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Angular Overlap Interpretation of the Magnetic Properties of Copper(II) Dimers

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A generalized angular overlap approach is suggested for the interpretation of the magnetic properties of transition metal dimers. The ferro- and antiferromagnetic coupling constants are related to the splitting of the ten d *orbitals of the two metal centres. Sample calculations are performed, using model complexes where the two metals are bridged by two ligands in square planar, square pyramidal and trigonal bipyramidal coordinations. The use of the diagrams in the rationalization of the magnetic properties of copper(II) dimers is discussed.*

Introduction

One of the more distinctive characteristics of dimeric transition metal complexes is that their magnetic properties differ notably from those of the monomers [1–7]. The model generally used for rationalizing the magnetic properties of dimers makes use of the Heisenberg–Dirac–van Vleck exchange Hamiltonian and of superexchange considerations [8, 9]. Only quite recently have models been proposed which relate the orbital energies of the dimer with the observed exchange coupling constants [9–15]. All the proposed models describe the interaction between the two metal atoms in the dimer by means of molecular orbital calculations or, at least, by means of molecular orbital symmetry parametrizations. Some of these models, however, use a ligand field approach in order to parametrize the orbital energies of each monomeric unit in the dimer and limit the molecular orbital treatment to the description of the interaction.

Glerup [12] in particular proposed that the orbital energies in the dimer can be obtained through a potential of the form:

$$V = V_A + V_B + V_{AB}$$

where V_A is the ligand field potential for metal atom A, V_B is the ligand field potential for metal atom B and V_{AB} is the interaction potential [16]. He did not give an explicit form to V_{AB}, but he accounted for its effects by means of symmetry considerations and on the basis of the baricenter rule of energies. A similar approach to the energies of L_5M–L–ML_5 dimers was suggested also by Schmidtke [17] and Kahn and Briat extended it to other chromophores [14, 18].

The advantages of a ligand field treatment over a molecular orbital one for the interpretation of the optical and magnetic properties of transition metal complexes are well known [19]. We wish therefore to report here a new angular overlap parametrization scheme of the orbital energies of transition metal dimers which is as general as possible. Further in order to check the validity of the suggested approach we report some sample calculations on model complexes, and show their use in the interpretation of the magnetic properties of several copper(II) dimers.

The Model

If the dimer is considered as formed by two monomeric moieties and the direct metal–metal interactions can be neglected the assumptions which support a ligand field treatment on one metal centre keep their validity. An explicit form of the ligand field potential can be given provided that the symmetry properties of the whole dimer are taken into account.

It is convenient to consider first the very simple dimer shown in Figure 1. It is known that the energy levels of the ligand orbitals can be parametrized using bonding parameters similar to the antibonding ones used to express the energies of the metal orbitals [20]. The ligand "sees" two metal atoms on opposite directions on the *z* axis, and their effects must be considered as additive. The bonding effect of the two identical metals on the *p* ligand orbitals will be $2e_\sigma$ for the p_z and $2e_{\pi s}$ and $2e_{\pi c}$ for the p_x and p_y

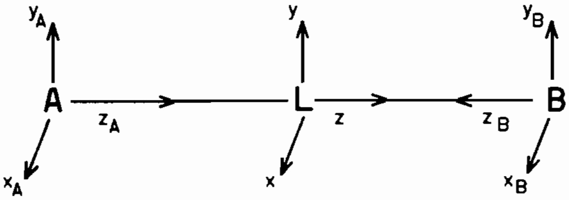

Figure 1. The coordinate axes for a linear symmetric dimer.

orbitals respectively. The metal orbitals which are responsible for this effect can be written in the form:

$$|d_g^{\lambda t}\rangle = (1/\sqrt{2})(|d_{\mathrm{A}}^{\lambda t}\rangle + |d_{\mathrm{B}}^{\lambda t}\rangle);\ |d_u^{\lambda t}\rangle = (1/\sqrt{2})(|d_{\mathrm{A}}^{\lambda t}\rangle - |d_{\mathrm{B}}^{\lambda t}\rangle) \qquad (1)$$

where λt, g, and u are symmetry labels of the $D_{\infty h}$ group and A and B refer to the two metal atoms. The overlap $\langle d_A | d_B\rangle$ has been neglected.

It is now apparent that the d_u^σ, $d_u^{\pi s}$ and $d_u^{\pi c}$ orbitals, which span the same irreducible representations of $D_{\infty h}$ as the p_z, p_x and p_y ligand orbitals respectively, will have the antibonding energies $2e_\sigma$, $2e_{\pi s}$ and $2e_{\pi c}$, while all the other metal orbitals will be non-bonding.

