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Exchange Coupling in Halo-Bridged Dinuclear Cu(II) Compounds: A Density Functional Study

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A density functional study of exchange coupling in halo-bridged dinuclear copper(II) compounds has been carried out. Coupling constants calculated for full unmodeled structures, as determined by X-ray diffraction, are in excellent agreement with experimental data, confirming the ability of the computational strategy used in this work to predict the magnetic behavior of such compounds. Model calculations have been used to examine the influence of several factors on the coupling constant: the nature of the bridging and terminal ligands, the coordination environment around copper atoms, and some structural distortions frequently found in this family of complexes. A ferromagnetic coupling is predicted when N-donor terminal ligands are present, especially for bromo-bridged systems, an interesting synthetic target.

1. Introduction

The phenomenon of exchange coupling between the spins of unpaired electrons located on different metal atoms in polynuclear compounds leads to interesting magnetic behaviors. This coupling is termed intramolecular ferro- or antiferromagnetism, depending upon whether the individual spins in the ground state show a parallel or antiparallel alignment, respectively. Since the discovery of intramolecular antiferromagnetism in copper(II) acetate monohydrate in 1951,[1] much experimental and theoretical work has been carried out to elucidate the mechanism of exchange coupling in polynuclear complexes. Dinuclear systems have been in this respect the most frequent target, and their relative simplicity has permitted the proposal of some magnetostructural correlations that are very useful for predicting magnetic properties of new compounds. Such a work has led to the now well-established field of molecular magnetism, that is, the synthesis and the study of the magnetic behavior of materials based on molecular entities.[2−7]

Dinuclear copper(II) complexes with monatomic bridges have been extensively studied, especially those containing two hydroxo bridging ligands. This family of compounds shows a structural homogeneity which has made possible the establishment of relationships between magnetic properties and the structural parameters of the bridge.[8−12] On the other hand, the compounds with two halo bridges have also been comprehensively studied, but the structural variety is much larger, and the existence of a correlation between their magnetic behavior and the structural parameters is less obvious than for hydroxo-bridged compounds.

In dihalo-bridged Cu(II) complexes, the metal atoms are usually five- or four-coordinated with different types of terminal ligands, giving as a result a wide range of values for the coupling constant, which may even change its sign

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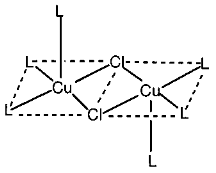
depending on these factors. When the metal atom is tetracoordinated by halide ions in a square-planar environment, antiferromagnetic coupling is found,[13−24] although in some cases the coordination environment around copper atoms is distorted toward a tetrahedral geometry because of the bulky counterions, thus changing the nature of the coupling from antiferromagnetic to ferromagnetic.[25,26] When the metal atoms are five-coordinated, the square-pyramidal environment is the most usual one, but a distortion toward a trigonal bipyramid can exist. Three different geometries of dinuclear dihalo-bridged Cu(II) complexes with square-pyramidal environment have been experimentally characterized: square pyramids sharing a basal edge (**1**), square pyramids sharing a base-to-apex edge with parallel basal planes (**2**), and square pyramids that also share a base-to-apex edge, but with perpendicular basal planes (**3**). The latter geometry, though, has been observed only in one case.[27]



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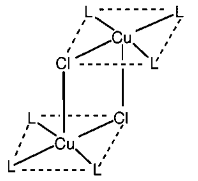

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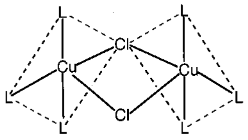

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As far as the magnetic properties are concerned, the compounds of type **1** show different magnetic behavior depending on the terminal ligands: when halide ions are present, the coupling is antiferromagnetic ($-30 < J < -100$ cm^{-1}),[13−18,20−24,28] whereas in the presence of N-donor ligands, the coupling is ferromagnetic ($J \sim +40$ cm^{-1}).[29] Compounds of type **2** show small coupling constants in all cases ($-10 < J < +10$ cm^{-1}),[30−37] and the only compound with geometry **3** known so far presents ferromagnetic coupling ($J = +43$ cm^{-1}).[27]

The large amount of synthesized and characterized dihalo-bridged Cu(II) complexes has led several authors to study the relationship between the exchange coupling constant and the molecular structure for this family of compounds. In particular, Willett et al.[20] found correlations between the experimental coupling constants and several structural parameters of the bridge region: the Cu−X−Cu bridging angle (**4**), the angle between the CuX_4 planes produced by a hinge distortion (**5**), the angle formed by the Cu_2X_2 plane that contains the bridge and the CuX_2 plane of the external X ligands (**6**), and the angle formed by the plane CuX_3, that contains one external X ligand, and the Cu_2X_4 plane (**7**). All the compounds considered by Willet are of the type $[Cu_2X_6]^{2-}$, with halide anions as terminal ligands. The $[Cu_2X_6]^{2-}$ complexes (X = Cl, Br) present a geometry that is strongly dependent on the nature of the countercation. When small counterions such as Li^+ or K^+ are present, the coordination environment of the copper atom is square-planar,[38,39] but in the presence of bulky cations such as Ph_4P^+ or Ph_4As^+, the coordination around copper is pseudotetrahedral (**6**).[25,40] A different magnetic behavior has been found for these two cases: the copper unpaired electrons are antiferromagnetically coupled for systems close to the square-planar limit but ferromagnetically coupled for those with a pseudotetrahedral geometry. Such a distortion has been extensively studied from the theoretical point of view. Hay et al. were the first ones to predict[41] in a qualitative way an antiferromagnetic coupling for both square-planar and tetrahedral coordination environments with a weaker coupling for intermediate geometries, in good agreement with experi-

