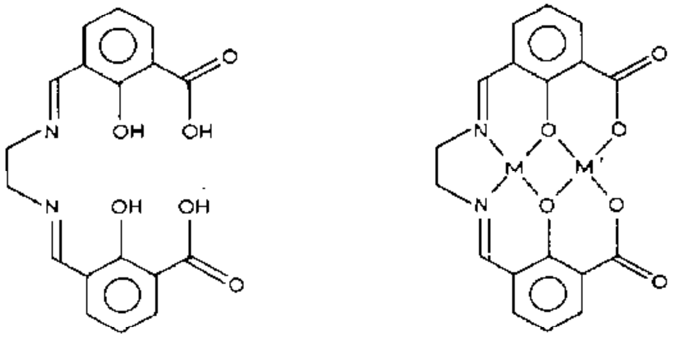


Fig. 13. Structure of the ligand $H_4(fsa)_2en$ and a representation of the coordination mode in binding two metals.

hibit antiferromagnetic interactions, these ligands will be described in cases where it may be possible, using suitable combinations of metal ions and structural modifications, to design ligands in which a ferromagnetic interaction between metals is a favorable occurrence. These ligands will be described in a later section; this section will concentrate on that ligand system which, by virtue of its structural and symmetry properties, has given rise to a number of heterobinuclear complexes in which a considerable intramolecular ferromagnetic effect has been observed.

In the last dozen years an extensive collection of publications has appeared on the complexes of the ligand formed by the Schiff base condensation of 3-formylsalicylic acid and ethylenediamine. The ligand *N*,*N'*-bis(2-hydroxy-3-carboxybenzylidene)ethylenediamine ($H_4(fsa)_2en$) forms a variety of complexes with metals (Fig. 13).

Much of the studies on these complexes, and on similar ones in which other diamines replace the ethylenediamine have been carried out by the research groups of Kida, Vidali and Kahn. It was Kida et al. who first showed [63] how the ligand could act to bind two dissimilar metal ions. The first heterobinuclear complex to be characterized contained square planar copper(II) in the inner compartment and an essentially octahedral nickel(II) ion in the outer hole. Two axial water ligands completed the coordination sphere around the latter ion. Later work established the structure of a heterobinuclear complex by X-ray analysis; the structure of Cu(II)Co(II)–$(fsa)_2en \cdot 3H_2O$ [64] proved to be very similar to that proposed for the Cu(II)–Ni(II) complex. The magnetic properties of the former heterobinuclear complex, as determined from magnetic susceptibility studies in the temperature range 77–300 K [65], were indicative of an antiferromagnetic interaction with $J = -75$ cm^{-1}. Thus the energy separation between the ground spin state ($S = 1/2$) and the excited spin quartet ($S = 3/2$) is $3J = -225$ cm^{-1}. The homobinuclear copper(II) complex Cu(II)Cu(II)-

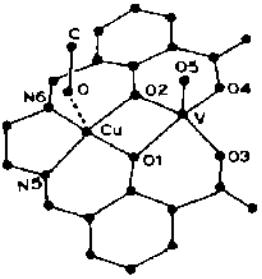


Fig. 14. Structure of $CuVO(fsa)_2en \cdot CH_3OH$.

$(fsa)_2en \cdot 2H_2O$, exhibits an even stronger antiferromagnetic effect, with $2J = -660\ cm^{-1}$ [66].

In recent years a major research effort by Kahn and co-workers has led to important advances in the theoretical treatment used to describe and rationalize the sign and magnitude of the magnetic interaction observed in binuclear complexes. As will be discussed in the theoretical portion of this section, Kahn has used homo- and hetero-binuclear complexes as a testing ground for this theoretical treatment. The results so far have been spectacular; to date three heterobinuclear complexes have been prepared in which a sizeable intramolecular ferromagnetic interaction is present, and the other binuclear complexes synthesized possess magnetic properties which can be largely explained using this theoretical framework.

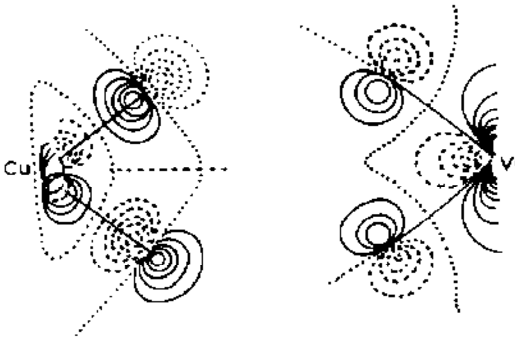
The first of these heterobinuclear complexes to be thoroughly characterized was $Cu(II)VO(II)(fsa)_2en \cdot CH_3OH$, which contains two square-pyramidal CuN_2O_3 and VO_5 geometries (Fig. 14) [67,68]. The metal ions and the axial oxygen atoms form a fairly rigorous mirror plane in the molecule, with both axial oxygens lying on the same side of the equatorial ligand plane. Magnetic susceptibility measurements down to 4 K prove that the molecule possesses a ground triplet state with a triplet–singlet separation $2J$ (or J, as Kahn defines it using a different spin Hamiltonian) of 118 cm^{-1}. Below 18 K an intermolecular antiferromagnetic interaction between adjacent $S = 1$ molecular spins becomes significant. Variable temperature EPR spectroscopy confirms the presence of the ground state triplet.

More recently, two other heterobinuclear complexes have undergone similar characterization. In one of these, $Co(II)Cu(II)(fsa)_2en \cdot 3H_2O$, a very strong ferromagnetic interaction is observed [69,70], although its magnitude has not been determined. The available evidence indicates that the cobalt(II) ion, which occupies the inner site in this complex, has a square-pyramidal geometry with one axial water ligand; the copper(II) ion has, presumably, a tetragonal geometry with two weakly-bound axial waters. Again an antiferromagnetic contribution from intermolecular interactions makes its presence felt below ca. 30 K. It should be noted that the isomeric complex in which the positions of the two metal ions are reversed shows completely different magnetic properties [71], exhibiting a net antiferromagnetic intramolecular coupling with $J = -52\ \mathrm{cm}^{-1}$. The reason behind this difference in magnetic behavior will be explained later in this section. In the third complex, $[\mathrm{Cu(II)Cr(III)(fsa)_2en(H_2O)_2]Cl \cdot 3H_2O}$ [72,73], the copper(II) ion occupies the inner compartment while a high-spin chromium(III), ligated by two axial waters, occupies the outer position. The interaction between the copper(II) $S = 1/2$ spin doublet and the chromium(III) $S = 3/2$ spin quartet gives rise to coupled states $S = 1, 2$. Experimentally the quintet state is stabilized with the quintet–triplet splitting $2J = +210\ \mathrm{cm}^{-1}$.

While these complexes represent the only ferromagnetically coupled molecular species based on this ligand to be synthesized to date, other homo- and hetero-binuclear complexes have been characterized by magnetic and spectroscopic techniques. These include $\mathrm{Cu(II)Cu(II)(fsa)_2en \cdot CH_3OH}$ ($2J = -650\ \mathrm{cm}^{-1}$) [74] and $\mathrm{Cu(II)Fe(III)(fsa)_2enCl(H_2O)(CH_3OH)]CH_3OH}$ ($2J = -78\ \mathrm{cm}^{-1}$) [73,75]. The large intramolecular antiferromagnetic coupling measured in the former complex should be compared with the theoretical value of ca. $-190\ \mathrm{cm}^{-1}$ expected using the linear $2J$ vs. ϕ correlation established by Hatfield and co-workers [29] ($\phi = 100.1°$ in this complex). This very strong antiferromagnetism is also found in other copper(II) systems in which ketonate oxygens bridge the copper(II) centers.

Having described the structures and magnetic parameters associated with the intramolecular ferromagnetic complexes studied by Kahn and co-workers [37–40,42], it is instructive to explain these magnetic properties using the molecular orbital framework constructed by Kahn and co-workers. It will be remembered that the di-μ-hydroxo-bridged copper(II) complexes owed their magnetic properties at values of $\phi < \phi_0$ to accidental orthogonality of the interacting magnetic orbitals. In the present case the orthogonality of the magnetic orbitals is strict, owing to the symmetry of the problem.

It will be useful to take a typical example of a completely characterized binuclear complex to help explain the relationships involved in this treatment. Consider the heterobinuclear Cu(II)VO(II) complex which has already been described [67,68] (Fig. 14). An important feature of this structure is that the two metal ions and two axial oxygens lie on a plane which is a mirror for the two square pyramids that make up the complex. The symmetries of the two metallic sites, and the overall molecular symmetry, are close to C_s. With the coordinate system defined with the x-axis along the metal–metal vector then the magnetic orbital ϕ_{Cu} for the copper(II) ion in the square-pyramidal geometry is derived from the d_{xy} metallic orbital, partially delocalized toward the terminal and bridging donor atoms due to a σ-type antibonding overlap $\langle d_{xy} \mid p_\sigma \rangle$. This magnetic orbital is antisymmet-



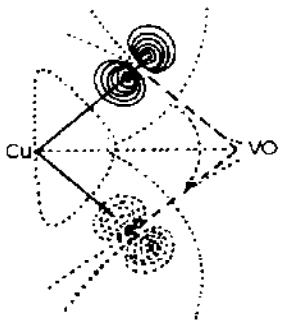


Fig. 15. Magnetic orbitals ϕ_{Cu} and ϕ_{VO}.

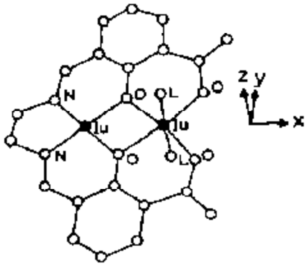
Fig. 16. Overlap density map for the Cu(II)VO(II) dimer. The solid and dashed lines represent positive and negative iso overlap density curves respectively. The dotted lines represent nodal zones.

ric with respect to the mirror plane and transforms as the a'' irreducible representation of the C_s point group. Similarly, the pertinent magnetic orbital ϕ_{VO} is derived from the $d_{x^2-y^2}$ metallic orbital, again partially delocalized toward the five oxygen donor atoms by a π-type antibonding overlap $\langle d_{x^2-y^2} | p_\pi \rangle$. This latter magnetic orbital is symmetric with respect to the mirror plane and transforms as the a' irreducible representation of the C_s point group. Thus by these symmetry considerations these two magnetic orbitals are orthogonal; i.e., $\langle \phi_{Cu} | \phi_{VO} \rangle$, the overlap integral, is zero, and $J_{AF} = 0$. The singlet–triplet splitting will be entirely due to J_F and a triplet ground state is expected. Experiment shows this to be the case. By considering the relative orientations of the magnetic orbitals in this complex, as well as their symmetries, the magnitude of the interaction can be rationalized. Figures 15 and 16 show a representation of the relevant magnetic orbitals and the overlap density map, as determined by extended Hückel calculations [68]. Notice that the same $2p$ orbitals centered on the bridging phenolate oxygens interact with ϕ_{Cu} to give a σ overlap and with ϕ_{VO} to give a π overlap. As a result the overlap density, which is defined by the relationship

$$\rho = \phi_{Cu}\phi_{VO} \tag{9}$$

has two strongly positive lobes around one oxygen and two equally strong negative lobes around the other (Fig. 16). Since these two lobes have exactly compensating density the overlap integral, $S = 0$. The two-electron exchange integral j has a magnitude which is related to the height (or depth) of either lobe and will then be the remaining factor, giving a net positive J ($J_F = 2j$).

