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Theoretical study of the exchange coupling in copper(II) binuclear compounds with oxamidate and related polyatomic bridging ligands†

Joan Cano,[a] Eliseo Ruiz,[b] Pere Alemany,[c] Francesc Lloret[a] and Santiago Alvarez[b]

[a] *Departament de Química Inorgànica, Universitat de València, Doctor Moliner 50, Burjassot, Spain*
[b] *Departament de Química Inorgànica and Centre de Química Teòrica, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain*
[c] *Departament de Química Física and Centre de Química Teòrica, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain*

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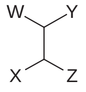
A theoretical density functional study of the exchange coupling has been carried out for binuclear copper(II) compounds with oxamidate and related bridging ligands: oxalate, oxamate, ethylenetetraamidate, dithiooxamidate, dithiooxalate, tetrathiooxalate, bipyrimidine and bisimidazole. Model calculations have been used to examine the influence of the donor atoms at the bridging ligand and of the ligands' orientation on the coupling constant. Estimates for the singlet–triplet gap of complete structures of *cis*- and *trans*-oxamidato-bridged complexes are reported. Comparison of these results with those obtained from qualitative models provides some insight into the limits of applicability of these methods for the study of magnetostructural correlations.

One of the most appealing features in the field of molecular magnetism is the ability of a bridging ligand to provide a pathway for exchange coupling between two transition metal atoms that are far apart.[1–3] In this regard, a largely explored set of bridging ligands are those formally derived from the oxalate dianion **1**, where W, X, Y and Z can be O, NR or S. Previous semiempirical molecular orbital studies[4,5] have indicated that the substitution of oxalato oxygen atoms by less electronegative ones should result in an enhanced antiferromagnetic interaction. In recent papers we have presented a computational approach to the calculation of exchange coupling constants, based on the use of density functional theory (DFT) and discussed *ab initio* approaches presented by other authors. Good quantitative approximations to known experimental values have been obtained for homobinuclear complexes, including hydroxo- and alkoxo-bridged[6,7] copper(II) compounds, azido-bridged complexes of Cu^{II}, Ni^{II} and Mn^{II},[8] as well as for several heterobinuclear complexes.[9] A study of copper(II) complexes with the oxalate bridge showed that a good theoretical description of the exchange coupling in systems with extended bridges can also be obtained with that methodology.[10]



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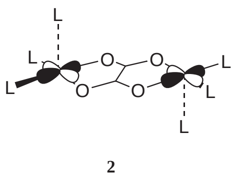

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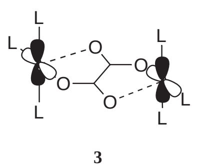

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The aim of the present work is to explore the ability of such a computational approach to reproduce the effects of chemical substitution at the oxalate bridging ligand on the exchange coupling between copper(II) ions, and to predict the behavior of some still unknown members of this family. In a previous study[10] we looked at different co-ordination environments around the Cu atoms in oxalato-bridged complexes, and found that strong antiferromagnetic coupling results only when the short copper–ligand bonds are coplanar with the bridging ligand. In such case, the singly occupied molecular orbitals (SOMOs) are built up from metal d orbitals well oriented to interact with the bridging ligand (**2**). On the other hand, when one of the copper–bridge distances is long (**3**), the interaction between the highest energy d orbitals through the bridge is poor and weak coupling results. Therefore, in this paper we will consider only those complexes with the coplanar topology in which the oxygen atoms of the oxalate bridge are partially or totally substituted by S atoms or NR groups. With this restriction in mind, we present the results of DFT calculations on model compounds of general formula $[(H_3N)_3Cu(\mu\text{-}C_2WXYZ)Cu(NH_3)_3]^{2+}$ (W, X, Y, Z = NH, O or S) in an attempt to obtain semiquantitative estimates of the effect of chemical substitution at the bridge donor atoms. We also studied how the participation of the donor atoms in an aromatic system affects the exchange coupling, taking as examples the bipyrimidine and bisimidazolate bridging ligands. For the case of the oxamidato bridge (W = Z = NH; X = Y = O), the effect of the orientation of the substituent and of the position of the terminal ligands on the exchange coupling constant has also been analysed. Finally, we will discuss the results obtained for five unmodelled complexes.

Computational methodology

A detailed description of the computational strategy adopted in this work has been given elsewhere[6] and is only briefly summarized here. For the evaluation of the coupling constant of each compound, two separate DFT calculations[11] are carried out, one for the triplet and another one for a broken-symmetry singlet state. The hybrid B3LYP method[12] has been used in all calculations as implemented in GAUSSIAN 94,[13] mixing the exact Hartree–Fock exchange with Becke's expression for the exchange[14] and using the Lee–Yang–Parr correlation

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† *Supplementary data available*: structural and magnetic data and references. For direct electronic access see http://www.rsc.org/suppdata/dt/1999/1669/, otherwise available from BLDSC (No. SUP 57523, 11 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/dalton).

