Exchange Coupling in Oxalato-Bridged Copper(II) Binuclear Compounds: A Density Functional Study

Joan Cano, Pere Alemany,* Santiago Alvarez, Michel Verdaguer, and Eliseo Ruiz*

Abstract: A theoretical study of the exchange coupling for a selected sample of oxalato-bridged binuclear Cu^{II} compounds is presented. Model calculations have been used to examine the influence of several factors on the coupling constants: a) the relative orientation of the two semioccupied orbitals, b) the nature of the terminal ligands, and c) various structural parameters. Singlet–triplet splittings calculated for complete structures, as determined by X-ray diffraction, are in excellent agreement with experimental data. Comparison of our results with those obtained from qualitative models provides some insight into the limits of applicability of these approximate methods for the study of magnetostructural correlations.

Keywords: binuclear complexes • copper • correlation analysis • density functional calculations • magnetic properties

Introduction

Polynuclear complexes of transition metals and their magnetic properties have been an area of intensive research in recent decades.[1–3] One of the most appealing features in this field is the variety of structural data and magnetic measurements that have been successfully correlated for many families of compounds. Despite the large amount of available data, the prediction of the magnetic behavior for new binuclear or polynuclear compounds is not perfect, mainly because of the subtle interplay between different factors determining the magnetic properties. The problem of the electronic structure of coupled polymetallic systems has attracted the attention of a large number of researchers, who have proposed several orbital models to describe the phenomenon of exchange interaction. However, controversy over the respective advantages and limits of each of these models is still alive.

From our point of view, one of the most fruitful approaches to the qualitative theoretical aspects of magnetostructural correlations is provided by the now-classical work of Hay, Thibeault, and Hoffmann (HTH).[4] These authors proposed a simple expression for the coupling constant between two symmetry-related magnetic centers and applied it to the study of the structural factors that affect the exchange interaction. For a binuclear system with two unpaired electrons the singlet–triplet splitting proposed by those authors is given by Equation (1), where J stands for the coupling constant and ε_1 and ε_2 are the energies of ϕ_1 and ϕ_2, the two singly

$$E_s - E_T = J = 2K_{ab} - \frac{(\varepsilon_1 - \varepsilon_2)^2}{(J_{aa} - J_{ab})} \qquad (1)$$

occupied molecular orbitals (SOMOs) of the complex.[5] K_{ab}, J_{aa}, and J_{ab} are two-electron integrals involving two localized orthogonal versions of these orbitals. Of the two terms in this equation, the first can be interpreted as a ferromagnetic contribution to the magnetic exchange constant, stabilizing the triplet state, while the second represents an antiferromagnetic term favoring a singlet ground state. For simplicity, the dependence of the coupling constant on small structural changes is generally supposed to arise mostly from the one-electron term $(\varepsilon_1 - \varepsilon_2)^2$, whereas all two-electron terms are assumed to remain approximately constant.

Although this approach has been employed often since its publication to obtain qualitative trends in magnetostructural correlations,[6–11] it is unable to provide quantitative results that would allow the prediction of magnetic properties for new compounds. The main drawback of such an approach, as normally applied, comes from the use of semiempirical calculations (i.e., the extended Hückel method) to estimate the one-electron term $(\varepsilon_1 - \varepsilon_2)$, since it only allows for a

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[*] Dr. P. Alemany, Dr. E. Ruiz, Dr. J. Cano, Prof. S. Alvarez
Departament de Química Inorgànica and
Departament de Química Física
Universitat de Barcelona, Diagonal 647
E-08028 Barcelona, Catalunya (Spain)
Fax: (+34) 3-402-12-31
Email:pere@linus.qui.ub.es

Prof. M. Verdaguer
Profesor Visitante Iberdrola de Ciencia y Tecnología
Permanent address: Laboratoire de Chimie des Métaux de Transition
URA CNRS 419, Université Pierre et Marie Curie
F-75252 Paris Cedex 05 (France)

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qualitative analysis of the influence of structural parameters on the exchange coupling. Alternative strategies based on the direct evaluation of the singlet–triplet energy splitting by ab initio methods have been successfully applied by various groups.[12–21] In order to obtain quantitative estimates of the coupling constant, one has to evaluate energy differences that are often smaller than 100 cm^{-1} (approximately 0.3 $kcal\,mol^{-1}$) from total energies seven orders of magnitude larger. Therefore much computational effort is involved in these calculations and their technical difficulty has prevented their extensive application to the analysis of magnetostructural correlations.

In a recent paper we presented a computational approach to this problem consisting in the use of density functional theory (DFT) for the calculation of coupling constants, and we discussed previous work in this area.[22] Good quantitative approximations to known experimental values were obtained for hydroxo- and alkoxo-bridged Cu^{II} binuclear compounds. One of the main advantages of this approach is its relative ease of application: thus coupling constants for binuclear compounds with over 50 atoms can be calculated with reasonable computational resources. In this paper we continue to explore the applicability of such an approach by studying the family of oxalato-bridged Cu^{II} compounds.