The same qualitative description can be applied to the complex $[Cu(II){-}Cr(III)(fsa)_2en(H_2O)_2]Cl \cdot 3H_2O$. In this complex the idealized symmetry is C_{2v}, as the Cr(III) ion is now six coordinate. The coordinates are



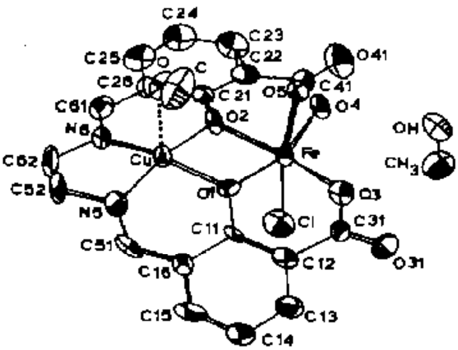


Fig. 17. Schematic representation of [Cu(II)Cr(III)(fsa)$_2$en(H$_2$O)$_2$]Cl·3H$_2$O.

Fig. 18. Crystal structure of [Cu(II)Fe(III)(fsa)$_2$enCl(H$_2$O)(CH$_3$OH)]CH$_3$OH.

defined as before (Fig. 17). As in the previous case, the unpaired electron centered on the copper(II) ion occupies an xy-type orbital in this symmetry which transforms as b_1. The three unpaired electrons around the chromium(III) ion are in magnetic orbitals based on the d_{xz}, d_{yz}, and $d_{x^2-y^2}$ metallic orbitals, and transform as b_2, a_2 and a_1, respectively. Again there is strict orthogonality and $J_{\mathrm{AF}} = 0$. Thus the sign of the intramolecular coupling in this complex can be accounted for, as before. The magnitude of the coupling, $J = +105\ \mathrm{cm}^{-1}$ [73], is similar to that observed in the Cu(II)VO(II) system. The J coupling constant can be expressed as the sum

$$J_{\mathrm{CuCr}} = 1/3\left(J_{b_1a_1} J_{b_1a_2} + J_{b_1b_2}\right) \tag{10}$$

It can be shown from the overlap density maps analogous to Fig. 16 that only the first component of the summation has a significantly large value. Assuming that $J_{b_1a_2} = J_{b_1b_2} = 0$, $J_{b_1a_1}$ is ca. $+300\ \mathrm{cm}^{-1}$. This is much larger than the $J_{b_1a_1}$ for the Cu(II)VO(II) complex, probably reflecting the fact that the vanadyl ion in this latter complex is pulled 0.44 Å out of the equatorial plane toward the axial oxygen, leading to a smaller overlap between the relevant magnetic orbitals. It appears that the copper(II)–chromium(III) framework bridged by two oxygens may provide a very favorable pathway for a ferromagnetic interaction.

The analogous complex with an iron(III) replacing the chromium(III) center has been synthesized and studied [73,75] (Fig. 18). In this complex the copper(II) is five coordinate with an axial methanol, while the iron(III) has one axial chloride and an axial water ligand. In the resulting C_{2v} symmetry the unpaired electron on the copper(II) ion transforms as a b_1 magnetic orbital as before. The five unpaired electrons on the iron(III) center transform as a_1 (d_{z^2} and $d_{x^2-y^2}$), a_2 (d_{yz}), b_1(d_{xy}), and b_2 (d_{xz}) magnetic orbitals, respectively. Since one of them transforms as b_1 there is no longer a net zero overlap in this system. The antiferromagnetic contribution J_{AF} will be expected to overwhelm the smaller ferromagnetic component. The overlap coupling constant can be expressed by the summation

$$J_{CuFe} = 1/5\left(J_{b_1a_1} + J_{b_1a_1'} + J_{b_1a_2} + J_{b_1b_1} + J_{b_1b_2}\right) \tag{11}$$

If it is assumed that the ferromagnetic $J_{b_1a_1}$ component is ca. $+300$ cm^{-1}, using the value derived from the Cu(II)Cr(III) dimer, then, if the $J_{b_1a_1'}$, $J_{b_1a_2}$, and $J_{b_1b_2}$ components are small as before, $J_{b_1b_2}$ will be ca. -700 cm^{-1}. The experimental data, obtained from magnetic susceptibility measurements down to 4.2 K [73], confirms the presence of a large net intramolecular antiferromagnetic effect.

A further instructive example concerns the homobinuclear copper(II) complex of this ligand. In this complex both magnetic orbitals have the same a'' symmetry and again $S \neq 0$. The observed singlet–triplet splitting of -650 cm^{-1} corresponds [74] to a very large net antiferromagnetic coupling. Of course this reasoning can be applied just as rigorously to the di-μ-hydroxo-bridged copper(II) complexes which have already been discussed in some detail. If the equatorial ligands are restricted to an exact plane, each copper(II) center has C_{2v} symmetry, and the interacting magnetic orbitals will be constructed from metallic orbitals with b_1 symmetry. The overlap is in principle non-zero, except when the bridging angle has the exact value to allow an accidental orthogonality to arise.

One last example should suffice to prove the generality of this symmetry-based argument. In the heterobinuclear Co(II)Cu(II) complex the inner cobalt(II) ion is five coordinate, with one axial water, while the outer copper(II) ion is bound to two waters [69,70]. This situation is slightly more involved than the others that have been described, as the cobalt(II) ion is orbitally non-degenerate. In C_{2v} symmetry the ground state for low-spin cobalt(II) can be either $^2A_1$ or $^2A_2$—there is some argument over which state is the more stable in this geometry. If $^2A_1$ is the ground state the unpaired electron on the cobalt(II) ion is described by a magnetic orbital of a_1 symmetry constructed by mixing the d_{z^2} and $d_{x^2-y^2}$ metallic orbitals. When $^2A_2$ is the ground state, the magnetic orbital has a_2 symmetry. In either case the magnetic orbital so formed is orthogonal to that derived from the d_{xy} metallic orbital on the copper(II) ion, which has b_1 symmetry. Consequently the exchange interaction should be, and is, ferromagnetic. Similar reasoning can be used to explain the interaction observed for the other positional isomer of this heterobinuclear complex. In this isomer [71] the cobalt(II) ion is six coordinate and has a $^4T_1$ ground term, which gives the terms $^4A_2 + ^4B_1 + ^4B_2$ in C_{2v} symmetry. An exchange interaction between the ground Kramers doublet and the spin doublet from the copper(II) leads to an antiferromagnetic coupling.

TABLE 2

Predicted nature and magnitude of the interactions between pairs of magnetic orbitals

	x^2-y^2	xz	yz	z^2	xy
x^2-y^2	from a to A	f	f	a	F
xz		a	from f to F	f	f
yz			a	f	f
z^2				from a to F	f
xy					from A to F

a = weakly antiferromagnetic
A = strongly antiferromagnetic
f = weakly ferromagnetic
F = strongly ferromagnetic

By the use of this general strict orthogonality hypothesis it should be possible to look for pairs of metal ions where, at least within the restrictions imposed by this ligand, a net intramolecular ferromagnetic interaction may be expected. By a consideration of the five possible types of magnetic orbitals, and their symmetry in O_h, C_{2v}, and C_s environments (those which have been found for complexes of the $H_4(fsa)_2en$ ligand), predictions have been made as to the size and magnitude of the intramolecular interactions [68]. These predictions are shown in Table 2. A few examples will be taken to illustrate the entries.

(i) $x^2-y^2 \leftrightarrow x^2-y^2$. Here there are two interactions to consider. The indirect interaction through the bridges will, because of the symmetry of the magnetic orbitals, give a strong antiferromagnetic coupling except when $\phi = \phi_0$. The direct metal–metal interaction will increase as this distance decreases and will always lead to an antiferromagnetic contribution. The sum of these factors leads to the expectation that this pairwise interaction will vary between a strong and weak net antiferromagnetism, depending on the bridge angle.

(ii) $x^2-y^2 \leftrightarrow xz, yz$. Since these interactions occur between orthogonal magnetic orbitals, regardless of the symmetry of the complex, and because the overlap density around each bridge is weak for these overlaps, a fairly small net ferromagnetic interaction will be observed in complexes of this type.

(iii) $z^2 \leftrightarrow z^2$. The d_{z^2}-based magnetic orbitals are only weakly delocalized towards the ligands in the molecular plane. The interaction will usually be weak but highly dependent on the size of the metal–oxygen–metal bridging angle. Accidental orthogonality may arise under fortuitous circumstances.

(iv) $xz \leftrightarrow x^2-y^2$. This is the situation which has been described in the Cu(II)VO(II) and Cu(II)Cr(III) systems. It causes a large net ferromagnetic interaction because of the strict orthogonality of the interacting magnetic orbitals.

(v) $xy \leftrightarrow xy$. In general this will give rise to a strong antiferromagnetic coupling because of the extensive delocalization of the pertinent magnetic orbitals towards the bridging oxygen atoms. Accidental orthogonality may be expected for ϕ ca. 90°.

(vi) $xz \leftrightarrow xz$, xy, yz, z^2. The xz orbital is only weakly delocalized towards the bridging oxygen atoms, and so the $xz \leftrightarrow xz$ interaction will be small, but of an antiferromagnetic nature since the interacting magnetic orbitals will have the same symmetry. The xz interactions with magnetic orbitals based on the other three metallic orbitals will give rise to a small ferromagnetic contribution. If the bridging atoms become less electronegative; e.g., nitrogen or sulfur instead of oxygen, the delocalization of the xz- and yz-based magnetic orbitals may become more extensive and the $xz \leftrightarrow yz$ interaction may become appreciably ferromagnetic.

E. OTHER COMPARTMENTAL COMPLEXES

(i) Schiff base complexes of 4-substituted-2,6-diformylphenols

This class of compartmental ligand, like those described in the previous section, is one in which a considerable variety of encapsulated metal ion and component organic precursors is possible. Figure 19 shows the binuclear complexes which can be made by a stepwise synthetic procedure, in which M and M′ may be the same or different metals.