Table 1 Calculated exchange coupling constants (cm^{-1}) for the model compounds $[Cu_2(\mu\text{-}C_2WXYZ)(NH_3)_6]^{2+}$ with different bridging ligands (**1**), and ranges of experimental values for complexes with the analogous bridges

Bridge	W[a]	X[a]	Y[a]	Z[a]	$-J_{calc}$[b]	$-J_{exp}$[c]	Ref.
Oxalate	O	O	O	O	293	284–402	24–38
Oxamate	NR	O	O	O	312	400–425	4, 39, 40
cis-Oxamidate	NR	NR	O	O	360	242–453	41–43
	NR	O	NR	O	347		
trans-Oxamidate	NR	O	O	NR	356	305–591	4, 43–63
Ethylenetetraamidate	NR	NR	NR	NR	358		
cis-Dithiooxalate	S	S	O	O	485		
	S	O	S	O	465		
trans-Dithiooxalate	S	O	O	S	391		
cis-Dithiooxamidate	NR	NR	S	S	504		
	NR	S	NR	S	553		
trans-Dithiooxamidate	NR	S	S	NR	473	523–730	64–66
Tetrathiooxalate	S	S	S	S	829	>800	23
Bipyrimidine	NR	NR	NR	NR	98	139–236	67–73
Bisimidazole	NR	NR	NR	NR	44		

[a] R = H for calculated values, φ = 120° (see **4**). [b] This work. [c] Detailed information is available as supplementary data (SUP no. 57523).

functional.[15] We have previously found that, among the most common functionals, the B3LYP method combined with the broken-symmetry[16–19] treatment (abbreviated as B3LYP-bs hereafter) provides the best results for calculating coupling constants.[6] A basis set of triple-ζ quality[20] was used for the Cu atoms in the calculations of the full structures, and of double-ζ quality[21] for Cu atoms in the model calculations as well as for other atoms in all calculations.

We choose to evaluate the coupling constant J from the calculated energies of the high spin (triplet) and broken-symmetry states according to expression (1) where S is the total

$$J = 2(E_{BS} - E_{HS})/S(S+1) \qquad (1)$$

spin for the high spin state, E_{BS} and E_{HS} are the calculated energies for the broken-symmetry and high spin states, respectively. For a discussion of the relationship between E_{BS} and the energy of the singlet state the reader is referred to recent papers by us and other authors.[9,22]

We note that the *experimental* values of the coupling constant J are usually obtained by fitting the spin hamiltonian to the temperature-dependent magnetic susceptibility data, measured in the solid state. Under such conditions, the structure of the molecules can suffer deviations from the optimum gas phase geometry due to *packing* forces. Since such small structural differences can result in significant 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.

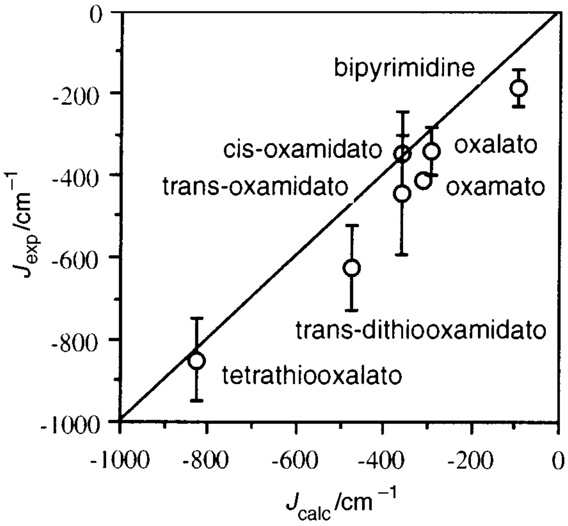
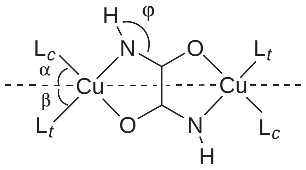


Fig. 1 Ranges of experimental exchange coupling constants for different families of binuclear copper(II) compounds with bridges of type **1**, represented as a function of the calculated value for the corresponding model compound (Table 1).

