Toward the Prediction of Magnetic Coupling in Molecular Systems: Hydroxo- and Alkoxo-Bridged Cu(II) Binuclear Complexes

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Abstract: Magnetic coupling constants ($2J$) of hydroxo- and alkoxo-bridged copper binuclear compounds have been evaluated to determine the accuracy of different density functional methods and to study the magnetic behavior of these compounds. Comparison between the calculated and experimental coupling constants for the complete structures of five compounds shows that the most successful computational strategy is the combination of the B3LYP method with the broken-symmetry approach. Calculations for model compounds of both families yield reasonable approximations to the values of magnetic coupling constants calculated for the full molecular structures. Our calculations show a correlation between the magnetic coupling constant and the Cu−O−Cu bridging angle and with the out-of-plane displacement of the hydroxo or alkoxo groups, in agreement with the experimental data. The counterions of the hydroxo-bridged complexes, when hydrogen bonded to the bridging hydroxo group, determine the extent of the out-of-plane displacement of its hydrogen atom and strongly influence the sign and magnitude of the magnetic interaction. The energy gap between the two singly occupied molecular orbitals is shown to determine the changes in the value of $2J$ for small structural variations.

1. Introduction

The magnetic behavior of materials based on molecular entities is a research area that has been widely explored from an experimental point of view.[1−3] One system that has been extensively studied is that of the binuclear complexes of transition metals, due mainly to the variety of their structures and magnetic properties. However, understanding the relation between the structure and magnetic properties of known compounds and predicting the magnetic behavior of new compounds are hindered by the complex nature of magnetic interactions. The failure to understand the key factors controlling magnetic properties prevents further development of experimental work in this field. A theoretical model of general applicability that would allow researchers to understand and predict the magnetic exchange has been much sought after in the last few decades. An early model aimed at shedding some light on the influence of orbital factors in the nature of magnetic coupling was put forward by Hay, Thibeault and Hoffmann.[4] For a system with two metal atoms, each bearing one unpaired electron, they proposed the following expression for the magnetic coupling constant:

$$2J = 2K_{ab} - \frac{(\epsilon_1 - \epsilon_2)^2}{J_{aa} - J_{ab}} \qquad (1)$$

where ϵ_1 and ϵ_2 are the energies of the singly occupied molecular orbitals (SOMOs) and K_{ab}, J_{aa}, and J_{ab} are two-electron integrals. The first and second terms in this equation give the ferromagnetic and the antiferromagnetic contributions to the overall

coupling constant, respectively. In this context, the dependence of the coupling constant on a structural parameter (bond angle or torsion angle) within a family of binuclear compounds is assumed to depend essentially on the one-electron term ($\epsilon_1 - \epsilon_2)^2$, adopting the approximation that the two-electron integrals are practically insensitive to such structural changes. This approach has been fruitfully used by several authors to deduce magnetostructural correlations in families of compounds that exhibit antiferromagnetic coupling.[5−9] However, this method has two major shortcomings: first, the study of ferromagnetic systems cannot be undertaken because the first term in eq 1 is taken as an unknown constant within a family of compounds and, second, results for different families of compounds cannot be compared because the two-electron terms, which are not considered, are supposedly different in each case.

An alternative strategy that overcomes these limitations is to adopt a quantitative approach by performing *ab initio* calculations of the magnetic coupling constant $2J$, where this quantity is the energy difference between the ground and first excited states (singlet and triplet for Cu(II) binuclear compounds). This approach, however, involves a highly challenging computational problem because the energy differences between these two states are on the order of 100 cm^{-1} (∼0.3 kcal/mol) or even smaller, and the system size that is of experimental interest is of at least 40 atoms. Given the degree of accuracy required in calculating the energy of both states, various authors have applied methods based on configuration interaction (CI), modeling the structure in order to limit the number of atoms in the calculations. The first work in this field was reported by Daudey et al., who used *ab initio* CI calculations with a perturbational scheme to

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calculate the magnetic coupling constant for Cu(II) binuclear systems with acetato,[10] hydroxo,[10] alkoxo,[11] and oxalato bridges[12] as well as for a Cu(II)−V(IV) heterodinuclear system.[13] The approach proposed by Daudey was subsequently employed by Haase et al. to study *N*-oxide,[14] hydroxo,[15] alkoxo/acetato[16] and terephthalato-bridged[17] Cu(II) dimers, and hemocyanin models.[18] More recently, Caballol et al. have proposed a new variational approach[19] to calculate small energy differences called difference-dedicated configuration interaction (DDCI), employing it to estimate coupling constants for dihalide-bridged Cu(II) dimers,[20,21] as well as for dichloride and azido-bridged Ni(II) binuclear complexes.[22] Stammler et al., employing model structures for oxo-bridged complexes of Ti(III), V(III), and Cr(III),[23,24] have calculated magnetic coupling constants at the CASSCF level, obtaining improved results using a multi-reference CEPA method.