Pilkington and Robson [76] synthesized the first members of this family, as homobinuclear complexes of copper(II), nickel(II), cobalt(II), man-

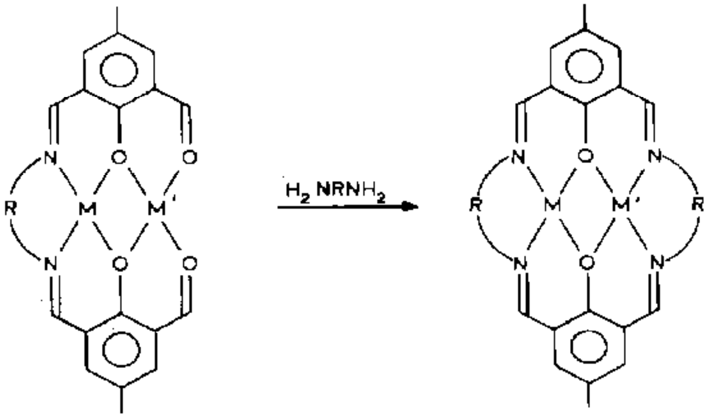
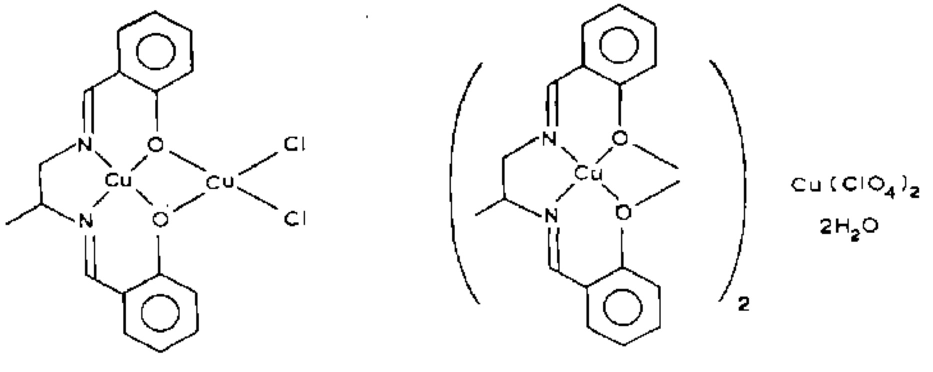


Fig. 19. Binucleating ligands formed from the Schiff base condensation of 4-methyl-2,6-diformylphenol with α, ω-diamines, in the presence of a template metal ion.

ganese(II), and iron(II). The template synthesis of these complexes involved the Schiff base condensation of 5-methylisophthalaldehyde (4-methyl-2,6-diformylphenol) with 1,3-diaminopropane in the presence of the appropriate metal salt. Following a procedure devised by Okawa and Kida [77], Gagné, Hendrickson and co-workers prepared a series of square pyramidal macrocyclic complexes [78] in which $M = M' =$ Mn(II), Fe(II), Co(II), Ni(II) and Cu(II). Variable temperature magnetic susceptibility measurements down to ca. 4 K showed that the net interaction in these homobinuclear complexes decreased in the order $J(\mathrm{Cu}) > J(\mathrm{Ni}) > J(\mathrm{Co}) > \mathrm{J(Fe)} > J(\mathrm{Mn})$, with the last named complex exhibiting a very small net ferromagnetic interaction ($J = +0.2\ \mathrm{cm}^{-1}$). The use of two axial ligands, to force the metals to lie in the macrocyclic plane, produced very similar results [79]. Studies on a number of heterobinuclear complexes have all shown a net antiferromagnetic interaction between the metal centers [80,81], a result which can probably be rationalized using the molecular orbital model of Kahn and co-workers. The heterobinuclear complexes which have been prepared are not ones in which a net ferromagnetic interaction would be expected to occur. The study of this class of ligand should be extended to include those complexes in which J might be positive, for example the Cu(II)VO(II) and Cu(II)Cr(III) systems. An additional research effort into heterobinuclear complexes of the precursor ligand L′ (Fig. 19) might be of special interest, as this binucleating ligand has obvious similarities to $H_4(\mathrm{fsa})_2\mathrm{en}$ (Fig. 13). Gagné et al. reported these complexes [80] but apparently did not study their magnetic properties, and instead used them as intermediates in the synthesis of the macrocyclic complexes.

(ii) Salicylaldimine derivatives: metal complexes as ligands

Metal complexes of tetradentate Schiff bases, such as the salicylaldimines, may act as bidentate chelating agents, coordinating through *cis* phenolate oxygens to form bi- and tri-nuclear complexes [82]. Figure 20 shows an example of this behavior in which Cu(II)(salmen) coordinates with copper(II) chloride to form a binuclear complex, or with copper(II) perchlorate to form a trinuclear species. In this sense the mononuclear complex can be considered as a bidentate ligand with the two phenolates acting as donors to a potential second metal. A considerable amount of research has been carried out on these systems, and Sinn and Harris have reviewed this area [83], much of which Sinn helped to develop. Most of the research has used copper(II) complexes of tetradentate Schiff bases (TSB) as ligands to coordinate to metal chlorides, and in this way complexes of general formula $\mathrm{Cu(II)TSB} \cdot \mathrm{MCl}_n$ have been synthesized, where $M =$ Mn(II), Fe(II), Fe(III), Co(II), Ni(II) and Cu(II). Without exception, only net antiferromagnetic



(a) (b)

Fig. 20. Structures of Cu(II)(salmen)·$CuCl_2$ and [Cu(II)(salmen)]$_2$·$Cu(ClO_4)_2$·$2H_2O$.

interactions have been observed, regardless of the diamine and salicylaldehyde used. For example, in Cu(II)(salen)·$CuCl_2$ $2J = -232$ cm^{-1} [84]. These measurements were generally carried out only to liquid nitrogen temperatures.

It was noted in the previous subsection that no studies had yet been initiated into the most promising candidates for a molecular ferromagnet. The same is true for this ligand family. A study of the VO(II)Cu(II) dimer included only room temperature magnetic data [85]; the moment obtained, 1.9 B.M. per complex molecule, was suggestive of a considerable antiferromagnetic coupling. It is probable that in this ligand system the "outer" ion in the complex would be appreciably distorted toward a tetrahedral geometry, a result which, as Sinn and co-workers noted [86], would lead to an increase in the antiferromagnetic contribution to the observed magnetic properties of the complex. In an attempt to repeat and extend this work, Okawa and Kida [87] provided strong evidence that the previous complex was in fact a diamagnetic V(V)Cu(I) complex contaminated with some mononuclear impurity. This work highlights a significant problem in the synthesis of binuclear complexes of this class of ligand. In general the mononuclear precursors are very insoluble and resist easy purification. An additional problem concerns the relative stabilities of the products which may be formed in any reaction. In theory the reaction of M(TSB) with $M'X_2$ may produce either M(TSB) or M′(TSB), the latter by metal exchange, as well as the desired heterobinuclear complex M(TSB)·$M'X_2$. If M(TSB) has a much lower stability constant than M′(TSB) then the reaction will produce only M′(TSB)·$M'X_2$. This situation arises, for example, when M = Zn and $M'X_2$ is a copper(II) or nickel(II) halide or perchlorate salt. If the relative stability constants of M(TSB) and M′(TSB) are similar, then the desired complexes can be isolated if they are removed from the reaction mixture quickly. In this way the positional isomers Cu(salen) $\cdot$ $NiCl_2$ and Ni(salen) $\cdot$ $CuCl_2$ have been synthesized.

(iii) Schiff base derivatives of 1,3,5-triketones and related ligands

It has been established that the number and type of donor atoms which bind to a metal ion have a profound effect on the physical and chemical properties associated with that metal, and that, under competitive conditions, certain metal ions have a clear thermodynamic and/or kinetic preference for certain ligand donor atoms. This leads to the conclusion that many novel binuclear complexes could be made using ligands which have the ability to coordinate two metals per molecule and which contain different kinds of donors. Examples of these types of ligands fill this review; some of the most versatile in this regard are the polyketonates (Fig. 21). The metal complexes of the 1,3-diketonates and their Schiff base derivatives have been the subjects of hundreds of papers and will not be discussed here. By comparison the higher homologs have received less attention. In recent years, however, the study of the metal complexes of the Schiff bases derived from 1,3,5-triketonates has become the focus of some attention. These ligands exhibit great versatility as regards substituents on the polyketonate backbone and the type of diamine used in the condensation (Fig. 22). The research groups led by Lintvedt and Fenton have exploited the variations inherent in this type of ligand in the synthesis of a wide range of homo- and hetero-binuclear complexes.

Conceptually, binuclear complexes of these ligands can be thought of as being a combination of the chelate of a mononuclear 1,3-diketonate and its Schiff base [88,89], a picture which enables the study of the spectroscopic properties of the binuclear product in a straightforward manner. Similarities between the mononuclear parents and the binuclear product result from the

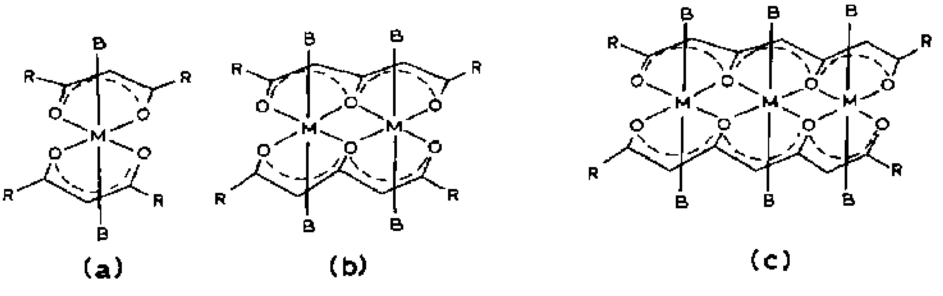


Fig. 21. General structures of (a) metal(1,3-diketonates), (b) metal(1,3,5-triketonates), and (c) metal(1,3,5,7-tetraketonates) [88].

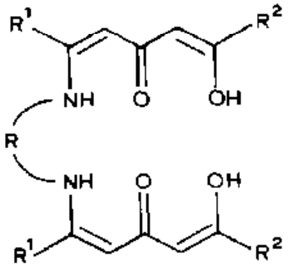


Fig. 22. Structure of the Schiff base adducts of 1,3,5-triketonates.

similar electronic states of the species, while differences in spectroscopic and magnetic properties can be ascribed to interactions between the metal ions via the bridging oxygens. The general scheme adopted to make heterobinuclear complexes of the Schiff base ligands is to prepare an easily characterized mononuclear chelate which can be isolated as a pure, stable positional isomer, and to use this precursor to coordinate the second metal. In this sense the scheme is entirely analogous to that adopted in the synthesis of heterobinuclear complexes of compartmental ligands described in previous sections.