Formally we can achieve these results by defining the following one-electron operator:

$$\mathbf{A} = |p_u^\sigma\rangle\langle p_u^\sigma| + |p_u^{\pi c}\rangle\langle p_u^{\pi c}| + |p_u^{\pi s}\rangle\langle p_u^{\pi s}| \qquad (2)$$

where the $p_u^{\lambda t}$ are the p ligand orbitals labelled by symmetry. The energies of the metal d orbitals in the dimer are found by a first order perturbation calculation. Considering for instance the σ orbital one finds:

$$\langle d_u^\sigma|\mathbf{A}|d_u^\sigma\rangle = \langle d_u^\sigma|p_u^\sigma\rangle\langle p_u^\sigma|d_u^\sigma\rangle = (1/2)[|\langle d_{\mathrm{A}}^\sigma|p_u^\sigma\rangle|^2 + |\langle d_{\mathrm{B}}^\sigma|p_u^\sigma\rangle|^2 - 2\langle d_{\mathrm{A}}^\sigma|p_u^\sigma\rangle\langle p_u^\sigma|d_{\mathrm{B}}^\sigma\rangle] = (1/2)[e_{\sigma\mathrm{A}} + e_{\sigma\mathrm{B}} + 2(e_{\sigma\mathrm{A}}e_{\sigma\mathrm{B}})^{1/2}] = 2e_\sigma^u$$

where we have used the definitions:

$$e_{\sigma\mathrm{M}} = |\langle d_{\mathrm{M}}^\sigma|p_u^\sigma\rangle|^2 \qquad \mathrm{M} = \mathrm{A}, \mathrm{B}$$

and considered that $e_{\sigma\mathrm{A}} = e_{\sigma\mathrm{B}}$ by symmetry and $\langle d_{\mathrm{A}}^\sigma|p_u^\sigma\rangle$ and $\langle p_u^\sigma|d_{\mathrm{B}}^\sigma\rangle$ are of opposite sign (see Figure 1). It is therefore possible to write in general:

$$\langle d_u^{\lambda t}|\mathbf{A}|d_u^{\lambda t}\rangle = 2\mathrm{e}_{\lambda t}^u \qquad (3)$$

all the $\langle d_g^{\lambda t}|\mathbf{A}|d_g^{\lambda t}\rangle$ being zero.

A first generalization of (2) can be made considering contributions of ligand orbitals with l values different from p. In this case (2) becomes:

$$\mathbf{A} = \Sigma_l\, \Sigma_{\lambda t}\, c_l^{\lambda t}|l_i^{\lambda t}\rangle\langle l_i^{\lambda t}|\ i = g, u \qquad (4)$$

in which the $c_l^{\lambda t}$ coefficient is required since ligand orbitals of different l can span the same irreducible representation of $D_{\infty h}$. Equation (3) then becomes:

$$\langle d_i^{\lambda t}|\mathbf{A}|d_j^{\lambda t'}\rangle = 2\delta_{ij}\delta_{\lambda\lambda'}\delta_{tt'}e_{\lambda t}^i \qquad (5)$$

where

$$e_{\lambda t}^i = \Sigma_l\, c_l^{\lambda t}|\langle d_i^{\lambda t}|l_i^{\lambda t}\rangle|^2 \qquad (6)$$

is different from zero only if $d_i^{\lambda t}$ has the same parity as the ligand orbital. Therefore for d metal orbitals up to six parameters (e_σ^g, e_σ^u, e_π^g, e_π^u, e_δ^g, e_δ^u) can be required to parametrize the orbital energies. This makes a noteworthy difference from the case of a monomeric complex, where only three parameters are required [20]. In the M–L–M dimer l ligand orbitals of different parity, which in the monomer M–L of $C_{\infty v}$ symmetry span the same irreducible representations, are now bases for different representations of $D_{\infty h}$. So for instance the e_σ^g parameter is relative to the σ bonding interaction with s or d ligand orbitals, while e_σ^g is relative to the σ interaction with the p ligand orbitals. However following the common assumption that the bonding interaction is mainly with the p orbitals [13] the relation (3) is valid and the number of parameters which must be used in the case of the dimer is the same as in the corresponding monomer.

In order to apply the model to real dimers a further generalization must be made. The most general unit which can be found in a dimer where the two halves are bridged by single atoms is that shown in Figure 2, where a ligand is unevenly shared by two different metal atoms. Since in general on each metal centre also other ligands will be present, it is convenient to define two coordinate systems (x_{A}, y_{A}, z_{A}) and (x_{B}, y_{B}, z_{B}) centered on metal A and B respectively, chosen according to the symmetry of each monomeric moiety. The bridge atom L will have angular coordinates θ_{A} and φ_{A} in the system of metal A, and θ_{B} and φ_{B} on metal B. According to the postulates of the angular overlap model [20], in order to define the effect of the bridge atom on the metal d orbitals, we have to pass to primed coordinate systems oriented as in Figure 2. The d orbitals defined in the not-primed and primed coordinate systems, $|\mathrm{M}u\rangle$ and $|\mathrm{M}u'\rangle$ respectively, are connected by the usual angular overlap matrix, $\mathbf{F}_d^{\mathrm{M}}$ (M = A, B). Finally we need a reference system, (X_{M}, Y_{M}, Z_{M}) on the ligand. In one-centre angular overlap model, it is assumed that the coordinate system on the ligand is parallel to that on the metal, but in a dimer there are two metals and one single choice is not possible. A convenient choice is that shown in Figure 2 with Z_{A} coincident with the A–L bond direction and X_{A} parallel to x'_{A}. Z_{B} and X_{B} are defined correspon-