Density functional theory (DFT) methods have also been employed to study magnetic coupling in molecular systems. Initially, the X−α method was used in several studies[25] but the aim was mainly to examine the electronic structure, charges, spin densities, and metal configurations rather than to calculate directly the magnetic coupling constants. This method provides results that correctly describe the sign of the constant but that give a poor estimate of its absolute value. The inclusion of the broken-symmetry approach proposed by Noodleman[26,27] in the study of magnetic interactions in Fe$_x$S$_x$ clusters[28,29] provided a new scheme for analyzing the electronic structure and for obtaining coupling constant values. This approach has been extensively analyzed[26−29] for both Hartree−Fock and density functional methods, showing that it provides the wave function with a "valence bond" character. Hence, the broken-symmetry approach is often called the "density functional valence bond" method when combined with density functional methods. Despite the widely reported ability of DFT methods to handle large systems, previous studies have generally used model structures to perform the calculations. Bencini et al. have used the X−α method linked with the broken-symmetry approach to study dihalide,[30] carbonato,[31] and oxo-bridged Cu(II) binuclear complexes and a Cu(II)−V(IV) heterodinuclear sys-tem.[32] Using the same method, Solomon et al. studied the electronic structure of the hemocyanin and tyrosinase active sites with a model of a dioxo-bridged Cu(II) complex.[33] Stranger et al., using a similar approach, have devoted several papers to the study of the magnetic interactions in halide-bridged Mo(III) binuclear systems[34,35] and, more recently, to the evaluation of the ability of the broken symmetry approach to optimize geometries in cases where the full symmetry method gives poor results.[36] There are also examples in which the broken symmetry method within the unrestricted Hartree−Fock framework has been used. Rappé et al. used it to study oxo-bridged Fe(III) complexes[37] and Ti(III) binuclear complexes,[38] and Yamaguchi et al., for Fe$_2$S$_2$ clusters.[39] Recently, DFT broken-symmetry calculations have been performed by several authors to study certain especially complicated systems, e.g. C$_2$[40] and Cr$_2$.[41,42]

The present paper has two separate goals. First of all, it tests the performance of modern density functional methods[43] in evaluating the magnetic coupling constants with different density functionals and basis sets. This should allow us to establish a computational strategy that meets three predetermined criteria: (a) it should give good quantitative estimates of the value of 2*J* for the full molecular structure of a variety of compounds, correctly predicting their ferro- or antiferromagnetic character (i.e., the sign of *J*) in all cases; (b) it should provide a correct description of the magnetostructural correlations for a family of analogous compounds represented by an idealized model in which only a limited set of structural parameters are varied; and (c) the method should be easily accessible to other researchers in the field through standard quantum chemistry packages. The second goal of this paper is to provide a quantitative study of the magnetic behavior of several hydroxo- and alkoxo-bridged Cu(II) binuclear complexes and to study the dependence of the magnetic coupling constant on their molecular structure through model calculations. These compounds provide a good case for theoretical studies since only one electron per center participates in the magnetic interaction and a large set of experimental data is available. The hydroxo-bridged binuclear complexes are also of particular interest because they exhibit either ferromagnetic or antiferromagnetic character depending on their geometry.

2. Computational Details

The magnetic coupling constant has been evaluated by calculating the energy difference between the singlet and triplet states:

$$E(S = 1) - E(S = 0) = -2J \tag{2}$$

Positive values of the coupling constant *J* indicate a triplet ground state with parallel spins (i.e., ferromagnetic character). For negative values of *J* the singlet state is lower in energy, with opposite spins on each