Fenton and co-workers have extended this work to various triketones and related species [90–94], and have in addition varied the diamine used to connect the two polyketonate moieties. The results which have been obtained are too extensive to detail here, however a few of the more significant results will be mentioned. Perhaps the most significant is that it has proved possible to prepare pure positional isomers of the copper(II) complex of Fig. 22, R = en, $R^1 = CH_3$, $R^2 = CH_3$ [92], in which the copper ion can be made to occupy either one of the two sites. The positional isomer formed has been found to depend on the acyclic ligand used. Both Fenton [92] and Lintvedt [95] have observed that using the unsymmetrical phenyl-substituted triketonte (Fig. 22, R^2 = phenyl), only the CuO_4 isomer could be prepared. The importance of this result lies in the fact that with these complexes as precursors there is a basis for the synthesis of heterobinuclear complexes. Such complexes have been isolated and the products characterized by a variety of spectroscopic techniques. To date no variable temperature magnetic susceptibility measurements have been published on any of these complexes, although the room temperature moment of 0.88 B.M. per metal atom measured for a Cu(II)VO(II) complex suggests an appreciable antiferromagnetic interaction in this particular compound. The results may be explained by a possible structural distortion of the binucleating ligand towards a tetrahedral geometry. In addition a direct metal–metal interaction cannot be excluded.

F. POLYNUCLEAR NICKEL(II) COMPLEXES

(i) Linear trimers

Most of the complexes described in this section contain β-diketones as chelating ligands bridging nickel(II) centers. As will be seen, these ligands possess certain intrinsic characteristics, such as stability and versatility, which lead to their occurrence in a number of complexes possessing a wide range of intramolecular magnetic interactions. Although several structural investigations had been carried out on nickel(II) chelates of 2,4-pentanedione (acetylacetone) and derivatives substituted at the terminal and methine positions [96–101], it was not until 1968 that a study [8] focused on the magnetic interactions exhibited by bis(acetylacetonato)nickel(II). Figure 23 shows the structure of this molecule, which crystallizes when anhydrous as a linear trimeric octahedral species [101]. Theoretical considerations on the structure of this complex suggested that the exchange integral between neighboring metal centers might be positive; i.e., that an intramolecular ferromagnetic interaction might be observed. This expectation was realized, giving the first example of such a situation to be verified, although a later, more detailed analysis [102] revised the original estimate of the positive coupling constant for the cooperative interaction from $J = +52$ cm^{-1} to $+26$ cm^{-1}. (Note that the two research groups responsible for these measurements used two slightly different forms of the HDVV Hamiltonian in their analysis.) An antiferromagnetic interaction of magnitude $J' = -14$ cm^{-1} couples the terminal nickel(II) ions. The theoretical discussion of the mechanisms leading to a ferromagnetic interaction in this system uses Anderson's solid-state valence bond approach [35]. As discussed in the original paper [8], a ferromagnetic exchange between adjacent nickel(II) ions arises using the HDVV spin-coupling model via an electron transfer plus

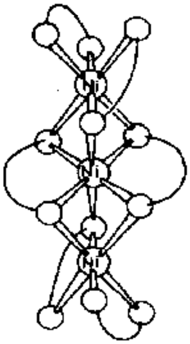
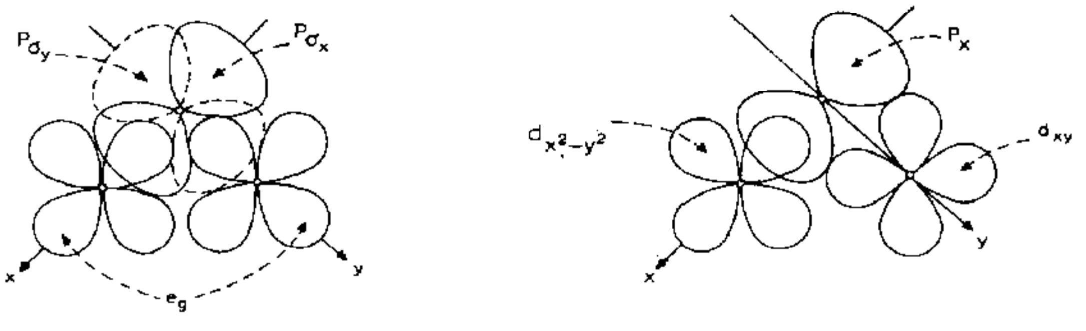


Fig. 23.Structure of the bis(acetylacetonato)nickel(II) trimer.



(a) (b)

Fig. 24. Orientation of p_x and p_y oxygen orbitals with respect to e_g and t_{2g} orbitals on two nickel(II) ions arranged at right angles.

intraatomic direct exchange mechanism. This type of interaction occurs when a half filled metal orbital overlaps with either an empty orbital or a completely filled orbital on a metal ion which also contains an unpaired electron in an orbital orthogonal to the one being overlapped. This situation arises in the present case because of the symmetry properties of the e_g-p-t_{2g} orbitals in the Ni-O-Ni system which are arranged at close to 90°. (The Ni–O–Ni bond angles actually vary between 76.5° and 89.3° so an idealized situation has been taken so that Anderson's theoretical approach to the theory of superexchange interactions can be applied.) Figure 24 shows the orientation of the appropriate nickel(II) and oxygen orbitals. Superexchange has been defined [35] by Anderson as the exchange effect caused by direct electron transfer from cation to cation using d orbitals which have been expanded by mixing with ligand orbitals of appropriate symmetry. For this transfer to occur the d orbitals must overlap and the spin of the transferred electron must be antiparallel to that on the acceptor cation, as required by the Pauli exclusion principle. As a result this effect will always be antiferromagnetic. In situation (a) of Fig. 24, overlap between adjacent e_g orbitals via the oxygen $p\sigma_x$ or $p\sigma_y$ orbitals cannot occur; the only oxygen orbital with a suitable energy and symmetry is the $2s$ orbital, and since its ability to expand the magnetic orbitals should be small, the superexchange interaction will therefore give only a small antiferromagnetic effect. On the other hand, situation (b) shows how a ferromagnetic contribution can arise via either of the overlap pathways $d_{x^2-y^2}$–p_x–d_{xy} or d_{xy}–p_y–$d_{x^2y^2}$. By either of these routes a pathway is provided for unpaired electron spin density originally located in an e_g orbital ($d_{x^2-y^2}$) to be delocalized onto a t_{2g} (d_{xy}) orbital; intra-atomic coupling between the t_{2g} and e_g subsets on each nickel center then couples the two ions with a resulting parallel spin. It can be shown, in a similar vein, that an antiferromagnetic interaction couples the terminal nickel ions via the π system of the two acetylacetonate groups which bridge them.

The application of the knowledge acquired in the study of the structural and magnetic properties of $[Ni(acac)_2]_3$ to other similar similar systems seems eminently reasonable. Many β-diketonate nickel(II) complexes have been synthesized, and spectroscopic data, as well as room temperature magnetic susceptibility measurements, have been collected. It thus seems somewhat surprising, given the novel magnetic properties of the "simplest" member of the family, that no variable temperature magnetic susceptibility studies have been performed on any other member of the class. In addition, no other X-ray structural determinations have been published. Nonetheless, enough circumstantial evidence has been gathered to show that, in at least a few cases, a similar trimeric nickel(II) structure exists over a temperature range. For example, bis(2,2-dimethyl-3,5-heptanedionato)nickel(II), $R^1 = R^5 = -CH(CH_3)_2$, $R^3 = H$ [97], is a green paramagnetic solid, suggesting an octahedral trimeric structure. In a non-coordinating solvent at ca. 0°C the solution is green, changing to red on heating to 50°C. Thus a temperature dependent trimer–monomer equilibrium exists in solution at intermediate temperatures. By contrast, bis(2,2,6,6-tetramethyl-3,5-heptanedionato) nickel(II), $R^1 = R^5 = -C(CH_3)_3$ [97], is a red diamagnetic monomer at room temperature. Bis(2,4-diphenyl-2,4-pentanedionato)nickel(II), $R^1 = R^5 =$ phenyl [98], is thought to exhibit a monomer–trimer equilibrium, with the solid trimer forming at ca. 185°C or under mechanical pressure. This behavior differs from that of the diisopropyl derivative just mentioned in that in the former the assciated form is the more stable, in solution at least, while heating causes dissociation. Presumably in the latter complex the bulky phenyl groups are forced into a configuration which allows oligomerization to occur, with the energy gained from bonding offsetting that lost due to steric repulsions.

A particularly interesting case where monomer–trimer equilibria occur concerns β-diketonates with extremely long hydrocarbon chains in place of the methyl groups of acetylacetone [103]. The complex in which $R^1 = R^5 = -(CH_2)_6CH_3$, $R^3 = H$, is a green liquid at room temperature. It appears that the large terminal groups destabilize the crystalline lattice of the trimer but are not sufficiently bulky to destabilize the trimer itself. Above 17°C it solidifies to form a green solid, and forms a purple monomeric solid if cooled below 0°C. The analogous complex where $R^1 = R^5 = -(CH_2)_8CH_3$, is isolated as a purple (monomeric) solid which turns to a green (trimeric) solid at 42°C. Between 42°C and 45°C a mixture of green solid, green liquid and purple liquid coexist, and between 45°C and 53°C the purple liquid disappears. Above 53°C the green solid melts and the usual monomer–trimer equilibrium exists in the melt, and also in solution. These results serve to show that bulky terminal groups on the β-diketonate ligand do not necessarily rule out trimer formation, unless the bulk occurs at the carbon atom on the $\mathbf{R}^1$ (or $\mathbf{R}^5$) group adjacent to the carbonyl substituent.

The preceding paragraphs have demonstrated how the presence of bulky groups at the terminal positions of the bridging diketonate ligand can influence the relative stabilities of monomer and trimer. The same situation holds true for substituents at the 3-(methine) position. Thus, the nickel(II) complexes of 3-phenyl-2,4-pentanedione [98] and 3-benzyl-2,4-pentanedione [104] are red diamagnetic square-planar solids. In toluene an equilibrium exists between the monomeric and trimeric forms. As dilution shifts the position of this equilibrium in favor of the monomer it is possible to measure equilibrium constants for the process

$$3NiL_2 \rightleftharpoons Ni_3L_6$$

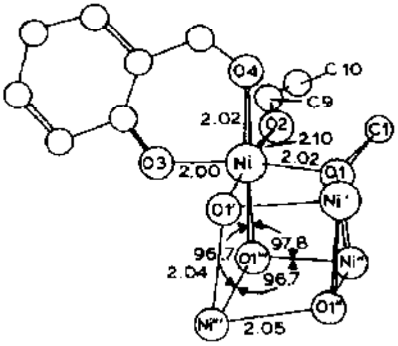
Experimentally $10 < K < 200$ [98]. As the analogous complex in which $R^3 = o$-tolyl is paramagnetic [105] it appears that steric considerations alone do not explain the relative stabilization of the monomeric and trimeric forms. In fact molecular models have suggested that there is no reason to expect appreciable steric interactions in these complexes which would destabilize the oligomeric form. It is proposed that electronic effects are important in this class of compounds. There is a clear correlation [105] between the acidity of the β-diketones and the properties of the resulting nickel(II) complex. Ligands with a high pK_a which give an anion which is a strong donor (Lewis base) donate considerable charge to the central metal ion and stabilize a low coordination number; i.e., a square-planar monomeric complex. Conversely, more acidic diketones give anions which are poorer electron donors and hence do not stabilize this state to the same extent. In such a way one can explain why the nickel(II) complex of 3-*o*-tolyl-2,4-pentanedione ($pK_a = 12.84$) is six-coordinate, while that of 3-phenyl-2,4-pentanedione ($pK_a = 13.76$) is four-coordinate, at room temperature. It should be emphasized that electronic effects alone cannot account for all the observed features of these complexes. As a general rule the acidity of the ligand (or more strictly, the basicity of the anion) is the principal factor in determining the structure of the 3-substituted diketonate complexes, while the size of the ligand, and specifically the amount of steric bulk on the carbon atoms on R^1 and R^5 adjacent to the carbonyls, usually decides the nature of the terminally-substituted complexes.