Computational Methodology

A detailed description of the computational strategy adopted in this work has been described elsewhere[22] and is only briefly reviewed here. For the evaluation of the coupling constant of each compound, two separate calculations are carried out by means of density functional theory,[23] one for the triplet and another for the singlet state. The hybrid B3LYP method,[24] as implemented in Gaussian-94,[25] has been used in all calculations, mixing the exact Hartree–Fock exchange with Becke's expression for the exchange[26] and with the Lee–Yang–Parr correlation functional.[27] A double-ζ quality basis set proposed by Ahlrichs has been employed throughout.[28] The presence of low-energy singlet states makes it difficult to evaluate accurately the energy of the lowest singlet by a single-determinant method. To solve this problem, broken-symmetry wavefunctions, as proposed by Noodlemann et al., have been used.[29–32] In the present case the valence-bond character imparted to the wavefunction by this approach gives acceptable results because it takes into account the three most relevant singlet configurations. We have found previously that, among the most common functionals, the B3LYP method combined with the broken-symmetry treatment (abbreviated as B3LYP-bs hereafter) is the strategy which provides the best results for calculating coupling constants.[22]

Abstract in Spanish: *En este trabajo se presenta un estudio teórico del acoplamiento magnético en compuestos dinucleares de cobre(II) con puente oxalato. Nuestro interés se ha centrado en el efecto que tienen sobre las constantes de acoplamiento a) la topología molecular, b) la naturaleza de los ligandos terminales y c) la variación de algunos parámetros estructurales. Los cálculos realizados considerando las estructuras completas de compuestos selecionados para determinar la diferencia de energía entre singulete y triplete proporcionan resultados en excelente concordancia con los datos experimentales. La comparación de nuestros resultados con los que se deducen de modelos cualitativos sencillos propuestos con anterioridad permite determinar los límites de aplicabilidad de éstos en el estudio de correlaciones magneto–estructurales.*

In earlier work, Noodleman et al. deduced the relationship [Eq. (2)] between the energy of the broken-symmetry state (E_{BS}) and those of the pure singlet (E_S) and triplet (E_T) states,[30] where S_{ab} is the overlap integral between the two localized orbitals. Two limiting cases can be foreseen for Equation (2). First, when each orbital is completely localized on one magnetic center (the so-called weak bonding regime), $S_{ab} = 0$ and the antiferromagnetic contribution vanishes,[32] resulting in Equation (3) for the relationship between the singlet–triplet splitting parameter J and the calculated energies, E_T and E_{BS}. Alternatively, for completely delocalized orbitals (strong bonding regime), $S_{ab} = 1$, and Equation (2) is simplified to Equation (4).

$$E_S = \frac{2}{1 + S_{ab}^2} E_{BS} - \frac{1 - S_{ab}^2}{1 + S_{ab}^2} E_T \qquad (2)$$

$$J = E_S - E_T = 2(E_{BS} - E_{BT}) \qquad (3)$$

$$J = E_S - E_T = E_{BS} - E_{BT} \qquad (4)$$

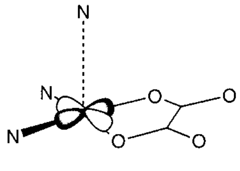
Although for practical cases S_{ab} should be relatively small, corresponding to an intermediate situation between these two limiting cases which would suggest the use of Equation (3), we have chosen to apply the approximation given in Equation (4), which has been found to reproduce better the experimental antiferromagnetic coupling constants of the related Cu^{II} hydroxo-bridged compounds in calculations performed with DFT-based methods that include a correlation term.[22] This approximation corresponds to describing the singlet state by means of a single-determinant wavefunction, in terms of which density functional theory is well defined.

The experimental magnetic susceptibility is measured from solid samples in which packing forces can induce small deviations from the optimum structure for the isolated molecules. Since such small structural differences can result in rather large changes in the calculated coupling constants, we use the molecular structure as found in the solid state rather than an optimized structure for the isolated molecule.

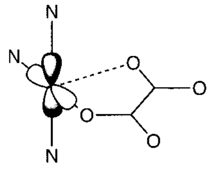
Results and Discussion

Influence of the coordination geometry on the exchange coupling: Some binuclear Cu^{II} complexes with an oxalato-bridging ligand, represented by the general formula $[(AA)Cu(\mu\text{-}C_2O_4)Cu(AA)]X_n$, have been structurally and magnetically characterized in recent years. In these complexes AA is a chelating ligand, typically a diamine, and X a counteranion or solvent molecule. Owing to the Jahn–Teller plasticity of the coordination sphere around Cu^{II}, this ion may appear as four-coordinate, or four-coordinate with a fifth ligand at a larger distance ([4+1] coordination), or with two weakly bound ligands ([4+2] coordination). In all three cases, four ligand bonds to the central ion (the shortest ones in the latter two cases) can be found approximately in a common plane giving square-planar, square-pyramidal, or pseudooctahedral coordination environments, respectively.

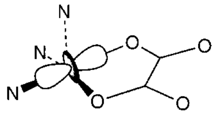
The local electronic structure of the d^9 ion is determined by its coordination geometry. In the three cases mentioned above, the unpaired electron is located in a $d_{x^2-y^2}$-type orbital pointing to the four atoms with short metal–ligand distances. Two different orientations of the basal plane with respect to the bridging ligand have been identified experimentally.[6] In the first case, with *N,N,N′,N′*-tetramethylethylenediamine (tmen) as chelating ligand,[33] the four short Cu–L distances correspond to two nitrogen atoms of tmen and two oxygen atoms of the oxalate ion. The SOMO can be described in this case as a $d_{x^2-y^2}$-type orbital coplanar with the oxalate molecule (**1a**). On the other hand, when the diamine AA is replaced by diethylenetriamine (dien) the basal plane is formed by the three nitrogen atoms of that ligand and one oxygen atom of the oxalate ion. In this case the unpaired electron is accommodated in a $d_{x^2-y^2}$-type orbital perpendicular to the plane of the bridging oxalate molecule (**1b**). A third, somewhat different, situation in which AA is replaced by *N,N,N′,N″,N″*-pentaethyldiethylenetriamine (petdien) has been described by Hendrickson.[34] In this case there is an approximately trigonal-bipyramidal coordination environment around the metal ion. The equatorial plane of this trigonal bipyramid is formed by two nitrogen atoms of the chelating ligand and one oxygen atom of the oxalate. The remaining oxygen atom of the oxalate and a third nitrogen atom from petdien provide the two apical ligands to complete the coordination sphere. The SOMO in this case is a d_{z^2}-type orbital directed along the pseudotrigonal axis (**1c**).



