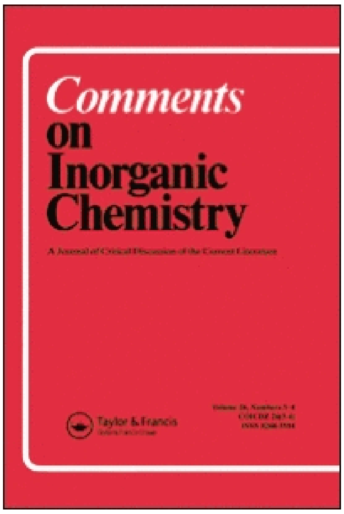


Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

Ferromagnetically Coupled Dinuclear Complexes

Olivier Kahn[a]
[a] Laboratoire de Spectrochimie des Eléments de Transition, ERA N° 672, Université de Paris-Sud, Orsay, France

To cite this Article Kahn, Olivier(1984) 'Ferromagnetically Coupled Dinuclear Complexes', Comments on Inorganic Chemistry, 3: 2, 105 — 132

To link to this Article: DOI: 10.1080/02603598408078132

URL: http://dx.doi.org/10.1080/02603598408078132

Ferromagnetically Coupled Dinuclear Complexes

The goal of this Comment is to propose a strategic approach to the design of ferromagnetically coupled dinuclear complexes. The theoretical aspect of the problem is discussed at two levels of approximation. At the first level only the metallic unpaired electrons are considered as active electrons; at the second the eventual spin polarization effects from the highest occupied orbitals of the bridging ligands are included. Three situations leading to ferromagnetic interaction are then presented, namely, the strict orthogonality of the magnetic orbitals, the accidental orthogonality and spin polarization effects. For each situation several examples are described. It is emphasized that the accidental orthogonality can be distroyed by a very small change of structural parameter, whereas the two other situations are less sensitive to such modifications. Finally, it is pointed out that in the case of ferromagnetic interaction there is great uncertainty in the energy gaps between low lying states deduced from the magnetic data.

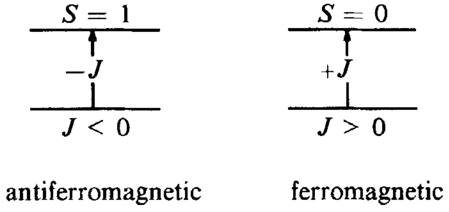
INTRODUCTION

In the last decade an extremely large number of dinuclear complexes have been synthesized in which the metal ions are exchange coupled. Increasingly, the crystal structures have been determined and the spectrum of the low lying states has been interpreted in light of the structural data.

It is well known that the interaction can be of an antiferromagnetic or ferromagnetic nature depending on whether the low-lying ground state has the lowest or the highest spin multiplicity. For instance, in copper (II) dinuclear systems the interaction between the single-ion spin doublet states leads to a pair of spin singlet and spin triplet

Comments Inorg. Chem.
1984, Vol. 3, Nos. 2–3, pp. 105–132
0260-3594/84/0303-0105/$18.50/0

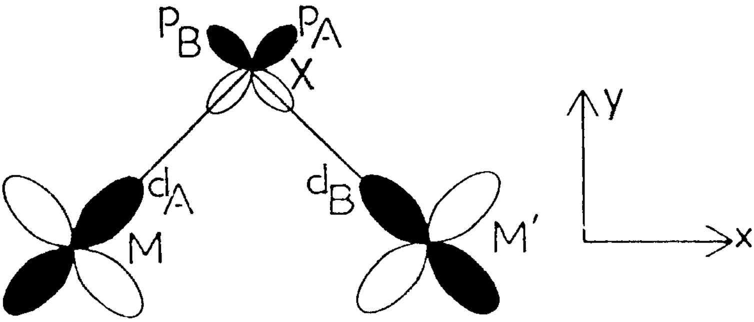
states. The ground state is the singlet in the case of antiferromagnetic interaction and the triplet in the case of ferromagnetic interaction as schematized in **1**, with a singlet-triplet (S-T) energy gap conventionally noted by *J*.



1

It must be emphasized here that *J* is a physical observable and not a parameter, the value of which could depend on the theoretical model used to describe the phenomenon.

At first sight one might expect the proportions of antiferro and ferromagnetically coupled complexes to be statistically close to 50/50. In fact, when examining the reported results one sees that this is far from being the case. Less than 5% of the perfectly characterized dinuclear complexes are reported as ferromagnetically coupled and in some cases the result may be questioned.[1,2] Moreover, the synthesis of such a complex generally was not the outcome of a strategic approach but an accidental result. In other words, the normal situation appears to be the one in which the interaction between the metal centers leads to weakly bonding molecular orbitals in which the metallic electrons tend to pair. In this respect, it is characteristic that Hoffmann and co-workers, in their theoretical approach of the exchange interaction, only discussed the variation of the antiferromagnetic interaction versus small structural changes.[3] The phenomenon of exchange interaction was then assimilated to a borderline case of very weak polycentric bonds. To our knowledge, prior to 1977 only solid state physicists or chemists such as Goodenough[4] and Kanamori[5] had suggested how a ferromagnetic interaction between two metal centers could arise; this represented one of the rules which, in principle, might allow a prediction of the nature of the interaction.[6] A good presentation of these rules has been given by Ginsberg.[7] From these rules a ferromagnetic interaction was expected in a copper(II) pair with a 90° CuXCu bridging angle as shown in **2**.



2

The metallic orbitals with an unpaired electron have *xy* symmetry. With conventional notation the exchange pathway along the CuXCu linkage may be written as $d_{\mathrm{A}\parallel}p_{\mathrm{A}\perp}p_{\mathrm{B}\parallel}d_{\mathrm{B}}$ and the orthogonality between the p_{A} and p_{B} atomic orbitals centered on the bridge X favors the ferromagnetic interaction.[7] We shall see later that the situation represented in **2** corresponds to what we call the accidental orthogonality of the magnetic orbitals. Several copper(II) as well as nickel(II) polymetallic systems with bridging angles close to 90° actually are ferromagnetically coupled, as predicted by the Goodenough–Kanamori rules. However, when applied to molecular systems this approach has a severe defect. It considers individually each MXM linkage and does not take into account symmetry of the system. When there are several bridging atoms it ignores the phase relations between the different MXM linkages. We shall see that the strict orthogonality of the magnetic orbitals, which is actually the most convenient way to achieve a ferromagnetic interaction, is based on these phase relations between the bridging atoms.

The goal of this Comment is to propose a strategic approach to the design of ferromagnetically coupled dinuclear complexes and to present some examples illustrating various facets of this approach. The plan will be the following: First, we shall focus on the theoretical aspect of the problem, then we shall approach successively the strict orthogonality of the magnetic orbitals, accidental orthogonality and spin polarization effects. Finally, we shall briefly discuss some specific difficulties in determining accurately the magnitude of the interaction in the case of ferromagnetic coupling. This Comment is mainly concerned with dinuclear species, even if the described approach is applicable to one-dimensional systems. It complements the excellent review paper on ferromagnetism in linear chains by Willett and Landee.[8]