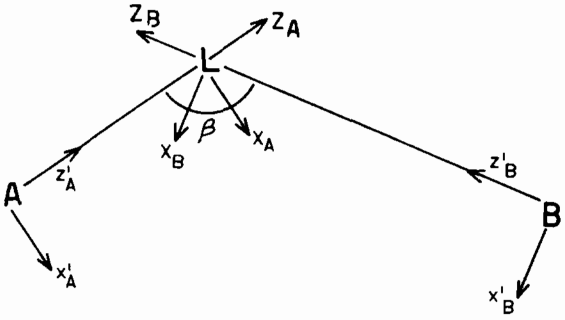

Figure 2. The coordinate axes for a bent asymmetric dimer. The y axes are not shown for the sake of simplicity. They are perpendicular to the A–L–B plane. Also the ($x_{\mathrm{A}}y_{\mathrm{A}}z_{\mathrm{A}}$) and ($x_{\mathrm{B}}y_{\mathrm{B}}z_{\mathrm{B}}$) axes (see text) are not shown.

dingly relative to B. The ligand orbitals in the two reference systems are related by the angular overlap matrix, $\mathbf{F}_l^L$. In order to have the ligand reference frame parallel to one of the metal frames it is necessary to use the most general angular overlap matrix which contains the three Eulerian angles φ, θ, and ψ [20]. All the above relations can be expressed in a formal way as shown below:

$$|\mathrm{A}u\rangle = \sum_{1}^{5}{}_{i}\, \mathbf{F}^{\mathrm{A}}_{ui} |\mathrm{A}i'\rangle \tag{7}$$

$$|\mathrm{B}u\rangle = \sum_{1}^{5}{}_{i}\, \mathbf{F}^{\mathrm{B}}_{ui} |\mathrm{B}i'\rangle \tag{8}$$

$$|\mathrm{L}lm_{\mathrm{A}}\rangle = \sum_{1}^{21+1}{}_{n}\, \mathbf{F}^{L}_{l,mn} |\mathrm{L}ln_{\mathrm{B}}\rangle \tag{9}$$

(7) and (8) refer to metal and (9) to ligand orbitals respectively. On the angular overlap matrix for the metal orbitals we have omitted the d index for simplicity purposes.

If we consider interactions only with the p ligand orbitals the potential can be written as

$$\mathrm{A} = \sum_{1}^{3}{}_{n} |\mathrm{L}pn_{\mathrm{A}}\rangle\langle \mathrm{L}pn_{\mathrm{A}}| = \sum_{1}^{3}{}_{n} |\mathrm{L}pn_{\mathrm{B}}\rangle\langle \mathrm{L}pn_{\mathrm{B}}|$$

where the second equality holds due to the orthogonality of the $\mathbf{F}_p^L$ matrix [20]. Using the assumptions of the angular overlap model one finds:

$$\langle \mathrm{A}v'|\mathrm{A}|\mathrm{A}u'\rangle = \sum_{1}^{3}{}_{n} \langle \mathrm{A}v'|\mathrm{L}pn_{\mathrm{A}}\rangle\langle \mathrm{L}pn_{\mathrm{A}}|\mathrm{A}u'\rangle$$
$$= \delta_{v'u'}\, e_{v\mathrm{A}}$$

$$\langle \mathrm{B}v'|\mathrm{A}|\mathrm{B}u'\rangle = \delta_{v'u'}\, e_{v\mathrm{B}}$$

with

$$|\langle \mathrm{M}v'|\mathrm{L}pn_{\mathrm{M}}\rangle|^2 = \delta_{v'n}\, e_{v\mathrm{M}} \quad (\mathrm{M} = \mathrm{A}, \mathrm{B}) \tag{10}$$

The matrix elements coupling an A and a B metal orbital can be computed in the following manner:

$$\langle \mathrm{A}u'|\mathrm{A}|\mathrm{B}v'\rangle = \sum_{1}^{3}{}_{m} \langle \mathrm{A}u'|\mathrm{L}pm_{\mathrm{A}}\rangle\langle \mathrm{L}pm_{\mathrm{A}}|\mathrm{B}v'\rangle$$

and by (9)

$$\langle \mathrm{A}u'|\mathrm{A}|\mathrm{B}v'\rangle = \sum_{1}^{3}{}_{m} \sum_{1}^{3}{}_{n}\, \mathbf{F}^{L}_{p,mn} \langle \mathrm{A}u'|\mathrm{L}pm_{\mathrm{A}}\rangle\langle \mathrm{L}pn_{\mathrm{B}}|\mathrm{B}v'|$$
$$\langle \mathrm{A}u'|\mathrm{A}|\mathrm{B}v'\rangle$$