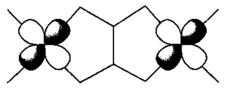
1a



1b

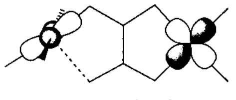


1c



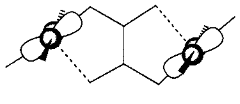
2a

coplanar



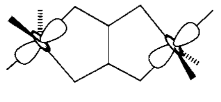
2b

perpendicular



2c

parallel



2d

trigonal-bipyramidal

When two Cu^{II} ions are combined in a binuclear compound, one can imagine several possibilities for the relative orientation of the two SOMOs, although only four of these have been realized experimentally (**2**). The first (**2a**), which will be called coplanar hereafter, is by far the most common one and has both SOMOs in the plane of the oxalato bridge. Magnetic measurements for different compounds with this orbital topology show that although a long distance (>5 Å) separates the metallic centers, an important antiferromagnetic exchange exists as evidenced by coupling constants in the range −300 to −400 cm^{-1}. For the other three orbital topologies much smaller coupling constants are found: −75 cm^{-1} in the perpendicular (**2b**) topology, from +1 to −37 cm^{-1} in the parallel one (**2c**) and −75 cm^{-1} in the trigonal-bipyramidal (**2d**) case. Qualitative reasoning, based on orbital overlap arguments, has been formulated to explain these values.[33, 35] While strong overlap of both SOMOs and oxalate-centered molecular orbitals is possible for the coplanar topology, this interaction is almost nonexistent in the complexes with a parallel arrangement of the two SOMOs. Compounds with perpendicular and trigonal-bipyramidal topologies provide intermediate situations.

In order to obtain a deeper insight into the influence of the coordination environment on the exchange, we have performed calculations on model compounds representative of each of the four topologies. In these models all terminal ligands have been replaced by ammonia molecules. Details of the geometric parameters used in these models can be found in the Appendix. The calculated coupling constants are presented in Table 1. Despite the important structural simplifications introduced in the model compounds, the trends are correctly described by our results. A fair agreement with the available experimental data is obtained for the coplanar and perpendicular cases. For the parallel topology, the sign of the calculated coupling constant is in disagreement with the reported experimental values. Nevertheless, its significantly small absolute value is clearly reflected in our calculations. In such cases with *J* values smaller than 10 cm^{-1} (singlet–triplet splittings of the order of 0.025 kcal mol^{-1}) it is difficult to obtain accurate results from a simplified model; this will be discussed below with the results obtained for the full structures. The disagreement between the calculated data and the experimental values for the compounds with trigonal-bipyramidal coordination at the two copper atoms has been attributed to the departure from perfect trigonal-bipyramidal coordination environments in the experimental structures,[34] resulting in a substantial decrease in the coupling constant. If one considers a model with different values for the two nonequivalent Cu–O distances, as in the experimental structure, the calculated coupling constant is reduced to −124 cm^{-1}. This value is closer to the experimental one (−75 cm^{-1}) but still too large. The difference is not due to the inaccuracy of the B3LYP-bs method, but to the poor representation of the molecular structure by the chosen model. For the model with the same geometry as the

Table 1. Calculated exchange constants (cm^{-1}) for the model compound $[(NH_3)_3Cu(\mu\text{-}C_2O_4)Cu(NH_3)_3]^{2+}$ with different topologies of the two SOMOs. The column labeled J_{est} corresponds to the empirical estimation of *J* proposed by Julve et al.,[33] by taking the average experimental value (−370 cm^{-1}) for the coplanar case as a reference value.

	Orbital topology	J_{calc}	J_{est}	J_{exp}	ref.
2a	coplanar	−293	−370	−300 to −400	see Table 3
2b	perpendicular	−86	−93	−75	[33]
2c	parallel	+10	≈0	+1.2 to −37	[33–38]
2d	trigonal-bipyramidal	−185	−165	−75	[34]

experimental structure for the coordination sphere around the copper atoms, calculation of the coupling constant results in a value of $-128\,\mathrm{cm}^{-1}$. Disagreement with the experimental data thus arises not only from the departure from the perfect trigonal-bipyramidal coordination environments as had been postulated in earlier work;[34] our results indicate that an important part of this disagreement is introduced by the simplification of the terminal ligands used in the model. This last affirmation is supported by a calculation for the complete experimental structure (see below), which gives a value of J much closer to the experimental one.