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Table 1. Magnetic Coupling Constants $2J$ (cm^{-1}) Calculated as the Singlet–Triplet Energy Difference Using Four Different DFT Methods with a Double-ζ Basis Set for the Complete Structure of Three Hydroxo-Bridged Complexes and Two Alkoxo-Bridged Compounds[a,b]

compd	θ (deg)	τ (deg)	$2J$				
			BLYP	BP86	BLYP-bs	B3LYP-bs	Exp.
A [Cu(bipy)OH]$_2$(NO$_3$)$_2$[59]	95.6	54.0	+4108	+4091	+57	+107	+172
B [Cu(tmeen)OH]$_2$Br$_2$[60]	104.1	0.0	−309	−392	−1206	−502	−509
C [Cu(eaep)OH]$_2$(ClO$_4$)$_2$[61]	98.8	44.0	+2565	+2602	−237	−22	−130
	99.5	60.0					
D [Cu(papen)]$_2$[62]	103.9	4.1	−1837	−1675	−2405	−769	$\sim$ −800
E [Cu(papo)]$_2$·2H$_2$O[63]	98.3	27.7	+1619	+1148	−777	−189	−128

[a] The values of θ and τ angles defined in **3** are provided to allow the comparison between the calculated $2J$ values using model and complete structures. Experimental values from references indicated are given for comparison. [b] Compilations of $2J$ values can be found in refs 57 and 58. [c] bipy, bipyridine; tmeen, tetramethylethylenediamine; eaep, 2-(2-ethylaminoethyl)pyridine; papen, 5-pyrrol-2-yl-4-azapentenolato; papo, *N*-picolinoyl-3-amino-1-propoxido.

copper atom giving rise to antiferromagnetic behavior. All the calculations have been performed using the Gaussian92/DFT[44] and Gaussian94[45] programs. Local spin density calculations have been carried out using the Slater exchange[46] and Vosko, Wilk, Nusair[47] (VWN) correlation functionals. Generalized Gradient Corrections have been introduced using the Becke exchange part[48] (B) and either the Perdew[49] (P86) or the Lee–Yang–Parr[50] (LYP) correlation parts. The adiabatic connection method using three parameters proposed by Becke[51] (B3LYP), mixing the Hartree–Fock contribution for the exchange, has been also used. The use of the broken symmetry approach in combination with the BLYP and B3LYP functionals will be indicated by BLYP-bs and B3LYP-bs in what follows. The complete avoidance of auxiliary functions to fit the electron density and the exchange-correlation potential in the calculation of Coulomb and exchange-correlation terms seems of particular importance in these calculations in view of the accuracy needed for the estimation of the magnetic coupling constant.

Experimentally, the magnetic susceptibility measurements are obtained from solid samples in which packing forces can produce small deviations from the structure of the isolated molecule. Hence, in our calculations, neither the model nor the complete structures have been optimized since very small variations in the geometry such as those induced by the packing forces can produce large changes in the calculated magnetic constant.

Four different basis sets have been tried out. In one of them we employed the pseudopotentials proposed by Hay and Wadt[52] (LANL2DZ) while the other three were the all-electron basis sets of double-ζ[53] (DZ), double-ζ with polarization (DZP), and triple-ζ[54] (TZ) quality proposed by Ahlrichs et al., including an additional p function for Cu in all cases. In all calculations, we have employed a pruned grid[55] of 75 angular points with 302 radial points (called finegrid in GAUSSIAN terminology). To check the influence of the grid on the accuracy of the results, we performed some test calculations increasing the size up to 99 angular points. The difference in the $2J$ values was only of some 0.2 cm^{-1}, so the use of the smaller grid can be considered acceptable in all the cases studied.

3. Results and Discussion

In this section, we first discuss the performance of the different DFT methods in estimating the $2J$ values. For this purpose, we chose five complete structures of hydroxo- and alkoxo-bridged copper complexes, including their counteranions. We use the complete structure rather than simplified models to enable a straighforward comparison between the calculated and experimental coupling constants. To complete the evaluation, we performed calculations on model structures to check their ability to qualitatively reproduce the dependence of the coupling constant on different structural parameters. The influence of the basis set was also analyzed for the model compounds.

3.1. Methodological Study. As it has been previously reported that local functionals overestimate the relative stabilization of the singlet state relative to the triplet state,[56] we directly evaluated the following four methods: two generalized gradient

functionals (BLYP and BP86) and the combination of the broken-symmetry approach with either the BLYP functional or the hybrid B3LYP method.

