Structural Modeling and Magneto−Structural Correlations for Hydroxo-Bridged Copper(II) Binuclear Complexes

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The influence of the simplifications introduced by modeling a molecular structure on the exchange coupling constant is studied for hydroxo-bridged Cu(II) binuclear complexes. This study focuses on the role of the terminal ligands and the counterions. The terminal ligands are responsible for marked changes in the exchange coupling constant, depending on their donor properties, while the counterions have an effect only when directly coordinated to the copper atoms. The study of the magneto−structural correlations for the hydroxo-bridged Cu(II) binuclear complexes has been extended by analyzing the influence of the Cu−O distance, the effect of the asymmetry at the bridging backbone, and the hinge distortion of the bridge. The increase in the Cu−O distance and the absence of the hinge distortion of the Cu_2O_2 ring substantially enhance the antiferromagnetic interaction.

1. Introduction

Bridged binuclear complexes of first-row transition metals have received much attention recently because of their condensed-phase magnetic properties.[1,2] One of the most extensively studied families from an experimental point of view is that of hydroxo-bridged Cu(II) binuclear complexes.[3,4] These compounds are also of particular interest from a theoretical point of view, since they provide examples of the simplest case of magnetic interaction involving only two unpaired electrons. These complexes exhibit ferromagnetic or antiferromagnetic character depending on their geometry. Hatfield and Hodgson found a linear correlation between the experimentally determined exchange coupling constant ($2J$) and the Cu−O−Cu bond angle (θ).[5] An antiferromagnetic character is found for complexes with θ larger than 98°, while ferromagnetism appears for smaller values of θ. Recently, we studied[6] the dependence of the exchange coupling constant for the hydroxo-bridged complexes on the molecular geometry using density functional calculations and found the same correlation with the Cu−O−Cu angle. Another structural feature that has a crucial role in the determination of the exchange coupling constant is the out-of-plane displacement of the hydrogen atom of the hydroxo group. If this atom is retained on the molecular plane, the magnetic behavior is predicted to remain antiferromagnetic for the whole range of the Cu−O−Cu bond angle. However, we found a correlation between the two structural parameters (both theoretically and experimentally), showing that small values of the Cu−O−Cu bond angle appear combined with large out-of-plane displacements of the hydrogen atom, resulting in a ferromagnetic character for these complexes.

Several theoretical approaches have been followed to study the magnetic behavior of molecular complexes, ranging from the qualitative method proposed by Hay et al.,[7] which analyzes the energy splitting between the two orbitals bearing unpaired electrons, to the more elaborate quantitative determinations of the $2J$ value using *ab initio* methods.[8−13] One of the crucial points in these computational studies is the choice of a model for the compound under study. This simplification is used within the semiempirical approaches to facilitate the analysis of the molecular orbitals, while in the case of the *ab initio* methods it is mandatory because the current technology does not allow handling of systems with a large number of atoms. This prevents direct comparison between the calculated magnetic constants using model structures with the experimental values. In a recent work, we proposed a computational strategy,[6] based on density functional theory,[14] that allows direct calculation of the exchange coupling constant with a good level of accuracy for the complete structure of molecular complexes with as many as 100 atoms. The complete structures were not optimized to allow comparison with the experimental coupling constant because very small variations of the geometry can induce large changes in the magnetic behavior, and the value of the coupling constant for an optimized structure can be notably different from that obtained for the experimental one, even if the two structures are similar.

In the analysis of magneto−structural correlations, it is useful to employ model structures because the main aim in this case is to study the variations of the magnetic behavior with structural

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parameters rather than to calculate the coupling constant. However, it is always interesting to determine the ability of these model structures to reproduce the exchange coupling constant of the complete structure. The model structures also offer the possibility of checking the approximation introduced by using the same geometry for the singlet and triplet states in the calculation.

The aim of this work is to study the influence of the simplifications introduced by modeling a molecule on the calculated exchange coupling constant for the family of hydroxo-bridged Cu(II) binuclear complexes. Furthermore, we analyze the effect of the geometry optimization for the singlet and triplet states on the calculated magnetic constant in model structures. Finally, we extend the study of the magneto−structural correlations for these complexes by analyzing the influence on the nature of the magnetic exchange of (i) the Cu−O distance, (ii) the effect of the asymmetry on the metal-bridge bonds, and (iii) the hinge distortion of the M_2O_2 core.