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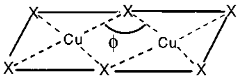
mental results. The same conclusion was reached later by Bencini and Gatteschi in their work within the density functional theory (DFT) framework[42] and by Caballol et al. by means of difference dedicated configuration interaction (DDCI) calculations.[43] Caballol and co-workers also studied the dependence of the coupling constant on the other structural parameters proposed by Willett and found a decrease of the antiferromagnetic coupling upon moderate distortion of the structure in the ways shown in **5** and **7**, in qualitative agreement with experimental data. Willett and co-workers also analyzed, within the extended Hückel framework, the effect of changing the nature of the terminal ligand on the coupling constant in copper(II) halide dimers,[44] finding a decrease of the antiferromagnetic coupling when the chloride and bromide terminal ligands are substituted by more electronegative O- or N-based ligands, in good agreement with experimental results.[45]



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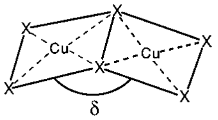

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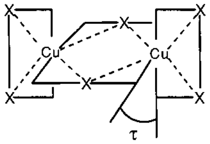

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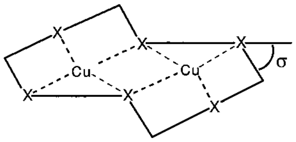

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Hatfield et al. studied compounds with geometry **2**, finding that the experimental coupling constant is correlated with the ϕ/R_0 ratio, where ϕ is the Cu−X−Cu angle and R_0 the longest Cu−X distance.[30] As stated previously, all these systems present minute coupling constants, and most of them are not dinuclear species but chain structures.

Although previous theoretical studies for dihalo-bridged Cu(II) dinuclear compounds have been reported,[41−44] there is still much work to be done because of the large structural variety of this family. The aim of this contribution is to examine the exchange coupling phenomenon for these compounds by applying a recently developed computational strategy that, as shown in our previous work,[46−55] is able to quantitatively reproduce the coupling constants for a great variety of compounds with different bridging ligands and/or paramagnetic centers. Coupling constants for a variety of full unmodeled structures as well as model calculations are reported, to examine the influence of several factors on the coupling constant, such as the nature of the bridging and terminal ligands, the coordination environment around copper atoms, and some structural distortions.

2. Computational Methodology

A detailed description of the computational strategy adopted in this work can be found elsewhere,[46,47,50,51,54] so we only briefly summarize its most relevant aspects. Using a phenomenological Heisenberg Hamiltonian, $\hat{H} = -J\hat{S}_1\cdot\hat{S}_2$, to describe the exchange coupling in a dinuclear compound, where J is the coupling constant, and S_1 and S_2 are the local spins on centers 1 and 2, respectively, the coupling constant J can be related to the energy difference between states with different spin multiplicity. For the case in which $S_1 = S_2$, the coupling constant may be obtained by using eq 1

$$E_{\mathrm{HS}} - E_{\mathrm{LS}} = -2JS_i(S_i + {}^1/_2) \qquad (1)$$

where E_{HS} and E_{LS} are the energies of the state with the highest and lowest total spin, respectively, and S_i is the local spin on each metal atom.

It has been found that, when using DFT-based wave functions, a reasonable estimate of the energy corresponding to the low spin state, E_{LS}, can be obtained directly from the energy of a broken-symmetry solution, E_{BS}.[50,56] In this case, introducing $S_i = {}^1/_2$ in eq 1, we arrive at the following expression for J:

$$J \approx E_{\mathrm{BS}} - E_{\mathrm{HS}} \qquad (2)$$

Experience has shown that this equation leads to a good agreement with experimental data for a large variety of compounds with exchange-coupled electrons.[46−48,50−55]

The hybrid, DFT-based B3LYP method[57] has been used in all calculations as implemented in Gaussian-94,[58] mixing the exact Hartree−Fock exchange with Becke's expression for the exchange functional[59] and using the Lee−Yang−Parr correlation functional.[60] Double-ζ quality basis sets[61] have been employed for all atoms.

3. Results and Discussion

3.1. Calculations for Full Structures. To check the accuracy of the computational procedure employed in this

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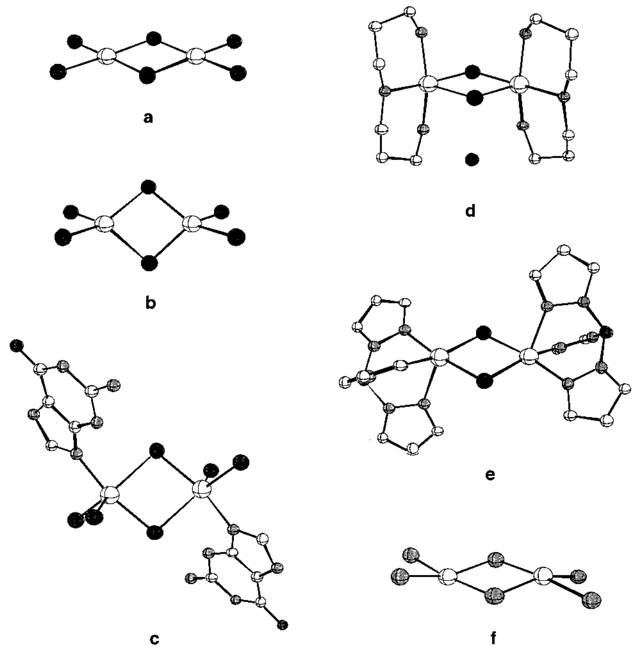

Figure 1. Crystal structures of chloro- and bromo-bridged dinuclear Cu(II) compounds whose coupling constants have been computed (Table 1). Large white spheres represent Cu atoms, large gray spheres, Br atoms, and black spheres, Cl atoms.