1
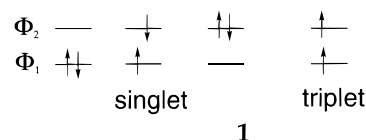
The results of the estimation of magnetic coupling constants using a DZ basis set for five different complexes are shown in Table 1. Values of $2J$ calculated with the generalized gradient approximation (BLYP or BP86 functionals) overestimate the ferromagnetic interaction for the ferromagnetic or weakly antiferromagnetic compounds (**A**, **C**, and **E**, in Table 1). In these cases, the calculated energy for the resulting singlet state is too high in comparison with that of the triplet, leading to an overestimation of the ferromagnetic coupling. For a d^9 binuclear compound, three different configurations give rise to low lying

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singlet states, while only one configuration is involved in the triplet state, as sketched in **1**, where Φ_1 and Φ_2 are the SOMOs (**2a,b**).[4]

2a   **2b**
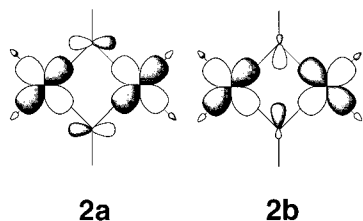
The contribution of these excited configurations to the lowest singlet state is important, and the noninclusion of these is responsible for the poor description of that state. For the strong antiferromagnetic complexes, this problem is minimized because there is a substantial energy gap between the ground and the excited singlet configurations. Hence, a monodeterminantal wave function is closer to the right solution for the ground state. In an attempt to adequately account for the excited singlet configurations, we performed calculations using the BLYP functional combined with the broken-symmetry method that provides a multiconfigurational character to the singlet wave function.[26,27] The use of broken symmetry in the singlet state calculations results in the localization of one SOMO on each metallic center, since the resulting low-spin solution is not a pure spin state but represents an averaged antiferromagnetic aligment of spins, as discussed by Noodleman.[28,29] Due to the presence of only one relevant configuration for the triplet state (**1**), the results are the same for this state regardless of the use of broken symmetry in the calculation. The coupling constants obtained using the BLYP-bs method correctly reproduce the sign of the experimental $2J$ values, but in the five cases, the calculated values overestimate the stability of the singlet state (Table 1).

In contrast with the local density methods, the unrestricted Hartree−Fock method provides an overestimation of the stabilization of the triplet state. This fact suggested us that the inclusion of the Hartree−Fock exchange provided by the B3LYP functional might correct the overestimation of the antiferromagnetic character found using the BLYP-bs method. The B3LYP-bs results (Table 1) confirm this idea, providing an excellent agreement between the experimental and calculated data for the five compounds. The largest absolute error is of *ca.* 100 cm^{-1} (less than 0.3 kcal/mol) for systems with 40−70 atoms. In contrast, when used without the broken symmetry approach, the B3LYP functional (results not shown) strongly overestimates the relative stability of the triplet state. We have also performed a similar study for the oxalato-bridged complexes,[64] for which the errors using the B3LYP-bs method are still smaller than those obtained for the hydroxo-bridged systems. The discrepancies with the experimental results for the hydroxo-bridged complexes could be associated to the uncertainty in the position of the hydrogen of the bridging ligand obtained using X-ray diffraction. As we will show later, this parameter is a crucial factor for the magnetic behavior of the hydroxo-bridged complexes. The B3LYP-bs method gives significantly improved results for the magnetic coupling constants compared with the BLYP or BLYP-bs methods, thus corroborating the overall impression given by different authors[65−68] that, in spite of its nonpure density functional

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Table 2. Magnetic Coupling Constants $2J$ (cm^{-1}) Calculated as the Singlet−Triplet Energy Difference Using Three Different DFT Methods with a Double-ζ Basis set for the Hydroxo- and Alkoxo-Bridged Model Structure (**3**) for Six Different Cu−O−Cu Angles (θ) and $\tau = 0°$

angle θ (deg)	hydroxo			alkoxo		
	BLYP	BLYP-bs	B3LYP-bs	BLYP	BLYP-bs	B3LYP-bs
95	+795	−1006	−174	−564	−1702	−408
97	+407	−1196	−252	−1043	−1875	−494
99	0	−1406	−336	−1415	−2131	−610
101	−405	−1619	−429	−1891	−2485	−737
103	−828	−1850	−543	−2292	−2774	−858
105	−1245	−2047	−651	−2704	−2953	−994

character, the B3LYP functional is actually the DFT method that provides the best results for calculating several molecular properties.

The comparison with calculations previously reported by other authors is difficult because, even in the case of the same complex, those results correspond to model compounds, not to the complete structure. Daudey et al.,[10] using a perturbative CI approach, obtained a value of −392 cm^{-1} for a model of the complex **B**{[Cu(tmeen)OH]$_2$Br$_2$} while the experimental value is −509 cm^{-1} and our calculated value is −502 cm^{-1}. Moreover, we have observed that small changes in the terminal ligands or the elimination of counterions causes changes of 50−60 cm^{-1}, making the direct comparison of methods inadequate with the available results.