The foregoing discussion should have emphasized the basic criterion for an intramolecular ferromagnetic interaction in these trimeric systems; the necessity of a Ni–O–Ni bond angle between adjacent nickel(II) ions of ca. 90° to enforce the necessary accidental orthogonality of the interacting metal-based magnetic orbitals. There is no reason to expect that the structure which has been studied in most detail, namely that of $[Ni(acac)_2]_3$, represents the only, or even the best, example of a linear nickel(II) trimer with a net positive J coupling constant. A report on a related nickel(II) trimer, containing a dioximato derivative of pentane-2,4-dione as a bridge between the two terminal nickel(II) centers, indicates [106] that oximes may have the ability to form suitable trimeric species with similar magnetic properties. In this work the magnetic susceptibility of di-μ-acetylacetonedioximato-dichlorooctaaquatrinickel(II) dihydrate and the bromide, iodide, and nitrate salts were measured in the range 90–305 K. Coupling constants of J ca. +20 cm^{-1} suggested an intramolecular ferromagnetic interaction between adjacent nickel centers. No attempt was made to detect any interaction between the two terminal nickel(II) ions. X-ray crystallographic determinations, combined with low-temperature magnetic susceptibility measurements, need to be carried out on other members of this class of molecular species to build up a clearer picture of the effect of these various perturbations, in the same way that a program of structural characterization has allowed a semi-quantitative description of the magnetic properties of the di-μ-hydroxo-bridged copper(II) and chromium(III) classes of dimers.

(ii) Tetrameric nickel clusters

While this class of complexes is small it deserves separate mention since the structures to be described underline the principles discussed in previous sections. It will be seen that, just as in the trimeric nickel(II) complexes, the intramolecular ferromagnetic effect arises by means of approximately orthogonal Ni–O–Ni bridges.

The first nickel(II) complex identified as a member of this class was characterized by Schrauzer and Kohnle [107] in 1964. On the basis of molecular weight determinations and spectral and magnetic evidence, they assigned to $Ni(sal)(OCH_3)(CH_3OH)$ (sal is the anion derived from salicylaldehyde) a cubane structure with nickel(II) and methoxy groups occupying alternate corners of a distorted cube. Figure 25 shows a representation of this structure, as determined by later workers [108]; this structure is of the isomorphous ethanol adduct, which gave crystals more suitable for an X-ray analysis. One can see that this cubane structure is actually considerably distorted from the ideal geometry; the Ni–O–Ni bridge angles are ca. 97.7°. However, magnetic susceptibility studies between 80 and 300 K [108] did indicate a weak ferromagnetic exchange interaction between the nickel(II) ions, with $J = +7$ cm^{-1} for the ethanol solvate and ca. $+4$ cm^{-1} for the analogous methanol solvate. More complete studies down to 4 K [109] have confirmed the essential results of the earlier studies. The molar susceptibility



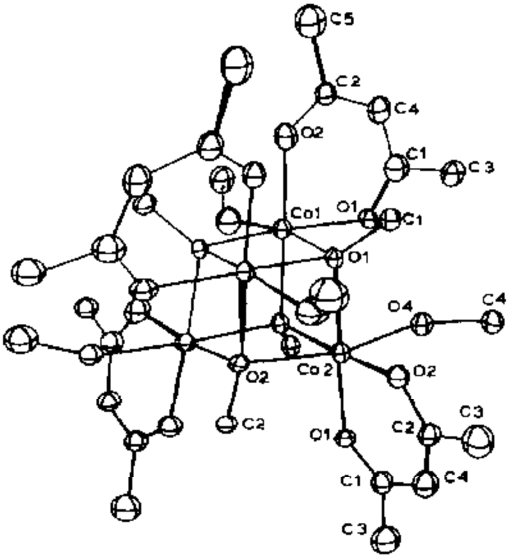


Fig. 25. Structure of $[Ni(sal)(OCH_3)(C_2H_5OH)]_4$.

Fig. 26. Structure of $[Co(acac)(OCH_3)(CH_3OH)]_4$.

data were fit to the theoretical equation for this system using the values $J = +7.46\ cm^{-1}$ and $g = 2.45$, although this fit used only the data collected above 80 K. Between 9.5 and 61.1 K the values $J = +4.97\ cm^{-1}$ and $g = 2.387$ more accurately represented the data. Zero field splitting and intermolecular effects prevented use of susceptibility measurements below 7.5 K. Measurements of the field dependent molar susceptibility gave magnetization data which proved that the $S = 4$ spin state was indeed the ground state, as opposed to four non-coupled $S = 1$ spins.

A very similar complex containing the anion of 2,4-pentanedione as a terminal chelate has been studied in some detail; the results of magnetic susceptibility measurements down to $< 2\ K$ [110] indicated the existence of an $S = 4$ ground state with $J = +7\ cm^{-1}$ between adjacent nickel(II) ions within a cluster. In addition, a much weaker intermolecular lattice ferromagnetic interaction was observed, thus making this complex a unique example of a species exhibiting both intra- and inter- molecular ferromagnetic spin coupling. Figure 26 shows the crystal structure of the isomorphous cobalt(II) complex, in which the M–O–M angles range from 94.6° to 98.6°.

It is not necessary to have chelating ligands to observe these types of structures. This is shown by the work of Kruger and Winter [111], who prepared clusters of the general formula $Ni(OR)X \cdot ROH$, where $R = -CH_3$ or $-CH(CH_3)_2$ and $X = Cl$, Br, I. Magnetic and spectral measurements on $Ni(OCH_3)Cl$ and its solvates suggested that the anhydrous compound

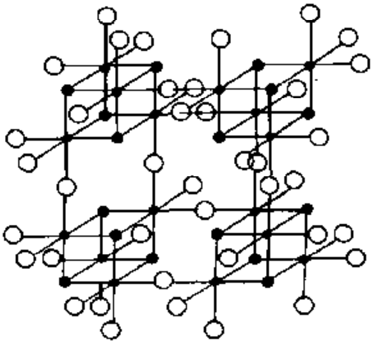


Fig. 27. Illustration of the proposed structure of $[Ni(OCH_3)Cl]_4$.

adopted a tetrameric cubane structure with methoxide bridges and linked by intermolecular chlorides (Fig. 27). Solvation by methanol breaks these intermolecular bridges. The magnetic susceptibility measurements to 90 K could be rationalized on the basis of an intramolecular ferromagnetic exchange with $J = +2.8$ cm^{-1}. Solvation increased this value to $+8.4$ cm^{-1} for $[Ni(OCH_3)Cl(CH_3OH)]_4$ and $+11.2$ cm^{-1} for $[Ni(OCH_3)Cl(CH_3OH)_2]_4$, suggesting that the halide bridges, which are broken by solvation, impart some antiferromagnetism between clusters. Supporting evidence comes from the magnetic behavior of the corresponding bromide and iodide complexes, which are known to provide more efficient pathways for superexchange between metal ions. Indeed in $[Ni(OCH_3)I]_4$, the magnetic moment at room temperature is strongly depressed, implying a dominant intermolecular antiferromagnetic interaction.

It was shown in the previous discussion of the linear nickel(II) trimers that the magnitude and sign of J will depend crucially on the Ni–O–Ni bond angles and, to a lesser extent, on the Ni–O bond lengths. Figure 28 represents schematically the appropriate metal and ligand orbitals whose

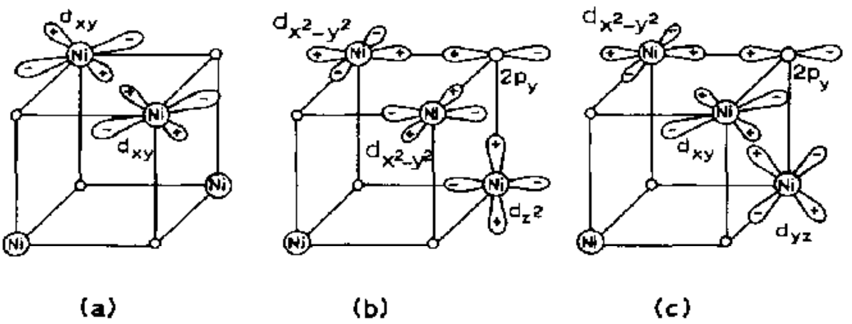


Fig. 28. Orientation of magnetically important metal and ligand orbitals in cubane-type tetrameric nickel(II) clusters.

overlap determines the net magnetism of these tetrameric systems [110]. The various pathways are as follows.

(a) $d_{x^2-y^2}$*(Ni(I))–2*p_y*(O)–*e_g*(Ni(II), Ni(III)) pathway (Fig. 28(b))*

Unpaired spin density on Ni(I) is transferred to a $2p_y$ oxygen orbital. Since this bridging orbital is orthogonal to both the $d_{x^2-y^2}$ and d_{z^2} orbitals of Ni(II) and Ni(III), respectively, this will give rise to a ferromagnetic component.

(b) $d_{x^2-y^2}$*(Ni(I))–2*p_y*(O)–*t_{2g}*(Ni(II), Ni(III)) pathway (Fig. 28(c))*

In this instance the bridging oxygen orbital is not orthogonal to either of the metal *d* orbitals on Ni(II) or Ni(III). This intraatomic direct exchange pathway gives rise to another ferromagnetic contribution.

(c) e_g*(Ni(I))–2s(O)–*e_g*(Ni(II), Ni(III)) pathway*

In this case all the metal e_g orbitals can overlap the oxygen $2s$ orbital. This superexchange will give an antiferromagnetic contribution to the observed magnetic behavior.

(d) e_g*(Ni(I))–2s(O)–*t_{2g}*(Ni(II), Ni(III)) pathway*

The $2s$ oxygen orbital is orthogonal to the t_{2g} orbitals on the acceptor metal ions, and hence this will lead to another ferromagnetic contribution.