Table 1. Experimental and Calculated Coupling Constants for Complete Structures of Some Dichloro- and Dibromo-Bridged Dinuclear Cu(II) Complexes

compound[a]	structure	geometry	J_{calcd} (cm^{-1})	J_{expt} (cm^{-1})	ref
(DBTTF)$[Cu_2Cl_6]$	**a**	**1**	−93.6	−93.1	16
$(Ph_4As)_2[Cu_2Cl_6]$	**b**	**1**	+50.8	+45.1	25
$[Cu_2Cl_6(Gua)_2]\cdot 2H_2O$	**c**	**1**	−60.0	−82.6	28
$[Cu_2Cl_2(dpt)_2]Cl_2$	**d**	**3**	+47.7	+42.9	27
$[Cu_2Cl_2(TPB)_2]$	**e**	**1**	+16.1	+33.7	29
$(^{i}PrNH_3)_2[Cu_2Br_6]$	**f**	**1**	−87.7	−132	18

[a] Abbreviations: DBTTF = dibenzotetrathiafulvalene cation; Gua = guaninium cation; dpt = dipropylenetriamine; TPB = tris(1-pyrazolyl)borate anion.

Table 2. Computed Coupling Constants (cm^{-1}) for Model Structures **1**−**3** Using Different Cu−Cl Distances

	Cu−Cl (Å)	Cu−Cl−Cu (°)	1	2	3
	2.31	90.0	+73.9	+10.1	+52.9
	2.48	90.0	+52.3	+4.0	+42.1
opt **1**[a]	2.47	97.7	−3.5		
opt **2**[a]	2.41	96.6		+4.7	
opt **3**[a]	2.53	97.8			+17.2

[a] opt stands for optimized structures. Other structural parameters can be found in the Appendix, Table 4.

work for the family of dihalo-bridged dinuclear Cu(II) complexes, we have performed calculations for several complete structures, most of which correspond to chloro-bridged complexes, and one to a bromo-bridged system. The structures for which the coupling constant has been computed represent the great structural variety found in this family of compounds (Figure 1). For dichloro-bridged complexes, we have considered structures in which the metal atom is either four- or five-coordinated, having in each case different coordination environments, and structures that are more or less distorted from the ideal geometry. We have only considered one complete structure of a dibromo-bridged complex, because most known dibromo compounds with experimentally measured coupling constants are not dinuclear, but chain structures.

We note that the experimental magnetic susceptibility used to obtain the coupling constant is measured from solid samples in which packing forces can induce small deviations from the minimum energy geometry of the individual molecules. So as to be able to compare our computed coupling constants for complete structures, we have used in our calculations the molecular structure as determined experimentally by X-ray diffraction rather than an optimized one, in which small changes with respect to the experimental structure could result in significant deviations of the calculated coupling constant.

The results (Table 1) show that the agreement between calculated and experimental coupling constants is excellent for this family of compounds (average error of 16 cm^{-1}), and the sign of the coupling constant is well reproduced in all cases. The largest absolute difference between experimental and calculated values, 44 cm^{-1}, corresponds to the bromo-bridged complex. However, considering that the coupling constants are obtained as energy differences that are calculated from total energy values 8 or 9 orders of magnitude larger, this maximum deviation should be considered as fair.

3.2. Exchange Coupling in Chloro-Bridged Compounds. After verifying the good agreement between calculated and experimental values of *J* for unmodeled structures, we analyze now the effects of different factors on the coupling constant by performing calculations on a model system. We have replaced the terminal ligands present in experimental structures by ammonia molecules and considered idealized structures (geometrical details for the model structures can be found in the Appendix). First, we analyze the influence of the molecular geometry on the coupling constant, and then, we study magnetostructural correlations for the distortions most frequently found in these compounds. Finally, we look at the effect of the terminal ligands on the coupling constant.

(a) Influence of the Geometry on the Exchange Coupling. As previously mentioned, three types of geometry have been experimentally characterized for this family of compounds, that differ in the way in which the metal atoms are connected (**1**−**3**). The structural parameters have been kept constant in the three models to study only the effect of the geometry on the coupling constant. For each geometry, two different Cu−Cl distances have been chosen: 2.31 Å, which corresponds to the average distance for the experimental structures of type **1**, and 2.48 Å, which is the distance for the only known structure of type **3**. The calculated coupling constant is positive in all cases (first and second rows in Table 2) but is much larger for geometries **1** and **3** than for **2**, in good agreement with experimental results.[31,32,36,37]

These results can be rationalized within the framework of the qualitative model proposed by Hay, Thibeault, and Hoffmann (HTH).[41] These authors obtained an approximate expression for the coupling constant of a homodinuclear complex with two unpaired electrons, eq 3. The first term in eq 3 ($2K_{ab}$) is positive and can be interpreted as a ferromagnetic contribution to the exchange coupling constant, responsible for the stability of the triplet state, whereas the second one is negative and represents an antiferromagnetic term favoring the singlet state.

$$E_S - E_T = J = 2K_{ab} - \frac{(\epsilon_1 - \epsilon_2)^2}{J_{aa} - J_{ab}} \tag{3}$$

Here, ϵ_1 and ϵ_2 are the energies of the two SOMOs of the complex, φ_1 and φ_2, whereas K_{ab}, J_{aa}, and J_{ab} are two-electron integrals involving localized orthogonal versions of the SOMOs. We have calculated the values of K_{ab} for the three geometries considered from the virtual β orbitals of the triplet state (unoccupied magnetic spin-orbitals, UMSOs), because the α spin density is located on more than two orbitals, whereas the HTH model was deduced considering only two orbitals. This approximation has been used previously by ourselves[62,63] and by other authors.[64] K_{ab} increases and ($\epsilon_1 - \epsilon_2$) decreases from **2** to **3** to **1**, while the values of J increase in the same order, but no clear correlation exists between these parameters and the calculated coupling constants.