THEORETICAL APPROACH

This theoretical part will be developed at two levels. We first assume that all the electrons of the molecular system but the unpaired electrons coming from the metals are passive.[9] This assumption implicitly requires that the doubly occupied molecular orbitals of the bridging and terminal ligands and the doubly occupied metallic orbitals are very low in energy with regard to the magnetic orbitals. These magnetic orbitals are defined as the singly occupied molecular orbitals for each monomeric fragment of the bimetallic system, made up of the metal ion surrounded by its terminal and bridging nearest neighbors.[10] The (nonphenomenological) electrostatic Hamiltonian of the system may then be written

$$\mathcal{H} = \sum_{i} h(i) + \sum \sum_{j>i} \frac{1}{r_{ij}}, \tag{1}$$

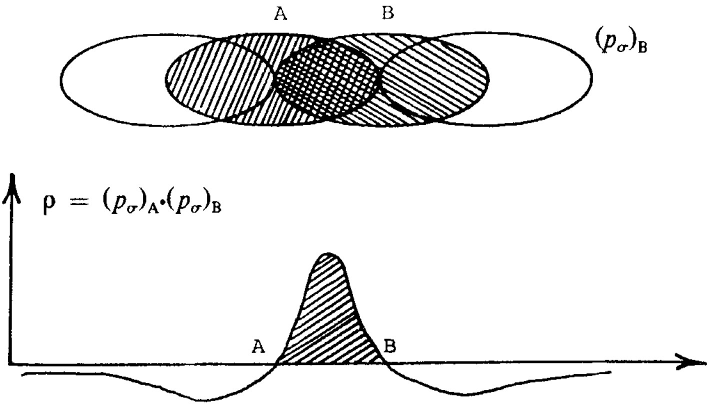
where the summation extends over the active electrons of the A-B dinuclear system. $h(i)$ is the one-electron Hamiltonian for the electron i and r_{ij} is an interelectronic distance. To simplify, we assume that there is just one unpaired (active) electron per interacting center described by the ϕ_A and ϕ_B magnetic orbitals, respectively. A and B may be identical or not. From the ground configuration $\phi_A\phi_B$ arise the two low lying spin states with $S=0$, $M_S=0$ and $S=1$, $M_S=0,\pm1$. The orbital parts of the corresponding wavefunctions are $[2(1\pm S^2)]^{-1/2}[\phi_A(1)\phi_B(2)\pm\phi_A(2)\phi_B(1)]$, where the plus sign holds for the spin singlet state ($S=0$, $M_S=0$) and the minus sign for the spin triplet state ($S=1$, $M_S=0$, ±1). The S-T energy gap J is easily obtained:

$$J = 4tS + 2\,(j - kS^2)/(1 - S^4), \tag{2}$$

where

$$\begin{aligned} S &= \langle \frac{\phi_A(i)}{\phi_B(i)} \rangle, \\ t &= \langle \frac{\phi_A(i)}{h(i)} - \frac{\alpha_A+\alpha_B/2}{\phi^A(i)} \rangle, \\ \alpha_{A(B)} &= \langle \frac{\phi_{A(B)}(i)/h(i)}{\phi_{A(B)}(i)} \rangle, \\ k &= \langle \frac{\phi_A(i)\phi_B(j)/r^{-1}{}_{ij}}{\phi_A(i)\phi_B(j)} \rangle, \\ j &= \langle \frac{\phi_A(i)\phi_B(j)/r^{-1}{}_{ij}}{\phi_A(j)\phi_B(i)} \rangle. \end{aligned} \tag{3}$$

t and S are of opposite sign so that $4tS$ is negative, as well as $-kS^2$. Therefore, the only positive term in Eq.(2) is $2j$. Whatever the sign of J, the positive contribution $2j$ is far from being negligible. For instance, in copper(II) acetate, J is equal to -286 cm^{-1}, i.e., the interaction is strongly antiferromagnetic. Nevertheless, $2j$ was found to be $+230$ cm^{-1} by *ab initio* calculation.[11] It is clear from Eq.(2) that the way to obtain a triplet ground state is to mimimize, or better, to cancel the overlap integral S. In this latter case, the magnetic orbitals are orthogonal and the triplet state is stabilized by $2j$ with regard to the singlet state. This orthogonality can be achieved in two ways. It can be strict when the two magnetic orbitals transform as different irreducible representations of the molecular symmetry group, or it can be accidental when $S = 0$, although the magnetic orbitals have the same symmetry. This accidental orthogonality can only occur for very peculiar values of the structural parameters. The concepts of strict and accidental orthogonalities can be clarified by an atomic analogy. A p_σ orbital and a p_π orbital are strictly orthogonal. This orthogonality holds whatever the interatomic distance. On the other hand, two p_σ orbitals give a nonzero overlap except for a quite peculiar value of the interatomic distance where the positive part of the overlap density exactly compensates the negative part, as shown in **3**.



3

To establish the relation (2) we only considered the ground configuration with an electron around each metal center. Above this ground configuration we have two charge transfer configurations ϕ^2_A and ϕ^2_B (if A is different from B), separated from $\phi_A\phi_B$ by $k^o_A - k$ and $k^o_B - k$ respectively, with

$$k^o_A = \left\langle \frac{\phi_A(i)\phi_A(j)/r_{ij}}{\phi_A(i)\phi_A(j)} \right\rangle \tag{4}$$

and the same expression for k^o_B, replacing A with B. From each charge transfer configuration arises a singlet state which may interact with the low lying singlet state and stabilize the latter. Therefore, the interaction between ground configuration and charge transfer configurations favors antiferromagnetic coupling. This second order effect vanishes when the magnetic orbitals are orthogonal.[12]

To summarize, at this first level, where only the unpaired electrons are considered as active electrons, the sole factor favoring ferromagnetic interaction is the two-electron exchange integral j. In contrast, the one-electron exchange integral S favors antiferromagnetic interaction. The problem for designing a ferromagnetically coupled dinuclear complex is to minimize S without making j too small.

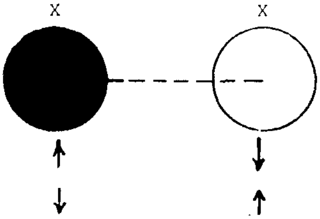
The active electron approximation loses its validity when low energy molecular orbitals, doubly occupied by the so-called passive electrons, no longer differ much in energy from the magnetic orbitals.

We do not intend to discuss this problem in detail, which has been recently investigated by Bominaar and Block.[13] However, we would like to show that these doubly occupied molecular orbitals can polarize the spin of the unpaired electrons to favor either the singlet state or the triplet state. Let us consider first the network **4**, where two metal centers A and B are bridged by an extended ligand X. . .X, X denoting the atoms bound to the metals.

$$A - X\ldots X - B$$

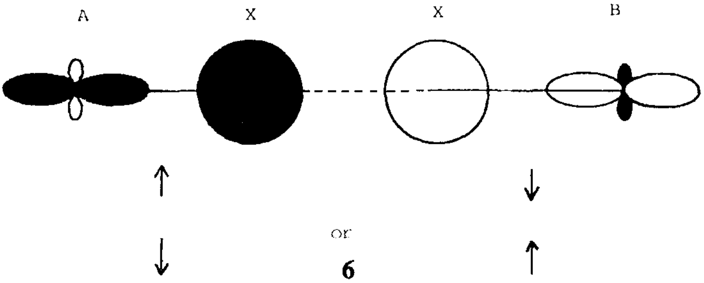
4

Let us assume that we have one unpaired electron per metal occupying the d_A and d_B orbitals and two paired electrons in the nonbonding molecular orbital of the X. . .X ligand, shown in **5**, with at each instant an electron of a given spin around one of the X atoms and an electron of the opposite spin around the other X atom.



5

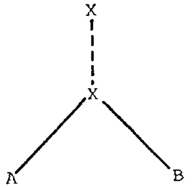
In the network **4**, **5** gives the molecular orbital **6**, with an electron of a given spin partially delocalized towards d_A and an electron of the opposite spin partially delocalized towards d_B.



6

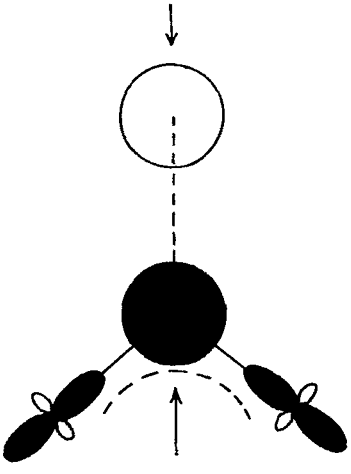
To respect the Pauli principle, for both d_A and d_B the unpaired metallic electrons will tend to have opposite spins, favoring the antiferromagnetic interaction.

Now let us suppose that the same X. . .X ligand bridges in an end-on fashion as shown in **7**.



7

In the network **7**, **5** gives the molecular orbital **8** with an electron of a given spin partially delocalized towards both d_A and d_B.



