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Magneto-Structural Correlations in Trinuclear Cu(II) Complexes: A Density Functional Study

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Summary. Density functional theoretical methods have been used to study magneto-structural correlations for linear trinuclear hydroxo-bridged copper(II) complexes. The nearest-neighbor exchange coupling constant shows very similar trends to those found earlier for dinuclear compounds for which the Cu–O–Cu angle and the out of plane displacement of the hydrogen atoms at the bridge are the two key structural factors that determine the nature of their magnetic behavior. Changes in these two parameters can induce variations of over $1000\,\mathrm{cm}^{-1}$ in the value of the nearest-neighbor coupling constant. On the contrary, coupling between next-nearest neighbors is found to be practically independent of structural changes with a value for the coupling constant of about $-60\,\mathrm{cm}^{-1}$. The magnitude calculated for this coupling constant indicates that considering its value to be negligible, as usually done in experimental studies, can lead to considerable errors, especially for compounds in which the nearest-neighbor coupling constant is of the same order of magnitude.

Keywords. Broken symmetry; Density functional calculations; Exchange coupling; Magnetic properties; Trinuclear transition metal complexes.

Introduction

One of the most prominent families of compounds in modern coordination chemistry is that of the polynuclear Cu(II) complexes which have been extensively studied in recent decades, specially in regard with their magnetic properties and the dependence of those properties on the molecular structure [1–8]. Although

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most attention has been focused either on the simplest representatives of this family, *i.e.*, dinuclear compounds, or on polymeric compounds with infinite chains, the presence of trinuclear or tetranuclear arrays of copper atoms at the active sites of enzymes has lead to an increased interest in compounds with intermediate nuclearity [9–15]. From the point of view of molecular magnetism these complexes are also particularly interesting since their intermediate position between the simplest dinuclear species and bulk materials may result in completely new magnetic properties.

Within the large family of polynuclear Cu(II) compounds that have been magnetically characterized, hydroxo-bridged dinuclear complexes have featured prominently in these studies, with *Hodgson* and *Hatfield* noting a correlation between the exchange coupling constant and the Cu–O–Cu angle [16, 17]. Evidences that other structural parameters may influence both the magnitude and the sign of the coupling constant continues to stimulate the interest in these compounds, especially those which feature unusual $Cu_2(\mu\text{-OH})_2$ core geometries. All these studies have led to now well-established magneto-structural correlations for dinuclear compounds that allow, at least in a semiquantitative manner, to predict the sign and the magnitude of exchange coupling.

However, the situation for compounds of higher nuclearity is still quite obscure. The usual procedure adopted in most of the published studies is to neglect next-nearest neighbor coupling constants, and to assume that the dominant nearest-neighbor constants behave with respect to structural changes in a very similar manner as in analogous dinuclear compounds [18–23]. In this contribution we adopt a computational approach to shed some light on magneto-structural correlations for trinuclear compounds. Extensive studies of this kind on hydroxo-bridged dinuclear Cu(II) compounds have been successfully employed in the evaluation of exchange coupling constants and their relation to molecular structure [24, 25]. We think that even if there are, up to the present, no reported experimental studies for their trinuclear analogues, these compounds form an excellent testing ground for magneto-structural correlations in compounds of higher nuclearity.

Results and Discussion

Evaluation of Coupling Constants in Trinuclear Systems

Exchange coupling in a polynuclear compound is usually described at a phenomenological level by a *Heisenberg* Hamiltonian:

$$\hat{H} = -\sum_{i>j} J_{ij}\hat{S}_i\hat{S}_j \tag{1}$$

where J_{ij} are the exchange coupling constants between each pair of coupled paramagnetic centers and $\hat{S}_i$, $\hat{S}_j$ are the spin moments of the different paramagnetic centers. The set of coupling constants involved in this expression can be obtained experimentally by fitting the measured magnetic susceptibility *versus* temperature curve to the theoretical expression derived for a system that obeys Eq. (1). In the following we will briefly describe a simple strategy to evaluate computationally the values for the set of *n* different coupling constants in a polynuclear compound using standard DFT calculations. For this purpose we will need first the energies corresponding to $n+1$ different spin distributions of our compound.