2. Computational Details

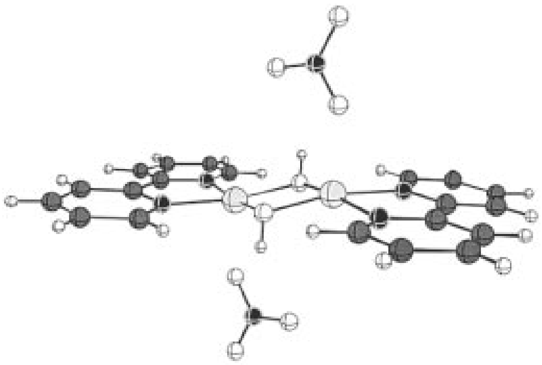
The exchange coupling constant for the hydroxo-bridged Cu(II) complexes was evaluated by calculating the energy difference between the singlet (S) and triplet (T) states (using $H = -2JS_1S_2$)

$$E_T - E_S = -2J \qquad (1)$$

Positive values of the coupling constant J indicate a triplet ground state (i.e., ferromagnetic character). For negative values of J, the singlet state is lower in energy, leading to antiferromagnetic behavior. All the calculations were performed using the double-ζ basis set proposed by Ahlrichs et al.,[15] with the help of the Gaussian 94 program.[16] The adiabatic connection method using three parameters proposed by Becke (B3LYP)[17] was used, mixing the Hartree−Fock contribution for the exchange with generalized gradient approximation functionals.[18,19] The presence of low-energy singlet states near the lowest singlet state makes the evaluation of its energy difficult within a single-determinant method. To solve this problem, Noodlemann et al.[20−22] proposed a broken-symmetry approach. Although the broken-symmetry wave function is a not pure spin state, we have used its energy as an approximation to that of the singlet state, which corresponds to the strong bonding regime proposed by Noodleman et al.[23] In a previous study, we found, after evaluating several functionals, that the B3LYP method combined with the broken-symmetry approach (indicated as B3LYP-bs in what follows) provides the best results for the calculation of coupling constants.[6]

3. Results and Discussion

3.1. Modeling of Hydroxo-Bridged Cu(II) Binuclear Complexes. We have investigated the effects of modeling the hydroxo-bridged Cu(II) complexes by performing calculations for the complexes $[Cu(bipy)(\mu\text{-}OH)]_2(NO_3)_2$ (**1**)[24] and $[Cu(t\text{-}meen)(\mu\text{-}OH)]_2Br_2$ (**2**).[25] The choice of these compounds covers a wide range of situations, since they present ferromagnetic and antiferromagnetic character, respectively. In the case of complex **1**, the counterions are close to the Cu atoms and the terminal ligand is an aromatic N-donor, while, in **2**, the counterions do not interact with the Cu atoms and an aliphatic amine acts as terminal ligand.



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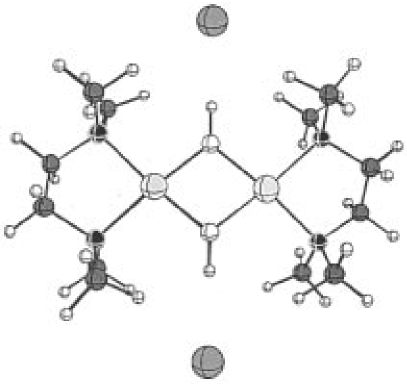