In order to have a compact expression for the matrix element, using (10), it must be recalled that for u', $v' = \delta s$ or δc $\mathbf{F}^{L}_{p,u'v'}$ is not defined. A formal way to overcome this inconvenience is to define a matrix $\mathbf{F}^*_p$ such that

$$\mathbf{F}^*_{p,ij} = \begin{cases} \mathbf{F}^{L}_{p,ij} \text{ for } i \text{ and } j = \sigma, \pi s, \pi c \\ 0 \text{ for } i \text{ or } j = \delta s, \delta c \end{cases}$$

The matrix element can now be written as

$$\langle \mathrm{A}u'|\mathrm{A}|\mathrm{B}v'\rangle = \mathrm{F}^*_{p,u'v'} (e_{u'\mathrm{A}}\, e_{v'\mathrm{B}})^{1/2}$$

Using (7) and (8) we obtain the required relations for the non primed basis functions:

$$\langle \mathrm{A}v|\mathrm{A}|\mathrm{A}u\rangle = \sum_{1}^{5}{}_{i}\, \mathbf{F}^{\mathrm{A}}_{vi} \mathbf{F}^{\mathrm{A}}_{ui} \langle \mathrm{A}i'|\mathrm{A}|\mathrm{A}i'\rangle$$
$$= \sum_{1}^{5}{}_{i}\, \mathbf{F}^{\mathrm{A}}_{vi} \mathbf{F}^{\mathrm{A}}_{ui}\, e_{i\mathrm{A}} \tag{11}$$

$$\langle \mathrm{B}v|\mathrm{A}|\mathrm{B}u\rangle = \sum_{1}^{5}{}_{i}\, \mathbf{F}^{\mathrm{B}}_{vi} \mathbf{F}^{\mathrm{B}}_{ui}\, e_{i\mathrm{B}} \tag{12}$$

$$\langle \mathrm{A}v|\mathrm{A}|\mathrm{B}u\rangle = \sum_{1}^{5}{}_{i} \sum_{1}^{5}{}_{j}\, \mathbf{F}^{\mathrm{A}}_{vi} \mathbf{F}^{\mathrm{B}}_{uj} \langle \mathrm{A}i'|\mathrm{A}|\mathrm{B}j'\rangle$$
$$= \sum_{1}^{5}{}_{i} \sum_{1}^{5}{}_{j}\, \mathbf{F}^{\mathrm{A}}_{vi} \mathbf{F}^{\mathrm{B}}_{uj} \mathbf{F}^*_{p,ij} (e_{i\mathrm{A}}\, e_{j\mathrm{B}})^{1/2} \tag{13}$$

Now we can parametrize the energies of weakly interacting dimers, making only the assumption, common to the one-centre angular overlap model, that the contributions from different ligands are additive [21]. Equations (11–13) show how a perturbation matrix can be constructed for every ligand using ten metal orbitals, five for metal A and five for metal B.

Calculations

All the calculations described below were performed using a CII 10070 computer. A FORTRAN program was written which used the angular overlap matrix defined in the previous section. The input parameters were the geometrical (θ, φ, ψ and β) and the bonding ones (e_σ, $e_{\pi s}$, $e_{\pi c}$) for each ligand. The program evaluates the angular overlap matrix for each ligand and sums the results over all the ligands. Diagonalization yields the eigenvalues and the eigenvectors.

In order to test our calculations, copper(II) dimers were considered since many spectral and magnetic data are available for these compounds [4, 22–26]. We will discuss doubly bridged dimers, which are by far the most common. We will consider dimers formed by two square planar moieties, and those formed by five-coordinate moieties, either square-pyramidal or trigonal bipyramidal. Dimers formed by six-coordinate moieties will not be considered explicitly, because they can be reconduced to the square pyramidal cases.

Some of the model complexes below were considered previously by Hoffmann [13]. In every case our calculations were found to yield the same pattern as the Extended Hückel calculations, thus confirming that our approach is correct.

The coordinate system used for the square planar dimers is shown in Figure 3. We have fixed the bonding parameters (e_σ and e_π for each ligand; for bridging ligands it is necessary to define e_σ and e_π on both the metal atoms) and considered first of all the effect of varying β, the M–X–M angles (Figure 4a). Throughout this paper we will use the symbol β to indicate the angles at the bridge ligands. The other

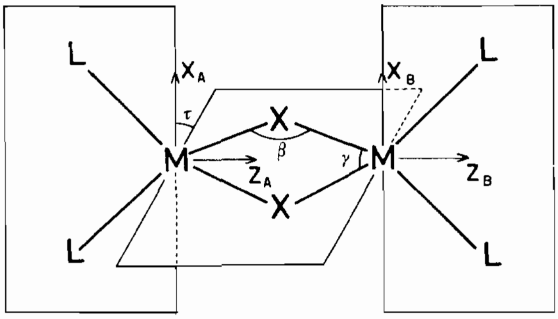

Figure 3. The coordinate system and the geometrical parameters for a general square planar dimer.

