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A Theoretical Study of the Nearest Cu···Cu Antiferromagnetic Exchange Coupling Interactions in [$LaCu_6$] and [YCu_6]

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A density functional study of the exchange coupling interactions between the two nearest Cu^{II} centers in [$LaCu_6$] and [YCu_6] is presented. Two approaches show that the Cu···Cu antiferromagnetic interactions increase with a decrease of the ionic radius of the diamagnetic central La^{III} and Y^{III} ions. However, the influence of the central ions on the Cu···Cu interactions is small compared to that of their structures according to our calculations. We therefore conclude that the stronger antiferromagnetic interactions between the two nearest Cu^{II} centers in [$LaCu_6$] than in [YCu_6] are not a result of the central La^{III} ion but the structure. The antiferromagnetic contributions of the direct overlap between the two nearest Cu^{II} magnetic orbitals also play a major role according to the calculations of the overlap integral S_{ij} based on Kahn's theory.

Introduction

In recent years, the synthesis and study of single-molecule magnets with high total spin that can be used to store data has received much attention.[1–15] Among these single-molecule magnets, heteropolynuclear transition-metal and rare-earth mixed complexes are of great interest due to their interesting structures and magnetic properties.[14,15] In a recent experimental study, Liu et al.[10] considered that the substitution of the central La^{III} ion with Y^{III} will decrease the antiferromagnetic exchange coupling interactions between the two nearest Cu^{II} ions in [$LaCu_6(\mu\text{-}OH)_3(HL)_2(L)_4$]($ClO_4$)$_2$·25$H_2O$[15] and [$YCu_6(\mu\text{-}OH)_3(HL)_2(L)_4$]($ClO_4$)$_2$·25$H_2O$[14] ($H_2L$ = iminodiacetic acid) clusters and that the direct overlap of Cu orbitals plays a minor role since this would enhance the antiferromagnetic coupling at shorter Cu···Cu separations. However, the above conclusions are not correct according to our calculations. Herein, we investigate the influence of the diamagnetic central ions La^{III} and Y^{III} and the effects of the direct overlap of Cu orbitals on the exchange coupling interactions between the two nearest Cu^{II} ions in the clusters [$LaCu_6$] and [YCu_6] by density functional theory (DFT).

Computational Methodology

Description of the Complexes and Models

Complex **1-La**[15] [$LaCu_6(\mu\text{-}OH)_3(HL)_2(L)_4$] ($H_2L$ = iminodiacetic acid) contains two parallel layers, each of which is composed of three Cu^{II} ions and three ligands. Six Cu^{II} ions form a trigonal prism with the La^{III} ion located in the center (see Figure 1). Each two nearest Cu^{II} centers are connected by bridging hydroxides. The Cu–O–Cu angles are 120.7°. The nearest Cu···Cu distance is 3.383 Å and the La···Cu distance is 3.509 Å. The structure of model **1-Y** is the same as that of complex **1-La** except that its central ion is Y^{III} not La^{III}. Complex **2-Y**[14] [$YCu_6(u\text{-}OH)_3(HL)_2(L)_4$] has a similar structure to that of **1-La** (see Figure 2). The Cu–O–Cu angles are 118.3°, the nearest Cu···Cu distance is 3.323 Å, and the Y···Cu distance is 3.447 Å. The structure of model **2-La** is the same as that of complex **2-Y** except

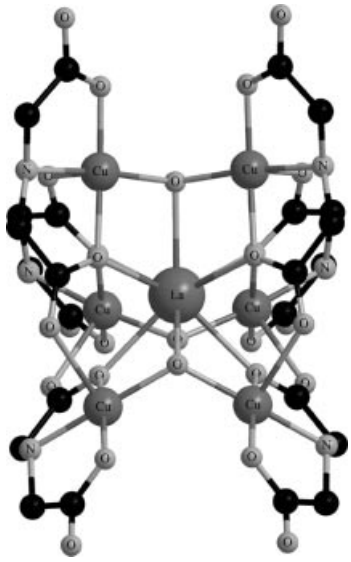

Figure 1. Structure of complex **1-La** ($LaCu_6$).