It is instructive to compare the calculated values with those predicted by Julve et al.[33] with empirical rules based solely on the overlap between magnetic orbitals. Taking J_a, the coupling constant for coplanar compounds, as a reference value, these authors suggest the following relationships between the J values in the different compounds (the subscripts correspond to the different orbital topologies in **2**): $J_b = J_a/4$, $J_c \approx 0$, and $J_d = 4J_a/9$. As can be seen from the values calculated with these relationships, a fair agreement with our calculated constants is also obtained, demonstrating an excellent predictive power of the empirical rules. In particular, both these rules and our calculation predict a much larger coupling constant for the compounds with trigonal-bipyramidal coordination of copper atoms than was found experimentally. The disagreement of the empirical rules with the experimental data in this case was also attributed to the departure of the coordination geometry from an ideal trigonal bipyramid.[33]

The calculated singlet–triplet splittings for the full structures of four compounds, including the complete chelating ligands, each one representing one of the orbital topologies **2**, are reported in Table 2. The counterions have also been included in the calculations for the complexes with coplanar and parallel topologies, but were omitted for the other two examples. In the case in which the SOMOs have a perpendicular topology (**2c**), only one counterion is included because the position of the other one in the crystal structure could not be determined unambiguously. For the compound with trigonal-bipyramidal topology, the counterions have been omitted because the tetraphenylborate anion is too large. It must be noted, however, that in previous work on hydroxo- and alkoxo-bridged complexes[36] it was shown that the noncoordinated counterions, such as the tetraphenylborate anion, are not relevant to the exchange interaction. The calculated J values are in excellent agreement with the experimental data. The ferro- or antiferromagnetic character of these compounds is correctly reproduced in all four cases, even in the parallel one, which presents quite a small coupling constant. The calculated constants are also in good qualitative agreement with those for the corresponding simplified models (Table 1), showing that the topology of the two SOMOs is the leading factor in determining this property. For the compound with a trigonal-bipyramidal coordination of the copper atoms, a sizeable deviation from the ideal coordination geometry results in a significant reduction of the calculated coupling constant compared with that found for the model compound (Table 1), which leads to excellent agreement with the experimental value.

In a related study on hydroxo- and alkoxo-bridged Cu^{II} compounds we found that suppression of two weakly coordinated nitrate counterions in a complete structure resulted in a change of $-34\,\mathrm{cm}^{-1}$ in the coupling constant.[36] A similar effect is probably the cause of the overestimation of the calculated coupling constants for the compound with a perpendicular arrangement. It should be borne in mind that for such a compound one of the counterions had to be excluded from the calculations because of the incomplete resolution of the crystal structure. It is noteworthy that our computational strategy provides good approximations to the coupling constants for relatively large structures such as the trigonal-bipyramidal representative, $[\{Et_5dien\}_2Cu_2(\mu\text{-}C_2O_4)]$, which contains 108 atoms and 540 basis functions.

If we compare the present results with the ab initio calculations of Daudey et al., who obtained a J value of $-295\,\mathrm{cm}^{-1}$ for $[tmen_2(H_2O)_2Cu_2(\mu\text{-}C_2O_4)](ClO_4)_2 \cdot 1.25\,H_2O$, the agreement between the two calculations is fair. However, such a comparison is not straightforward as Daudey et al. used a simplified structural model for their calculations.

Influence of the terminal ligands on the exchange coupling: Once the main topological factors concerning the role of the bridge are understood, it is important to analyze the effect of the nature of the terminal ligands on the magnitude of the magnetic coupling when the orbital topology is kept constant. A quantitative estimate of such an effect would be even more desirable and would be useful in order to gain better control of the coupling constant when new compounds are being designed. On the theoretical side, one needs to know how the modeling of such ligands affects the calculated values of J. In a previous qualitative theoretical study on oxalato-bridged Ni^{II} binuclear complexes,[37] we showed that the terminal ligands affect the magnitude of the coupling, and therefore become indirectly involved in the superexchange mechanism. This effect is related to the energy of the lone-pair orbitals of the donor atom: other things being equal, the less electronegative donors induce a stronger antiferromagnetic coupling. This is due to a greater hybridization of the $d_{x^2-y^2}$-type metal orbital towards the bridge, induced by better σ-donor terminal

Table 2. Experimental and calculated coupling constants (cm^{-1}) by means of the B3LYP-bs method for four selected complete structures.

	Type	J_{calc}	J_{exp}	ref.
$[(tmen)_2(H_2O)_2Cu_2(\mu\text{-}C_2O_4)]$[a]$(ClO_4)_2 \cdot 1.25\,H_2O$	coplanar (**2a**)	-339	-385	[33]
$[(dien)Cu(\mu\text{-}C_2O_4)Cu(H_2O)(tmen)](ClO_4)_2$	perpendicular (**2b**)	-101	-76	[33]
$[(bpca)_2Cu_2(\mu\text{-}C_2O_4)]$	parallel (**2c**)	$+1.5$	$+0.3$	[35,36]
$[\{Et_5(dien)\}_2Cu_2(\mu\text{-}C_2O_4)](BPh_4)_2$	trigonal-bipyramidal (**2d**)	-82	-75	[34]

[a] Abbreviations: tmen = N,N,N′,N′-tetramethylethylenediamine; dien = diethylenetriamine; bpca = bis(2-pyridylcarbonyl)amido; Et$_5$dien = 1,1,4,7,7-pentaethyldiethylenetriamine.