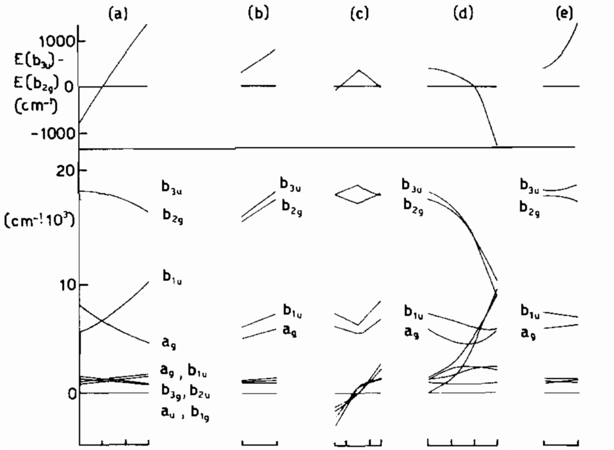

Figure 4. Energy level diagrams for square planar dimers. (a): the effect of varying β with $e_\sigma^L = e_\sigma^X = 6000$, $e_\pi^L = e_\pi^X = 600$ cm^{-1}, τ = 0°, δ = 180°; (b), (c), (d) and (e): the effect of changing e_σ^X, (e_π^X/e_σ^X), τ, δ in turn with $e_\sigma^L = 6000$, $e_\pi^L = 600$ cm^{-1}, β = 95°. The L–M–L angle is 90°. Upper: Energy differences between the two highest energy levels.

geometrical parameters are defined in the caption to Figure 4, and the dimers were considered to possess an inversion centre. All the ligands were considered as equivalent at this stage.

The effect of varying all the other parameters has been considered by varying them in turn, one at a time. So the effect of varying the nature of the bridge ligand has been simulated by changing the e_σ and e_π/e_σ parameters and keeping all the other bonding and geometrical parameters constant, with β = 95° (Figure 4b, 4c). Besides π antibonding effects of the ligand on the metal orbitals also π bonding effects were taken into account. These can occur with ligands which have low lying empty π orbitals, and in the angular overlap scheme they correspond to negative values of e_π.

The effect of what was called "tetrahedral distortion" [27] was also considered (Figure 4d), by changing the angle τ of Figure 3 from 0° to 90°.

Finally we have considered the effect of changing the dihedral angle δ between the two CuL_2X_2 planes (Figure 4e). In terms of the classification suggested by Lintvedt [28] this corresponds to passing from type *b* to type *d* complexes. For the bridge ligands the angle β was kept constant. In order to do this however it was necessary to change slightly the X–Cu–X angles, γ, according to the relation $\gamma = 2\sin^{-1}[\sin(\delta/2)\sin(\beta/2)]$.

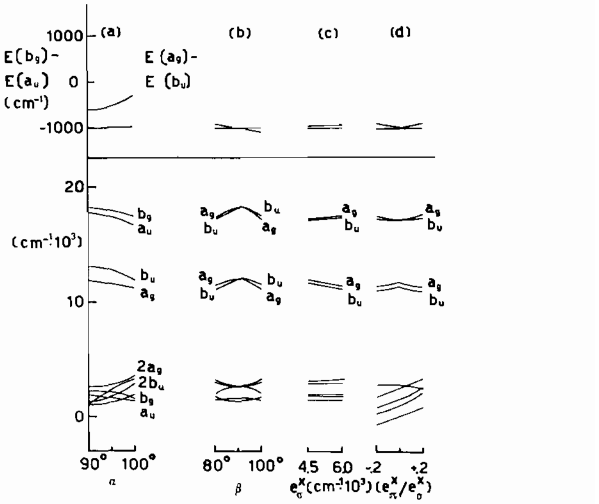

Figure 5. Energy level diagrams for five coordinate square pyramidal dimers. (a): the effect of varying α in the model dimer shown in Figure 6, with $e_\sigma^L = e_\sigma^X = 6000$, $e_\pi^L = e_\pi^X = 600$ cm^{-1}, β = 95° and the L–M–L and X–M–X angles at 90°; from left to right the effect of changing the geometrical parameters for the model dimer of Figure 7. (b): $e_\sigma^L = e_\sigma^X = 6000$, $e_\pi^L = e_\pi^X = 600$ cm^{-1}, α = 90°. (c) and (d): $e_\sigma^L = 6000$, $e_\pi^L = 600$ cm^{-1}, β = 80°, α = 90°. The L–M–L and L–M–X angles are 90°. Upper: Energy differences between the two highest energy levels.