On the other hand, we have also calculated the coupling constant for the optimized structures with geometries **1**−**3,** so as to be able to compare their relative stabilities and whether the results for J are similar to those obtained with models. The optimized structures differ a bit from the models used, with the metal environment distorted toward a trigonal bipyramid in geometries **2** and **3** and with slightly longer Cu−Cl bonds and larger Cu−Cl−Cu angles (Table 2). The calculated coupling constants show a significant change with respect to those obtained for model systems, but this is because the optimized structural parameters are considerably different from the ones used in the models, especially the Cu−Cl distances and the Cu−Cl−Cu angles that play an important role in the exchange coupling mechanism. The most stable geometry is **2**, in good agreement with the large number of known compounds that adopt this structure,[30−33,36,37,65,66] but geometries **3** and **1** are only 3.2 and 5.1 kcal/mol higher in energy, respectively.

(b) Magnetostructural Correlations. The experimental structures of chloro-bridged dinuclear Cu(II) compounds often deviate from the ideal geometries adopted in our model compounds, being distorted in a similar way to that observed for the optimized structures. In this section, we analyze the effect of the most common distortions on the coupling constant using model compounds with ammonia molecules as terminal ligands.

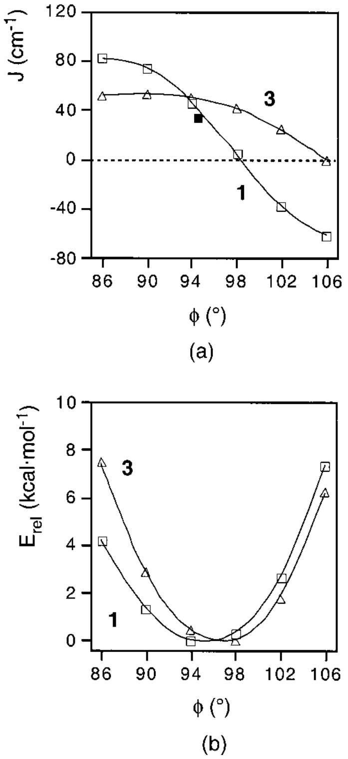

Figure 2. (a) Dependence of the coupling constant J on the Cu−Cl−Cu bridging angle ϕ for geometry types **1** (□) and **3** (△) of the model compound $[Cu_2Cl_2(NH_3)_6]^{2+}$, for a Cu−Cl distance of 2.31 Å. ■ corresponds to the experimental compound of type **1** with such a Cu−Cl distance.[29] (b) Relative energy of the ferromagnetic state at the different steps of the distortion.

Effect of the Bridging Angle. First of all, we have studied the dependence of the coupling constant on the Cu−Cl−Cu bridging angle for geometry types **1** and **3**, keeping the Cu−Cl distance and all other structural parameters fixed. Two Cu−Cl distances have been probed: 2.31 and 2.48 Å. The same behavior is observed regardless of the Cu−Cl distance: the ferromagnetic coupling decreases when the Cu−Cl−Cu bridging angle increases (Figure 2a). The nature of the coupling changes from ferro- to antiferromagnetic at an angle of approximately 98° for geometry **1**, but at a much larger angle for geometry **3** (∼106°).

The energy of the triplet state varies little within the whole range of bridging angles considered (less than 8 kcal/mol), presenting its minimum for structures with angles between 94° and 98° in geometries **1** and **3** (Figure 2b), in good agreement with the experimental data. The only known compound of type **1** whose coupling constant has been experimentally measured, $[Cu_2Cl_2(TPB)_2]$ (TPB = tris(1-pyrazolyl)borate),[29] presents an average Cu−Cl distance of 2.31 Å and a bridging angle of 94.5° and fits well into the theoretical magnetostructural correlation (Figure 2a). On the other hand, the angle of about 97° obtained for the minimum energy structure of type **3** is in disagreement with the experimental value found for the only known structure of this type, 91.4°. However, it is seen from Figure 2b that only about 2 kcal/mol are needed to reach such a structure. Modelization of terminal ligands and/or crystal packing

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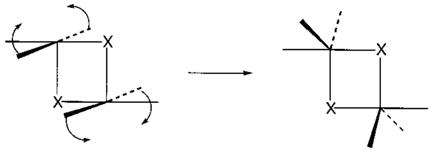
forces within the solid state could be responsible for such a disagreement between the theoretical gas phase structure and the experimental one.

Effect of the Bond Distance. We have also studied the dependence of the coupling constant on the Cu−Cl distance for structures of type **1**, keeping the bridging angle (94°) and other structural parameters constant. When the Cu−Cl distance decreases from 2.51 to 2.11 Å, the coupling constant increases from +29 to +113 cm^{-1}. The strongest ferromagnetic coupling corresponds to the shortest Cu−Cu distance (3.09 Å), and thus, we can infer that the superexchange mechanism is more important than the direct mechanism, even at such short distances. If this were not the case, the coupling would become more antiferromagnetic upon decreasing the Cu···Cu distance. The energy of the triplet state changes extensively within the range of Cu−Cl distances considered (about 60 kcal/mol), the most stable structures being those with the longest Cu−Cl distances (from 2.31 to 2.51 Å).