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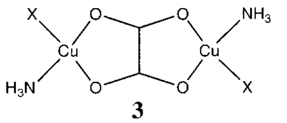
ligands. A similar observation was made by Escuer et al.[38] from their comparison of N-donor and O-donor ligands. As the previous studies were based only on the analysis of the one-electron contribution to the coupling constant, here we present DFT calculations for a series of compounds in which only a terminal ligand is changed (**3**, X = F, Cl, Br, or I), to see whether the same effect is found when the two-electron terms are considered also. The results, shown in Figure 1, confirm the previous findings. Furthermore, the effect of the equatorial ligands is approximately additive, as can be seen for the following series of compounds in which equatorial ammonia ligands are gradually substituted by chlorides: $[Cu_2(\mu\text{-}C_2O_4)(NH_3)_6]^{2+}$, $J = -295\ cm^{-1}$; *trans*-$[Cu_2(\mu\text{-}C_2O_4)(NH_3)_4Cl_2]$, $J = -230\ cm^{-1}$; $[Cu_2(\mu\text{-}C_2O_4)(NH_3)_2Cl_4]^{2-}$, $J = -195\ cm^{-1}$. In contrast, substitution of the axial ammonia ligands by chlorides produces a change in the opposite direction: a J value of $-293\ cm^{-1}$ for $[Cu_2(\mu\text{-}C_2O_4)(NH_3)_6]^{2+}$ changes to $-318\ cm^{-1}$ in $[Cu_2(\mu\text{-}C_2O_4)(NH_3)_4Cl_2]$.



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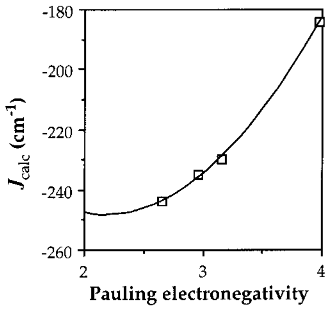
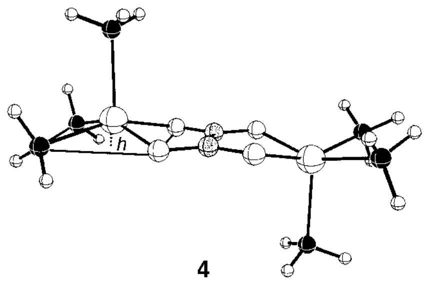


Figure 1. Dependence of the calculated J value on the electronegativity of the terminal ligands X in compounds of type **3**. See the Appendix for a definition of the structure used in the calculations.

Magnetostructural correlations for compounds with coplanar topology: Compounds with a coplanar topology of the SOMOs form the most extensively studied family of oxalato-bridged binuclear complexes of Cu^{II}. The 12 known compounds (Table 3),[34, 39–44] with coupling constants ranging from -330 to $-402\ cm^{-1}$, thus provide the oportunity to establish correlations between these values and the structural variations found in the complexes. We report in this section the results of a series of calculations on the complexes $[(AA)Cu(\mu\text{-}C_2O_4)Cu(AA)]X_n$, modeled by $\{[(NH_3)_2Cu(\mu\text{-}C_2O_4)Cu(NH_3)_2](NH_3)_2\}^{2+}$. The relevant structural parameters used for such calculations are given in the Appendix. In this type of compound, the copper ions exhibit square-pyramidal coordination with two oxygen atoms of the oxalato bridge and two nitrogen atoms of the terminal ligand occupying the base of the pyramid. The counterion X or a solvent molecule completes the coordination sphere by occupying an axial site (replaced in our model by NH_3). Taking an idealized square-planar $N_2Cu(C_2O_4)CuN_2$ molecular framework with square-planar N_2CuO_2 fragments as a starting point for the description of the geometry in these compounds, the deviation of the experimental structures from the planar model can be described by three parameters:

a) The coordination of the fifth ligand X induces an out-of-plane displacement of the Cu atom, quantified by the parameter h_M, as shown in **4**.



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b) The base of the pyramid and the oxalato bridge are not always coplanar, giving rise to either a chair (**5a**) or a boat (**5b**) conformation. A negative dihedral angle (γ) between the mean planes containing the two sets of basal ligands and the plane of the oxalato molecule indicates a boat conformation.

c) The four donor atoms on the basal plane are not perfectly planar, showing a tetrahedral distortion (**6**). An

Table 3. Structural and magnetic data for binuclear oxalato-bridged complexes of the type $[(AA)Cu(\mu\text{-}C_2O_4)Cu(AA)]X_n$. A positive value for γ indicates a chair conformation, a negative value a boat conformation.

AA	X	donor set	h_M (Å)	γ (°)	α (°)	J_{exp} (cm^{-1})	Ref.
phen[a]	NO_3	O_2N_2/O	0.27	16.9	3.3	-330	[42]
bpy	Cl	O_2N_2/Cl	0.37	-15.0	4.3	-330	[43]
bpy	ClO_4	O_2N_2/O	0.18	12.0	7.4	-376	[45]
bpy	BF_4	O_2N_2/O	0.16	10.4	7.2	-378	[45]
bpy	PF_6	O_2N_2/F	0.08	3.2	0.0	-385	[43]
bpy	NO_3	O_2N_2/O	0.16	3.2	4.4	-386	[45]
bpy	SO_4	O_2N_2/O	0.18	10.5	8.1		[48]
bpy	saccharide	O_2N_2/O	0.12	4.09	7.0		[49]
bzpm	PF_6	O_2N_2/O	0.19	8.9	0.0	-349	[46]
tmen	PF_6	O_2N_2/O	0.21	10.0	8.5		[50]
tmen	ClO_4	O_2N_2/O	0.18	8.4	4.8	-385	[33]
			0.15	12.0	6.3		
tmen	O*t*Bu	O_2N_2/O	0.34	7.8	0.0		[51]
mpz	PF_6	O_2N_2/O	0.24	13.9	5.3	-402	[47]
mpz	NO_3	O_2N_2/O_2	0.06	2.1	0.4	-284	[52]

[a] Abbreviations: phen = phenantroline; bpy = 2,2′-bipyridine; bzpm = bromazepam; tmen = N,N,N′,N′-tetramethylethylenediamine; mpz = mepirizole.