The resulting magnetism of a cubane-type nickel(II) cluster will depend on the relative importance of these four pathways, which will in turn depend on the relative overlap integrals, the Ni–O bond lengths, the bridging Ni–O–Ni angles, and the relative energies of the interacting nickel and oxygen orbitals. In all the cases described in this section the ferromagnetic pathways predominate to give a small ferromagnetic effect. This result is obtained in spite of the measured bridging bond angles in these tetramers which range from ca. 94° to 99°. It appears then that the size of the bridging angle, while of definite importance, is not the only factor which decides the magnitude of the intramolecular magnetic interaction.

G. CHROMIUM(III) DIMERS

In a previous section, the structural and low-temperature studies which have been carried out on di-μ-hydroxo-bridged copper(II) complexes were detailed, and a linear correlation was described relating the singlet–triplet splitting energy and the Cu–O–Cu bridging angle (ϕ). In more recent years this treatment has been extended to the electronically somewhat more complex chromium(III) [d^3–d^3] system; the work of Pederson, Hodgson, Hatfield, and Güdel and their research groups has been especially notable in

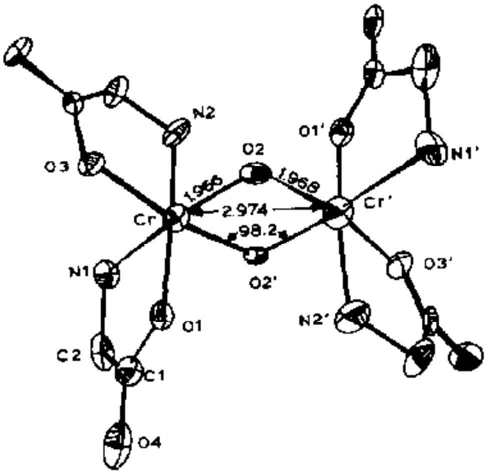


Fig. 29. Structure of $[Cr(gly)_2(OH)]_2$.

this area. As one might expect, because of the competing ferro- and antiferromagnetic contributions to the overall magnetism, the dependence of the observed magnetic properties on the measured structural parameters of these dimers is outwardly less simple than in the copper(II) case. However, some correlations have been noted and will be presented here.

Most of the chromium(III) dimers that have been studied have the molecular formula $[CrL_m(OH)]_2^{n+}$, where L is a mono- or bidentate ligand [112–125]. Figure 29 shows the structure of the first of these complexes to be characterized by X-ray crystallography [124], $[Cr(gly)_2(OH)]_2$. In this particular complex $\phi = 98.2°$. Unfortunately, as is often the case when solving the structures of large molecules, the bridging hydrogen atoms were not resolved in this analysis. This meant that the dihedral angle (θ) between the CrOCrO plane and the O–H bond was not determined, and since recent work has established the major significance of this parameter, one cannot, strictly speaking, described the above complex as being completely structurally characterized.

It is interesting to compare the present knowledge of these complexes with the state of affairs pertaining ten years ago. The progress that has been made in the understanding of this area should lead to optimism in regard to the advances which are probable in the same time span in other branches of this subject.

By the middle of the last decade it was thought that a simple correlation related the singlet–triplet splitting and the bridging angle, entirely analogous to that already seen for the structurally similar copper(II) dimers [125]. The slope of the plot of $2J$ vs. ϕ was much less than that for the copper(II) complexes, with a very similar crossover point at ca. 97.6°. The available

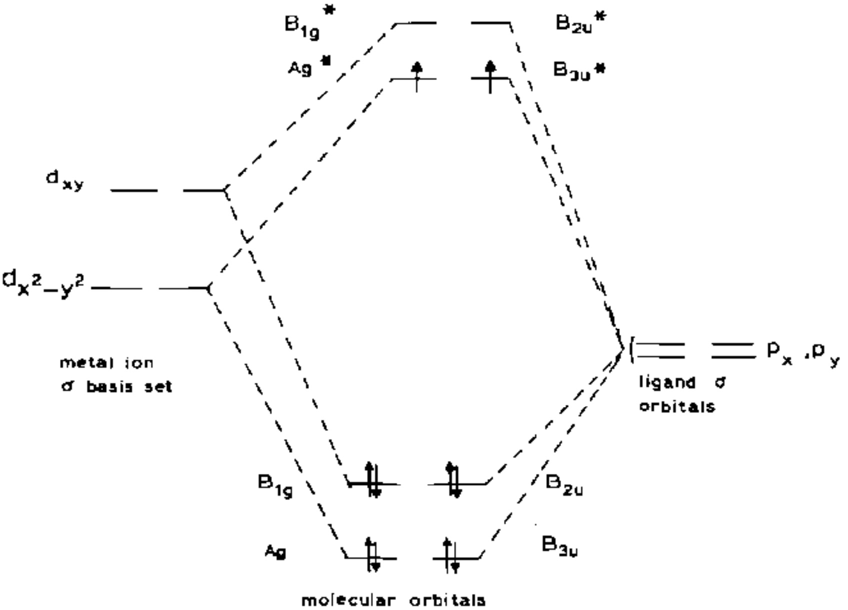


Fig. 30. Molecular orbital diagram for the σ-orbitals in the CrOCrO plane assuming D_{2h} symmetry and $\phi = 90°$.

structural information, which was rather scanty, was used to rationalize the observed magnetic properties on a molecular orbital basis, as shown below. Figures 30 and 31 show the molecular orbital diagrams [125] which can be constructed from the appropriate metal and oxygen orbitals, depending on whether ϕ equals 90° or is considerably greater than 90°. In these diagrams the x-axis is defined as being along the Cr–Cr vector, with the y-axis perpendicular to it along the O–O direction. Assuming planarity of the four atoms in the bridging ring, the system is close to D_{2h} symmetry. It can be shown that for $\phi = 90°$, the ten electron system (for chromium(III), neglecting the oxygen s electrons) gives rise to a triplet ground state (Fig. 30), while for $\phi > 90°$, a singlet state is stabilized (Fig. 31). The slope of the plot of the singlet–triplet splitting energy ($2J$, or ΔE) vs. ϕ can be explained on the same basis. In the copper(II) dimers the unpaired electrons are localized on $d_{x^2-y^2}$ orbitals (using the axes imposed by the D_{2h} symmetry) which point directly at the bridging oxygen orbitals, while in the chromium(III) case the relevant orbitals containing unpaired spin are t_{2g} orbitals which point between these bridge orbitals. Hence, a smaller overlap occurs between the interacting orbitals in this latter case, with ΔE being smaller for the chromium(III) dimers, for any particular value of ϕ, than in the analogous copper(II) complexes.

More recent research into the magnetic properties of these complexes has indicated that the preceding desription is not sufficient to provide a com-

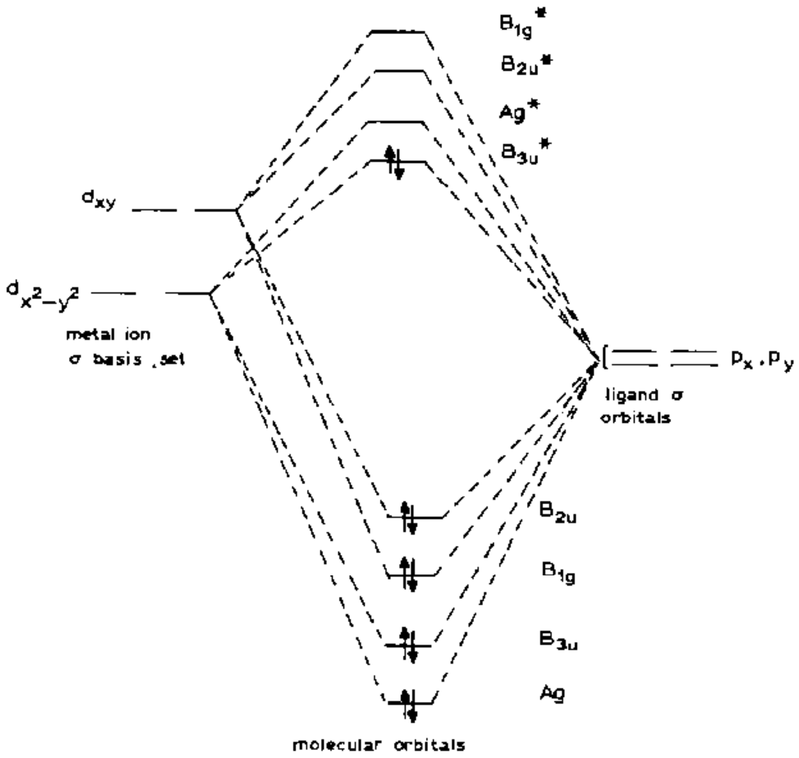


Fig. 31. Molecular orbital diagram for the σ-orbitals in the CrOCrO plane, assuming D_{2h} symmetry and $\phi > 90°$.

plete picture of the correlation between the magnetism and structural parameters in these coupled systems. The more complete model correlates the magnitude of the superexchange interaction with three structural parameters r, ϕ, and θ, where r is the chromium-bridging oxygen bond length and ϕ and θ have already been defined (Fig. 32).

To date nearly a score of dimers of the type $[\mathrm{CrL}_m(\mathrm{OR})]_2^{n+}$ have been completely structurally characterized, where L is a mono- or bidentate ligand and R is a hydrogen or alkyl group, and, with accurate measurements

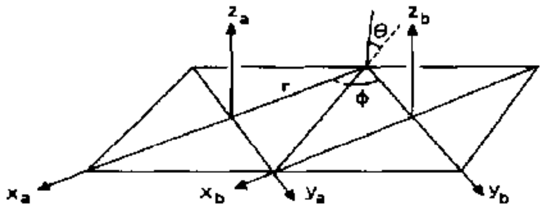


Fig. 32. Definition of structural parameters and coordinate system for di-μ-hydroxochromium(III) complexes.

of the dihedral angle θ now possible, a clearer picture is emerging of the effects of the structural and electronic variations on the superexchange processes in these dimers. This model, due to Pedersen and co-workers [126], uses angular overlap calculations based on Anderson's superexchange model. The theory will not be described here, but the final theoretical expression for J is

$$J = J_{\mathrm{AF}} - J_{\mathrm{F}} = \mathrm{e}^{-a(r-1.8)}\Big[b\cos^4\theta/\{1-\sin^2\theta/\tan^2(\phi/2)\}^2 - c\sin^2\phi/\{1-\cos\phi\}^2\Big] \tag{12}$$

In this rather involved equation J is the observable exchange coupling constant, defined as the difference between the antiferromagnetic and ferromagnetic contributions to the magnetic interactions of the ground state. The parameters a, b, and c will depend on the triplet–singlet separation ΔE as well as on $10Dq$ for the chromium(III) system and on interelectronic repulsion parameters. The measured structural and magnetic data have been fitted to this equation using a least-squares technique and gave J coupling constants that on the whole agree remarkably well with those determined experimentally.