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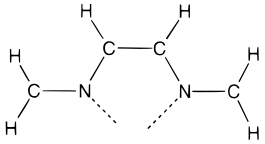
The calculated exchange coupling constants for complexes **1** and **2** and related models are shown in Table 1. Let us first check the influence of the nature of the terminal ligand. Later, we will analyze the effect of the counterions. The results for the different models of the ferromagnetic compound (**1**) show that a model of the bipy ligand as in **3a** (where the donor N atoms have the same environment as in bipy) yields practically the same result as with the whole bipy ligand. The lack of the two additional C atoms directly bonded to the donor N atoms (ligand **3b**) causes an increase of +40 cm^{-1} in the 2J value. Substitution of bipy by amines, such as ethylendiamine or ammonia, results in a decrease in the 2J value of 47 and 26 cm^{-1}, respectively, as compared to the complete structure. For the models of the antiferromagnetic complex (**2**), a clear decrease in the antiferromagnetic coupling results as the substituents of the N atom are excluded. In brief, the replacement of each substituent on the N-donor atoms by H raises the value of 2J by about +10 cm^{-1}. The conclusion regarding both series of results is that the strength of the antiferromagnetic coupling shows the same trend as the basicity of the terminal ligand: tmeen ($pK_b = 3.29$) > en ($pK_b = 4.07$) > NH_3 ($pK_b = 4.75$) > aromatic N-ligand ($pK_b = 8.77$).



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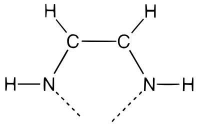

3b

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Table 1. Exchange Coupling Constants $2J$ (cm^{-1}) Calculated as the Singlet−Triplet Energy Difference Using the B3LYP-bs Method with a Double-ζ Basis Set for the Structures of the Hydroxo-Bridged Cu(II) Binuclear Complexes **1** ($\theta = 95.6°$, $\tau = 54.0°$), and **2** ($\theta = 104.1°$, $\tau = 0.0°$) and for Related Model Structures

complex[a]	calcd	exptl
$[\mathrm{Cu(LL)}(\mu\text{-OH})_2\mathrm{Cu(LL)}](\mathrm{NO}_3)_2$		
LL = bipy (**1**)	+107	+172[b]
LL = **3a**	+110	
LL = **3b**	+150	
LL = NH_3	+81	
LL = en	+60	
$[\mathrm{Cu(bipy)}(\mu\text{-OH})_2\mathrm{Cu(bipy)}]^{2+}$	+73	
$[\mathrm{Cu(LL)}(\mu\text{-OH})_2\mathrm{Cu(LL)}]\mathrm{Br}_2$		
LL = tmeen (**2**)	−502	−509[c]
LL = en	−402	
LL = NH_3	−354	
$[\mathrm{Cu(tmeen)}(\mu\text{-OH})_2\mathrm{Cu(tmeen)}]^{2+}$	−498	

[a] bipy = bipyridine; tmeen = tetramethylethylenediamine; en = ethylenediamine. [b] Reference 24. [c] Reference 25.

Neglect of weakly coordinated counterions (complex **1**) causes a decrease of 34 cm^{-1} in the $2J$ value. In contrast, for complex **2**, in which the bromide anions are far from the copper atoms, the value of the coupling constant remains practically unchanged when the counterions are disregarded in the calculations.

3.2. Analysis of the Geometries of the Model Compounds. The calculation of the exchange coupling constant using *ab initio* methods involves a subtle problem that is the choice of the geometry for the studied complex. At first glance, it would be desirable to optimize the geometries for both the singlet and the triplet states, and calculate the $2J$ value with the energies obtained for the optimized geometries. However, we wish to compare the calculated $2J$ values with the experimental data obtained for the compound in a condensed phase, in which small deviations from the optimum geometry for the isolated molecule may be present, induced by the intermolecular forces in the crystal. Such geometry differences can lead to large changes in the magnetic behavior. Thus, to allow comparison with the experimental values, it seems adequate to use the experimental structure to perform the calculation of the coupling constant. Adopting this criterion implies the additional supposition that such geometry is valid for both the singlet and the triplet states. In fact, the experimental structure corresponds to the average of the singlet and triplet molecules resulting from thermal population of those states at the experimental temperature. To check if this approximation introduces a sizable error in the evaluation of exchange coupling constants, we have calculated $2J$ for the model structure **4** as the energy difference between the singlet and triplet states in their optimized geometries (see Table 2).