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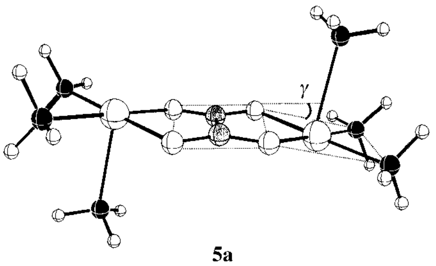

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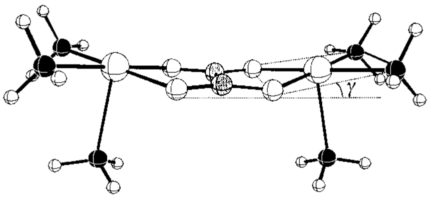

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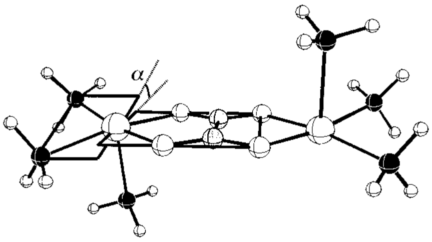

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adequate parameter to describe this distortion is the dihedral angle α formed between the O-Cu-O and N-Cu-N planes. A value of $\alpha \approx 0°$ indicates an ideal planar situation. Such a distortion is found to be less relevant for the oxalato-bridged compounds ($\alpha \approx 7.2°$) although it has been shown to have a major importance in the related tetrathiooxalato-bridged compounds.[11]

The experimental values of h_M, γ, and α, together with the coupling constants of several oxalato-bridged Cu^{II} complexes, are presented in Table 3. The effect of these distortions was analyzed previously with the one-electron approximation for oxalato- and bipyrimidine-bridged Cu^{II} compounds.[6, 45] In the first case only the influence on the coupling constant of the bending deformation leading to chair conformations was examined. For the bipyrimidine-bridged compounds the qualitative study predicts that the out-of-plane displacement of the copper atoms and the bending deformation should have effects of similar magnitude on their magnetic behavior.

In order to calibrate more precisely the effect of the out-of-plane displacement of the Cu atoms on the coupling constant, which was predicted previously on a qualitative basis, we have calculated J for the model compound **4** as a function of h_M. The results are presented in the upper panel of Figure 2. Comparison with related experimental data (Figure 2, lower panel) shows that the trend is reproduced well by the model calculations, even if the calculated curve is shifted by some $+100\,cm^{-1}$ relative to the experimental one. The displacement of the copper atoms out of the basal plane has a strong influence on the value of the coupling constant: the larger the distortion, the less antiferromagnetic J becomes.

An additional finding of interest is that the two structural distortions represented by γ and h_M are not independent. According to our DFT calculations, the larger the bending angle γ the more important is the displacement of the copper atoms from the ligand plane. The experimental data for 13 independent molecules of oxalato-bridged complexes show an analogous trend (Figure 3), although with some dispersion which is to be expected given the variety of compounds under consideration. The compound with an equatorial tmen and an axial $tBuO^-$ ligand has a disordered crystal structure and has been omitted from Figure 3.

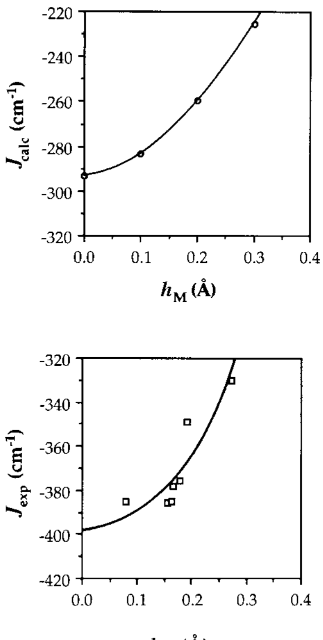


Figure 2. Variation of the coupling constant J with the out-of-plane displacement of the Cu^{II} ion (h_M, **4**). Upper panel: calculated for the model compound $\{[(NH_3)_2Cu(\mu\text{-}C_2O_4)Cu(NH_3)_2](NH_3)_2\}^{2+}$ (bending angle γ kept constant). Lower panel: experimental results for the $[(AA)Cu(\mu\text{-}C_2O_4)Cu(AA)]X_n$ family of complexes (AA = bidentate diamine; X = H_2O, NO_3^-). See Table 3 for references.

In order to gain further insight into the factors that govern the exchange interaction, we have analyzed separately the effect of the bending distortion leading to either a chair (**5a**) or a boat (**5b**) conformation. The behavior of the calculated coupling constant as a function of such distortions is presented in Figure 4. Interestingly, the two distortions are predicted to have quite different effects on the coupling constant. Whereas the bending of the molecule leading to a chair conformation strongly affects the exchange coupling, making it less antiferromagnetic, the bending that leads to a boat conformation has practically no effect on the coupling constant.

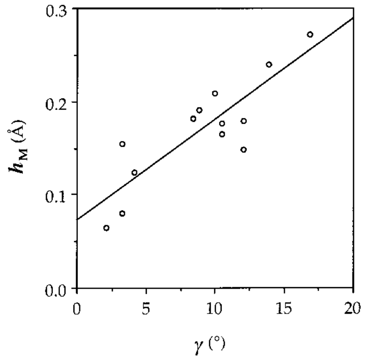


Figure 3. Out-of-plane displacement of the Cu atoms (h_M) as a function of the dihedral angle between the basal plane and the oxalato bridge (γ) in oxalato-bridged Cu^{II} binuclear compounds. See Table 3 for references.