To check the influence of the basis set on the calculation of the magnetic coupling constant and to corroborate the performance of different functionals obtained for the complete structures, we carried out calculations using the model structure[69] shown in **3** (for the alkoxo-bridged model, the hydrogen is replaced by a methyl group) by varying the Cu−O−Cu (θ) angle while maintaining the H or C atom of the bridge in the molecular plane ($\tau = 0°$).


3
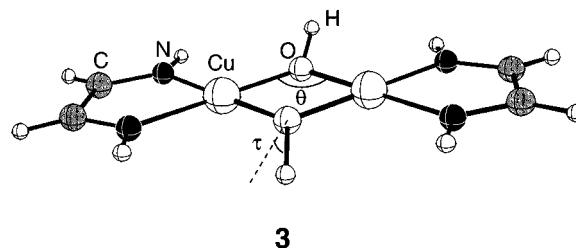
The calculated coupling constants for the hydroxo- and alkoxo-bridged models with three different methods (BLYP, BLYP-bs, and B3LYP-bs) are shown in Table 2. These results confirm the general trends found for the complete structures: the BLYP method provides a poor description of weak antiferromagnetic systems (see, for example, hydroxo compounds with $95° < \theta < 99°$), and both BLYP and BLYP-bs methods overestimate the stabilization of the singlet state, giving too large coupling constants for complexes with strong antiferromagnetic character (see, for example, hydroxo compounds with $\theta < 103°$ and alkoxo compounds with $\theta \geq 97°$). The B3LYP-bs method gives results within the range of experimental values for both families of compounds and all values of θ. Moreover, the

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(69) The following structural parameters were used for the model calculations: Cu−O = 1.9 Å; Cu−N = 2.0 Å; C−N = 1.34 Å; N−H = 1.0 Å; C−H = 1.0 Å, and O−H = 0.9 Å. Cu−N−C = 115°; H−C−N = 123.25°; H−N−Cu = 122.5°, and Cu−Cu−N = 138.5°.
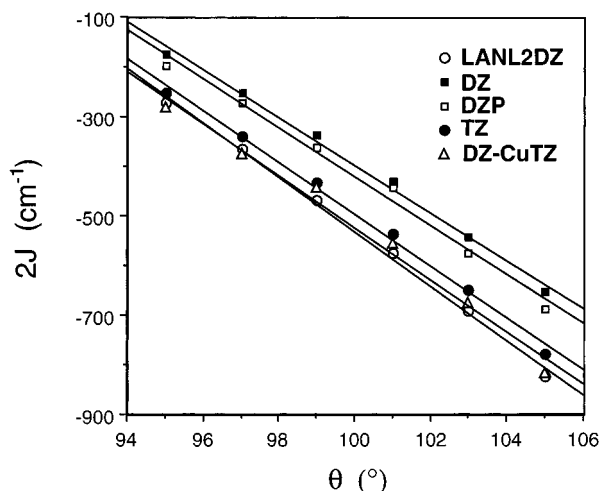
Figure 1. Magnetic coupling constants ($2J$) for Cu(II) hydroxo-bridged complexes calculated with the B3LYP-bs method for model **3** with $\tau = 0°$ as a function of bridging angle θ using five different basis sets.

models with the calculated values for $\theta \approx 104°$ (Table 2) are in fair agreement with the experimental ones for compounds **B** (hydroxo-bridged) and **D** (alkoxo-bridged), which have values of τ close to 0° (as assumed in our model).

In Figure 1, we show the variation of $2J$ with the Cu$-$O$-$Cu angle, calculated using the B3LYP-bs method with five different basis sets (see the Computational Details for a description of the basis sets employed) for the hydroxo-bridged model. In all cases, a linear variation of $2J$ with θ is obtained in agreement with the correlation found for the experimental data by Hatfield and Hodgson.[70] This behavior is analyzed in more detail in the next section.