Influence of the bridging donor atoms

The calculated values of the singlet–triplet gap for the different model complexes $[(H_3N)_3Cu(\mu\text{-}C_2WXYZ)Cu(NH_3)_3]^{2+}$ with polyatomic bridges **1** analogous to the oxalate anion (W, X, Y, Z = NH, O or S) are presented in Table 1. The range of reported experimental values for each family of compounds is also given for comparison. It must be noted first that the model calculations predict in all cases an antiferromagnetic behavior, as experimentally found. Furthermore, the model calculations give a good approximation to the upper limit for the experimental values of J in each family of compounds. We note that in a previous study[7] of hydroxo-bridged copper(II) complexes we found that the simplifications adopted in the model compounds can affect the calculated values of J by as much as 150 cm^{-1}. A scatter plot (Fig. 1) nicely illustrates the good semi-quantitative description achieved with the model calculations. The calculated values confirm the qualitative trend established by Verdaguer and co-workers[4,23] using semiempirical extended Hückel theory for this family of bridging ligands, that progressive substitution of oxygen by less electronegative donor atoms such as nitrogen or sulfur results in increasingly stronger antiferromagnetic coupling. The exception to this rule comes from the aromatic bridging ligands bipyrimidine and bisimidazole, which show much weaker coupling than the analogous non-aromatic ligand, ethylenetetraamidate. Although a large part of the variation in the values of J can be attributed to the electronegativity of the donor atoms, the wide range of values experimentally found within each family of compounds clearly indicates that other factors are affecting the extent of the exchange coupling to a significant degree.

In contrast to the effect of substitution of donor atoms, which accounts for changes in the coupling constant of up to 600 cm^{-1}, different substitution patterns for the same set of donor atoms affect the values of J by less than 90 cm^{-1}. Hence, the different isomers of the oxamidato bridging ligand give quite similar values of $|J|$ (347–360 cm^{-1}). The differences are larger among the isomers of dithiooxalate (391–485 cm^{-1}) and dithiooxamidate (473–553 cm^{-1}). The fact that the bipyrimidine and bisimidazolate bridging ligands give much weaker antiferromagnetic coupling ($J = -98$ and -44 cm^{-1}, respectively) than the model non-aromatic ligand ethylenetetraamidate ($J = -358$ cm^{-1}) is associated to the delocalization of the lone pair orbitals throughout the aromatic system, resulting in poorer overlap with the metal d orbitals. The effect of the decreased overlap is a smaller splitting of the SOMOs, found in our calculations to be of 3373, 3151 and 8151 cm^{-1} for bipyrimidine, bisimidazolate and ethylenetetraamidate, respectively. Further evidence for such enhanced delocalization will be presented below when discussing the spin density distribution.



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Notice that we are adopting some crude approximations in the model compounds that deserve some discussion. (i) All terminal ligands are substituted by ammonia molecules. Changes in the nature of one terminal ligand (*e.g.* from F$^-$ to I$^-$) induce changes in J as large as 60 cm^{-1} for the oxalato-bridged complexes,[10] and even the substitution of one hydrogen by a carbon atom[7] in a NH$_3$ ligand shifts the calculated J to negative values, hence the analogous modelling at the bridging atoms is likely to affect the calculated coupling constant to a larger extent. (ii) The bond distances and angles are kept fixed in the idealized structures. The orientation of the substituent R (measured by the angle φ) and other structural parameters (**4**) may have a significant influence on the coupling constant, as will be discussed in more detail below. (iii) The substituents at the donor N atoms are replaced by hydrogen. For the copper(II) hydroxo-bridged complexes we have shown[7] that each hydrogen substituted for a carbon atom at the terminal amine ligands decreases the value of the calculated antiferromagnetic coupling constant by about 10 cm^{-1}. Hence, the analogous modelling at the bridging atoms is likely to affect the calculated coupling constant to a larger extent. (iv) The counter ions are not included in the calculations, but when weakly bound to the two Cu atoms they usually induce a shift of the calculated J toward positive values. In summary, the present calculations are not aimed at obtaining quantitative estimates of the values of the coupling constant, but rather at detecting the trends in this parameter along the family of the bridging ligands topologically equivalent to the oxalate anion.

Magnetostructural correlations for oxamidato-bridged compounds

The effect of the orientation of the substituent at the bridging nitrogen atoms in the oxamidato-bridged complexes is studied in this section. We also study how the orientation of the terminal ligands influences the magnitude of the exchange coupling constant. The effects of other distortions (such as the out of plane displacement of the Cu atoms, or the angle between the plane of the bridging ligand and the basal plane of the copper co-ordination sphere) were previously analysed using semiempirical calculations for oxalato- and bipyrimidine-bridged copper(II) compounds,[5,74] and with the present B3LYP-broken symmetry approach for oxalate complexes.[10]