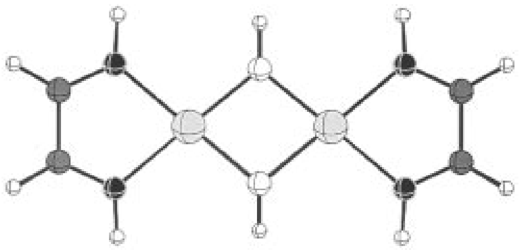

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Table 2. Optimized Structural Parameters Calculated for the Triplet and Singlet (with and without Broken-Symmetry) States of Model Structure **4** Using the B3LYP Method with a Double-ζ Basis Set[a]

	triplet	singlet-bs	singlet	exptl
Cu−O (Å)	1.915	1.917	1.925	1.892−2.006
Cu−N (Å)	2.037	2.033	2.008	1.981−2.036
O−H (Å)	0.977	0.979	0.988	
N−C (Å)	1.291	1.291	1.294	1.293−1.417
C−C (Å)	1.492	1.492	1.490	1.464−1.486
Cu−O−Cu (deg)	101.2	102.2	106.1	95.6−103.6
N−Cu−N (deg)	79.5	79.7	81.3	80.6−81.7
Cu−N−C (deg)	114.8	114.6	113.6	113.2−115.5
N−C−C (deg)	115.5	115.6	115.8	113.9−115.4

[a] The range of experimental values for the selected structural parameters obtained for the hydroxo-bridged Cu(II) binuclear complexes from the Cambridge Structural Database are provided for comparison.

The results show that the triplet and singlet states calculated using the broken-symmetry approach have very similar structures. However, if the geometry is optimized for the singlet state without the broken-symmetry approach, significant differences for the structural parameters are obtained, especially for the copper coordination sphere and the $\mathrm{Cu}_2\mathrm{O}_2$ framework. These results agree well with those found by Lovell et al.[26] for binuclear Cr(III) and Mo(III) complexes, who found considerable differences in the optimized geometry for the ground state with and without broken symmetry. The most significant difference corresponds to the Cu−O−Cu angle (θ), which changes by 1° between the two states. We have previously seen[6] that varying θ by 1° induces a change in $2J$ of ∼50 cm^{-1}.

The influence of using different geometries for singlet and triplet states on the exchange coupling constant is at most 30 cm^{-1} (i.e.,∼ 5%). In the present case, a $2J$ value of −547 cm^{-1} is found by using both optimized structures, in comparison with the value of −577 cm^{-1} found when the optimized singlet geometry was employed for both states. In summary, the theoretical evaluation of $2J$ for this family of complexes has an intrinsic uncertainty of *ca.* 30 cm^{-1} associated with the uncertainty of the molecular structures of the singlet and triplet states.

3.3. Magneto−Structural Correlations in Hydroxo-Bridged Cu(II) Binuclear Complexes. Previous studies devoted to magneto−structural correlations in hydroxo-bridged Cu(II) compounds focused mainly on the influence of the Cu−O−Cu angle on the exchange coupling. In a recent paper,[6] we also found the out-of-plane displacement of the hydrogen atom of the hydroxo group to be of great importance. A clear example of the importance of this factor can be found in phenoxide-bridged compounds. Recently, Thompson et al.[27] synthesized a family of binuclear Cu(II) complexes using macrocyclic ligands with a double phenoxide bridge. These authors found that such complexes are more strongly antiferromagnetic than the related hydroxo- and alkoxo-bridged families. This finding can be explained by the coplanarity of the phenoxide group with the $\mathrm{Cu}_2\mathrm{O}_2$ ring imposed by the rigidity of the macrocyclic ligand. Indeed, the out-of-plane shifts of the hydrogen or carbon atoms in the hydroxo- and alkoxo-bridged families reduce the antiferromagnetic coupling, while this displacement is hindered in the phenoxide-bridged macrocyclic complexes.

(a) Influence of the Cu−O Distance on the Magnetic Behavior. Analysis of the Cu−O distances for the hydroxo-

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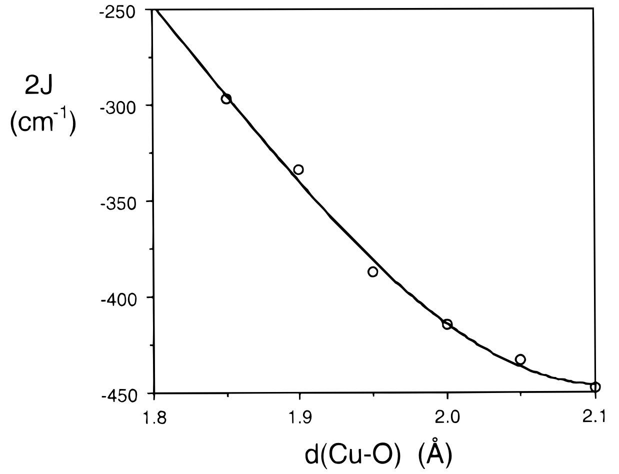