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that the central ion is La^{III} not Y^{III}. In all the complexes and models, the six Cu^{II} centers are symmetry equivalent. A thorough description of the above complexes can be found in the literature.[14,15] To be able to compare our calculated coupling constants for complete structures with the experimental values, we used the experimentally determined molecular structure rather than an optimized one in our calculations because small changes to the experimental structure could result in significant deviations of the coupling constant.

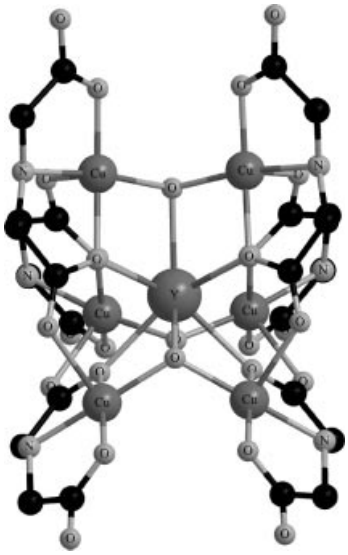

Figure 2. Structure of complex **2-Y** (YCu_6).

Calculation of the Exchange Coupling Constants

There are two different approaches to calculate the exchange coupling constants for polynuclear complexes.[3–5] In all calculations, the spin-orbit coupling is not considered, so the magnetic anisotropy needs not be considered. The first approach consists of evaluating the exchange coupling constant, J_{ij}, between two paramagnetic metal centers i and j in the hexanuclear molecule by calculating the energy difference between the highest and broken-symmetry spin states of a model molecule in which the metal atoms, except for i and j, are substituted by diamagnetic Zn^{II} cations. This approach has been used to calculate the exchange coupling interactions of hexanuclear complexes many times and has proven to give good results compared to the experimental ones.[3–5,16] The second approach is to calculate the different spin-state energies of hexanuclear complexes and use the Heisenberg Hamiltonian to obtain the exchange coupling constants between different metal centers.[3–5,16,17] This is a more rigorous approach for evaluating J for polynuclear complexes than the first one. How to use these two approaches will be discussed thoroughly below.

First of all we will discuss the first approach. The magnetic interactions between Cu^{II} metal ions were studied on the basis of density functional theory (DFT) coupled with the broken-symmetry approach (BS).[18–20] The exchange coupling constants J were evaluated by calculating the energy difference between the high-spin state (E_{HS}) and the broken-symmetry state (E_{BS}) by assuming that the spin Hamiltonian is defined as shown in Equation (1).

$$\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2 \quad (1)$$

If the spin-projected approach is used, the equation proposed by Noodleman[18–20] to extract the J value for a binuclear transition-metal complex becomes

$$J = \frac{E_{BS} - E_{HS}}{4S_1S_2} \quad (2)$$

For all the models, where $S_1 = 1/2$, $S_2 = 1/2$ for Cu^{II}, we derive Equation (3) from (2),

$$J = E_{BS} - E_{HS} \quad (3)$$

while with the non-projected approach[21]

$$2J = \frac{E_{BS} - E_{HS}}{2S_1S_2 + S_2} \quad (4)$$

where S_1 and S_2 are the total spins of the two interacting paramagnetic centers and S_1 is assumed to be greater than S_2 for heterodinuclear complexes.

For all the models, we derive Equation (5) from (4).

$$J = (E_{BS} - E_{HS})/2 \quad (5)$$

There are a lot of discussions as to whether Equation (4) can be used to calculate J.[21–27] Adamo and co-workers consider that Equation (4) corresponds strictly to the limit of complete overlap between the magnetic orbitals and such a hypothesis is not sustained,[22,23] although it can give good J results compared to experiment.[21,24,25] Ruiz and co-workers[26,27] think that the spin-projected approach [Equation (2)] introduces a double counting of the static correlation contributions due to the multi-determinant character of the broken symmetry solution obtained with the common functional that includes a self-interaction error. However, the non-projected approach [Equation (4)] can remove the self-interaction correction (SIC)[28] error and give better J values. A detailed discussion of the two approaches can be found in the literature.[21–27] In this paper, Equations (2) and (4) are both used to calculate the J values. The differences in the calculated J values using the two approaches will be discussed below.