Comparison of the results obtained with the DZ and DZP basis sets indicates that the polarization functions do not induce important changes in the calculated magnetic coupling constant. However, the use of a TZ basis set shifts the $2J$ results by approximately 90 cm^{-1} to antiferromagnetic values relative to the results obtained with the DZ and DZP basis sets. When using a TZ basis set only for the copper atoms and a DZ set for the other atoms (DZ-CuTZ), the results are very close to those obtained with the TZ basis set for all atoms. This shows that for the calculation of magnetic coupling constants it is the quality of the basis set on the copper atoms which is most important. The results obtained using pseudopotentials are very close to those provided by the TZ basis set, but the SCF convergence of the calculations is considerably poorer than for the all electron basis set. Similar results (included in the Supporting Information) have been obtained for model calculations on alkoxo complexes. As a further test of the basis set dependence, we have repeated the calculation of the coupling constant for [Cu(bipy)OH]$_2$(NO$_3$)$_2$ and [Cu(tmeen)OH]$_2$Br$_2$ using the DZ-CuTZ basis set. The newly calculated values are $+124$ and -555 cm^{-1}, respectively, while the results with the DZ basis set were $+107$ and -502 cm^{-1}. These values indicate a considerably smaller influence of the basis set for the complete structures (less than 50 cm^{-1}) than for the model structures, probably due to the large number of functions included in the whole molecule that can complement the copper basis set. In summary, the DZ basis set seems to be a good compromise between the accuracy and computational requirements for this kind of calculations, although DZ-CuTZ would be preferred for smaller systems or as larger computing resources become available.

3.2. Dependence of the Magnetic Behavior on the Molecular Structure. Since the computational strategy proposed in this paper might adequately account for the coupling constants of several compounds, we decided to analyze its ability to provide a good qualitative description of the dependence of $2J$ on the structural parameters within a large family of compounds through model calculations. The calculated values of $2J$ for the hydroxo-bridged model compound **3** are presented in Figure 2 as a function of the angle θ for two different sets of calculations. The experimental values are also represented as solid circles with the corresponding value of τ annotated besides. In the first set of calculations (dashed line), θ was varied keeping the hydrogen groups coplanar with the Cu$_2$O$_2$ ring ($\tau = 0°$). The calculated values for the model compounds are in good agreement, with the experimental values in those complexes with small values of τ (complexes **B** and **D** in Table 1).

In another set of calculations (solid line) we optimized the angle θ for fixed values of τ, and the singlet-triplet splitting for each (θ, τ) pair was represented as a function of θ. The calculations for the planar model predict an antiferromagnetic behavior for the whole range of θ values, whereas the out-of-plane displacement of the hydrogen atoms results in weaker antiferromagnetic and eventually ferromagnetic couplings. It becomes clear that a good theoretical description of the magnetic behavior of these compounds cannot be achieved if the position of the hydrogen atom (τ angle) is not taken into account. Since the analysis of the molecular structures reveals that the out-of-

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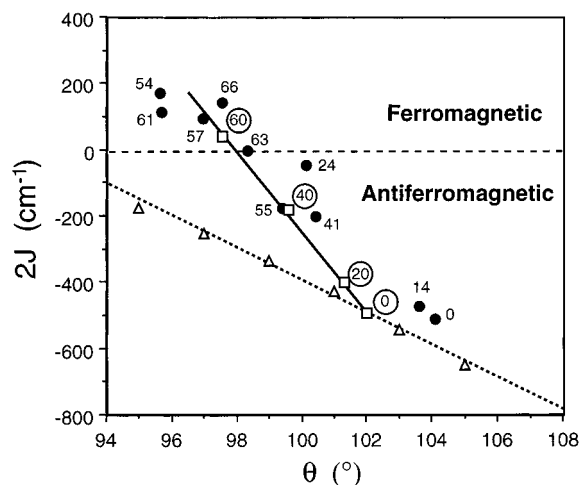
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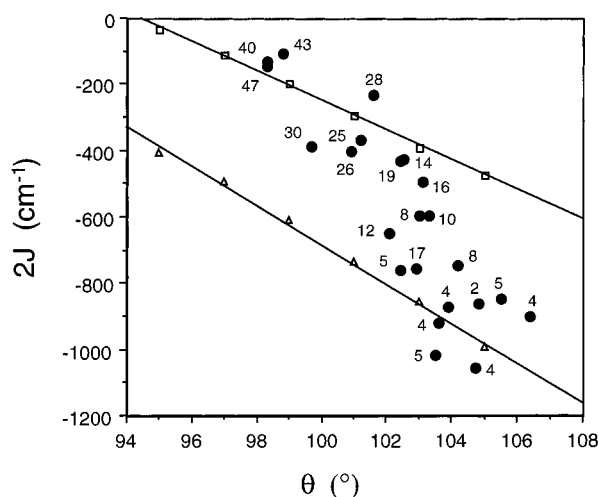
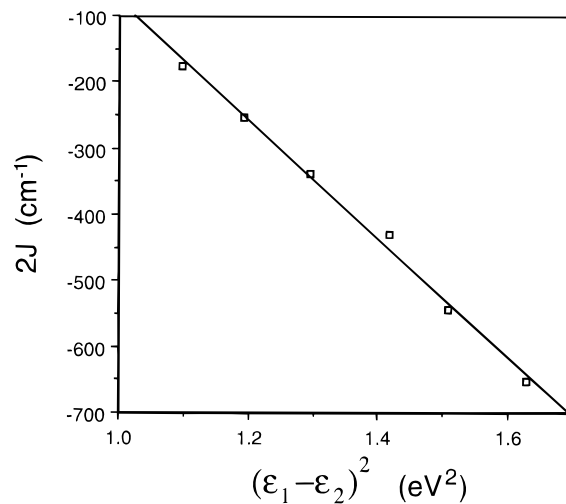(96) Broer, R.; Maaskant, W. J. A. *Chem. Phys.* **1986**, *102*, 103.