Figure 1. Representation of the calculated 2*J* value (B3LYP-bs method with a double-ζ basis set) for model **4** as function of the Cu−O distance.

bridged Cu(II) binuclear complexes[24,25,28−37] shows a range of values between 1.90 and 1.99 Å, the average value being 1.93 Å. To check the influence of the Cu−O distance on the magnetic behavior, we calculated the coupling constant for the model structure **4** with a Cu−O−Cu angle $\theta = 99°$ while keeping the hydrogen atoms of the hydroxo bridge in the Cu_2O_2 plane.[38] The six calculated values of 2*J* (Figure 1) show that a shortening of the Cu−O distances diminishes the antiferromagnetic coupling. Since zero coupling is expected at large distances, in the limit of noninteracting fragments, a maximum antiferromagnetic coupling is predicted for a Cu−O distance over 2.0 Å. The calculated 2*J* values indicate that uncertainties in the experimental values of the Cu−O bond distances (i.e., 0.003−0.006 Å) would produce an uncertainty of about 4−5 cm^{-1} in the coupling constant.

Two possible mechanisms to account for the exchange interaction in the hydroxo-bridged Cu(II) binuclear complexes are the direct interaction between the copper atoms and the superexchange interaction through the hydroxo bridge. The decrease in the Cu−O distance causes a reduction in the Cu···Cu distance, which increases the direct interaction and the ferromagnetic contribution. Simultaneously, these changes will produce an increase in the overlap between the orbitals on the Cu atoms and the bridge, increasing the antiferromagnetic character of the compound. The calculated 2*J* values seem to indicate that the reduction of the Cu−O distance mainly affects the ferromagnetic term, diminishing the overall antiferromagnetic character of the complex.

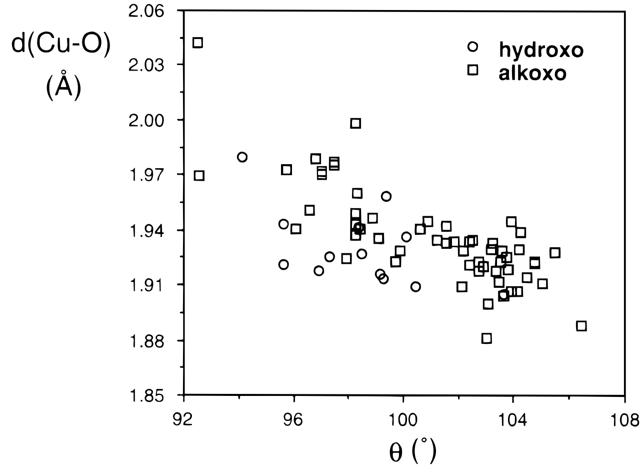

Figure 2. Representation of the average value of the four Cu−O bond distances as function of the average of the two Cu−O−Cu angles for hydroxo- and alkoxo-bridged Cu(II) binuclear complexes.

Table 3. Calculated Coupling Constants 2*J* (Singlet−Triplet Energy Difference; B3LYP-bs Method with Double-ζ Basis Set) for the Model Structure **5** with Two Different Cu−O−Cu Angles (θ_1, θ_2)[a]

symmetric		asymmetric				
θ (deg)	2*J* (cm^{-1})	θ_1 (deg)	θ_2 (deg)	θ_m (deg)	Δ (deg)	2*J* (cm^{-1})
95	−205					
97	−279	95	99	97	4	−305
99	−362	97	101	99	4	−385
101	−454	99	103	101	4	−472
103	−554	101	105	103	4	−567
105	−660					
		97	99	98	2	−330
		99	101	100	2	−416
		101	103	102	2	−510
		98	99	98.5	1	−345

[a] θ_m is the average value and Δ the difference between θ_1 and θ_2. The 2*J* values corresponding to the symmetric models are provided for comparison.