As an illustration of this procedure we will start with the simplest possible case, a dinuclear compound with two identical paramagnetic centers with $S_i = 1/2$. The *Heisenberg* Hamiltonian used to fit the experimental data in this case contains a single coupling constant J_{12}:

$$\hat{H} = -J_{12}\hat{S}_1\hat{S}_2 \tag{2}$$

For this system we need to consider the two spin distributions shown schematically in **1**, which correspond to a ferromagnetic high spin (Φ_{HS}) and an antiferromagnetic low spin state (Φ_{LS}), respectively. The diagonal elements of the *Heisenberg* Hamiltonian are:

$$E_{\mathrm{HS}} = \langle \Phi_{\mathrm{HS}} | \hat{H} | \Phi_{\mathrm{HS}} \rangle = -\frac{J_{12}}{4} \tag{3a}$$

and

$$E_{\mathrm{LS}} = \langle \Phi_{\mathrm{LS}} | \hat{H} | \Phi_{\mathrm{LS}} \rangle = +\frac{J_{12}}{4} \tag{3b}$$

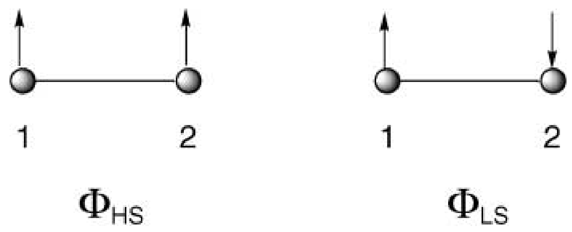
By taking the difference of these two equations we can evaluate the exchange coupling constant for this case:

$$E_{\mathrm{HS}} - E_{\mathrm{LS}} = -\frac{J_{12}}{2} \tag{4}$$

The calculation of E_{HS} and E_{LS} using quantum chemical methods is, however, not straightforward. The main problem arises when one wants to evaluate the energy for the spin distribution corresponding to the antiferromagnetic state. The single determinant Φ_{LS} is not a proper wave function of the $\hat{S}^2$ operator and it corresponds to a broken symmetry solution. Within the *Hartree-Fock* methodology it has been demonstrated that using spin-projection techniques one arrives at an expression that is identical to [4]. However, in previous works we have shown that the use of DFT-based calculations in this equation leads to poor results. Excellent agreement with experimental values for a large variety of compounds is obtained if no spin projection is applied. The resulting equation in this case is:

$$E_{\mathrm{HS}}^{\mathrm{DFT}} - E_{\mathrm{LS}}^{\mathrm{DFT}} = -J_{12} \tag{5}$$

The reader interested in the origin of the differences between both approaches may find an extensive discussion on this topic in references [24, 26, 27].



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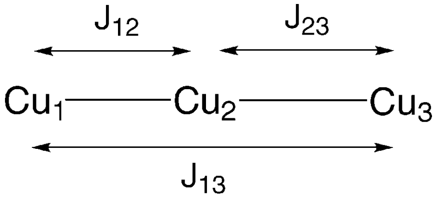

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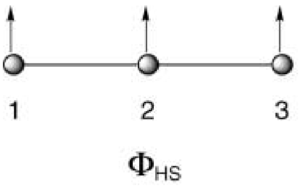

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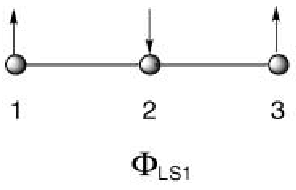

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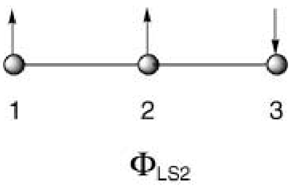


3c

Generalization of these equations to the case in which the two paramagnetic centers bear different spins, S_1 and S_2, respectively, can be obtained by introducing a new factor in Eqs. (4) and (5):

$$E_{\mathrm{HS}} - E_{\mathrm{LS}} = -(2S_1S_2)J_{12} \tag{6}$$

and

$$E_{\mathrm{HS}}^{\mathrm{DFT}} - E_{\mathrm{LS}}^{\mathrm{DFT}} = -(2S_1S_2 + S_2)J_{12} \tag{7}$$

respectively, where $S_1 > S_2$ [28].