8

Again, to respect the Pauli principle the metallic electrons will tend to have the same spins, favoring the ferromagnetic coupling.

To conclude this section we can say that three strategies can lead to a ferromagnetic interaction, namely, the strict orthogonality of the magnetic orbitals, accidental orthogonality and spin polarization by ligands of type **5**, bridging in an end-on manner.

This situation of strict orthogonality has been realized for the first time in the heterodinuclear complex CuVO(fsa)$_2$en·CH$_3$OH,[14] the structure of which is shown in Figure 1. The main feature of this structure is that the molecular symmetry is very close to C_s, with a mirror plane containing the metal ions perpendicular to the plane of the macrocycle. The magnetic orbital ϕ_{Cu} centered on a copper (II) ion in a 4+1 environment is constructed from the d_{xy}metallic orbital and is partially delocalized towards the oxygen and nitrogen atoms surrounding the copper owing to a σ-type antibonding overlap $\langle d_{xy}/p_\sigma\rangle$. This magnetic orbital is antisymmetric with regard to the mirror plane. It transforms as a'' in the C_s group. The magnetic orbital ϕ_{VO} is constructed from the $d_{x^2-y^2}$ metallic orbital and is

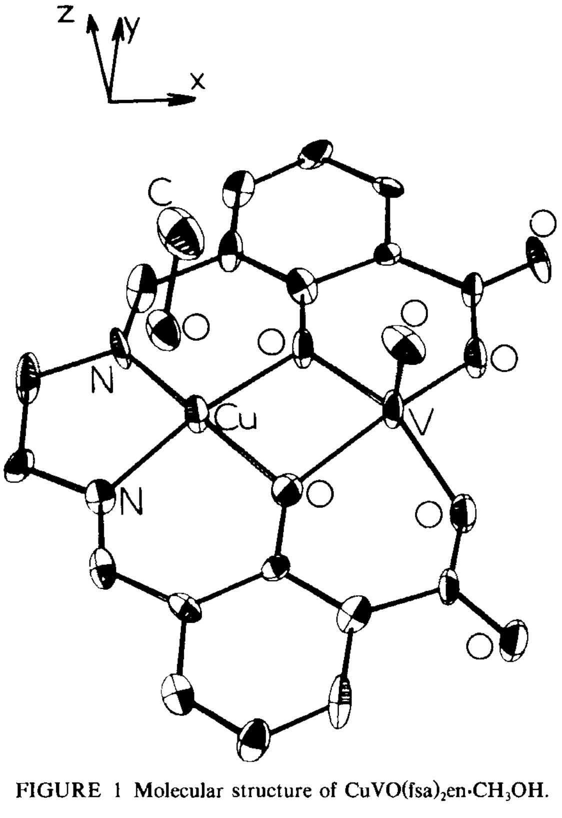


FIGURE 1 Molecular structure of CuVO(fsa)$_2$en·CH$_3$OH.

partially delocalized towards the oxygen atoms of the macrocycle owing to the π-type antibonding overlap $\langle d_{x^2-y^2}/p_\pi \rangle$. This magnetic orbital is symmetric with regard to the mirror plane and transforms as a'. Thus, the overlap integral $\langle \phi_{\mathrm{Cu}}/\phi_{\mathrm{VO}} \rangle$ is identically zero. The magnetic properties confirm that the interaction is actually ferromagnetic with a triplet state stabilized by 118 cm^{-1} with regard to the singlet state. The shape of the magnetic orbitals shown in Figure 2 allow us to understand why $J = 2j$ is relatively large.[10] J may be expressed as

$$J = 2\int_{\text{space}} \frac{\rho(i)\rho(j)}{r_{ij}}\, d\tau i\, d\tau j \tag{5}$$

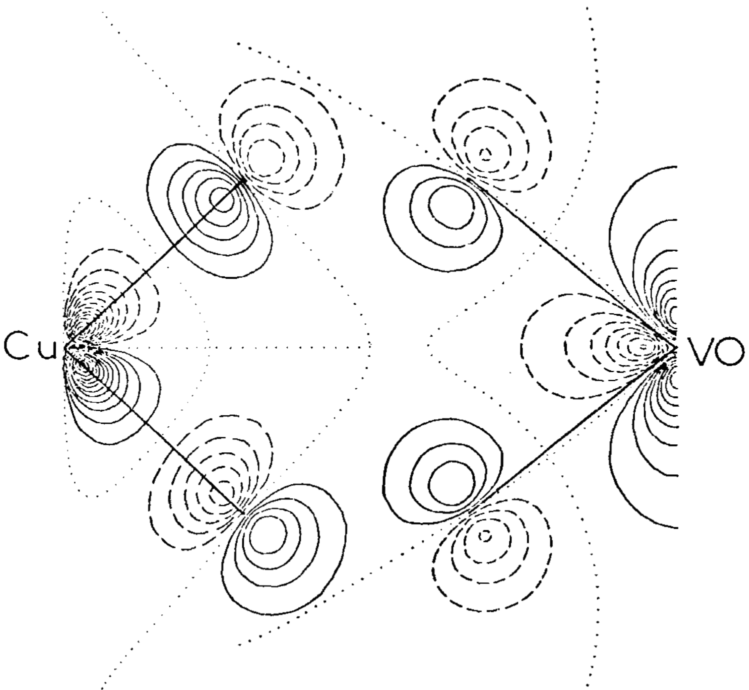


FIGURE 2 Magnetic orbitals ϕ_{Cu} and ϕ_{VO} in CuVO(fsa)$_2$en·CH$_3$OH. The solid lines represent the positive isovalue curves and the dashed lines the negative zones. The dotted lines represent the nodal zones.

where $\rho(i)$ is the overlap density between the magnetic orbitals:

$$\rho(i) = \phi_{Cu}(i)\phi_{VO}(i). \tag{6}$$

Figure 3 represents the overlap density map in the plane of the macrocycle, which exhibits two strongly positive lobes around one of the bridges and two strongly negative lobes around the other bridge. We can write

$$\rho(i) \simeq \rho_1(i) + \rho_2(i), \tag{7}$$

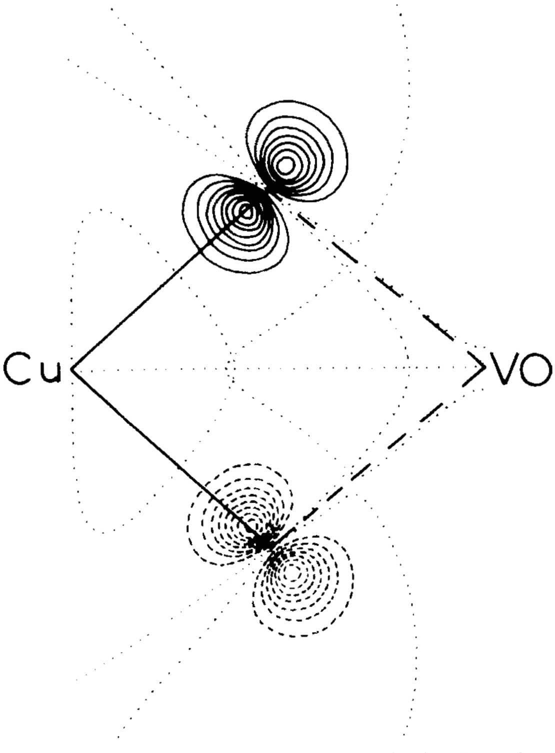


FIGURE 3 Map of the overlap density $\rho = \phi_{Cu} \cdot \phi_{VO}$ in the plane of the macrocycle of $CuVO(fsa)_2en \cdot CH_3OH$. The solid lines represent the positive isooverlap density curves and the dashed lines the negative ones. The dotted lines represent the nodal zones.

where the indices 1 and 2 refer to the surroundings of the one and the other bridges. The overlap integral S becomes

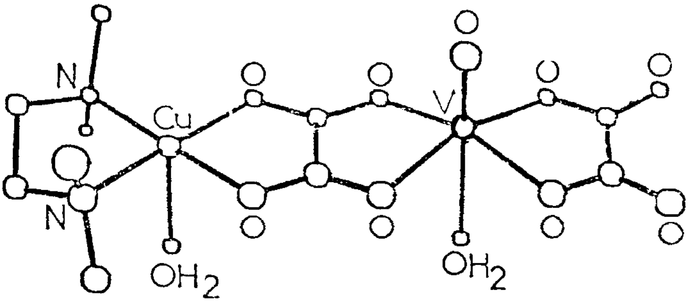
$$S = S_1 + S_2, \tag{8}$$

which is exactly zero since $S_1 = -S_2$. The two-electron exchange integral j may be written

$$j = j_1 + j_2 + 2\int_{\text{space}} \frac{\rho_1(i)\rho_2(j)}{r_{ij}}\, d\tau\, d\tau_j. \tag{9}$$

j_1 and j_2, which are quasi one-center integrals, are by far the most important terms in Eq.(9). They are equal and positive. Their value is related to the magnitude in the absolute value of the local overlap densities ρ_1 and ρ_2. It follows that j, and hence J, is large in $CuVO(fsa)_2en{\cdot}CH_3OH$.