The energy level diagrams relative to five-coordinate square pyramidal complexes are shown in Figure 5. Two different geometries can occur, differing from one another in the way in which the two square pyramidal moieties join to form the dimer [28]: the two bridging ligands can be both equatorial on the two metal centers, or one is equatorial for metal A and axial for metal B, and the other is axial for metal A and equatorial for metal B. These two models and the chosen reference systems are shown in the Figures 6 and 7. The first case, corresponding to Figure 6, can be considered as derived from the square planar case described above by the addition of a ligand in an axial position. It is of interest to notice that this has little effect on the splitting of the highest orbitals (Figure 5a). We considered also the possibility of removing the copper ions from the plane of the pyramid, according to the model shown in Figure 6, *i.e.* the α angle was varied from 90°. The variation was performed so that the symmetry of the model compound is C_{2h}, conserving therefore an inversion

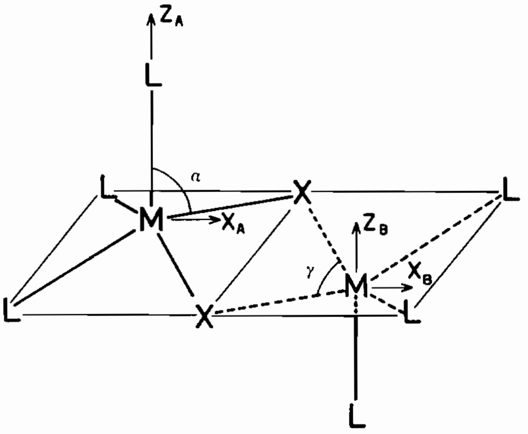

Figure 6. The coordinate system and the geometrical parameters for a square pyramidal dimer with the two bridging ligands in equatorial position.

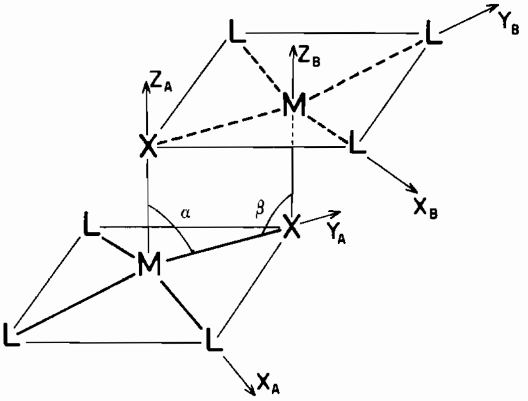

Figure 7. The coordinate system and the geometrical parameters for a square pyramidal dimer in which a bridging ligand is in axial position for one metal and in equatorial position for the other metal.

centre. This means that the L_4X_2 moiety is planar, as is the M_2X_2 moiety. The variation of the angle α was performed by keeping constant the β angles. In order to obtain this result a small deformation of the γ angle was required, according to the relation $\gamma = 2\cos^{-1}[\cos(\beta/2)/\sin\alpha]$.

The diagrams for dimers whose geometry corresponds to the model of Figure 7 are shown in Figure 5b, c, d. The symmetry of the dimer is C_{2h}, and a variation of the angle β causes a variation also of the angle α according to the relation $\alpha + \beta = 180°$. It is apparent that in the present case the predicted splitting of the energy levels is very small – smaller than that calculated in all the previous cases. The effect of decreasing the values of the parameters is that of decreasing the splitting and a similar pattern is followed for a decrease in the value of the ratio e_π/e_σ.

In Figure 8 are shown the coordinate systems used for trigonal bipyramidal dimers. Also in the present case a deformation of the β angle was taken into account, this time however no rearrangement of the rest of the molecule was considered (Figure 9a). The splitting appears to be small and increases very little for small deviations of β from 90°, while it increases far more rapidly as β becomes larger than 100° (Figure 9a). The effect of the variation of the e_σ and e_π/e_σ parameters is shown in Figure 9b, c.

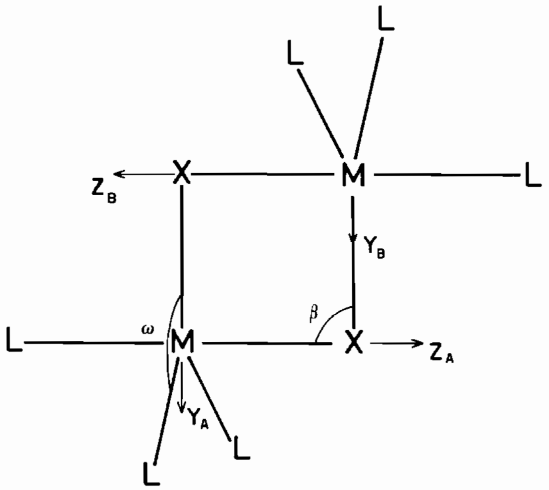

Figure 8. The coordinate system and the geometrical parameters for a trigonal bipyramidal dimer.