Effect of the Coordination Geometry. A common distortion from the ideal structure that is found for dinuclear five-coordinated Cu(II) compounds with two chloride bridges is one that changes the coordination environment of the Cu atoms from square-pyramidal to trigonal-bipyramidal.[27,28,67−72] We have studied the effect of this distortion on the coupling constant for geometries **2** and **3**. The degree of this type of distortion (**8** and **9** for each of the geometries, respectively) can be described within the formalism of continuous symmetry measures.[73,74] The two ideal structures for a pentacoordinate complex are the trigonal bipyramid (TBP) of D_{3h} symmetry and the square pyramid (SP) of C_{4v} symmetry.[75] Intermediate geometries can be described by the departure of their geometry from that of the ideal structures. In this work, we use the trigonal-bipyramidal symmetry measure S(TBP) to characterize distorted structures. Because the ideal trigonal bipyramid is not uniquely defined (any $M-L_{ax}/M-L_{eq}$ ratio gives a trigonal bipyramid with D_{3h} symmetry), we arbitrarily choose the equidistance trigonal bipyramid as the reference shape for evaluating S(TBP). An equidistance trigonal bipyramid will thus have S(TBP) = 0, while the S(TBP) value for an equidistance ML_5 square pyramid with the M atom on the plane formed by four ligands is 7.34. The pentacoordinated structures considered in this work show S(TBP) values that range from 6.53 for the structure closest to the square pyramid to 1.28 for that closest to the trigonal bipyramid. Departures from the values corresponding to the ideal polyhedra are due to the different M−L distances found in our structures. In our models, the Cu−Cl distance (2.48 Å), the Cu−L distance (2.00 Å), and the Cu−Cl−Cu bridging angle (98°) have been kept constant.



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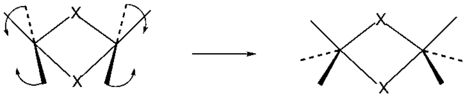

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For type **2** compounds, the coupling constant decreases moderately (from +16 to −3.2 cm^{-1}) when the square-pyramidal environment changes to trigonal-bipyramidal, in agreement with experimental results.[28,67,69] However, for the same change of coordination environment, a moderate ferromagnetic coupling builds up (from −0.3 to +16 cm^{-1}) for compounds with geometry of type **3**. The most stable structure corresponds to an intermediate geometry, S(TBP) = 2.21, in agreement with the optimized structures previously presented (S(TBP) for optimized **2** and **3** are 1.61 and 1.37, respectively). The structures corresponding to the square-pyramidal and trigonal-bipyramidal coordinations are about 4 and 11 kcal/mol above the energy minimum, respectively, regardless of the geometry type **2** or **3**.

(c) Influence of the Terminal Ligands on the Exchange Coupling Constant. An interesting relationship between the electronegativity of the coordinating atom in the terminal ligand and the strength of the antiferromagnetic coupling was found out by Willett within the extended Hückel framework.[44] These results are in agreement with experimental data, because a decrease of the antiferromagnetic coupling is seen when halide terminal ligands are subtituted by N-donor ligands.[27−29,45,76]

The effect of changing the terminal ligands not directly involved in the superexchange pathway has been studied theoretically in other families of compounds. For oxalato-bridged compounds,[52] an increase in the electronegativity of the equatorial terminal donor atoms results in a stronger antiferromagnetic coupling. The effect is inverted, however, when the replacement is at the axial position. For hydroxo-bridged compounds,[46] the strength of the antiferromagnetic coupling shows the same trend as the basicity of the ligand, whereas this trend is reversed for oximato-bridged compounds.[54] To explain the observed shifts in the coupling constant, a detailed analysis of the SOMOs for each particular case is needed, and no general rules can be established.

The model structure considered in this section differs sligthly from that used previously, because the Cu atoms are in the present case square-planar four-coordinated, as found in compounds with halide terminal ligands that we

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Table 3. Values[a] for Model Compounds $[Cu_2Cl_2L_2]^{2+}$

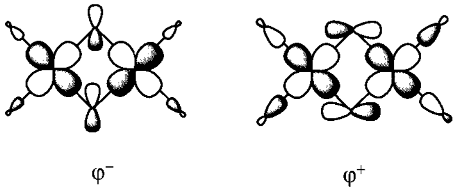
	L = en	L = NH_3	L = bipy
J (cm^{-1})	49.0	49.4	89.0
$\epsilon^+ - \epsilon^-$ (cm^{-1})	917	821	−189
pK_b	4.07	4.75	8.77

[a] Calculated exchange coupling constants, J; energy splitting between SOMOs, $\epsilon^+ - \epsilon^-$; and the experimental pK_b values for such terminal ligands. Cu−Cl−Cu bridging angle is 94°.

want to study here. To check the effect of the fifth ligand, we have computed the coupling constant for alternative models in which the Cu atom is four- or five-coordinated, keeping the same structural parameters (Cu−Cl = 2.31 Å and Cu−Cl−Cu = 94°) and using ammonia molecules as terminal ligands. The results, +46 and +49 cm^{-1} for square-pyramidal and square-planar environments, respectively, show the small influence of the axial ligand. This small change can be understood considering that the orbital that bears the unpaired electron is in the basal plane of the square pyramid, and its mixing with the orbitals of the apical ligand is very small for symmetry reasons.

We have studied the effect on the coupling constant of different terminal N-donor ligands, and these results have then been compared with those for chloride terminal ligands. The computed coupling constants obtained for the square-planar model structures, together with experimental pK_b values and computed SOMO energy splittings for different terminal ligands, are shown in Table 3.

It can be seen that models with ethylenediamine and ammonia as terminal ligands show a weaker ferromagnetic coupling than that with bipyridine. These results can be explained, in a qualitative manner, by means of the energy splitting of the SOMOs. For model compounds with en and NH_3, the lowest energy SOMO is the out-of-phase combination of the metal orbitals φ^- (**10**), and the energy differences between the two SOMOs are of the same order for both compounds (Table 3). On the other hand, for the model compound with bipy, the in-phase combination of the metal orbitals φ^+ (**10**) is more stable than φ^-, but the energy gap between them is about 1 order of magnitude smaller than in the model compounds with en and NH_3. In agreement with the HTH model, eq 3, the compound with bipy, with a smaller orbital gap, should present a stronger ferromagnetic coupling if we consider as a first approximation that the two-electron integrals appearing in eq 3 remain roughly constant when changing the terminal ligands.