Now we interpret the more rigorous second approach. If one neglects spin-orbit coupling effects, the Hamiltonian for a general extended structure is given by Equation (6).

$$\hat{H} = \sum_{i>j}(-2J_{ij}\hat{S}_i\hat{S}_j) \quad (6)$$

where $\hat{S}_i$ and $\hat{S}_j$ are the spin operators of the different paramagnetic centers and the J_{ij} values are the coupling constants between all the paramagnetic centers. Here, we only consider the exchange interactions between nearest neighbors. This fact, together with the presence of additional symmetry elements in the structure, normally results in a reduced set of J_{ij} values.

For complexes **1-La** and **2-Y**, 15 pair-wise coupling constants can in principle be calculated (see Figure 3), but these are reduced by symmetry to yield only three independent coupling constants for a symmetric structure:

$$J = J_{12} = J_{34} = J_{56};\ J' = J_{15} = J_{26} = J_{35} = J_{46} = J_{13} = J_{24};\ J'' = J_{16} = J_{25} = J_{36} = J_{45} = J_{14} = J_{23} \quad (7)$$

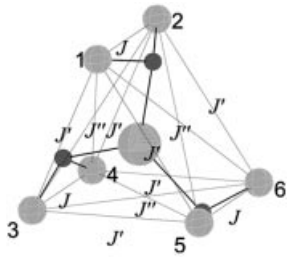

Figure 3. A sketch of the interactions between each Cu^{II} center.

For the systems studied here, we only need to calculate four different spin configurations for each of the models **1-La**, **1-Y**, **2-Y**, and **2-La**, namely **A** ($S = 0$), **B** ($S = 0$), **C** ($S = 1$), and **F** ($S = 3$; see Figure 4). From the calculated relative energies of these spin configurations, we can extract exchange coupling constants by associating them to energy expressions obtained as a sum of pair-wise interactions, as introduced in the Heisenberg Hamiltonian. Given the energy differences between the four spin states, we can evaluate the exchange coupling constants *J*.

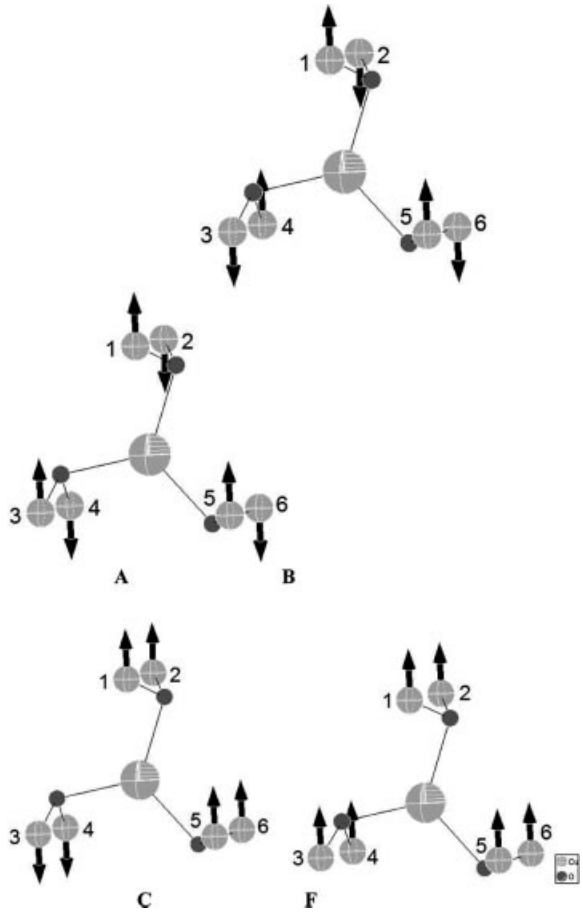

Figure 4. Four spin states: **A** ($S = 0$), **B** ($S = 0$), **C** ($S = 1$), and **F** ($S = 3$) for all the models.