When modelling the compounds with one or more nitrogen donor atoms a question that arises is which orientation to choose for the substituent (taken in our models as a hydrogen atom). We note that experimental values for such angles (φ in **4**) are found in the range 110–127° for the *trans*-oxamidato-bridged complexes. We have calculated the coupling constant for the model oxamidato complex at different values of φ, while keeping the rest of the structure fixed. A minimum is found at $\varphi = 115°$, both in the singlet and in the triplet state, although angles as large as 125° require only 2.5 kcal mol^{-1}. In the experimental structures, though, the substituent at the N donor is usually a pendant arm bearing another donor atom that occupies a terminal co-ordination position, thus forming a chelate ring. Hence, the value of φ is not determined by the electronic preference of the CNR group in the oxamidato ligand, but rather by the strain of the chelate ring. We have therefore calculated the dependence of the singlet–triplet gap on the angle φ (Fig. 2), and found that the antiferromagnetic coupling is made stronger upon increasing φ. Although the changes in the calculated J are not very large, the trend is consistent with the variations that appear in the experimental data. Notice that the corresponding structures can be classified in two groups, depending on whether the substituent at the N atom forms a five- or six-membered chelate ring, which appears to be the factor that determines the value of φ. The dependence of J on φ can be attributed to changes in the degree of hybridization and in the orientation of the nitrogen lone pair orbitals, as schematically depicted in **5**.

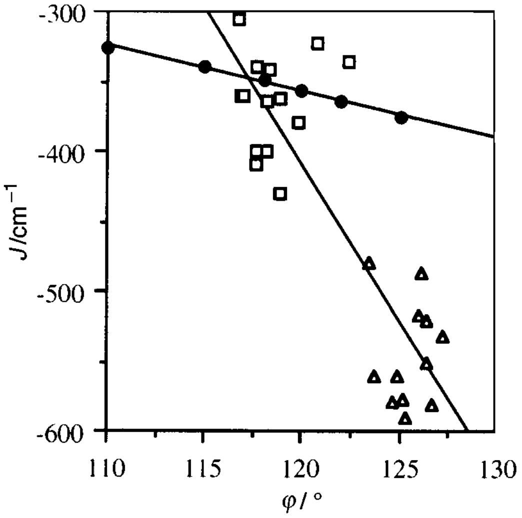
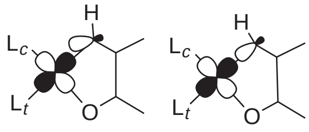


Fig. 2 Calculated J (dark circles) as a function of the HNC bond angle φ (see **4**) for the *trans*-oxamidato-bridged copper(II) model complex and experimental values for related compounds in which the N and O donors form five- (triangles) or six-membered (empty squares) chelate rings. For experimental values and references see supplementary data (SUP no. 57523).



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Although our calculations show a dependence of J on φ that qualitatively reproduces the experimental trend, the calculated J vary much less with φ than the experimental values. For example, experimental changes in φ of about 10° account for a difference in the calculated J values of about 40 cm^{-1}, while differences of up to 300 cm^{-1} are experimentally observed (Fig. 2). This fact suggests that other structural factors such as the position of the terminal ligands (defined by the angles α and β in **4**) also affect the coupling constant to a significant degree. Model calculations in which the bond angle α is varied while the rest of the geometry is kept frozen indicate that antiferromagnetism is enhanced for larger values of α (Fig. 3, circles). The simultaneous variation of the position of the two terminal ligands has a similar effect (Fig. 3, squares). In the experimental structures the *trans*-oxamidato-bridged complexes with five-membered chelate rings have larger values of α (55–60°) than those with six-membered chelate rings (40–45°), but similar values of β. Hence, the orientation of the terminal ligands in the former case favors a stronger antiferromagnetic coupling, reinforcing the influence of the orientation of the substituent at the bridging nitrogen (angle φ) discussed above. These two

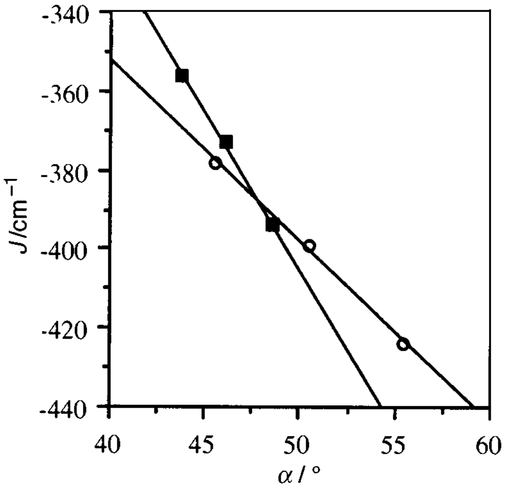
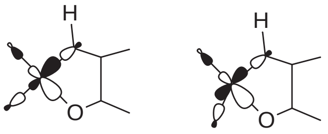


Fig. 3 Calculated exchange coupling constant for the *trans*-oxamidato-bridged binuclear compound **4** (W = Z = NH X = Y = O) as a function of the bond angle α with other bond angles frozen ($\beta = 42.5$, $\varphi = 124.5°$; circles), and as a function of α when β is simultaneously varied (with $\beta = \alpha$, $\varphi = 124.5°$; squares).

effects account for the different ranges of values of J experimentally found for the two families of chelates. The effect of the orientation of the terminal ligands is associated with the induced changes in the hybridization of the d orbitals that build up the SOMOs, as schematically illustrated in **6**: the larger the hybridization toward the bridging nitrogen atom, the stronger is the antiferromagnetic coupling, as expected from the Hay–Thibeault–Hoffmann model (see below). Such an effect results from the different electronegativity of the N and O donor atoms of the bridging ligand, that makes overlap between d_{xy} and the nitrogen lone pair orbital decisive in determining the gap between the two SOMOs.