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Because there is a considerable amount of known chloro-bridged Cu(II) dinuclear compounds with chloride anions as terminal ligands,[13−18,25,26] it is also interesting to study the effect on J of replacing N-donor ligands by chloride anions. The calculations show that a change from ferromagnetic to antiferromagnetic behavior occurs when the N-donor terminal ligands are substituted by chloride anions, in good agreement with experimental results. A value of −59 cm^{-1} is found for the four-coordinated model structure with a Cu−Cl_{term} distance of 2.00 Å, and a sligthly weaker coupling is found (−30 cm^{-1}) for the experimental Cu−Cl_{term} distance of 2.26 Å. The energy gap between SOMOs is slightly larger than in the case of N-donor ligands, in good agreement with the calculated antiferromagnetic behavior. However, comparison of the orbital energy gaps between the two families of compounds is not straightforward, because the two-electron integrals in eq 3 are strongly affected by the substitution of the donor atoms of the terminal ligands.

We have also studied the effect of the terminal chloride anions on the coupling constant for geometry type **3**, in which the Cu atom is five-coordinated. For a Cu−Cl distance of 2.48 Å and a Cu−Cl−Cu bridging angle of 90°, there is a moderate decrease of the ferromagnetic coupling (from +42 to +26 cm^{-1}) when the ammonia molecules are replaced by chlorides, showing that this effect is not as important as for the case of square-planar compounds.

3.3. Exchange Coupling in Fluoro- and Bromo-Bridged Compounds.

(a) $[Cu_2X_2(NH_3)_4]^{2+}$ Systems (X = F, Cl, and Br). The effect of the bridging ligands on the coupling constant has been also studied, replacing chloro by fluoro or bromo bridging ligands. A square-planar model structure with average experimental distances has been considered (see the Appendix for the geomerical details), using ammonia molecules as terminal ligands, and a range of bridging angles from 90° to 102° was explored. A different behavior is observed depending on the bridging ligand: A ferromagnetic coupling ($J \approx 100$ cm^{-1}) is found through the whole range of angles considered for the bromo-bridged compound, whereas the chloro- and fluoro-bridged systems become antiferromagnetic at large angles (Figure 3a). This effect is more important for the fluoro-bridged compound, for which antiferromagnetism is predicted even at 94°.

An analysis of the energy of the triplet states for the different structures shows that the minimum energy for chloro- and bromo-bridged systems is found between 94° and 98°. For fluoro-bridged systems, on the contrary, this minimum is found at larger angles, about 102° (Figure 3b). The amount of energy needed to change the aforementioned angle a few degrees is, however, not considerable. The only compound with this type of geometry with a measured coupling constant, $[Cu_2F_2(mppzH)_4](BF_4)_2$ (mppzH = 3-methyl-5-phenylpyrazole),[76] fits very well in the trend obtained for the computed values of J (black square in Figure 3a). The average Cu−F distance for this compound is 1.92 Å, and the Cu−F−Cu bridging angle, 98.9°, consistent with those used in the model.

To check the validity of the model structures that have been used through this analysis, partial geometry optimiza-

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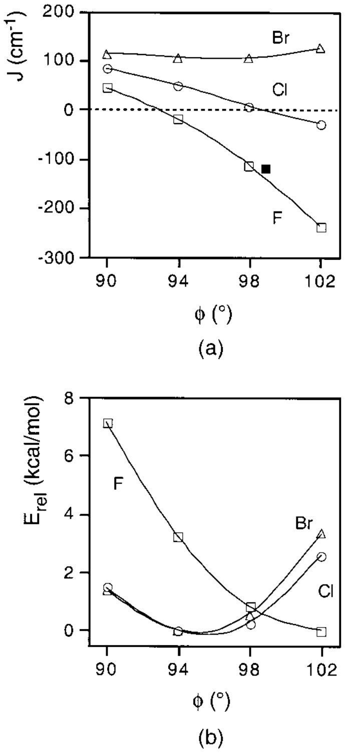


Figure 3. (a) Dependence of the coupling constant J on the Cu−X−Cu bridging angle ϕ for square-planar model compounds $[Cu_2X_2(NH_3)_4]^{2+}$, where X = F (□), Cl (○), or Br (△). ■ corresponds to the only known experimental fluoro-bridged compound.[76] (b) Relative energy of the ferromagnetic state at the different steps of the distortion.

tions for the parameters of the bridge have been performed for each system. The optimal Cu−X distances and Cu−X−Cu bridging angles are shown in the Appendix (Table 5). The coupling constants computed for each optimized structure (−282, −7.7, and +86.5 cm^{-1} for X = F, Cl, and Br, respectively) are in agreement with the values obtained in the previous magnetostructural correlation (Figure 3a).

(b) $[Cu_2X_6]^{2-}$ Systems (X = F, Cl, and Br). Given the considerable amount of experimental data available for compounds containing the $[Cu_2X_6]^{2-}$ anions, we have considered it appropriate to analyze the variations of the exchange coupling constant when simultaneously changing the halide ions at the bridging or at the terminal positions. We have used model systems with the same Cu−X$_{bridge}$ distances as for the model with ammonia terminal ligands, but with average experimental Cu−X$_{term}$ distances (see Appendix, Table 5). The computed coupling constants obtained for a wide range of Cu−X−Cu bridging angles are shown in Figure 4.