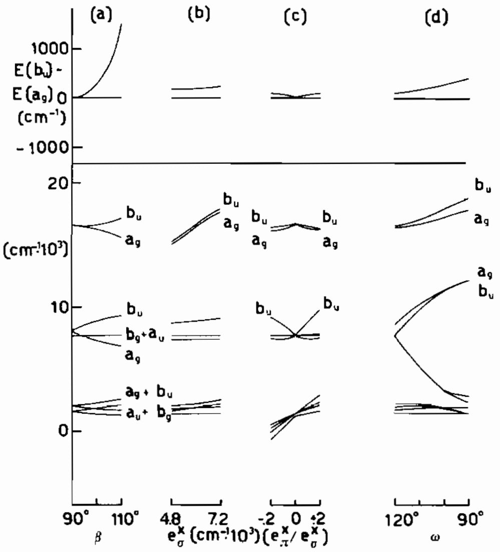

Figure 9. Energy level diagrams for five coordinate trigonal bipyramidal dimers. (a): the effect of varying β with $e_\sigma^L = e_\sigma^X = 6000$, $e_\pi^L = e_\pi^X = 600$ cm^{-1}, $\omega = 120°$; (b) and (c): the effect of changing e_σ^X and (e_π^X/e_σ^X) respectively with $\beta = 100°$, $\omega = 120°$; (d): the variation of ω with $e_\sigma^L = e_\sigma^X = 6000$, $e_\pi^L = e_\pi^X = 600$ cm^{-1}, $\beta = 95°$. The axial ligands have been kept orthogonal to the ML_2 plane. Upper: Energy differences between the two highest energy levels.

The square pyramidal and trigonal bipyramidal complexes can be easily interconverted one into the other by changing the angle ω of Figure 8. When it is

120°, the complex is trigonal bipyramidal, while when $\omega = 90°$ the complex is square pyramidal. The effect of this interconversion on the splitting is shown in Figure 9d.

Survey of Experimental Results

The calculations of the previous section show how it is possible to express the orbital energies of transition metal dimers using an angular overlap approach. It is now important to check if the calculations can be used in interpreting the magnetic properties of copper complexes.

In the MO scheme suggested by Hoffmann [13] the separation in energy between the two lowest singlet and triplet states is given by

$$E_S - E_T = J = 2K_{ab} - \frac{(\epsilon_1 - \epsilon_2)^2}{J_{aa} - J_{ab}}$$

where E_S and E_T are the energies of the singlet and of the triplet respectively, J and K are coulomb and exchange integrals respectively, a and b are localized molecular orbitals centered on the two different metal atoms, ϵ_1 and ϵ_2 are the energies of the two highest molecular orbitals. Hoffmann showed that in a series of complexes the most rapidly changing parameters are the differences in orbital energies $(\epsilon_1 - \epsilon_2)$ and therefore he focused the attention on this parameter. An increase in the splitting of the two highest molecular orbitals would favour an antiferromagnetic coupling between the two metal ions, while a decrease of the splitting would favour a ferromagnetic behaviour. In our model it is necessary to substitute the angular overlap energies to the molecular orbital energies. It is worth noting that the main advantage of the angular overlap approach over the molecular orbital one is that in the angular overlap the parameters to be used are, at least in principle, the same which are commonly used for the interpretation of the spectral and magnetic properties of monomeric complexes [29].

In the last years the number of attempts to interpret by the angular overlap approach all the properties which depend on the electronic structure of the complexes has steadily increased [30–33] and the possibility to use them also for the interpretation of the spectral and magnetic properties of dimers appears tempting. As a matter of fact it is only with models which can use easily the same sets of parameters to interpret the largest number of experimental data that it can be hoped to understand fully the electronic properties of low symmetry complexes.

Several attempts have been performed to give reasonable sets of radial parameters for copper(II) complexes with various donor atoms, relating them also to the metal–ligand distance [34, 35]. In the above calculations we chose the values of $e_\sigma = 6.000$ cm^{-1}, which compares well with the values suggested for nitrogen and oxygen ligands [34]. Also calculations with different starting values of e_σ and e_π/e_σ were performed, in order to check if changing the bonding parameters might alter the qualitative behaviour which was shown in Figures 4, 5, 9. In general it was found that for reasonable values of the parameters the pattern of the levels was not substantially altered.

We will now consider the series of square planar and square pyramidal di-hydroxo bridged copper(II) complexes discussed by Hatfield and Hodgson [36–39]. They related the experimental J values to the variation of the Cu–O–Cu, β, angle throughout the series. These complexes appear to be well suited for such a correlation because the bridge ligand is not changed throughout the series, and the metal–hydroxo ligand distances appear to be substantially constant (the extreme values are 190 and 195 pm). The diagram of Figure 4a can be used to confirm on a theoretical ground the suggested relation, since the energy difference $E(b_{3u}) - E(b_{2g})$ increases dramatically as β departs from 90°, and as stated above an increase in the orbital energy separation $(\epsilon_1 - \epsilon_2)$ increases the tendency to antiferromagnetic coupling. The transition from a ferromagnetic to an antiferromagnetic coupling has been found experimentally for β values of ~98°.

If one looks more into the detail of the series of complexes described by Hatfield and Hodgson several points can be raised. As a matter of fact, although all the complexes in the series are reasonably similar to each other, some differences do exist, and they might influence the value of J. First of all the nature of the non-bridge ligands. Our calculations show that this should not be a major effect, at least as long as the b_{3u} and b_{2g} orbitals remain the highest ones. In the series there are both square planar and square pyramidal complexes. In the latter case the α angles are different from 90°, and this deviation may play a role. For instance the difference in the bridge angle between the strictly similar $[Cu(bpy)OH]_2(NO_3)_2$ [39] and $[Cu(bpy)OH]_2SO_4 \cdot 5H_2O$ [40], where bpy is 2,2'-bipyridyl, is of only 1°, but J in the latter is +172 cm^{-1} and only +48 cm^{-1} in the former. The two complexes have very low symmetries, so it is necessary to make some idealization of the structures in order to discuss them. Since the axial ligand is closer to the metal in the sulphate derivative as compared to the nitrate it might be argued that α is larger in the sulphate. According to our calculations (Figure 5a) an increase in α increases the splitting of the levels, thus decreasing the ferromagnetic coupling.