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A non-negligible effect should also be ascribed to the small changes observed in the bond distances between the Cu atom and the bridging ligand. For the family with five-membered chelate rings, the Cu–N distance changes little (1.90–1.95 Å), and the same happens within the family with six-membered rings (1.95–1.98 Å), although the variation of the Cu–N distance between the extremes of the two series is large enough as to affect significantly the value of the coupling constant. However, test calculations carried out for the *trans*-oxamidato complex (with $\alpha = 55.5$, $\beta = 42.5$, $\varphi = 125°$) indicate that a change in the Cu–N distance from 1.98 to 1.90 Å shifts the value of J from -424 to -434 cm^{-1} only.

In summary, the large variation experimentally observed for the coupling constant within the family of oxamido-bridged copper complexes should be attributed to the joint effect of several structural parameters. Two of these, the orientation of the substituent and the position of the terminal ligands, are combined together in the experimentally known compounds due to the existence of chelate rings of different size involving the bridge substituent and one terminal ligand.

Calculations for full structures

Given the fact that several structural and constitutional factors affect the value of J in model calculations, direct comparison of such model calculations with experimental values is not straightforward. Hence, we have performed calculations for a few complete structures of oxamidato-bridged complexes (Table 2), to find that the agreement with the experimental values (average error of 148 cm^{-1}) is not better than that obtained with model calculations. This fact is surprising, since a good agreement between calculated and experimental values had been found for full structures in other families of compounds.[6,8,10] For compounds **A**–**D** the calculated and experimental J values differ by less than 120 cm^{-1}. Although such deviation is larger than those found for a variety of other binuclear complexes,[75] it is probably acceptable for strongly antiferromagnetic systems, especially if one considers the minute energy differences being calculated for big molecules such as **C**, that contains 64 atoms and 458 basis functions. Calculated coupling constants for compounds **E** and **F**, on the other hand, are off by more than 200 cm^{-1}. Notice also that the present results are comparable to those reported for two of the model complexes by Charlot *et al.*[76] through a perturbative treatment of the configuration interaction problem.

We note that the largest errors appear for complexes with pseudohalides (N_3^- or NCO^-) as terminal ligands. Therefore we decided to keep molecule **F** as in the experimental structure, but replaced the azido ligand by ammonia and the ethyl groups that connect bridging and terminal ligands by hydrogens. Surprisingly, the calculated J in that case (-439 cm^{-1}) is much closer to the experimental one. Even a model $[Cu_2(\mu\text{-oxamidate})(NH_3)_2(H_2O)_2]^{2+}$ with the same bond distances and angles as in the experimental structure gives a calculated J of -432 cm^{-1}. It might well be that the large error obtained for the full structure is associated with a poor description of the electronic structure in the presence of pseudohalide terminal ligands, but previous results for other systems with azido bridging and terminal ligands[8] make this an unconvincing explanation. Another possibility is that in the process of measuring the magnetic susceptibility data some structural changes have occurred to the compound and thus the reported coupling constant does not correspond to the crystal structure. This is a situation that has been found by some of us and other authors previously in a number of cases, either in exchange coupled binuclear complexes[77,78] or in spin crossover mononuclear systems,[79] and is mostly associated to the vacuum made in the sample compartment when cooling down to liquid helium temperatures.

Evaluation of the one- and two-electron contributions

In the light of our results, we discuss in this section the approximate expression deduced by Hay, Thibeault and Hoffmann[80] (referred to from here on as the HTH model) for the coupling constant of a binuclear complex with two unpaired electrons, eqn. (2). Here, ε_1 and ε_2 are the energies of

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

φ_1 and φ_2, the two SOMOs of the complex,‡ and K_{ab}, J_{aa}, and J_{ab} are two-electron integrals involving localized orthogonal versions of these orbitals. Of the two terms in eqn. (2), the first one can be interpreted as a ferromagnetic contribution to the magnetic exchange constant, responsible for the stability of the triplet state, while the second one represents an antiferromagnetic term favoring a singlet ground state.