The evolution of the calculated J as a function of the bending angle γ in the chair and boat distortion modes can be

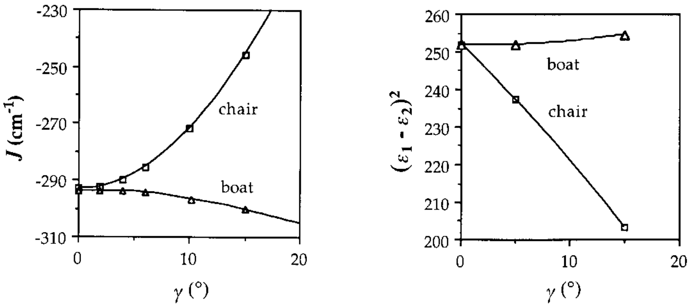
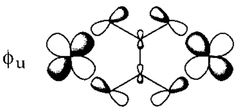


Figure 4. Left: variation of the calculated coupling constant as a function of the dihedral angle (γ, **5a, 5b**) between the CuL_4 and oxalato planes in the chair and boat conformations for the model binuclear compound $\{[(NH_3)_2Cu_2(\mu\text{-}C_2O_4)Cu(NH_3)_2](NH_3)_2\}^{2+}$ with coplanar topology (the Cu atoms are kept in their basal O_2N_2 planes). Right: variation of the square of the energy gap between the two SOMOs as a function of the same distortion.

traced back to the variations in the energy gap between the two SOMOs, ϕ_u and ϕ_g (**7a**, **7b**) as calculated for the triplet state (Figure 4, right-hand panel). In effect, the decrease of the energy gap brought about by the chair distortion results in a smaller antiferromagnetic contribution [the second term in Eq. (1)], and hence in less negative values of J. To be more precise, the energies of the two SOMOs do not change appreciably when the molecule is boat-distorted, whereas only the ϕ_u orbital is seen to increase in energy upon chair distortion, thus reducing the gap as shown in Figure 4 (right-hand panel). The increase in energy of ϕ_u with increasing γ results from mixing of the out-of-plane lone-pair orbital of the oxalato bridge π_u (**8**), which is allowed by symmetry in the chair but not in the boat distortion. In contrast, the ϕ_g orbital, which is allowed by symmetry to combine with π_u for the boat distortion, does not mix with it appreciably, and therefore its energy remains practically unchanged by each distortion.



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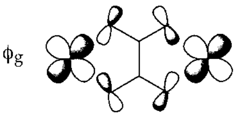

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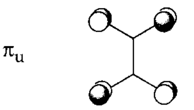

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Finally, we have analyzed the distortion towards a tetrahedral geometry of the Cu atoms (**6**) and found that it induces changes smaller than 0.1 cm^{-1} in the value of J for changes in the angle α of up to 10°. However, if the latter distortion is carried to its extreme, with the two Cu atoms in a tetrahedral environment ($\alpha = 90°$), the coupling becomes much less antiferromagnetic ($J_{calc} = -106$ cm^{-1}).

Evaluation of the one- and two-electron contributions: An interesting question concerns the analysis of our results obtained with the simple HTH model.[4] How good is the hypothesis, usually employed in qualitative theoretical studies, that the two-electron terms in Equation (1) are practically constant when small structural distortions occur? For this purpose the gap between the two SOMOs has been extracted from our DFT calculations on the triplet. We restrict the present analysis to the most important structural distortion, namely the displacement of the copper atoms from the basal planes. The coupling constant calculated for different values of h_M is plotted (Figure 5) as a function of the corresponding values of $(\varepsilon_1 - \varepsilon_2)^2$, and show a clear linear dependence, as expected from the HTH model. Although one cannot assume that similar results should be found for other magneto-structural correlations, these results suggest that there is a sound theoretical basis for the qualitative application of the HTH model.

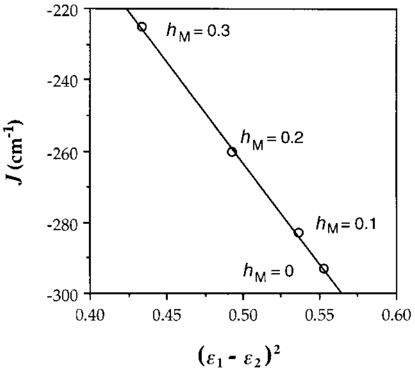

Figure 5. Singlet–triplet energy splitting, J, calculated for $\{[(NH_3)_2Cu_2(\mu\text{-}C_2O_4)Cu(NH_3)_2](NH_3)_2\}^{2+}$ as a function of the separation between the two SOMOs $(\varepsilon_1 - \varepsilon_2)$ [eV^2] in the triplet state when the copper atoms are moved out of the basal plane. The magnitude of this displacement [Å] is indicated for each point on the curve.