$$E_A - E_F = 6J + 2(J' - J'') \quad (8)$$

$$E_A - E_B = 8(J' - J'') \quad (9)$$

$$J = \frac{(E_A - E_F)}{6} - \frac{(E_A - E_B)}{24} \quad (10)$$

Although the J' and J'' values are very small and have no corresponding experimental equivalents, we also calculated these values using the second approach. The equations to extract J' and J'' are:

$$J' = \frac{(E_C - E_F)}{4} + \frac{(E_A - E_B)}{16} \quad (11)$$

$$J'' = \frac{(E_C - E_F)}{4} - \frac{(E_A - E_B)}{16} \quad (12)$$

Density functional calculations were performed using the Amsterdam Density Functional (ADF, version 2004.01[29–31]) package for the four model clusters. Illas et al.[32] have shown the strong dependence of the calculated *J* with respect to the exchange-correlation functionals chosen, therefore several exchange-correlation functionals were used to evaluate *J*. In the calculations of *J* using ADF, the local density approximation (LDA) made use of the Vosko, Wilk, and Musair[33] (VWN) local correlation functional. A series of generalized gradient approximations (GGAs), namely the Perdew–Wang 1991 (PW91),[34] the Perdew–Burke–Ernzerhof (PBE),[35] and the recently developed OPTX-Perdew (OP86)[36,37] and OPTX-Perdew–Burke–Ernzerhof (OPBE)[35–37] functionals were examined. The tau-dependent meta-GGAs such as VSXC[38] and tau-HCTH[39] were also examined. For Cu and Zn, the TZV2P basis set (a basis set of triple-ξ quality[40] with two polarization functions) was applied. For La and Y, the TZV2P basis set (a basis set of triple-ξ quality[40] with one polarization function) was applied. The DZP basis set (a basis set of double-ξ quality[40] supplemented with one polarization function) was used for the other atoms (C, N, O and H). The inner core shells of C (1s), N (1s), O (1s), Cu (1s,2s,2p), Zn (1s,2s,2p), Y (1s,2s,2p,3s,3p,3d), and La (1s,2s,2p,3s,3p,3d,4s,4p,4d) were treated with the frozen core approximation. The accuracy parameter (accint) for the numerical integration grid was set to 4.0 for all complexes. The convergence standard of the system energy was set to be smaller than 10^{-6} eV in order to reach the precision required for the evaluation of *J*.

Results and Discussion

Evaluation of *J* for Each Model

The calculated and experimental values are shown in Table 1. The *J* values calculated using the first approach with Equation (2) for all the models show larger differences

with respect to the experimental values. However, there is a good improvement in the calculated ones obtained using Equation (4). The reason for this has been mentioned above. However, we obtain the same qualitative description of the magnetostructural correlations from the *J* values calculated using both Equation (2) and Equation (4). For models **1** (**1-La** and **1-Y**), the *J* values calculated using the two approaches with all the functionals are consistent with the experimental values. However, for models **2** (**2-Y** and **2-La**), the calculated *J* values using the first approach (BS-DFT) with all functionals except for the meta-GGA tau-HCTH show a large difference from the experimental values. In the BS-DFT approach we used Zn^{II} to replace the Cu^{II} to calculate the *J* values and did not consider the influence of the other Cu^{II} center. This approximation is acceptable for models **1** because the *J′* and *J″* values are very small compared to *J*. However, the *J′* and *J″* values for models **2** are similar to that of *J* and so the influence of the other Cu^{II} cannot be ignored. The BS-DFT approach therefore gives inaccurate *J* values for models **2**, although the second approach, which considers the influence of all the Cu^{II} centers, gives better ones. The second approach is therefore a more rigorous one for evaluating Cu···Cu interactions irrespective of whether they are strong or weak, as we reported in our previous papers.[41,42]

For **1-La**, the *J* values calculated with the meta-GGA VSXC are the closest to the experimental value[15] (–12.0 cm^{-1}). However, the VSXC functional gives poor *J* values for **2-Y**. Although the first approach gives the opposite sign for complex **2-Y**, both approaches with all the functionals show that the antiferromagnetic interactions between the two nearest Cu^{II} centers in complex **1-La** are stronger than those in complex **2-Y**, which is consistent with the experimental results. It can be seen that the calculated *J* values are qualitatively correct (indeed, some are in good agreement with the experimental ones) and empirically scale the *J* with respect to experiments.