For the hydroxo- and alkoxo-bridged Cu(II) binuclear complexes, we have previously found[6] that the two most important structural parameters from the point of view of the exchange coupling, the Cu−O−Cu angle (θ) and the out-of-plane displacement of the hydrogen atoms of the hydroxo bridge, are correlated. Small values of θ appear combined with large out-of-plane displacements of the hydrogen atoms, both favoring a ferromagnetic character. We analyzed the Cambridge Structural Database[39] in search of a possible correlation between the experimental Cu−O distances and Cu−O−Cu angles. In order to have a large number of experimental data, we also included the alkoxo-bridged Cu(II) binuclear complexes for which analogous magneto−structural correlations have been established.

The results of this search (Figure 2) indicate some degree of correlation between these parameters although the points are far from being perfectly aligned. It should be borne in mind that a large number of complexes with different ligands are included in the plot and in these cases good correlations are not usual. In contrast to the relation between θ and the out-of-plane shift of hydrogen atoms,[4] the values of the θ angle and Cu−O bond distances affect the magnetic character in opposite ways. Thus, complexes with small θ angles that diminish their antiferromagnetic character normally have a large Cu−O bond distance that results in an increase in the antiferromagnetic character, as discussed above.

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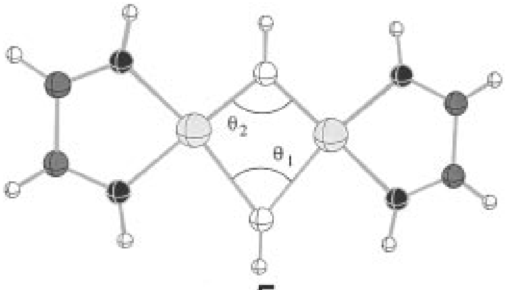
(b) Effect of the Asymmetry in the Cu−Hydroxo Bonds. Previous studies of the magneto−structural correlations in hydroxo-bridged Cu(II) binuclear complexes have been limited to the study of compounds with symmetric Cu_2O_2 backbones. However, many of the hydroxo-bridged Cu(II) binuclear complexes have an asymmetric Cu_2O_2 unit. Normally, when an asymmetric compound is included in the linear correlation between the coupling constant and the Cu−O−Cu angle proposed by Hatfield and Hodgson,[5] the average Cu−O−Cu angle is used. We attempted to evaluate how good this approximation is by performing calculations on model **5** with two different Cu−O−Cu bridge angles (θ_1 and θ_2; see Table 3).



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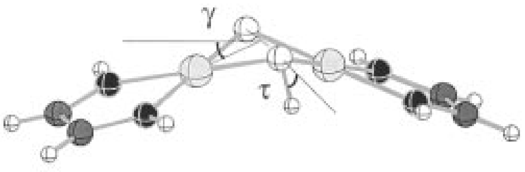
The Cu−O−Cu angle was changed by fixing the Cu−O distance (1.90 Å) for the bridge with a larger angle and increasing the Cu−O distances for the bridge with a smaller angle. Thus, the Cu···Cu distance for the asymmetric model is the same as that for the symmetric complex with the larger Cu−O−Cu angle. In all cases, the calculated 2*J* values for the asymmetric model structures show value intermediate between those of the two related symmetric structures, close to that corresponding to a symmetric structure with the average angle. To check the influence of the Cu−O distance, we performed two calculations in which the fixed distance (1.90 Å) is assigned to the bridge with the smaller angle, decreasing the Cu−O distance for the larger angle, and the Cu···Cu distance corresponds to the symmetric model with the smaller angle. In this case, the coupling constants for the complexes with (θ_1, θ_2) values of (95, 99°) and (97, 101°) are -261 and -348 cm^{-1}, respectively. These values are smaller than those obtained with the average angle (-279 and -362 cm^{-1}), while the those calculated at greater Cu−O distance (the 2*J* values were -305 and -385 cm^{-1}) are larger than those corresponding to the average angle. This agrees with the results of the previous section, where we saw that an increase in the Cu···Cu distance produces a stronger antiferromagnetic coupling.