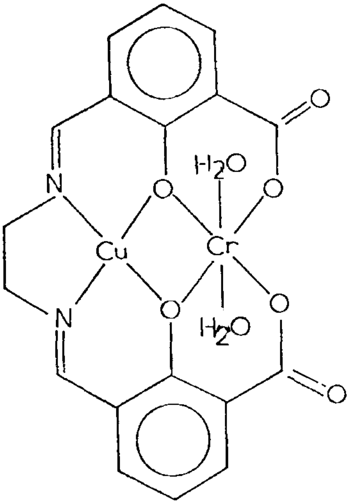
The strict orthogonality of the magnetic orbitals in a Cu(II)VO(II) pair is not sufficient to obtain a large ferromagnetic interaction. In the complex $(tmen)Cu(C_2O_4)VO(C_2O_4){\cdot}3H_2O$, [15] schematized in **9**, the magnetic orbitals ϕ_{Cu} and ϕ_{VO} do not give any region of strong overlap density.



9

The two metal ions interact through the oxalato bridge, as proven by the EPR spectrum, which is not the simple superposition of what would be expected for noncoupled Cu(II) and VO(II) ions. However the S-T energy gap is between 0.3 and 1 cm^{-1}.

This strategy of strict orthogonality has been generalized to the system with four active electrons $[\mathrm{CuCr(fsa)_2en{\cdot}(H_2O)_2}]\ \mathrm{Cl{\cdot}3H_2O}$ shown in **10**. The symmetry of the complex is C_{2v}. The unpaired electron around copper (II) occupies an *xy*-type magnetic orbital transforming as b_1 and the three unpaired electrons around chromium (III) occupy x^2-y^2, yz and xz-types transforming as a_1, a_2 and b_2, respectively.



10

The three pairs of magnetic orbitals $b_1 - a_1$, $b_1 - a_2$ and $b_1 - b_2$ are orthogonal and the interaction between Cu(II) single-ion doublet state and Cr(III) single-ion quartet state leads to a ground $S = 2$ and an excited $S = 1$ pair of states.[16]

Replacing Cr(III) by Fe(III), we obtain the complex $\mathrm{CuFe(fsa)_2}$ $\mathrm{en{\cdot}\ ClH_2O \cdot 2CH_3OH}$, the structure of which is shown in Figure 4. The five magnetic orbitals around Fe(III) transform as a_1 (z^2 and $x^2 - y^2$), a_2 (yz), b_1 (xy) and b_2 (xz), assuming a C_{2v} molecular symmetry. One of them strongly overlaps with the b_1 magnetic orbital around Cu(II), which favors the antiferromagnetic interaction. The

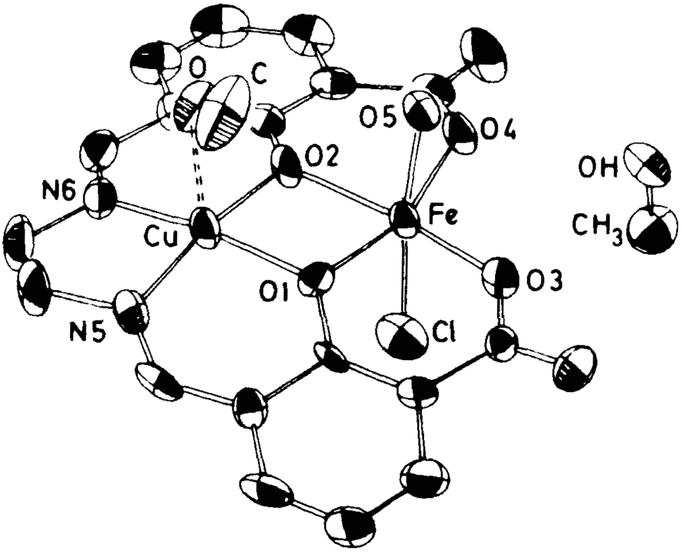


FIGURE 4 Molecular structure of CuFe(fsa)$_2$en·Cl(H$_2$O)·2CH$_3$OH.

interaction between the single-ion doublet state for Cu(II) and the single-ion sextet state for Fe(III) leads to a ground $S = 2$ and an excited $S = 3$ pair of states.[16] The most noteworthy point of the comparison Cu(II) Cr(III) and Cu(II) Fe(III) is that in both complexes the ground state is a spin quintet. In Cu(II)Cr(III) this state arises from a ferromagnetic interaction due to the strict orthogonality of the magnetic orbitals; in Cu(II) Fe(III) it arises from an antiferromagnetic interaction due to the strong overlap of the b_1 magnetic orbitals. The magnetic curves of the two complexes are given in Figure 5 and the spectra of the low lying states as deduced from the magnetic data are given in Figure 6. In both cases the ground quintet state undergoes a large zero-field splitting.

ACCIDENTAL ORTHOGONALITY OF MAGNETIC ORBITALS

The situation of accidental orthogonality has been obtained in planar networks like **11**, with M = Ni(II) or Cu(II), and X = OH$^-$ or Cl$^-$. Let us focus on the copper(II) dimers. The overlap density

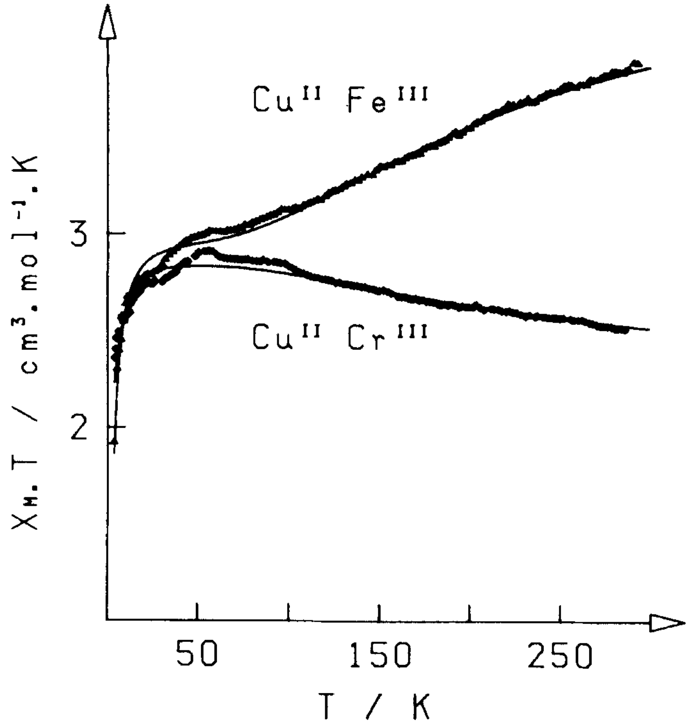


FIGURE 5 Experimental (▲ and ◆) and theoretical temperature dependencies of $\chi_M T$ for $CuCr(fsa)_2en{\cdot}(H_2O)_2\,Cl{\cdot}3H_2O$ and $CuFe(fsa)_2en{\cdot}Cl(H_2O){\cdot}2CH_3OH$.