Another geometric distortion whose effect might be important was noticed by Lintvedt [28]. He considered the two complexes $[Cu(bpy)OH]_2SO_4 \cdot 5H_2O$ [40] and bis(picolinoyl)3-amino-1-propoxidiaquocopper(II) dihydrate [41]. Both of them have CuO_2 bridges, with very similar β angles (97° for the former and 98° for the latter). Although the oxygen ligands are different, hydroxo in the former and alkoxo in the latter, the two bond distances are identical. The two complexes are square pyramidal, but the planes of the pyramids in the dimers are not parallel, making a dihedral angle of 172° in the hydroxo and 164° in the alkoxo dimer. The J values are +48 and -130 cm^{-1} respectively. According to the diagram of Figure 4e it is apparent that the separation of the two highest molecular orbitals increases as the dihedral angle δ decreases, thus providing a justification to the transition from ferromagnetic to antiferromagnetic coupling observed for the two complexes above.

The above examples require that the problem of the nature of the bridging atom be investigated. Lintvedt [28] noticed the difference between $[Cu(teen)OH]_2ClO_4$ [42] and $[Cu(BAA)py]_2$ [28], where teen is *N,N,N',N'*-tetraethylethylenediamine and BAA is benzoylacetylacetone. In both cases the angle β is 103°, but in the former the bridge is an hydroxo group, while in the latter it is a keto oxygen. The bridge bond distances are larger in the $[Cu(BAA)py]_2$ complex than in $[Cu(teen)OH]_2ClO_4$ (195 against 190 pm), and the antiferromagnetic coupling follows the same pattern ($J = -370$ cm^{-1} for the former and -205 cm^{-1} for the latter). If it is assumed that the main difference between the two sets of donor atoms is due to the different bond distances, a large decrease in the π bonding effects must be expected. Such effects might be responsible for the increase of J, since a decrease of π effects increases the splitting of the highest orbitals according to the diagram of Figure 4c.

Another structurally interesting class of compounds is that of pyridine-*N*-oxide dimers, which typically have very strong antiferromagnetic interactions [43]. In a reported structure [44] the β angle is very large, 108°, and this factor can have a large influence on the magnetic coupling. Other factors which could be of interest are the long distances (197–203 pm), which decrease the π bonding effects as compared to the hydroxo bridged complexes discussed above, and increase consequently the antiferromagnetic interactions.

An example of the so called "tetrahedral distortion" has been found by Sinn [27], who suggested that the effect of this distortion is to lower the antiferromagnetic coupling constant, *i.e.* complexes where the distortion is operative should have less negative J values as compared to those where it is not present. This result can be rationalized using the diagram of Figure 4d which shows that on increasing τ, the separation of the highest orbitals is lowered. A similar distortion was observed also in the $Cu_2Cl_6^{2-}$ dimers [45], and the same consideration apply also in that case.

Finally we want to mention the complexes whose structures can be reconducted to the models of Figure 7 and 8. The examples of square pyramidal complexes are numerous, and they are in general characterized by small magnetic effects, either ferro- or antiferromagnetic in nature. Sinn [46] collected many examples of this class of compounds reporting strong antiferromagnetic coupling only in one case in which $\beta = 101°$. Our model calculations suggest that in every case the magnetic interactions are small, a large angle stabilizing antiferromagnetic effects. A trigonal bipyramidal complex was reported by Bertrand [47], in which the low magnetic moment (1.1 μ_B at room temperature) was interpreted as a proof of strong antiferromagnetic exchange. This is in line with the observed large β angle of 110° and with the diagram of Figure 9a.

In all the above discussion the symmetry of the complexes was always kept as high as possible in order to reduce the number of parameters to a minimum. However, most of the complexes described have lower symmetries, and in principle low symmetry components might have large influence on the magnetic properties. Another factor which has been purposedly ignored in the above discussion is the possibility of non linearly ligating ligands [48]. As a matter of fact, most of the ligands considered are non linearly ligating. Although the suggested model can easily take into account both the low symmetry components and the non linear ligation, it appears that the problem at present is largely overparametrized, and that more experimental data are required in order to help in fixing the values of the parameters. In particular we have used e_σ and e_π values corresponding to those calculated for interpreting the *d–d* transition, but the problem is still open for assigning the values of the parameters of the bridge ligands. It appears that accurate studies of the electronic spectra of the dimers could in principle provide the required information. However, we feel that the model in its present form is suited to substitute the superexchange considerations with semiquantitative calculations, and that σ, π, in-plane, out-of-plane superexchange pathways can be easily computed also in the case of low symmetry dimers.

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