Extension of this procedure to obtain the set of coupling constants for a polynuclear compound with more than two paramagnetic centers is quite straightforward and it will be illustrated here in the case of trinuclear Cu(II) compounds in which each paramagnetic center bears a single unpaired electron ($S_i = 1/2$). For a symmetric compound in which two of the three copper atoms are equivalent (**2**), the exchange coupling is defined by two independent coupling constants $J_{12} = J_{23}$ and J_{13}. In this case we must evaluate the energy for three different spin distributions in order to obtain two equations that relate the values of the coupling constants with the evaluated energies. The most convenient procedure to find these two equations is based on the fact that the *Heisenberg* Hamiltonian for the polynuclear system [1] is built as a simple sum of pairwise spin interactions. If we consider the high-spin state shown schematically in **3a** and the low-spin states **3b** it is easy to see that the energy difference between these two states will have only two contributions. The first one will arise from the pair $S_1 \cdots S_2$ which is in a parallel alignment in **3a** and in an antiparallel one in **3b**. The same occurs for the spin pair $S_2 \cdots S_3$. Since the energy difference between the parallel and antiparallel alignments within each pair is given by Eq. (5) using a DFT-based method, the total energy difference between the two spin arrangements will be

$$E_{\mathrm{HS}}^{\mathrm{DFT}} - E_{\mathrm{LS1}}^{\mathrm{DFT}} = -2J_{12} \tag{8}$$

It is important to note that J_{13} does not appear in this equation because we have the same alignment for the $S_1 \cdots S_3$ pair in both spin distributions.

The equation needed to evaluate J_{13} can be obtained from the high-spin solution **3a** and the low-spin distribution **3c**. In this case the two spin pairs that contribute to the energy difference are $S_2 \cdots S_3$ and $S_1 \cdots S_3$. Using Eq. (5) for each pair, the total energy difference is:

$$E_{\mathrm{HS}}^{\mathrm{DFT}} - E_{\mathrm{LS2}}^{\mathrm{DFT}} = -J_{12} - J_{13} \tag{9}$$

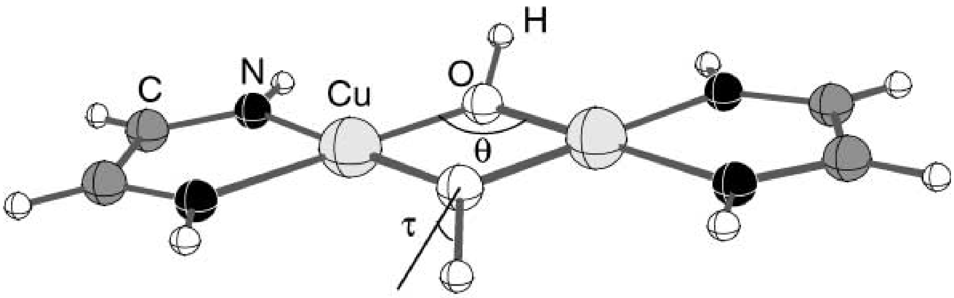
Note that the coupling constant between nearest neighbors, J_{12}, is independent from the energy of the intermediate state Φ_{LS2}. In case we want to obtain only this value (J_{13} is usually taken to be strictly zero in many experimental studies) we would need only to compute the energies of the high spin and the low-spin state Φ_{LS1}.

Computational Details

All DFT calculations were performed using the hybrid B3LYP functional [29] as implemented in the Gaussian98 package [30]. Basis sets proposed by *Schaefer et al.* were employed throughout, of triple-ζ quality for the transition metal atoms [31] and double-ζ quality for all other atoms [32]. Due to the small magnitude of the exchange coupling constants all energy calculations must be performed including the SCF = *Tight* option of Gaussian to ensure sufficiently well converged values for the state energies.

Magneto-Structural Correlations for Trinuclear Hydroxo-Bridged Cu(II) Compounds

In previous works we have performed a detailed computational analysis of the influence of the molecular geometry on the exchange coupling constants for hydroxo- and alkoxo-bridged Cu(II) dinuclear compounds using the model compound shown in **4** (for the alkoxo-bridged compounds the hydrogen atoms on the bridges are replaced by methyl groups) [24, 25]. The reader must be aware that in those publications we employed a slightly different *Heisenberg* Hamiltonian using $2J$ instead of J as multiplicative factor. The most important conclusion obtained in those works is that two key structural parameters dictate the nature of the exchange coupling in these compounds: the Cu–O–Cu angle θ, and the out-of-plane displacement of the hydrogen atom (or alkoxo group) at the bridge, measured by the angle τ. The general conclusion is that for large values of the Cu–O–Cu angle ($\theta > 100°$) and the hydrogen atoms lying in the plane ($\tau = 0°$) strong antiferromagnetic coupling is expected ($J_{12} < -400\,\mathrm{cm}^{-1}$). If θ is decreased or if the hydrogen atoms are pulled out of the Cu_2O_2 plane, the antiferromagnetic character is decreased. Ferromagnetic coupling can be achieved, for instance, in hydroxo-bridged compounds with $\theta < 98°$ and $\tau = 60°$. A detailed analysis of the variation of the ground state energy with the molecular geometry at the Cu_2O_2 ring shows, however, that both parameters are indeed not independent, so that small values of θ imply large out of plane deviations