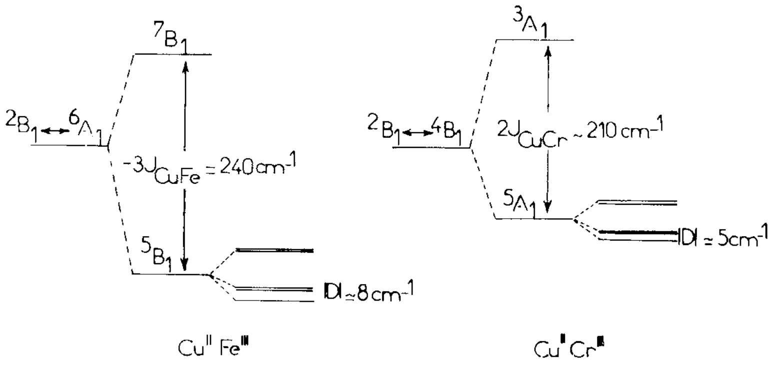
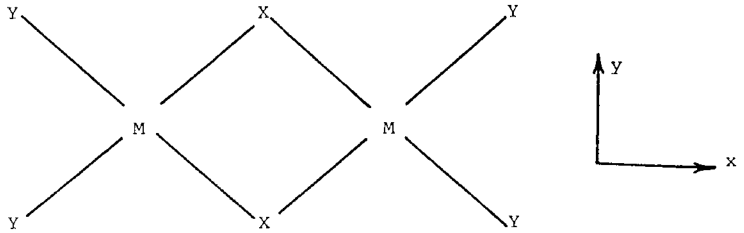


FIGURE 6 Low lying states in the Cu (II) Cr (III) and Cu (II) Fe (III) complexes.



11

between two magnetic orbitals like that shown in Figure 2 has the shape given in Figure 7 with, around each bridge, two lobes of a given sign along the x direction and two lobes of the opposite sign along the y direction. For a CuXCu bridging angle close to 90°, the positive lobes of the overlap density exactly compensate the negative lobes, so that S is zero although the two MO have the same symmetry and the interaction is expected to be ferromagnetic.[10] When the bridging angle increases, the extrema of the overlap density along the x direction are more pronounced than those along the y direction. Therefore, S is different from zero and quickly becomes the dominant factor in Eq.(2); the interaction becomes antiferromagnetic.

Another way to see the phenomenon of accidental orthogonality consists of noting that in a symmetric complex like **11**, $-2t/(1 - S^2)$ is the energy gap between the two molecular orbitals constructed from the two magnetic orbitals for the triplet pair state. It follows that Eq.(2) may be rewritten

$$J = -2\,\Delta S\ /\ (1 + S^2) + 2\,(j - ks^2)\ /\ (1 - S^4). \qquad (10)$$

To first order it is usual to assume that t and S are proportional, hence that Δ varies as S. In this approximation the accidental orthogonality may then be defined as the crossover of the two singly occupied molecular orbitals in the triplet state. For the system **11** of D_{2h} symmetry, these molecular orbitals shown in Figure 8 transform as b_{1g} and b_{2u}, respectively. When X = OH^- and Y = NH_3 an extended Hückel calculation gives the curves of Figure 9 with a crossover around 90°.[17] Experimentally, in planar di-μ-hydroxo copper (II) dimers, the triplet actually has been found to be the ground

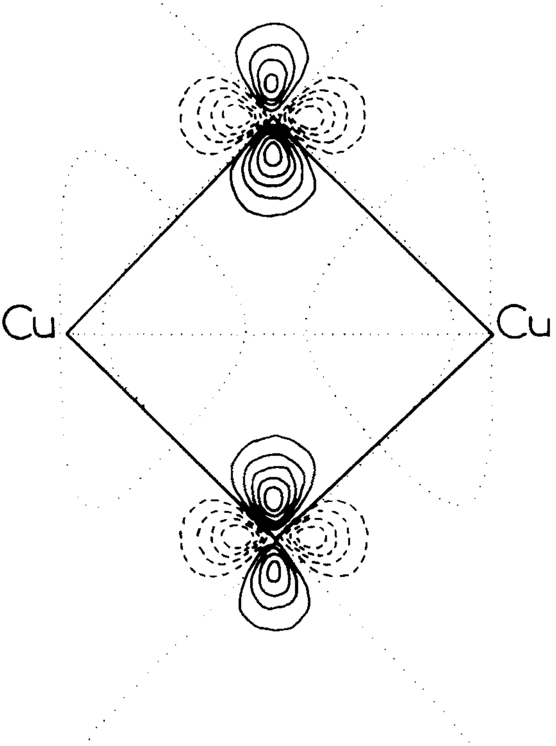


FIGURE 7 Map of the overlap density between the magnetic orbitals in planar bibridged copper (II) dimers.

state for any bridging angle smaller than 97.5°.[18] The same situation of ferromagnetic interaction due to the accidental orthogonality of the magnetic orbitals was found in di-μ-chloro copper (II)[19,20] and nickel (II) dimers.[21-25]

The essential characteristic of the accidental orthogonality is that it is destroyed by a very small change of the structural parameters even if the molecular symmetry as a whole is not modified. In contrast, in the case of strict orthogonality such a small change causes only a slight modification of the magnitude of the ferromagnetic interaction.

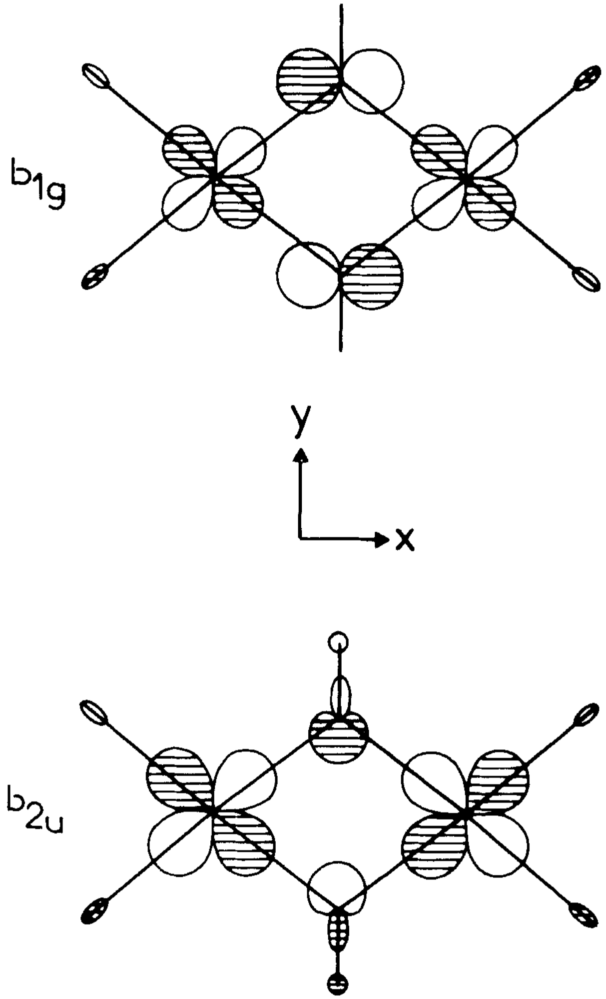


FIGURE 8 Molecular orbitals constructed from the magnetic orbitals in planar bi-bridged copper (II) dimers.

SPIN POLARIZATION EFFECT

The conditions leading to the stabilization of the state of highest spin multiplicity by the spin polarization effect have been presented above.