A least-squares fitting of the calculated data to Equation (1) allows us to obtain numerical estimates for the two-electron terms: $2K_{ab} = +17.4$ cm^{-1} and $(J_{aa} - J_{ab}) = 1.78 \times 10^5$ cm^{-1}. The value of K_{ab} is especially interesting, since it gives an estimate of the maximum possible ferromagnetic interaction ($J = 2K_{ab}$) predicted by the HTH model when the two SOMOs are degenerate (i.e., when $\varepsilon_1 - \varepsilon_2 = 0$). Our numerical estimate of $2K_{ab}$ for the oxalato-bridged Cu^{II} compounds indicates that only weak ferromagnetic coupling should be expected in the most favorable case within this family. However, it should be remembered that in order to obtain a numerical estimate in this way we have arbitrarily assumed that the linear behavior observed for the calculated data (Figure 5) can be extrapolated to the point $\varepsilon_1 - \varepsilon_2 = 0$. Estimates for these values obtained by Daudey et al. with an ab initio perturbative CI approach and a set of orthogonalized orbitals are $2K_{ab} = 1440$ cm^{-1} and $J_{aa} - J_{ab} = 1.27 \times 10^5$ cm^{-1}. In an earlier study of fluoro-bridged Cu^{II} compounds[46] and in our recent study of hydroxo- and alkoxo-bridged Cu^{II} compounds,[22] similar values for $J_{aa} - J_{ab}$ ($\approx 1.0 \times 10^5$ cm^{-1}) were obtained. However, differences in the values of K_{ab} obtained in different ways make it highly desirable to pursue further a feasible method of calculating as precisely as possible an average value for a particular family of compounds. No experimental evidence for strongly ferromagnetic oxalato-bridged Cu^{II} has yet been reported, in good agreement with the small limiting value of K_{ab} found in our calculations; only weak ferromagnetic coupling has been reported for Cu^{II} oxalato-bridged dimers or chains in which every two neighboring copper ions are connected in a parallel arrangement (**2c**) with J values of 0.3, 0.67 and 1.22 cm^{-1}.[47–49] A small positive J value (approximately $+1$ cm^{-1}) was also found in an oxalato-bridged copper(II)–vanadyl complex in which the magnetic orbitals, (x^2-y^2) for Cu^{II} and xy for V^{IV}, are orthogonal since they belong to different irreducible representations.[50] An interesting synthetic target would be a compound with different coordination spheres for the two Cu atoms, designed to give orthogonal SOMOs, in order to achieve the most favorable situation for a ferromagnetic coupling. One such possibility would be a compound with one Cu atom in a square-planar or square-pyramidal environment, and the other Cu atom in a tetrahedral conformation ($\alpha = 90°$ in **6**). The topology of the SOMOs in that case indicates that they are strictly orthogonal; hence $J = 2K_{ab}$. We have performed a calculation for such a hypothetical structure, obtaining a coupling constant $J = +23$ cm^{-1}, in good agreement with the above estimate of $2K_{ab} = +17$ cm^{-1}.

Conclusion

In this contribution we have applied a recently developed computational strategy to investigate exchange interactions in oxalato-bridged copper(II) complexes. Our results for model compounds indicate that the topology of the two SOMOs is a key factor in determining the magnitude of the magnetic exchange. A maximum antiferromagnetic coupling ($-300 > J > -400$ cm^{-1}) is achieved when both $d_{x^2-y^2}$-type SOMOs lie on the same plane as the bridging oxalate ligand. For the least favorable case, with both SOMOs in planes perpendicular to the oxalate, very weak antiferromagnetic coupling ($J \approx -10$ cm^{-1}) is expected. These findings are fully confirmed by calculation of the coupling constants for four selected complete structures, for which excellent agreement between calculated and experimental data is obtained.

The effect of several structural distortions has been analyzed for a model compound with a coplanar arrangement of the two SOMOs, showing that the most important changes in J are related to the displacement of the Cu atoms away from their basal planes. A structural correlation was also found between the degree of bending of the basal planes (γ) and the out-of-plane displacement of the copper ions (h_M). The accuracy of the method used in this work for the evaluation of coupling constants, together with its moderate demand for computer time, opens up novel routes towards the ab initio prediction of the magnetic behavior of new compounds.

Appendix

Calculations for the model compounds $[Cu_2(\mu\text{-}C_2O_4)(NH_3)_6]^{2+}$ were carried out with the following structural parameters: Cu–O = 1.98 Å; large Cu–O = 2.18 Å; $Cu\text{–}N_{eq}$ = 2.01 Å; $Cu\text{–}N_{ax}$ = 2.40 Å; N–H = 1.05 Å; C–C = 1.56 Å; C–O = 1.25 Å; Cu-O-C = 110°; C-C-O = 117°; Cu-N-H = 109°; O-Cu-N = 93.2°. For the models including halide ligands we have replaced one ammonia molecule by the corresponding halide, with the following bond distances: Cu–F = 1.85 Å; Cu–Cl = 2.25 Å; Cu–Br = 2.356 Å; Cu–I = 2.594 Å.

Acknowledgments: The computing resources at the Centre de Supercomputació de Catalunya (CESCA) were generously made available through a grant of Fundació Catalana per a la Recerca. Financial support for this work was provided by DGYCIT through project number PB95-0848-C02-01. Additional support came from CIRIT through grant 1995SGR-00421. The positive interaction between the French and Spanish researchers has been facilitated by the Acción Integrada Hispano–Francesa number 1995-88B. J.C. thanks the Ministerio de Educación y Ciencia for a doctoral grant. The visit of M. V. to Barcelona was made possible by courtesy of Iberdrola, through its Profesores Visitantes Iberdrola de Ciencia y Tecnología program.

Received: June 30, 1997 [F743]

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[5] Note that this expression corresponds to the use of the Heisenberg hamiltonian $\mathcal{H} = -JS_1S_2$ for the fitting of the experimental susceptibility data. In other instances the hamiltonian used is $\mathcal{H} = -2JS_1S_2$, for which the singlet–triplet gap in Equation (1) is $E_S - E_T = 2J$.

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