Figure 2. Magnetic coupling constants ($2J$) for Cu(II) hydroxo-bridged complexes calculated with the B3LYP-bs method using a double-ζ basis set for model **3** as a function of bridging angle θ. The black circles correspond to the experimental values,[59,60,71–78] and the dashed line gives the calculated values (triangles) for the planar model ($\tau = 0°$). The squares represent the values calculated for the optimized θ at a fixed value of τ (circled numbers). The uncircled labels indicate the value of τ for each experimental structure.

Figure 3. Magnetic coupling constants ($2J$) for Cu(II) alkoxo-bridged complexes calculated with the B3LYP-bs method using a double-ζ basis set for model **3** changing the bridging hydroxo group for a methyl group as a function of bridging angle θ. The black circles correspond to the experimental values,[62,63,79–95] and the solid lines give the calculated values (triangles) for the planar model ($\tau = 0°$) and the squares for the model with $\tau = 40°$. The uncircled labels indicate the value of τ for each experimental structure.

plane position of the hydrogen atoms is determined in most cases by hydrogen bonding with the counteranions, the choice of counterions can be of the utmost importance in determining the sign and magnitude of the magnetic coupling. The differences between the experimental and calculated values of $2J$ for the complete structures should not be attributed only to limitations of the computational approach. It should be borne in mind that the calculations are performed for the molecular structures usually refined at high temperature. It would be desirable to have the low-temperature structure available so as to evaluate the energy of the ground electronic state better. Furthermore, the inaccuracies in the localization of the hydrogen atoms of the hydroxo bridges induce uncertainty in the calculated value of $2J$.

Both the theoretical results and the experimental data show a correlation between the out-of-plane displacement of the hydrogen atoms and the bridging angle θ: a large τ value is associated with a small θ, which also favors a more positive value of $2J$. The existence of such correlation may be the reason why the importance of τ has not been discussed previously. When the correlation between the two structural parameters is taken into account (squares in Figure 2), the agreement between the coupling constants calculated for the model complex and the experimental data is remarkable. The approximations implicit in the use of model **3** give errors of 20–30% in the value of $2J$ while correctly predicting the sign of the exchange interaction. We have also studied model **3** substituting H for CH_3 in the bridge, to analyze the magnetostructural correlations found for the alkoxo-bridged complexes. The calculated values of $2J$ for the alkoxo-bridged model compound are presented in Figure 3 as a function of the angle θ for two different values of τ (0° and 40°, triangles and squares, respectively, in Figure 3). The experimental values are also represented as solid circles with the value of τ indicated besides. A good agreement is found: almost all experimental values are placed inside the region delimited by the two lines corresponding to $\tau = 0°$ and $\tau = 40°$. Roughly the same features discussed above for the hydroxo-bridged complexes were found. A correlation between both angles emerges, showing that small values of θ appear combined with the largest values of τ, and these structures have the weakest antiferromagnetic character. The main difference

Figure 4. Singlet–triplet energy separation, $2J$, calculated for the hydroxo-bridged model compound **3** with $\tau = 0°$ (B3LYP-bs method and a double-ζ basis set) as a function of the square of the split between the two SOMOs in the triplet state.

is that all of the alkoxo-bridged complexes are predicted to be antiferromagnetic for τ values smaller than 40°, in good agreement with the available experimental data, although ferromagnetic behavior might be expected for larger values of τ.