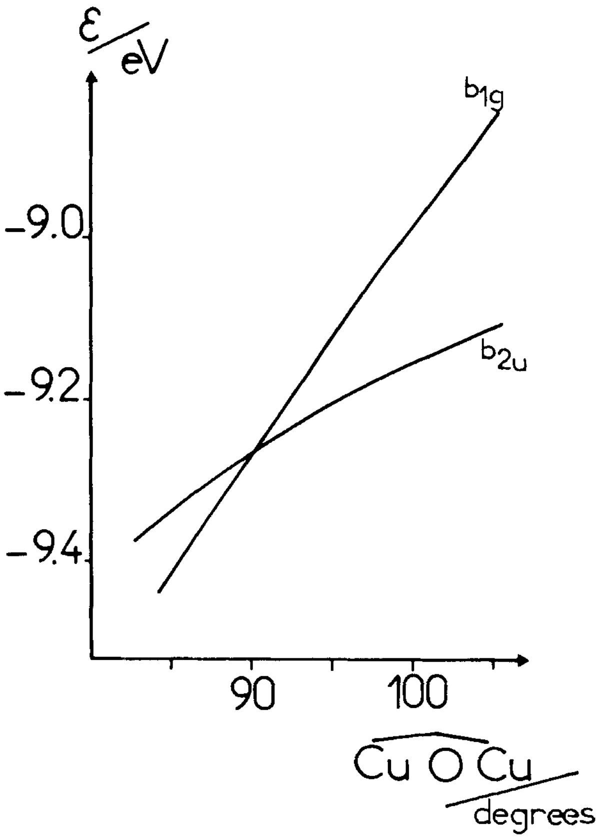
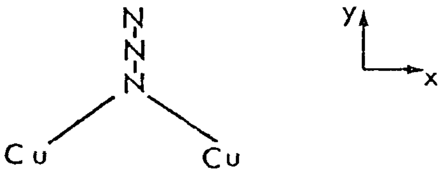


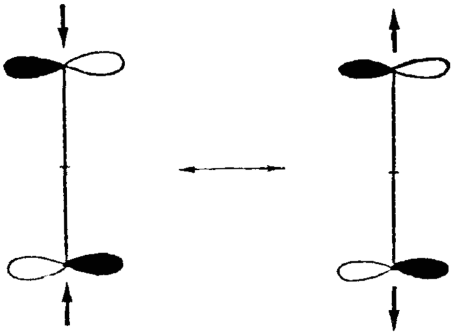
FIGURE 9 Variations of the energies of the two molecular orbitals constructed from the two magnetic orbitals versus the bridging angle in planar di-μ-hydroxo copper (II) dimers.

These conditions are perfectly fulfilled in copper (II) dinuclear complexes with one or two azido bridges like **12**.



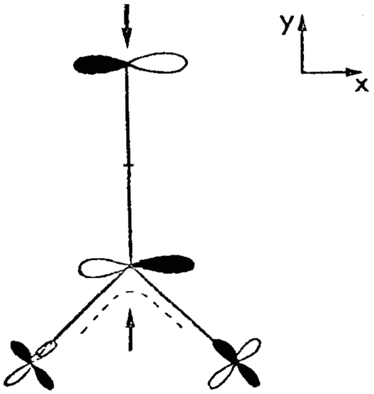
12

In fact, this mechanism has been proposed for the first time to account for the magnetic properties of the complexes of this kind.[26] Calculation of the electronic structure of $N^-{}_3$ reveals that the $(\Pi g)^4$ highest occupied molecular level is largely separated in energy from both the occupied levels just below and the empty levels just above.[27] Moreover, this $(\Pi g)^4$ level is close to the metallic levels. In each Πg molecular orbital at each instant, an electron with α spin is localized around one of the terminal nitrogen atoms and the other electron of the same orbital, with β spin, is localized around the other terminal atom as shown in **13**.



13

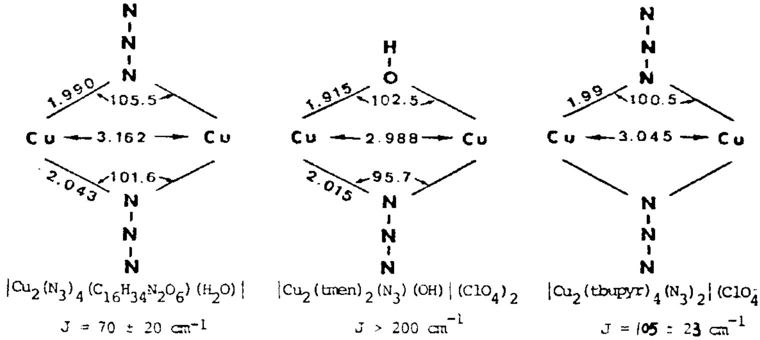
When $N^-{}_3$ bridges in an end-on fashion, the electron of the bridging nitrogen (say with α spin) is partially delocalized towards the d_{xy} metallic orbitals in the bonding molecular orbital schematized in **14**.



14

This delocalization is a function of the overlap $\langle (d_{xy})_{\text{cu}}\ /\ (p_x)_{\text{N}} \rangle$ and of the energy gap between d_{xy} and Π_g. It gives an instantaneous density of α spin in each of the two d_{xy} metal orbitals. Therefore, each unpaired electron localized in its magnetic orbital with a preponderant metallic character will have a probability of β spin larger than 0.5. This favors the triplet state.

Three copper (II) dinuclear complexes with one or two end-on azido bridges have been synthesized and structurally characterized so far. In the first of them, $Cu_2(N_3)_4(C_{16}H_{34}N_2O_6)(H_2O)$, the $Cu(N_3)_2Cu$ bridging network is located inside a cryptate cavity.[28] In the second we have an end-on azido bridge and an hydroxo bridge.[26] Its molecular structure is shown in Figure 10. The last, the structure of which is shown in Figure 11, also has two end-on azido bridges.[29] Their magnetic properties have been investigated. The geometry of the bridging networks and energy gaps J are compared in **15**.



15

The three complexes have a triplet ground state largely stable with regard to the singlet state. In $[Cu_2(tmen)_2(N_3)(OH)]\ (ClO_4)_2$ the triplet state is so stabilized with regard to the singlet state that even at room temperature this latter state is almost depopulated. The magnetic behavior is very close to the Curie law expected for an $S = 1$ state well separated in energy from the excited states. For $[Cu_2(tbupyr)_4(N_3)_2]\ (ClO_4)_2$ with tbupyr = 4-tertiobutylpyridine, we give the magnetic curve and the X-band EPR spectrum at 4.2 K in Figure 12. Both are typical of a triplet ground state.

From **15** one sees that the ferromagnetic interaction in μ-(end-on) azido copper (II) complexes does not seem to be destroyed by small

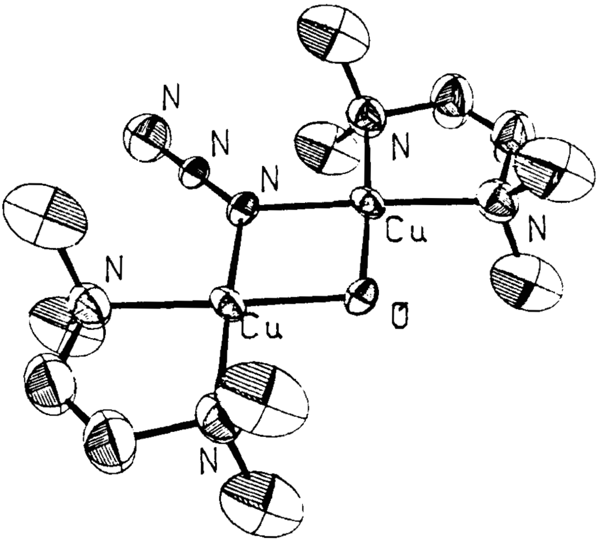


FIGURE 10 Structure of the dinuclear cation $[Cu_2(tmen)_2(N_3)(OH)]^{2+}$.