While this treatment has been applied successfully to all of the di-μ-hydroxo-bridged chromium(III) dimers structurally characterized to date, as well as some alkoxo-bridged systems, it is by no means certain that this model is the only one which will explain the magnetic data that have been collected on these dimers. Hatfield, Hodgson, and co-workers have characterized a large number of these dimeric hydroxo-bridged complexes using variable temperature magnetic susceptibility measurements as well as X-ray structural analyses. Their accumulated data reveal a correlation between the singlet–triplet splitting ΔE and ϕ/r. In their measurements the singlet–triplet separation is defined from the Hamiltonian

$$\mathscr{H} = -2J\hat{\mathbf{S}}_1\cdot\hat{\mathbf{S}}_2 - j(\hat{\mathbf{S}}_1\cdot\hat{\mathbf{S}}_2)^2 \tag{13}$$

where J is the isotropic bilinear exchange coupling and j is a biquadratic coupling constant [127]. $\Delta E = 2J - 6.5j$, and ϕ and r are as defined in Fig. 32. (It should be pointed out that Pedersen uses the Hamiltonian $\mathscr{H} = J\hat{\mathbf{S}}_1\cdot\hat{\mathbf{S}}_2 - j(\hat{\mathbf{S}}_1\cdot\hat{\mathbf{S}}_2)^2$ in his work.) Scaringe et al. [117] have extended the molecular orbital treatment first presented by Hoffmann and co-workers [43] to these chromium(III) dimers and have been able to account qualitatively for the variation of the exchange coupling with the structural features in the complexes. As yet no quantitative calculations have been performed. A result which proceeds from this work is the possibility that only two of the parameters ϕ, θ, and r used by Pedersen are truly independent, although more structural and theoretical work is needed to confirm this hypothesis.

It may seem strange that so much space has been devoted to the preceding discussion of a class of complexes in which by far the majority of members exhibit a net antiferromagnetic intramolecular coupling. In fact only one complex has been observed to exhibit a net ferromagnetic effect [112], with $J = 1.1$ cm^{-1}. It is interesting to note that in this complex, $Na_4[Cr(mal)_2OH]_2 \cdot 5H_2O$ (mal is the malonate dianion), $\phi = 99.3°$, an angle which would not have been predicted to lead to a net ferromagnetic interaction, using the early ΔE vs. ϕ correlation. This analysis has attempted to demonstrate the utility of relatively simple molecular orbital concepts in giving a semiquantitative picture of the magnetic coupling in complexes with more than one unpaired electron on each metal ion, and to show how, in theory at least, only a few structural parameters need be altered to produce novel polynuclear complexes with expected magnetic properties. The extension of molecular orbital theory to the next logical family of dimeric complexes, the di-μ-hydroxo-bridged iron(III) system, is obviously not a simple matter, but similar structure–magnetism correlations may well turn out to be equally valid there. Some recent work on dinuclear iron(III) systems containing -OR bridges (R = hydrogen, alkyl, or aryl) has, in fact, presented evidence [128] that this is so, although no example of a net ferromagnetic interaction has yet been reported.

H. OTHER SYSTEMS

The survey that has been presented here represents a fairly complete coverage of the main classes of ligands and structural features which can, under favorable circumstances, give rise to intramolecular ferromagnetic interactions. As in all reviews, there are certain cases which resist easy classification and can be best filed under "miscellaneous". Some of these complexes are mentioned here without detailed discussion. This is because these compounds tend, for the most part, to be unique examples, which may be of intrinsic interest but are not likely to give rise to new families of novel ferromagnetic molecules. Those that will be described in somewhat greater depth include classes of compounds which exemplify the structure–magnetism correlations discussed earlier, and which may provide future examples of strongly ferromagnetic molecules. The metalloporphyrin cation radicals exemplify such a class.

(i) Dibridged nickel(II) dimers

The earlier section on nickel(II) clusters indicated that the mechanism of the superexchange interaction in these complexes could not be described using the conceptually simple model which works so well for the di-μ-hy-

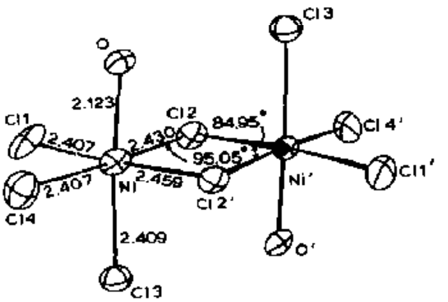


Fig. 33. Structure of the $[Ni_2Cl_8(H_2O)_2]^{4-}$ anion in $(PDA)_2[Ni_2Cl_8(H_2O)_2]$.

droxo-bridged copper(II) dimers and the heterobinuclear compartmental complexes. This is also true for the few ferromagnetic nickel(II) dimers that have been subjected to detailed study, although some progress has been made in this field. Most of these complexes are nickel(II) chloride dimers, although complexes with thiocyanate and phenolate (from a salicylaldimine ligand) bridges have also been characterized. Figure 33 shows the dimeric unit of $(PDA)_2[NiCl_4(H_2O)]_2$; PDA = propylenediammonium cation) [129], with pertinent structural information. This complex, which has a distorted octahedral geometry around each nickel(II) center, represents one of three main types of nickel(II) dimers which have been characterized. The other two classes are five-coordinate, with geometries most accurately described as based on either a trigonal bipyramid or square pyramid. The complex di-μ-chloro-dichlorobis(bis-3,5-dimethylpyrazolyl)methane)dinickel(II) prepared by Reedijk and co-workers [130] is a good example of a dimer which could be grouped in either of these latter two classes; however, based on its magnetic properties, it should probably be classified as a distorted trigonal bipyramid. This classification will be rationalized below.

Following the theoretical work of Ginsberg, who prepared and analyzed the magnetic properties of the first ferromagnetically coupled molecular species $[Ni(en)_2X]_2Y_2$ (X = Y = Cl, Br; X = NCS, Y = I) [131,132], the model used to fit the magnetic data in these dimeric systems uses the spin Hamiltonian

$$\mathscr{H} = -2J\hat{S}_1\cdot\hat{S}_2 - D\left(\hat{S}_{1z}^2+\hat{S}_{2z}^2\right) - g\beta H\hat{S}_z - 2zJ'\hat{S}_z < \hat{S}_z > \qquad (14)$$

In this equation J is the exchange integral for the intradimer interaction between nickel(II) ions with spin operators $\hat{S}_1$ and $\hat{S}_2$. D is the axial zero-field splitting of the ${}^3A_2$ ground state and zJ' allows for an interdimer exchange interaction. The effect of an external magnetic field H along the z direction accounts for the remaining parameter $\hat{S}_z$, the spin operator for the z component of total dimer spin. In spite of the apparent complexity of the relationship it has been possible to fit experimental data to this expression in several magnetic susceptibility studies. These studies have found small ferromagnetic coupling constants, with the largest measured to date having $J = +16$ cm^{-1} (assuming $zJ \neq 0$) [133]. The combined structural and magnetic data suggest the following conclusions.

(a) The sign and magnitude of the exchange interaction is sensitive to the size of the Ni–Cl–Ni bridging angle, a result first obtained by Barraclough and Brookes [134] and since confirmed by other groups. A linear relationship between J and ϕ has not, however, been observed [135,136].

(b) Magnetic orthogonality of the interacting orbitals is a prerequisite to a net ferromagnetic interaction, a result which is discussed more fully elsewhere in this article.

(c) In general, those complexes with a six coordinate or trigonal-bipyramidal geometry exhibit a ferromagnetic interaction, while those dimers with square-pyramidal coordination tend to give a negative coupling constant J. The dimethylpyrazolyl complex mentioned previously [130] has a coupling constant $J = +2.6$ cm^{-1}.

(ii) Other chloro-bridged copper(II) systems

The earlier discussion of the properties of some chloro-bridged copper(II) dimers showed that the sign and magnitude of the magnetic coupling between copper centers depends on the exact structure of the complex, and in particular on the bridging angle ϕ. Other chloro-bridged complexes have been studied in which the relationship between structure and magnetic properties is not so clearly defined, although the same principles undoubtedly hold. Most of these complexes are polymeric chain compounds, which do not, strictly speaking, fit into this review. However they will be described briefly because the results of magnetic studies on these species provide additional evidence in support of the molecular orbital models which have been devised to correlate the magnetic behavior of simpler dimeric systems.

Single-chloride copper(II) chains have been structurally characterized by Reedijk and co-workers [137]. Figure 34 gives a schematic illustration of the chain compounds CuL_2Cl_2, where L is DMSO, Im, or maep. This structure is also adopted by Cu(caf)(H_2O)Cl_2. In these complexes the geometry is best described as tetragonal pyramidal. The Cu–Cl–Cu bridging angles vary between 114° (maep) and 145° (DMSO). The former complex exhibits a weak net intramolecular ferromagnetism with $2J = +1.58$ cm^{-1}. It is probable that the overall crystal and molecular packing forces determine the relative orientations of the CuL_2Cl_2 units with respect to the bridge, and that the sign of $2J$ is determined by these effects.

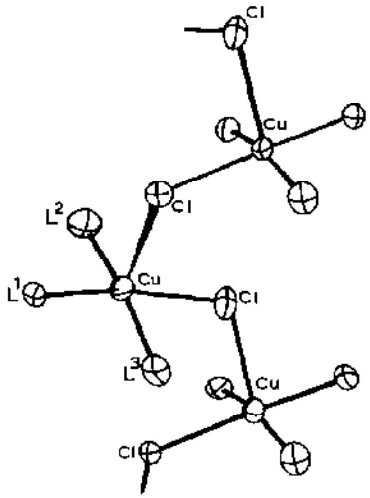


Fig. 34. Structure of the single chloride-bridged copper(II) chain complexes $[CuL_2Cl_2]_x$.

The magnetic susceptibility data for the above complexes can be described very closely using the series expansion for the Heisenberg model for ferromagnetically coupled $S = 1/2$ ions, originally derived by Baker et al. [138]. This model also fits the observed magnetic properties of the complexes $[CuCl_2(TMSO)]$ and $[CuCl_2(DMSO)]$ [139–141], in which the five-coordinate copper(II) ions are bridged by two chlorides and the oxygen of the sulfoxide. A mean-field correction for an antiferromagnetic interaction with a small coupling constant J', probably transmitted via Cu–O–S $\cdots$ S–O–Cu interactions, is necessary to fit the data at low temperatures. The values of $|J/J'|$ ca. 50 (TMSO) and 25 (DMSO) [141] show these complexes to be less than perfect one-dimensional systems. The complex $(CH_3)_4NCuCl_3$ contains distorted copper octahedra linked by three chloride bridges, only one of which is symmetrical [142]. Low-temperature susceptibility studies [143] lead to values of $J = +42\ \text{cm}^{-1}$ and $|J/J'| < 10^{-4}$. This latter value is the lowest yet observed in a ferromagnetic $S = 1/2$ chain and describes this compound as a fairly rigorous one-dimensional Heisenberg ferromagnet. (It should be pointed out that because of the form of the expansions used in fitting the observed magnetic susceptibility in an $S = 1/2$ Heisenberg model, these intramolecular coupling constants are often quoted in the form J/k, with units of Kelvins. The values quoted here have been converted from these units to the more commonly used reciprocal centimeters.)