Such an expression is very useful, since it provides a basis for explanation of the magnetic behavior, despite its little quantitative predictive ability. Hence, the dependence of the coupling

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‡ Notice that this expression corresponds to the use of the Heisenberg hamiltonian $H = -JS_1S_2$ employed for the fitting of the experimental susceptibility data. In other instances the hamiltonian used is $H = -2JS_1S_2$, for which the singlet–triplet gap in eqn. (2) is $E_S - E_T = 2J$.

Table 2 Experimental and calculated coupling constants (cm^{-1}) for complete structures of some oxamidato-bridged copper(II) binuclear complexes

Compound[a]	Refcode[b]	φ/°	$-J_{model}$[c]	$-J_{calc}$	$-J_{exp}$	Ref.
A *cis*-[Cu_2(apox)bipy][ClO_4]$_2$	dobfij	117	346	351	440	41
B *trans*-[Cu_2(apox)(N_3)$_2$]·$2H_2O$	licvic	119	353	465	362	55
C *cis*-[Cu_2(apox)(phen)(ClO_4)$_2$]	sucpub	117	346	376	453	42
D [Cu_2(bedox)][BPh_4]$_2$	cimaih	126	430	430	550	46
E *trans*-[Cu_2(dmeox)(NCO)$_2$(H_2O)$_2$]	pegsav	125	376	365	560	53
F *trans*-[Cu_2(dmeox)(N_3)$_2$(H_2O)$_2$]	yirmob	125	376	284	591	52

[a] Abbreviations: apox = *N,N*′-bis(3-aminopropyl)oxamidate-*N,N*′*,O,O*′ (also abbreviated by some authors as oxpn); bedox = bis(6-ethyl-3,6-diazaoctyl)oxamidate; bipy = 2,2′-bipyridine; dmeox = *N,N*′-bis[2-(dimethylamino)ethyl]oxamidate (also abbreviated by some authors as bdmox); phen = 1,10-phenanthroline. [b] The code with which each crystal structure is unequivocally identified in the Cambridge Structural Database. [c] Calculated for the model compound [$Cu_2(\mu\text{-}C_2WXYZ)(NH_3)_6$]$^{2+}$, using the experimental value of φ.

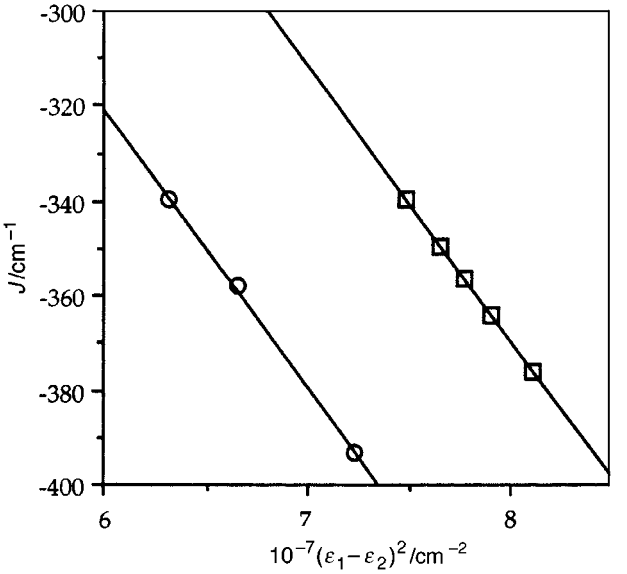

Fig. 4 Calculated exchange coupling constant as a function of the square of the energy gap between the two SOMOs for two different bridging ligands, oxamidate (squares) and ethylenetetraamidate (circles), as obtained by varying the bond angle φ. All values in cm^{-1}.

constant on structural parameters is generally supposed to arise from the one-electron term $(\varepsilon_1 - \varepsilon_2)^2$, while all two-electron terms are assumed to remain approximately constant within a family of analogous compounds. Therefore, a simple analysis of the dependence of the energy of the SOMOs on the structural parameters allows one to explain magnetostructural correlations in terms of such basic concepts as atomic electronegativity and orbital overlap. Such a qualitative approach, or a similar one proposed by Kahn,[76] has been employed by numerous researchers to explain qualitative trends in magnetostructural correlations.[5,23,81–84]

The present calculations offer the possibility of assessing the usual approximation that the two-electron terms in eqn. (2) (J_{aa}, J_{ab} and K_{ab}) are approximately invariant upon small structural distortions. For this purpose we have extracted the gap between the two SOMOs from our DFT results for the triplet state in the model *trans*-oxamidato- and ethylenetetraamidato-bridged complexes, at different values of the angle φ (**4**). The calculated coupling constant is then plotted (Fig. 4) as a function of the corresponding values of $(\varepsilon_1 - \varepsilon_2)^2$. A neat linear dependence appears in both cases, as expected from the HTH approximation [eqn. (2)]. These results are in keeping with a clear correlation found between the degree of participation of the copper 3d orbitals in the SOMOs and the value of J for the family of compounds reported in Table 1, confirming the orbital control of the coupling constant in these compounds. Although one cannot assume that similar results should be found for other magnetostructural correlations, the present findings suggest that there is a sound theoretical basis for the qualitative application of the HTH approximation. An intriguing result is that the two model complexes give practically the same estimate for $J_{aa} - J_{ab}$.