The assumption of Hay, Thibault, and Hoffmann, that small changes in structural parameters affect only the one-electron contribution to the coupling constant, has been checked by plotting the calculated $2J$ values as a function of $(\epsilon_1 - \epsilon_2)^2$. ϵ_1 and ϵ_2 are the orbital energies of the two SOMOs in the triplet state for the model compound **3** when θ is varied for a fixed value of τ (see Figure 4). The linear dependence expected from eq 1 is found for both the hydroxo- and alkoxo-bridged (included as Supporting Information) complexes. A similar behavior has been found for the out-of-plane hydrogen shift (not shown in the figure). In this case, the value of $(\epsilon_1 - \epsilon_2)^2$ decreases when the hydrogen atoms are separated from the Cu_2O_2 plane, resulting in a reduction of the antiferromagnetic character. From our calculations, it is seen that the energy of SOMO **2a** is

practically unaffected by the distortion whereas the energy of SOMO **2b** increases with τ. The analysis of the wave function **2b** indicates that the oxygen 2p contribution increases with τ (going from an sp to an sp^2 hybridization of the oxygen orbital contribution), resulting in a stronger antibonding Cu−O character because of the better energy match of oxygen 2p orbital than oxygen 2s orbital with the metal 3d orbital.

Our calculations suggest that there is a sound theoretical basis for the analysis of magnetic correlations based on the study of the variations of the HOMO−LUMO gap with geometry. They are consistent with the results of Broer and Maaskant on a fluoro-bridged model, for which the calculated two-electron integrals were seen to be approximately constant.[96]

4. Conclusions

In the present paper, modern density functional methods were used to calculate magnetic coupling constants in hydroxo- and alkoxo-bridged Cu(II) binuclear complexes. Analysis of the computational results for five complete structures showed that the functionals based on the generalized gradient approximation (BLYP and BP86) provide poor results for ferromagnetic or weak antiferromagnetic compounds due to an inaccurate description of the singlet state. The inclusion of the broken-symmetry approach combined with the BLYP functional partially solved this problem but overestimates the relative stability of the singlet state for strong antiferromagnetic complexes. A method combining the B3LYP functional with the broken-symmetry approach is the most successful one and provides results which are in good agreement with the experimental data. The study of the influence of the basis set on the model calculations using the B3LYP-bs method indicates that, in all cases, the variation of the coupling constants with geometrical parameters follows similar trends for the hydroxo- and alkoxo-bridged complexes. Significant changes in the calculated coupling constant were only obtained upon increasing the quality of the basis set for the copper atom. These changes were less significant for the complete structures than for the model systems.

The study of the dependence of the magnetic coupling constant for the hydroxo-bridged complexes with the molecular geometry using model structure calculations showed a correlation with the Cu−O−Cu angle as previously proposed by Hatfield and Hodgson from experimental data, but also with the out-of-plane displacement of the hydrogen atom in the hydroxo group. The ferromagnetic character is favored when θ diminishes and the out-of-plane displacement of the hydrogen atom increases. These results are in agreement with the experimental results, which show that the experimental complexes with ferromagnetic character have values of θ smaller than 98° and τ values larger than 50°. The influence on the magnetic behavior of the counterions present in the structures can be explained, since these counterions normally interact through hydrogen bonds with the hydroxo group, hence determining the extent of the out-of-plane displacement of the hydrogen in the bridging hydroxo group.

The approach proposed by Hay, Thibeault, and Hoffmann was investigated. We found a linear correlation between the calculated 2*J* value and the square of the energy gap between the two singly occupied molecular orbitals for structural variations in the whole range of θ values. A similar correlation is found for the out-of-plane displacement of the hydrogen atoms. These findings suggest that the two-electron terms present in eq 1 remain approximately constant for small geometry changes, and therefore, the energy gap between the two singly occupied molecular orbitals determines the changes in the 2*J* values for small structural variations.

The present conclusions seem to provide an affirmative answer to the question of whether DFT methods can provide an accurate description of the magnetic coupling constants in binuclear transition metal systems. In this respect the B3LYP-bs method fulfills the three requirements that we have proposed: (a) a good quantitative estimation of the magnetic coupling constants for the complete structures, (b) a correct qualitative description of the magnetostructural correlations, and (c) a method available in standard quantum chemistry packages easily accessible to other researchers in the field.

Supporting Information Available: Two figures, one comparing the magnetic coupling constant for the alkoxo model using four different basis sets and the other showing the correlation between the calculated 2*J* values and the square of the energy gap between the two singly occupied molecular orbitals for the alkoxo model (3 pages). See any current masthead page for ordering and Internet access instructions.

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