Chain compounds containing two halide bridges are also known [144–147]. Most of these exhibit net intramolecular antiferromagnetic coupling. Some examples have been observed in which the intrachain coupling leads to a net ferromagnetic interaction. These include the linear chains (cyclohexylam-

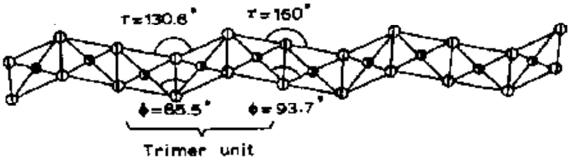


Fig. 35. Structure of $3CuCl_2 \cdot 2dx$, with relevant structural parameters.

monium)copper(II) chloride (CHAC) and (cyclopentylammonium)copper(II) chloride (CPAC) [145,146]. For the former compound $\phi = 86.0°$ and $J = +74$ cm^{-1}, which represents quite an appreciable ferromagnetic interaction for a copper(II) system. Another unusual example is provided by the complex $3CuCl_2 \cdot 2dx$ (dx = 1,4-dioxane) [148] (Fig. 35). The structure consists of a symmetrically dibridged linear chain in which pairs of bridges with $\phi_1 = 85.5°$ and $\delta_1 = 130.6°$ are separated by bridges in which $\phi_2 = 93.7°$ and $\delta_2 = 180°$. In magnetic terms, each adjacent pair of ϕ, δ bridges defines a ferromagnetically coupled trimer, coupled antiferromagnetically to adjacent trimeric units in the same chain. Fortunately for the sake of the resulting analysis there are no close interchain contacts and so no interchain interactions are expected. Analysis of the magnetic data collected on this complex [148] leads to an intratrimer coupling $J = +131$ cm^{-1} and a smaller intertrimer interaction $J' = -10.6$ cm^{-1}. Although this compound has an unusual structure, the observed magnetic properties can be rationalized by observation of the structural parameters. Thus, the intratrimer bridging angle, $\phi_1 = 85.5°$, which is almost identical to that observed for (CHAC)$CuCl_3$, clearly suggests that a ferromagnetic interaction is possible, on the basis of the analysis of the $Cu_2Cl_6^{2-}$ dimeric anions. Similarly, the angles $\phi_2 = 93.7°$ and $\delta_2 = 180°$, are sufficiently large to explain the small intertrimer antiferromagnetic interaction. The difference between the dihedral angles in the di-μ-chloro-bridged species should be noted. For $3CuCl_2 \cdot 2dx$ $\delta_1 = 130.6°$, while in (CHAC)$CuCl_3$ $\delta = 155.8°$. The increase in the ferromagnetic interaction seen in the former compound merely reflects the prediction of Charlot et al. [47] that a fold in the dimer along the Cl–Cl vector leads to a decreased antiferromagnetic contribution to the net magnetic properties of the compound. Of course this folding will also decrease ϕ; nonetheless, the result is valid, as theoretical calculations by Bencini and Gatteschi have demonstrated [149].

(iii) Pyridine N*-oxides and other bridged copper(II) dimers*

Figure 36 shows the structure of bis(μ-pyridine-*N*-oxide)bis-[bis(nitrato)(pyridine-*N*-oxide)copper(II)] [150,151], the first exchange-coupled copper(II) dimer to have a triplet spin ground state authenticated by

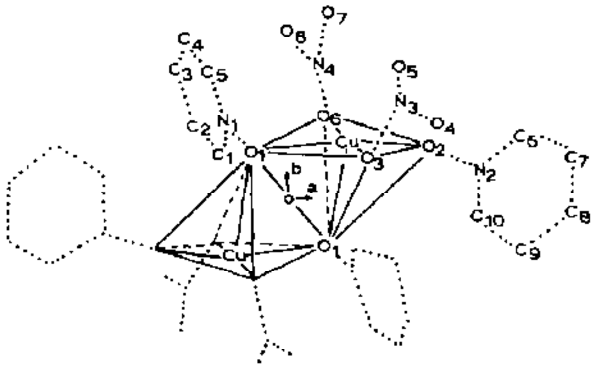


Fig. 36. Structure of dimeric bis(pyridine-*N*-oxide)copper(II) nitrate.

low-temperature magnetic susceptibility and EPR measurements [152]. $2J$ has been estimated at ca. $+10\ \mathrm{cm}^{-1}$ for this complex [153]. Each copper(II) ion has a distorted square-pyramidal geometry in which the copper–copper separation is 3.458 Å and the copper–oxygen–copper bridging angle 102.9°. The 4-methyl substituted complex also exhibits a small net ferromagnetic effect with $2J =$ ca. $+2\ \mathrm{cm}^{-1}$, while the analogous 4-methoxy derivative is reported to have a singlet ground state, with $2J = -2\ \mathrm{cm}^{-1}$ [153]. The chloride salt of the unsubstituted dimer has a rather different structure [154–156] in which each copper center is in a distorted tetrahedral environment. Magnetic susceptibility measurements on this complex [154] indicate a strong antiferromagnetic interaction with $2J = -650\ \mathrm{cm}^{-1}$. Finally, measurements over the 90–300 K range on the complex bis-μ-(quinoline-*N*-oxide)copper(II) chloride [156] indicate an exceptionally large stabilization of a ground triplet state where $2J =$ ca. $+200\ \mathrm{cm}^{-1}$. This remarkable value must be viewed as rather suspect given the lack of lower temperature data.

The case of bis(μ-pyridine-*N*-oxide)bis[bis(nitrato)(pyridine-*N*-oxide) copper(II)] is one that has been the subject of some debate in recent years. Carlin and co-workers [157] have reinvestigated the early work by Hatfield et al. on this complex and, on the basis of low-temperature magnetic susceptibility and magnetization measurements, state that no ferromagnetic interaction is in fact present, and that this complex behaves as if it has two isolated $S = 1/2$ spins. Hatfield notes in an accompanying paper [158] that EPR spectroscopy unequivocally showed a triplet state signal in the mixed metal system $[\mathrm{Cu}_x\mathrm{Zn}_y(\text{4-R-pyNO})_4(\mathrm{NO}_3)_4]$ ($\mathrm{R} = \mathrm{H}, \mathrm{CH}_3, \mathrm{OCH}_3$), in which some of the copper(II) dimer was doped into an isomorphous zinc dimer matrix. The discrepancy between these measurements only serves to emphasize the need for careful studies, using a variety of complementary magnetic and spectroscopic techniques, in order to distinguish among the various alternative intraatomic, intramolecular, and intermolecular interactions which become experimentally significant at very low temperature.

As well as the hydroxo-, chloro-, and *N*-oxide-bridged systems that have been described here, other miscellaneous systems involving carbonate [159], diethyldithiocarbamate [160], tyrosinate [161], glyoximate [162], salicylaldimate [163], pyrazine [164], and oxydiacetate [165] have been observed to exhibit a net ferromagnetic interaction between adjacent copper(II) centers. Information on these systems is at present too sparse to justify any discussion of their properties here.

(iv) Manganese(II) phthalocyanine

The magnetic behavior of transition metal phthalocyanines has been investigated intensively, since these complexes are known to exhibit anisotropic semiconductive and photoconductive properties. In general these studies show a strong intermolecular antiferromagnetic interaction but manganese(II) phthalocyanine appears to exist in the rare $S = 3/2$ spin state with a weak ferromagnetic interaction between neighboring molecules, as demonstrated by its positive Weiss constant of 10 K [166,167]. In agreement with this static susceptibility measurement, the Curie temperature, as measured by relative a.c. susceptibility measurements [168], is 8.6 K. The crystal structure of nickel(II) phthalocyanine, with which the manganese(II) complex is isomorphous, shows square-planar units stacked with an intermolecular distance of 3.4 Å. Two nitrogens of each molecule lie directly above and below manganese ions belonging to nearest neighbors, thus supplying a possible pathway for a superexchange interaction.

(v) Iron(II) bis(dithiocarbamates)

These complexes of general formula $\mathrm{Fe(III)X(S_2CNR_2)_2}$, where X is a halogen and R an alkyl group, are of interest in that they exhibit the relatively uncommon $S = 3/2$ spin ground state. In general they crystallize in a tetragonal pyramidal C_{2v} geometry with the halide at the axial site. The chloro complex exhibits a weak intermolecular ferromagnetic interaction ($J < 2\ \mathrm{cm}^{-1}$) [169,170] with an intermolecular exchange via the sulfur atoms of the extensively delocalized dithiocarbamate ligand giving rise to the observed magnetic properties. The analogous bromo derivative behaves as a simple paramagnet, while the iodide shows intermolecular antiferromagnetic coupling.

(vi) Metalloporphyrin π-radical cations

In the last few years a number of metalloporphyrin radical cations have been synthesized, whose magnetic properties provide further support for the molecular orbital approach to intramolecular ferromagnetic effects. It can readily be seen that a metalloporphyrin radical cation in strict D_{4h} symmetry must have orthogonal magnetic orbitals, regardless of the central metal ion. The five metal *d* orbitals (z^2, x^2-y^2, xy, xz, and yz) have a_{1g}, b_{1g}, b_{2g}, e_g, and e_g symmetry, respectively, while the radical will have either a_{1u} or a_{2u} symmetry. Thus no antiferromagnetic interaction is expected ($J_{AF}=0$) and the complex will behave either as a magnetically uncoupled $S=5/2$, $S=1/2$ system or as a strongly ferromagnetically coupled $S=3$ system. This situation occurs in the π-radical complex [Fe(III)(OClO$_3$)(TPP$^{\cdot}$)]. As yet, definitive magnetic susceptibility studies to low temperature have not been carried out to determine which of these possibilities fits the observed magnetic properties more accurately [171–173]. This case should be contrasted with the situation prevailing in some other M(TPP$^{\cdot}$) systems. In these complexes, for example [Fe(III)Cl(TPP$^{\cdot}$)]$^+$, ruffling of the macrocycle leads to a net C_{2v} symmetry around the metal. In this lowered symmetry the *d* orbitals (z^2, x^2-y^2, xy, xz, and yz) have symmetries a_1, a_1, a_2, b_1, and b_2, and the ligand orbitals transform as a_1 (a_{2u}) and a_2 (a_{1u}). A net overlap is now possible, and these complexes will show an intramolecular antiferromagnetic interaction [172–174].

The magnitude of the coupling constant J in these systems will depend on the central metal; i.e., which *d* orbitals are involved, and whether the radical cation has an a_{1u} or a_{2u} ground state. It would thus appear that a family of new species exhibiting a variable, controlled, intramolecular ferromagnetic interaction could be made by the use of appropriate metal ions and substituted porphyrins. The chromium(III), copper(II) and vanadyl(II) ions, which have been studied in other binuclear complexes, are particularly attractive candidates in this regard.

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