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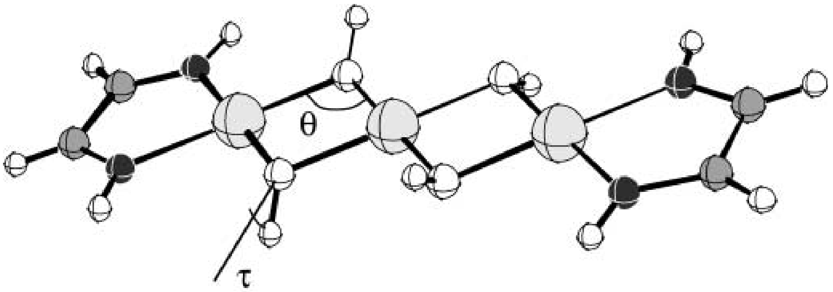

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of the hydrogen atom or the alkyl groups at the bridge. Although the same qualitative behavior is predicted for hydroxo and alkoxo-bridged compounds, the latter show stronger antiferromagnetic coupling for geometries with the same pair of (θ, τ) values.

The main aim of this work is to find out if these magneto-structural correlations still hold for analogous linear trinuclear compounds. In this case the additional coupling constant between next-nearest neighbors and its variation with the molecular geometry must be also considered. The model employed for the calculations on trinuclear compounds **5** is just an extension of that used earlier for dinuclear compounds (see **4**), keeping the nature of the terminal ligands and all geometric parameters the same [24, 25].

The nearest-neighbor exchange coupling constant J_{12} for the hydroxo-bridged trinuclear complex shows a very similar dependence on θ (Fig. 1) to that found for the dinuclear model. Antiferromagnetic coupling is expected for all values of θ if the hydrogen atoms on the bridge are kept on the Cu_2O_2 plane. The absolute values of J_{12} are very similar to those calculated for the dinuclear model, with the largest deviation found for large values of θ. Pulling the hydrogen atoms out of the plane decreases the antiferromagnetic coupling between nearest neighbors, in the same way as in dinuclear compounds. Nearest-neighbor ferromagnetic coupling is expected for $\theta < 99°$ and $\tau > 60°$.

Exchange coupling between next-nearest neighbors is practically unaffected by the distortion of the molecular geometry (Fig. 2). An average value of

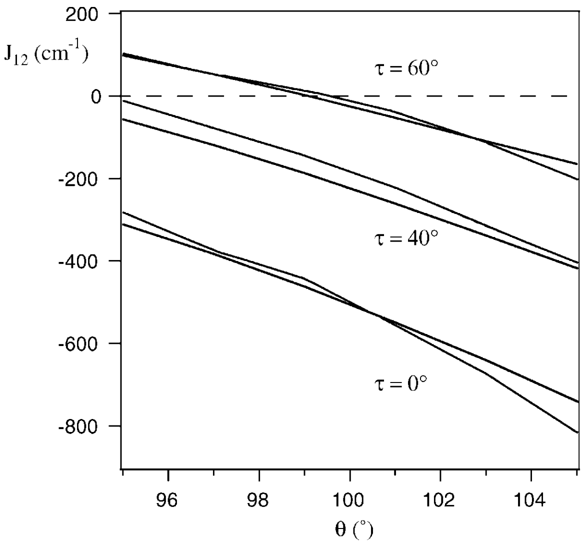

Fig. 1. Nearest-neighbor coupling constant J_{12} calculated for the trinuclear model compound with different values of τ; for comparison, the values obtained for the coupling constant in a dinuclear model with the same geometry are also indicated with dashed lines