(c) Hinge Distortion in Hydroxo-Bridged Cu(II) Binuclear Complexes. Some of the hydroxo-bridged Cu(II) binuclear complexes show a hinge distortion,[40−42] which results in roof-shaped molecules (**6**). Kahn et al.,[41,42] using extended-Hückel calculations and the Hay−Thibeault−Hoffmann[7] (HTH) model, predicted that such distortion should reduce the antiferromagnetic coupling. We analyzed the influence of the hinge distortion on the exchange coupling in the hydroxo-bridged Cu(II) binuclear complexes by calculating 2*J* with the model structure shown in **6** using the experimental structural parameters.[41,42] The results (Figure 3) indicate that the hinge distortion reduces the antiferromagnetic coupling, possibly reaching a ferromagnetic behavior for small values of θ, which is consistent with the qualitative predictions of Kahn et al. The influence of the “out-of-plane” shift of the hydrogen atoms is analogous to that observed for the planar model: it displaces the exchange coupling constant toward ferromagnetic values. However, for the model with the hinge distortion, the influence of the out-of-plane shift of the hydrogen atoms on the 2*J* value is larger than for the planar structure.[6]



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If we compare our results with the structural data for the hinge-distorted complexes synthesized by Kahn et al.[41,42] ($[Cu_2(\mu\text{-}OH)_2(CyNH_2)_4](ClO_4)_2$, complex **A**; $\theta_m = 98.1°$, $\gamma = 22°$, and $\tau = 35°$) and by Martens et al.[40] ($[Cu_2(\mu\text{-}OH)_2(\text{bipy−crown−bipy})]BF_4$, complex **B**; $\theta_m = 96.6°$, $\gamma = 15°$, and $\tau = 29$ and 59°), ferromagnetic behavior will be expected for these two compounds (Figure 3). The experimental results for the latter complex ($2J = +16$ cm^{-1}) agree well, but those for the former ($2J = -256$ cm^{-1}) are in strong disagreement with our calculations. To further check that our results are not biased by the use of a model compound, we calculated 2*J* for the two compounds with a minimum amount of modeling, consisting of replacing the cyclohexylamine ligands by methylamine in the first case and suppressing the crown ether linked to the bipyridine ligand in the second. The calculated values ($2J = -32$ and $+90$ cm^{-1}, respectively) are consistent with the experimental signs. The fact that this calculation yields an antiferromagnetic coupling constant for complex **A** whereas the model calculations of Figure 3 would predict ferromagnetism is in keeping with the effect seen in section 3.1 when a saturated amine is replaced by an unsatured one (see Table 1). Although weaker antiferromagnetic behavior is predicted for complex **A** than is seen experimentally, this may be due to the uncertainty in the position of the hydroxo H atoms as determined by X-ray diffraction. If these hydrogens were aligned with the Cu atoms (i.e., $\tau = 0°$; see Figure 3), a strong shift to negative values of 2*J* would be expected. Calculations on the idealized molecule assuming $\tau = 0°$ yield a 2*J* value of -450 cm^{-1}, thus supporting the hypothesis giving the hydrogen position as the reason for the disagreement between the calculated and experimental coupling constants.

Recently, Rentschler et al.[43] synthesized a family of compounds using polysiloxanolates to encapsulate copper atoms. One of these compounds has six encapsulated atoms of copper in a metal layer. The copper atoms have a square-planar coordination with two oxygen atoms as bridging ligands. The experimental Cu−O−Cu angle is 92.8°, and using the correlation proposed by Hatfield and Hodgson for the hydroxo-bridged compounds, a 2*J* value of about $+250$ cm^{-1} would be expected. It is remarkable that a compound with this Cu−O−Cu angle should present the strongest ferromagnetic behavior for these families with Cu_2O_2 rings. However, the experimental 2*J* value obtained for this compound is $+42$ cm^{-1}. The small value of

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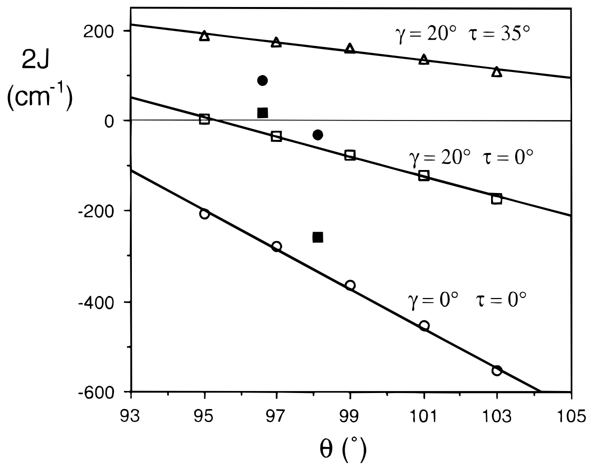