It is seen that bromo compounds present a more pronounced antiferromagnetic coupling than chloro and fluoro complexes for the whole range of bridging angles, although for larger values a crossing is predicted. Up to 100°, compounds with bromide are more antiferromagnetic than those with chloride, in agreement with experimental results (data and references in the Appendix, Table 6), represented as black circles (chloro) and black triangles (bromo) in Figure 4. The calculated energy shows a similar behavior as in the previous case: the minimum for bromo and chloro compounds is found at smaller values of bridging angles (about 98°) than for the fluoro ones (about 102°), and the energy needed to distort the structure is minute (less than 4 kcal/mol to change the angle in a range of about 8°).

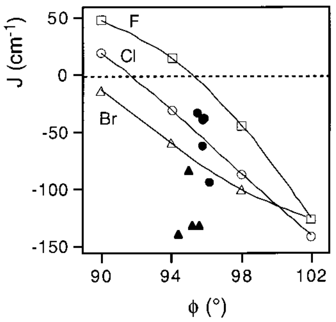
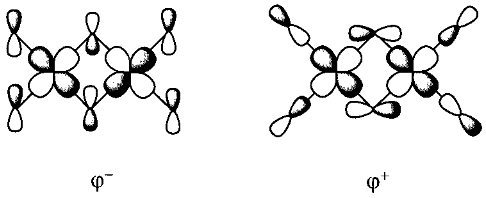


Figure 4. Dependence of the coupling constant J on the Cu−X−Cu bridging angle ϕ for square-planar model compounds $[Cu_2X_6]^{2-}$, where X = F (□), Cl (○), and Br (△). ● and ▲ correspond to experimental values for chloro- and bromo-bridged compounds, respectively (see Appendix, Table 6).

Finally, we have studied the influence of the X$_{term}$−Cu−X$_{term}$ angle on the coupling constant. For each structure within the range of bridging Cu−X−Cu angles analyzed, we have performed an optimization for the X$_{term}$−Cu−X$_{term}$ angle, keeping all other structural parameters constant. It is found that this parameter only varies about 4° when the bridging angle changes from 90° to 102°, but there are no significant variations either in the values of the computed coupling constants or in the relative energies of the structures. Thus, the influence of the X$_{term}$−Cu−X$_{term}$ angle on the coupling constant is negligible.

It is very interesting to note here the totally different behavior of the coupling constant when N-donor terminal ligands are replaced by halide anions. In the former case, the coupling is ferromagnetic for most of the systems considered, whereas our calculations predict antiferromagnetic coupling when halide terminal ligands are present. An especially interesting case is that of the bromo-bridged compounds, in which strongly ferromagnetic coupling is found for the range of Cu−Br−Cu angles considered in $[Cu_2Br_2(NH_3)_4]^{2+}$ (Figure 3a), but moderately antiferromagnetic coupling results in $[Cu_2Br_6]^{2-}$(Figure 4). A possible reason for such a dramatic change in the magnetic coupling is the very different topology of the orbitals of the donor atom within the SOMOs in each case. The π-basic character of the halides must play an important role in the exchange coupling of $[Cu_2Br_6]^{2-}$ systems, because there is a significant change in the shape of the SOMOs at the terminal positions, especially in the out-of-phase combination (**11**) compared to $[Cu_2Br_2(NH_3)_4]^{2+}$ (**10**).



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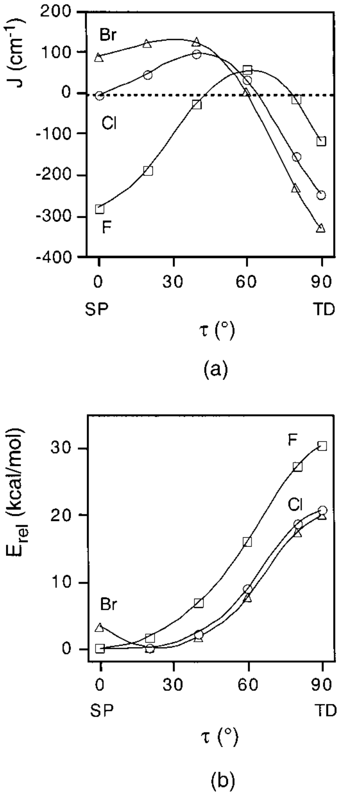


Figure 5. (a) Dependence of the coupling constant *J* on the τ angle (see **12**) for model compounds $[Cu_2X_2(NH_3)_4]^{2+}$ (X = F, Cl, or Br). (b) Relative energy of the ferromagnetic state at the different steps of the distortion. SP stands for square-planar, and TD, for tetrahedral coordination environments of the Cu atom.

Table 4. Structural Parameters Used for Model Compounds $[Cu_2Cl_2(NH_3)_6]^{2+}$ with Geometries **1**−**3** and Some of Their Optimized Values[a]

	model (**1**−**3**)	opt **1**	opt **2**	opt **3**
Cu−Cl	2.31/2.48	2.47	2.41 (eq) 2.80 (ax)	2.53 (eq) 2.58 (ax)
Cu−N	2.00	2.06 (eq) 2.19 (ax)	2.05	2.05
N−H	1.02			
Cu−Cl−Cu	90	97.7	96.6	97.8 (eq) 95.0 (ax)
trans-N−Cu−N	180		153.4	150.0
Cl−Cu−N	90	156.8 (eq)	168.2 (eq)	171.0 (eq)
Cu−N−H	109			

[a] Distances are in angstroms, and angles, in degrees.