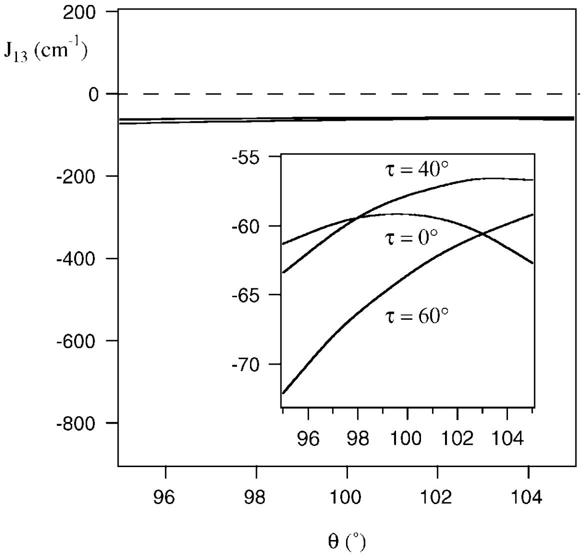

Fig. 2. Next-nearest-neighbor coupling constant J_{13} calculated for the trinuclear model compound with different values of τ; the same curves are shown in the inset using an expanded scale for the coupling constant

approximately $-60\,\mathrm{cm}^{-1}$ is observed for J_{13} in all cases. The magnitude of this parameter indicates that although roughly constant, the usual approximation in experimental studies which consider this value as negligible is, at least, doubtful. A detailed analysis shows that J_{13} is more sensitive to geometry changes for cases with larger τ values. It is interesting to note that in trinuclear compounds with the

Table 1. Calculated exchange coupling constants (cm^{-1}) using trinuclear models in which one of the Cu(II) ions is replaced by a diamagnetic Zn(II) ion. Coupling constants obtained for the trinuclear Cu(II) model with the same molecular geometry are given in parenthesis

θ	τ	J_{12}	J_{13}
95°	60°	+ 82.7 (+ 97.8)	− 90.3 (− 72.1)
101°	60°	− 88.5 (− 53.4)	− 90.8 (− 62.4)
105°	0°	− 833.4 (− 740.0)	− 129.8 (− 62.7)

hydrogen atoms far from the Cu_2O_2 plane, the situation in which the values of J_{12} and J_{13} are similar is possible. For the compound with $\theta = 101°$ and $\tau = 60°$, for example, the computed values of J_{12} and J_{13} are -88.5 and $-90.8\,\mathrm{cm}^{-1}$, respectively.

An alternative way to estimate the exchange coupling constants in a trinuclear compound is the replacement of one of the three Cu(II) paramagnetic centers by a diamagnetic ion such as Zn(II). These Cu_2Zn models are equivalent in their magnetic behavior to dinuclear Cu(II) complexes for which the coupling constant can be evaluated using Eq. (5). If one of the terminal Cu atoms is replaced by Zn in the model, the calculation yields an approximation to the nearest neighbor coupling constant J_{12}. On the other hand, if the central Cu atom is replaced, the computed exchange coupling constant is comparable to J_{13} in the trimer. Calculations of the coupling constants by this alternative procedure for three significative structures (Table 1) confirm the general trends found for the coupling constants evaluated for the copper trinuclear compounds, although slightly stronger antiferromagnetic coupling is found in all cases. The only case in which a significant discrepancy between the two methods is found is that of $\theta = 105°$ and $\tau = 0°$, for which the value for J_{13} in the model with Zn is twice that found for the trinuclear copper compound.

Concluding Remarks

Nearest-neighbor exchange coupling in trinuclear hydroxo-bridged copper(II) complexes shows very similar trends to those found earlier for dinuclear compounds for which the Cu–O–Cu angle and the out of plane displacement of the hydrogen atoms at the bridge are the two key structural factors that determine their magnetic behavior. A variation of more than $1000\,\mathrm{cm}^{-1}$ can be obtained by a suitable change in these two parameters. Coupling between next-nearest neighbors is, on the contrary, found to be nearly independent from structural changes in the Cu_2O_2 core. The usual approach of considering a practically negligible coupling constant between the terminal atoms in linear trinuclear compounds is, however, questioned by the relatively important value of the coupling constant predicted by our calculations. The good agreement between calculated and experimental coupling constants obtained using the same computational scheme for other dinuclear and tetranuclear compounds gives us confidence on the general trends found for the case of linear trinuclear hydroxo-bridged copper(II) compounds for which no experimental data have been published.

Acknowledgments

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