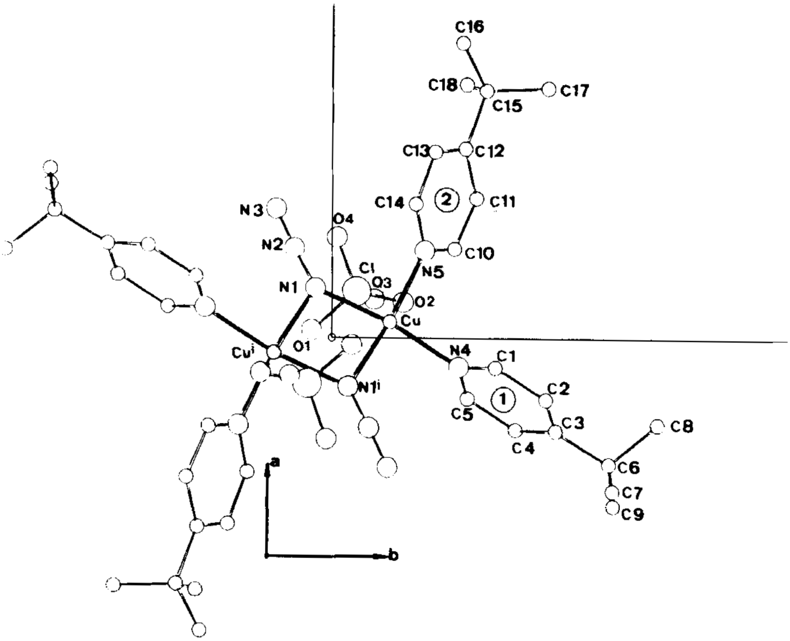


FIGURE 11 Projection of the structure of Cu_2 (tbupyr)$_4$ $(N_3)_2$ $(ClO_4)_2$ down to the *ab* crystallographic plane.

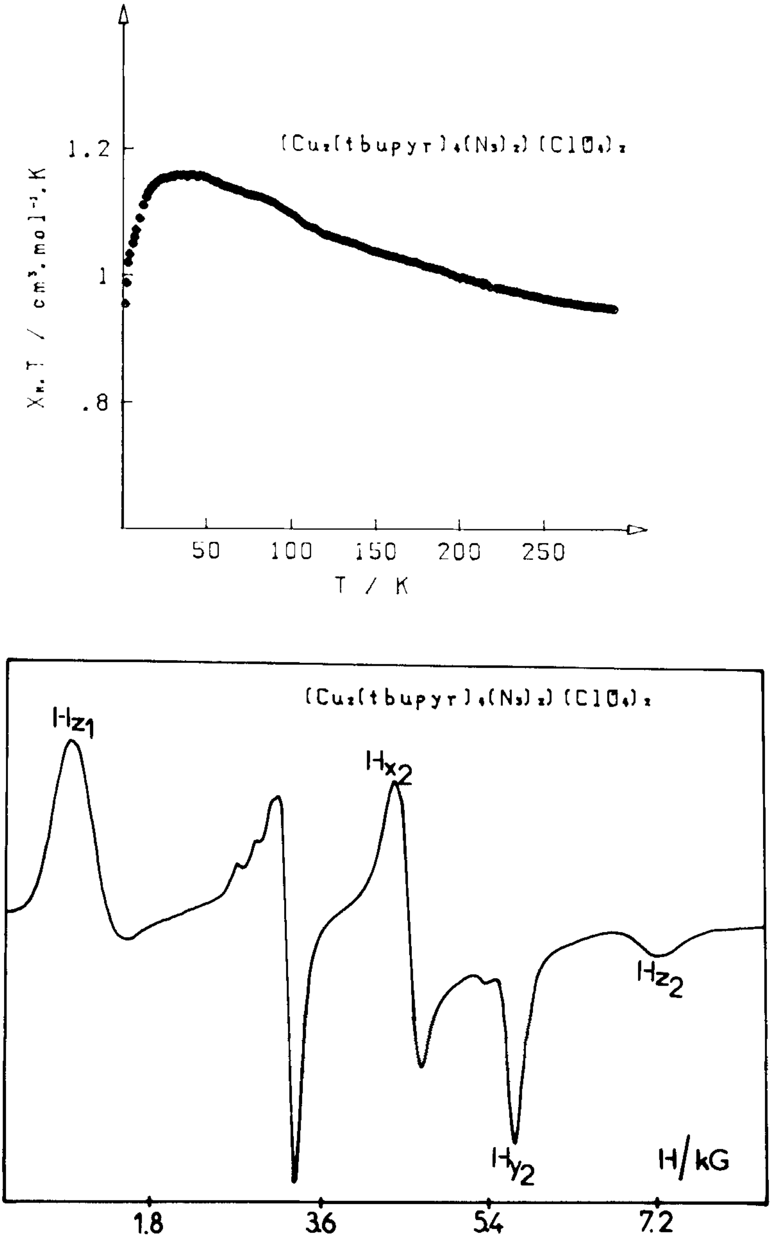


FIGURE 12 Magnetic susceptibility and X-band powder EPR spectrum at 4.2 K for $[Cu_2(tbupyr)_4(N_3)_2](ClO_4)_2$.

structural changes e.g., in the CuNCu bridging angle. This confirms that the stabilization of the triplet state cannot be interpreted as an accidental orthogonality of the magnetic orbitals. The mechanism of the spin polarization effect presented in the previous section does not suggest a dramatic dependence of the S-T energy gap on a small change of CuNCu.

It is difficult to imagine a bridge more appropriate to stabilize the triplet state than the end-on azido ligand. The spin polarization effect is magnified by the quasiabsence of overlap density in Π_g which pushes away the two paired electrons occupying the same molecular orbital towards the two extremities of the system. With less symmetric ligands like NCO^- or NCS^- the effect is expected to be less pronounced.

DETERMINATION OF *J* IN FERROMAGNETICALLY COUPLED DINUCLEAR COMPLEXES

In this section our purpose is to discuss briefly some specific difficulties in determining accurately the relative energies of the low lying states in the case of ferromagnetic interaction. Without loss of generality we can restrict ourselves to the interaction between two identical single-ion doublet states. The molar magnetic susceptibility is then

$$\chi_M = \frac{2N\beta^2 g^2}{kT}\left[3 + \exp\left(-\frac{J}{kT}\right)\right]^{-1}, \tag{11}$$

where the constants N, β and k have their usual meaning. The best way to detect a triplet ground state is to plot $\chi_M T$ versus T. The high temperature limit is $(\chi_M T)_{T\to\infty} = N\beta^2 g^2 / 2k$ and the low temperature limit is $(\chi_M T)_{T=0} = 2N\beta^2 g^2 / 3k$. One sees that when cooling down to very low temperature, $\chi_M T$ increases at most, by one-third of its high temperature value. When the ferromagnetic interaction is large, $J > 80\ \mathrm{cm}^{-1}$, even at room temperature the singlet excited state is only weakly populated and $\chi_M T$ may already be close to the low temperature limit $2N\beta^2 g^2 / 3k$. In other words, if J is determined as usual by minimizing the R factor defined by $\Sigma\ [(\chi_M T)^{obs} - (\chi_M T)^{calc}]^2 / \Sigma\ (\chi_M T)^{obs\ 2}$, the minimum of the R versus J plot is very smooth and the accuracy of the J value is poor even if the magnetic measurements have been carefully carried out. To illustrate this difficulty we consider the magnetic data of Figure 12 concerning $[Cu_2(tbupyr)4(N_3)_2]$ $(ClO_4)_2$. At room temperature, $\chi_M T$ is equal to 0.95 $cm^3mol^{-1}K$, which is already significantly larger than what would be expected for two noninteracting copper (II) ions. $\chi_M T$ increases when cooling down, reaches a broad maximum in the range 60–18 K with $\chi_M T = 1.15 \pm 0.02$ $cm^3mol^{-1}K$ and finally decreases when cooling down to pumped liquid helium temperature. This behavior in the range of the very low temperatures is attributed to small intermolecular effects and to account for these, χ_M in Eq.(11) is multiplied by $T / (T - \theta)$ where θ is a Weiss constant. It follows that the three variable parameters are J, g and θ. The curve of Figure 13 is obtained by minimizing R for different values of J. This curve confirms that the minimum of R is very smooth. If an uncertainty of 0.01 $cm^3mol^{-1}K$ on each of the 160 experimental points is assumed, which actually corresponds to an extremely careful experiment, all