Figure 3. Calculated coupling constants (2*J*) for Cu(II) hydroxo-bridged complex **6** (B3LYP-bs method, double-ζ basis set) as a function of the bridging angle θ. The circles correspond to the calculated values for the planar model ($\gamma = 0°$ and $\tau = 0°$). The squares and the triangles represent the values calculated for model **6** by fixing $\gamma = 20°$ with $\tau = 0°$ and $\tau = 35°$, respectively. The black squares correspond to the experimental values for the complexes with hinge distortion[40,41] while the black circles represent the calculated values with simplified structures.

the angle τ in this complex is responsible for the reduced ferromagnetic coupling in comparison with the predicted value. In this case, as discussed previously, the out-of-plane shift of the substituent at the bridging oxygen increases the ferromagnetic coupling.[6] The Cu_2O_2 ring for the polysiloxanolato complex shows an asymmetric distortion with $\gamma_1 = 27°$ and $\gamma_2 = 31°$. From Figure 3, for a hydroxo complex with structural parameters ($\theta = 93°$, $\gamma = 20°$, and $\tau = 0°$) close to those of the polysiloxanolato complex ($\theta_m = 92.8°$, $\gamma_m = 29°$, and $\tau = 0°$), our model calculations predict a ferromagnetic behavior with a 2*J* value of *ca.* $+50$ cm^{-1}. Such value is in excellent agreement with the one found experimentally for this complex ($+42$ cm^{-1}).

4. Conclusions

The influence of the structural simplifications on the calculated values of the exchange coupling constant and some magneto−structural correlations were checked for hydroxo-bridged Cu(II) binuclear complexes by using the B3LYP broken-symmetry approach. The following conclusions were reached from this study:

(1) The terminal ligands affect the exchange coupling according to their basicity, decreasing the magnitude of the antiferromagnetic coupling in the order tmeen > en > NH_3 > aromatic N-ligand. Therefore, when modeling the terminal ligands for theoretical studies, one must preserve as far as possible the basic character of the terminal ligands.

(2) The inclusion of the counterions in the calculation of the exchange constant appears to be important only when they are coordinated to the metallic centers.

(3) Geometry optimization for model structures shows that the triplet state and the singlet state calculated using the broken-symmetry approach have similar structures. For the optimized geometry of the singlet state without broken-symmetry, significant differences for the structural parameters are obtained in comparison with those for two other structures, especially for those involving the copper atoms. An uncertainty in the calculated coupling constant of *ca.* 30 cm^{-1} was estimated to be associated with the use of the same structure for the calculation of the singlet and triplet states.

(4) An increase in the bridging Cu−O distance within the range of the experimental values markedly increases the antiferromagnetic coupling, but for larger Cu−O distances a decrease in the antiferromagnetic coupling should be expected.

(5) The values of the coupling constant for hydroxo-bridged Cu(II) binuclear complexes with two different values of the Cu−O−Cu angle can be estimated approximately as the average of the exchange coupling constant for the two symmetric complexes with each value of the Cu−O−Cu angle.

(6) The hinge distortion of the Cu_2O_2 rings reduces the antiferromagnetic character. Our results also show that, for a complex with a distorted Cu_2O_2 ring, the influence of the positions of the hydrogen atoms on the bridge is greater than that for the nondistorted structure.

The structural requirements for a hydroxo-bridged Cu(II) binuclear compound with a strong ferromagnetic coupling are: small Cu−O−Cu angles, short Cu−O distances, large out-of-plane shifts of the hydrogen atoms on the bridge, and hinge-distorted Cu_2O_2 rings.

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Supporting Information Available: A listing of the corresponding bibliographic references for the data used in Figure 2, which were obtained from the Cambridge Structural Database (4 pages). Ordering information is given on any current masthead page.

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