Table 5. Structural Parameters Used for Model Compounds $[Cu_2X_2(NH_3)_4]^{2+}$ (X = F, Cl, and Br) and Some of Their Optimized Values[a]

	F	Cl	Br
Cu−X	1.91	2.31	2.44
Cu−X (opt)	1.94	2.38	2.54
Cu−N	2.00	2.00	2.00
$Cu-X_{term}$	1.95	2.26	2.35
N−Cu−N	90	90	90
Cu−X−Cu (opt)	101.8	97.2	96.8

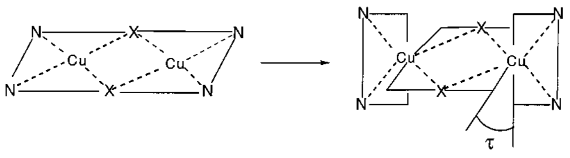
[a] Distances are in angstroms, and angles, in degrees.

Table 6. Experimental Coupling Constants and Cu−X−Cu Bridging Angles for Compounds with the $[Cu_2X_6]^{2-}$ Anion (X = Cl and Br) Represented in Figure 4 along with Their References

compound[a]	Cu−X−Cu (°)	J_{expt} (cm^{-1})	ref
(DBTTF)$[Cu_2Cl_6]$	96.2	−93.1	16
$K_2[Cu_2Cl_6]$	96.0	−38	15
(melH$_2$)$[Cu_2Cl_6]$	95.8	−38	23
(morphH)$_2[Cu_2Cl_6]$	95.8	−61	13
$(^iPrNH_3)_2[Cu_2Cl_6]$	95.5	−32	24
$K_2[Cu_2Br_6]$	95.6	−132	13, 21
$(Me_2NH_2)_2[Cu_2Br_6]$	95	−83	20, 22
$(^iPrNH_3)_2[Cu_2Br_6]$	95.2	−132	18
$(Et_2NH_2)_2[Cu_3Br_8]$	94.4	−139	19

[a] Abbreviations: DBTTF = dibenzotetrathiafulvalene cation; melH$_2$ = melaminium cation; morphH = morpholinium cation.

(c) Magnetostructural Correlation: Distortion from Square-Planar to Tetrahedral Coordination. Because of the wealth of theoretical work reported for this type of distortion in $[Cu_2X_6]^{2-}$ complexes,[41−43] we will limit our study of this distortion to another family of related compounds, the halo-bridged dinuclear Cu(II) complexes with ammonia molecules as terminal ligands. The calculations have been performed using model structures with optimized parameters in the bridge region (see Appendix, Table 5). The structural parameter that describes this distortion is the angle τ formed by the Cu_2X_2 and the CuN_2 planes (**12**). τ = 0° corresponds to a square-planar coordination, and τ = 90°, to a tetrahedral coordination.



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An increase of the calculated ferromagnetic coupling constants is observed when coordination environments between the two limits (τ = 40° or 60°) are considered, regardless of the halide bridge (Figure 5a). For fluoro-bridged systems, the antiferromagnetic coupling (about −300 cm^{-1}) found for square-planar systems (τ = 0°) becomes ferromagnetic (about +50 cm^{-1}) for a distorted structure with τ ≈ 60°. For chloro- and bromo-bridged compounds, the maximum coupling corresponds to structures with τ ≈ 40° (Figure 5a). When the coordination environment is tetrahedral (τ = 90°), the unpaired electrons are coupled antiferromagnetically regardless of the halide bridge considered.

The lowest energy structure is the one with square-planar coordination (τ = 0°), except for bromo-bridged complexes for which the minimum corresponds to τ = 20° (Figure 5b). Less than 7 kcal/mol is needed to distort it from τ = 0° to 50°, in good agreement with the experimental structures that present a τ angle within this range.[25,40] In the three cases, the energy becomes unattainable for larger τ angles, being greater than 20 kcal/mol for tetrahedral coordination environments.

From the results obtained in this magnetostructural correlation, we think that it would be interesting to synthesize bromo or chloro dinuclear Cu(II) compounds with N-donor terminal ligands so as to get new compounds with ferromagnetic behavior.

4. Concluding Remarks

In this contribution, we have applied a recently developed computational strategy to investigate exchange interactions in dihalo-bridged Cu(II) dinuclear complexes. The influence on the coupling constant of several factors related to the nature of the bridging and terminal ligands, the coordination environment around the copper atoms, and structural distortions of a given geometry have been analyzed through calculations using model structures. Dichloro-bridged compounds have been more thoroughly studied, showing that the most important factors that influence the coupling mechanism are the following: (i) the way both copper atoms are connected, (ii) the structural variations in the bridging region, and (iii) the nature of the terminal ligands. An important result is that the presence of N-donor terminal ligands seems to favor ferromagnetic coupling, whereas replacement by halide anions results in antiferromagnetic behavior. We have also seen a decrease in the ferromagnetic coupling when the Cu−Cl−Cu bridging angle increases, regardless of the model structure considered. The accuracy of the method used in this work, together with its moderate demand for computer time, has also allowed us to investigate the effect of the nature of the halide bridge on the coupling constant, as well as that of a structural distortion experimentally found for the related $[Cu_2X_6]^{2-}$ family of compounds. A completely different magnetic behavior is seen when changing the nature of the terminal ligands, especially for bromo-bridged compounds: moderate ferromagnetic coupling is found for N-donor terminal ligands, but antiferromagnetic coupling for halide anions. It is also interesting to stress the enhancement of the ferromagnetic coupling found for structures presenting coordination environments between square-planar and tetrahedral in the $[Cu_2X_2(NH_3)_4]^{2+}$ family, in analogy with the previous results for $[Cu_2X_6]^{2-}$ compounds. This family of compounds is suggested as an interesting synthetic target, because it might present ferromagnetic coupling between the unpaired electrons.

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Appendix

The bond lengths and angles of model compounds used throughout this work, along with the most characteristic structural parameters obtained from geometry optimizations are shown in Tables 4−6.

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