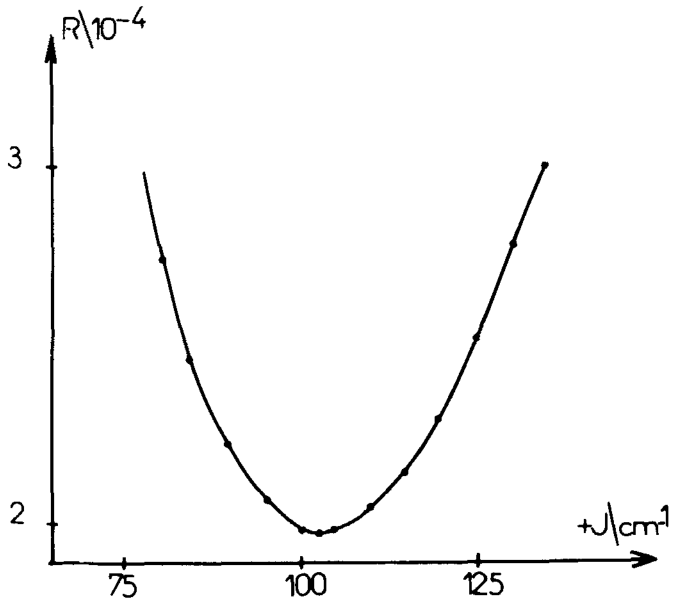


FIGURE 13 R versus J plot for $[Cu_2\ (tbupyr)_4\ (N_3)_2]$ $(ClO_4)_2$ (see text).

the J values corresponding to an R factor between the minimal value 1.97×10^{-4} and $1.94 \times 10^{-4} + \Sigma 10^{-4} / \Sigma (\chi_M T)^{obs\,2} \simeq 2.8 \times 10^{-4}$ are physically acceptable. Therefore, the J value deducted from the magnetic data must be given as 105 ± 23 cm^{-1} (see Figure 13). Note that this difficulty does not occur in the case of antiferromagnetic interaction. The theoretical susceptibility is then much more sensitive to small variations of J.

CONCLUSION

The design of new compounds exhibiting desired physical properties is certainly one of the main challenges in Inorganic Chemistry. The next few years will see great expansion of this kind of molecular engineering of magnetic electrical, optical and phase transition properties. This Comment concerns one of these aspects, the design of ferromagnetically coupled dinuclear complexes. Until recently, rare complexes of this kind could be considered peculiarities and the only known strategy of obtaining them was the accidental orthogonality of the magnetic orbitals, i.e., the orthogonality along each bridging linkage, generally due to a bridging angle close to 90°. This approach can give the expected result. This has been the case for copper(II) or nickel(II) dimers and linear chains. However, this accidental orthogonality is fragile. It can be distroyed by a very small change of structural parameter that is difficult to control during synthesis. On the other hand, strict orthogonality, if not easy to obtain from the synthesis, seems much less problematic for the ferromagnetic nature of the interaction. The magnitude of this interaction may then be estimated from overlap density considerations. These are of course far from being rigorous. They represent a topological approach to the problem.

We have also suggested another way to impose the nature of the interaction using a bridging ligand with an extended nonbonding highest occupied molecular orbital. Depending on whether such a peculiar ligand bridges in an end-on or an end-to-end fashion, it can polarize the spins of the metallic unpaired electrons to favor the ferro or the antiferromagnetic interaction. The theoretical framework of the phenomenon is not yet fully established. However, spectacular results were obtained with the azido ligand, which has a quite remarkable ability to stabilize the singlet state or the triplet state in copper(II) dinuclear complexes, depending on whether the bridge is of the end-to-end or end-on type.

Finally, we have pointed out a specific difficulty in the investigation of ferromagnetically coupled polymetallic systems: The energy gaps between the low lying states are difficult to determine accurately using the usual bulk techniques like magnetic susceptibility from the EPR intensity. Direct spectroscopic methods such as inelastic neutron scattering[30] would be particularly useful.

Acknowledgment

I wish to express my deepest gratitude to my co-workers, without whom this work could not have been realized.

OLIVIER KAHN
Laboratoire de Spectrochimie des Eléments de Transition,
ERA N° 672, Université de Paris-Sud,
91405 Orsay, France

References

1. R. L. Carlin, R. Burriel, R. M. Cornelisse and A. J. Van Duyneveldt, Inorg. Chem. **22**, 831 (1983).
2. W. Hatfield, Inorg. Chem. **22**, 833 (1983).
3. J. P. Hay, J. C. Thibeault and R. Hoffmann, J. Am. Chem. Soc. **97**, 4885 (1975).
4. J. B. Goodenough, Phys. Rev. **100**, 564 (1955).
5. J. Kanamori, J. Phys. Chem. **10**, 87 (1959).
6. P. W. Anderson, in *Magnetism, Vol. 1,* edited by G. T. Rado and H. Suhl (Academic, New York, 1963), Chap. 2.
7. A. P. Ginsberg, Inorg. Chim. Acta Rev. **5**, 45 (1971).
8. R. D. Willett, R. M. Gaura and C. P. Landee, in *Extended Linear Chain Compounds, Vol. 3,* edited by J. S. Miller (Plenum, New York, 1983), Chap. 3.
9. J. J. Girerd, Y. Journaux and O. Kahn, Chem. Phys. Lett. **82**, 534 1981).
10. O. Kahn and M. F. Charlot, Nouv. J. Chim. **4**, 567 (1980).
11. P. de Loth, P. Cassoux, J. P. Daudey and J. P. Malrieu, J. Am. Chem. Soc. **103**, 4007 (1981).
12. G. Van Kalkeren, W. W. Schmidt and R. Block, Physica **97B**, 315 (1979).
13. E. L. Bominaar and R. Block, Physica, in press.
14. O. Kahn, J. Galy, Y. Journaux, J. Jaud and I. Morgenstern-Badarau, J. Am. Chem. Soc. **104**, 2165 (1982).
15. M. Julve, M. Verdaguer, R. Claude, M. F. Charlot and O. Kahn, submitted to Inorg. Chim. Acta.

16. Y. Journaux, O. Kahn, J. Zarembowitch, J. Galy and J. Jaud, submitted to J. Am. Chem. Soc.
17. M. F. Charlot, S. Jeannin, Y. Jeannin, O. Kahn, J. Lucrèce-Abaul and J. Martin-Frère, Inorg. Chem. **18**, 1675 (1979).
18. V. M. Crawford, H. W. Richardson, J. R. Wasson, D. J. Hodgson and W. E. Hatfield, Inorg. Chem. **15**, 2107 (1976).
19. R. D. Willett, J. Chem. Phys. **44**, 39 (1966).
20. J. Livermore, R. D. Willett, R. Gaura and C. P. Landee, Inorg. Chem. **21**, 1304 (1982).
21. A. P. Ginsberg, R. L. Martin, R. W. Brookes and R. C. Sherwood, Inorg. Chem. **11**, 2884 (1972).
22. D. M. Duggan and D. N. Hendrickson, Inorg. Chem. **13**, 2929 (1974).
23. E. J. Laskowski, T. R. Felthouse, D. N. Hendrickson and G. Long, Inorg. Chem. **15**, 2908 (1976).
24. K. O. Joung, C. J. O'Connor, E. Sinn and R. L. Carlin, Inorg. Chem. **18**, 804 (1979).
25. Y. Journaux and O. Kahn, J. Chem. Soc. Dalton **1979**, 1575 (1979).
26. O. Kahn, S. Sikorav, J. Gouteron, S. Jeannin and Y. Jeannin, Inorg. Chem., in press.
27. J. F. Wyatt, I. H. Hillier, V. R. Saunders, J. A. Connor and M. Barber, J. Chem. Phys. **54**, 5311 (1971).
28. J. Commarmond, P. Plumere, J. M. Lehn, Y. Angus, R. Louis, R. Weiss, O. Kahn and I. Morgenstern-Badarau, J. Am. Chem. Soc. **104**, 6330 (1982).
29. S. Sikorav, I. Bkouche-Waksman and O. Kahn, submitted to Inorg. Chem.
30. H. U. Güdel, A. Stebler and A. Furrer, Inorg. Chem. **18**, 1021 (1979).