A least squares fitting of the calculated data using eqn. (1) allows us to obtain numerical estimates for the two-electron terms for the two model complexes analysed here (Table 3). The value of K_{ab} is especially interesting, since it provides a rough idea of the maximum possible ferromagnetic interaction ($J = 2K_{ab}$) predicted by the HTH model to correspond to strictly degenerate SOMOs (*i.e.* $\varepsilon_1 - \varepsilon_2 = 0$). Our numerical estimates of $2K_{ab}$ for the compounds under study in this paper are similar to those obtained previously for oxalato-bridged copper(II) compounds at a similar level of theory,[10] and predict that only weak ferromagnetic coupling should be expected in the most favorable case within these families, as compared to the much larger value estimated for the hydroxo-bridged copper(II) compounds.[6] Let us recall, however, that in order to obtain such a numerical estimate we have arbitrarily assumed that the linear behavior observed for the calculated data can be extrapolated to $\varepsilon_1 - \varepsilon_2 = 0$. No experimental evidence for strong ferromagnetic oxalato- or oxamidato-bridged copper(II) complexes has yet been reported, in good agreement with the small limiting value of K_{ab} found in our calculations. Only very weak ferromagnetic coupling has been found for copper(II) oxalato-bridged dimers or chains,[85–87] with J values of at most 1.2 cm^{-1}, although the orbital topologies of these compounds are different (*e.g.* **3**) to that discussed here (**2**). How much significance should be attached to these values is a question that requires a wider knowledge of such parameters than presently available. Clearly, the values of the analogous integrals obtained through *ab initio* calculations by other authors[76] differ by one order of magnitude from the present estimates, and further study of the factors that determine the two-electron terms and the development of efficient means of calculating them should provide a powerful tool for the design of exchange coupled systems.

To check if the Hay–Thibeault–Hoffmann approximation can be applied to the family of Cu^{II} with bridging ligands that differ in the donor set (*i.e.* **1**, where W, X, Y, Z = O, N, H or S), we have analysed the energy gaps between the two SOMOs for all the model compounds of Table 1, by comparing them to the corresponding estimate for J. A correlation consistent with eqn. (2) is found only for those molecules in which the two Cu atoms are symmetry related (*i.e.* W = Z, X = Y, or W = Y, X = Z) and the donor set is composed only of oxygen or nitrogen donor atoms. This result indicates that the two-electron terms in eqn. (2) are sensitive to the molecular symmetry as well as to important changes in the electronic structure attached to electronegativity perturbations (*i.e.* substitution of four O or N donors by four S donors).

Spin density distribution

Since there is a general belief that the spin density at the bridging atoms in binuclear complexes should be related to the sign and magnitude of the exchange coupling constant, we are systematically exploring the spin density distribution in the high-spin state of binuclear complexes.[88] The most relevant

Table 3 Estimated values of the two-electron contributions to the exchange coupling constant for three families of binuclear copper(II) complexes. All values in cm^{-1}

Bridge	$2\,K_{ab}$ DFT	$2\,K_{ab}$ *ab initio*	$J_{aa} - J_{ab}$ DFT	$J_{aa} - J_{ab}$ *ab initio*	Ref.
Oxalate	17	720	1.8×10^5	1.3×10^5	10, 76
Oxamidate	94		1.7×10^5		This work
trans-Dithiooxamidate		382		8.8×10^4	76
Ethylenetetraamidate	32		1.7×10^5		This work
OH^-	824		7.2×10^4		6
OR^-	599		6.1×10^4		6
N_3^-	1150 ± 300		$(1.4 \pm 0.4) \times 10^5$		8

Table 4 Calculated atomic spin densities for the triplet state of complexes of type $[Cu_2(\mu\text{-}C_2WXYZ)(NH_3)_6]^{2+}$ **1** with $\varphi = 120°$

W	X	Y	Z	Cu(WX)	Cu(YZ)	W	X	Y	C(WY)	C(XZ)
O	O	O	O	0.696	0.696	0.066	0.066	0.066	−0.003	−0.003
NH	O	O	O	0.684	0.700	0.092	0.078	0.066	−0.001	−0.004
NH	NH	O	O	0.665	0.697	0.100	0.100	0.068	0.000	0.000
NH	O	NH	O	0.678	0.678	0.112	0.070	0.112	0.000	0.000
NH	O	O	NH	0.686	0.686	0.087	0.075	0.075	−0.003	−0.003
NH	NH	NH	NH	0.672	0.672	0.083	0.083	0.083	0.010	0.010
S	S	O	O	0.542	0.783	0.170	0.170	0.026	−0.010	−0.010
S	O	S	O	0.626	0.626	0.159	0.051	0.159	−0.001	−0.001
S	O	O	S	0.629	0.629	0.158	0.058	0.058	−0.001	−0.001
S	S	NH	NH	0.546	0.809	0.173	0.173	0.010	−0.004	−0.004
S	NH	S	NH	0.609	0.609	0.165	0.083	0.165	−0.010	−0.010
NH	S	S	NH	0.607	0.607	0.080	0.163	0.080	0.000	0.000
S	NH	NH	S	0.607	0.607	0.163	0.080	0.080	0.000	0.000
S	S	S	S	0.557	0.557	0.147	0.147	0.147	−0.006	−0.006
Bipyrimidine				0.654	0.654	0.056	0.056	0.056	0.012	0.012
Bisimidazole				0.667	0.667	0.072	0.072	0.072	0.001	0.001

atomic spin densities obtained from our calculations on the triplet state of the molecules studied here are presented in Table 4. It is noteworthy that only 50 to 70% of the unpaired spin density is located at the Cu atoms, with the strongest delocalization corresponding to the S-bonded Cu atoms. The spin density at the bridging donor atoms is always positive and increases with decreasing electronegativity of that atom. The combined spin density at a copper atom and its two bridge donors is almost constant for the different compounds (0.84–0.89). Only for the bisimidazole (0.81) and bipyrimidine (0.77) bridges a larger amount of spin density is delocalized through the aromatic ring. This means that the covalence of the copper–terminal ligand bonds is little affected by the nature of the bridging ligand. The spin densities at the central atoms of the bridging ligands are small or negative in most cases, indicating that the spin delocalization and spin polarization mechanisms approximately cancel out.

The effect of the orientation of the bridge substituent (indicated by the angle φ) on the spin density distribution of the *trans*-oxamidate model compound, and its relationship with the coupling constant, are consistent with the above discussion on electron delocalization. Hence, the electron delocalization measured by the spin density at the bridging N atom is larger at $\varphi = 125°$ than at $\varphi = 115°$ ($\rho_N = 0.095$ and 0.085, respectively), and the antiferromagnetic coupling is also stronger in the former case ($J = -376$ and -340 cm^{-1}, respectively).

Concluding remarks

In this contribution we have applied a recently developed computational strategy to investigate exchange interactions in copper(II) complexes with oxamidate and related polyatomic bridging ligands. Model calculations of the exchange coupling constant for a series of complexes in which the bridging donor atoms are varied give a good approximation for the upper limit of the experimental values in each family of compounds. These results confirm previous qualitative studies that associated the changes in those values to the electronegativity of the bridging donor atoms. While the effect of substitution of the donor atoms accounts for changes of up to 600 cm^{-1} in the coupling constant, that parameter varies by less than 90 cm^{-1} for the isomers of a given bridging ligand. The bipyrimidine and bisimidazolate bridges give a poorer antiferromagnetic coupling as a result of the delocalization of the lone pair orbitals throughout the aromatic skeleton. Calculations for a few unmodelled oxamidato complexes predict a strong antiferromagnetic coupling in all cases, consistent with the experimental findings, although the calculated values do not reproduce the differences found among such complexes.

The effect on the coupling constant of the orientation of the substituent at the nitrogen donor atoms of the bridging ligand has been analysed for two model compounds, and the singlet–triplet gap is seen to be enhanced by larger φ angles. Also the orientation of the terminal ligands is seen to affect the magnitude of the coupling constant. Such angle dependences explain the stronger antiferromagnetic coupling observed for those complexes in which the bridging and terminal donors are forming five-membered chelate rings, compared to that for the six-membered chelate analogues. The magnetostructural correlations found are seen to be orbitally controlled, with the values of J depending on the square of the energy gap between the two SOMOs as originally proposed by the approximation of Hay, Thibeault and Hoffmann. The likelihood of finding ferromagnetic behavior within a family of compounds is analysed by obtaining an estimate of the exchange integral through that approximate expression of the exchange coupling constant.

In the model complexes studied the degree of unpaired electron delocalization associated with changes in the electronegativity of the bridging donor is seen to determine the spin density distribution at the copper and bridging donor atoms, whereas a tiny spin density at the carbonaceous backbone of the bridges is the result of opposing spin delocalization and spin polarization contributions. Delocalization of the lone pair orbitals throughout aromatic bridging ligands, such as bipyrimidine or bisimidazole, is reflected in a smaller spin density at the donor atoms, and in weaker antiferromagnetic coupling.

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