In their studies, Liu et al.[14] considered that the strength of the antiferromagnetic interactions between the two nearest Cu^{II} centers for the above two complexes is due to the central ions. They concluded that the stronger antiferromagnetic interactions in complex **1-La** are because its central ion is La^{III}, which has a greater ionic radius, and the direct overlap of metal orbitals plays a minor role. Whether the central ions have a dominant effect on the interactions between the two nearest Cu^{II} ions will be discussed in the following section.

Effects of the Central Ions on the Interactions Between the Two Nearest Cu^{II} Ions

To investigate the effects of the central ions on the interactions between the two nearest Cu^{II} ions, we replaced the La^{III} in complex **1-La** with Y^{III} to obtain the model **1-Y** and also substituted Y^{III} with La^{III} in complex **2-Y** to obtain the model **2-La**. From the calculated *J* values of **1-La** and **1-Y** (Table 1), we can see that substituting La^{III} with Y^{III} enhances the interactions between the two nearest Cu^{II} centers, which is opposite to the conclusion reached by Liu et al.[14] From the calculated *J* values of **2-Y** and **2-La**, we find that replacing Y^{III} with La^{III} weakens the interactions, although the first approach with the GGAs PW91, PBE, OP86, and OPBE gives almost the same *J* values for **2-Y**

Table 1. Experimental *J* and calculated *J*, *J′*, and *J″* values [cm^{-1}] for models **1** (**1-La** and **1-Y**) and **2** (**2-La** and **2-Y**) obtained from the two approaches (one is the BS-DFT approach and the other approach is to obtain the J_{ij} by calculating the energies of several pure spin states) with several LDA, GGA, and meta-GGA functionals.

	1-La					**1-Y**				
	Dinuclear model		Full structure			Dinuclear model		Full structure		
	J [cm^{-1}]		*J* [cm^{-1}]	*J′* [cm^{-1}]	*J″* [cm^{-1}]	*J*(cm^{-1})		*J* [cm^{-1}]	*J′* [cm^{-1}]	J″ [cm^{-1}]
	Equation (2)	Equation (4)				Equation (2)	Equation (4)			
VWN	–68.0	–34.0	–33.7	5.1	6.0	–91.0	–45.5	–40.1	7.2	7.8
PW91	–49.2	–24.6	–22.5	6.1	8.3	–65.4	–32.7	–26.8	6.9	8.9
PBE	–49.2	–24.6	–22.4	6.4	8.4	–65.2	–32.6	–26.7	7.0	9.0
OP86	–34.4	–17.2	–16.0	6.7	8.4	–54.0	–27.0	–21.3	7.7	9.2
OPBE	–33.4	–16.7	–15.2	7.3	9.0	–53.0	–26.5	–20.1	8.2	9.8
VSXC	–26.3	–13.2	–10.5	7.3	9.4	–47.1	–23.6	–16.4	8.6	10.5
tau-HCTH	–33.9	–17.0	–15.9	7.5	7.7	–61.9	–30.9	–23.1	9.2	9.4
Exp.			–12.0[11]							
	2-Y					**2-La**				
	Dinuclear model		Full structure			Dinuclear model		Full structure		
	J [cm^{-1}]		*J* [cm^{-1}]	*J′* [cm^{-1}]	*J″* [cm^{-1}]	*J* [cm^{-1}]		*J* [cm^{-1}]	*J′* [cm^{-1}]	*J″* [cm^{-1}]
	Equation (2)	Equation (4)				Equation (2)	Equation (4)			
VWN	15.0	7.5	–12.3	3.0	0.4	23.6	11.8	–6.8	2.9	0.7
PW91	38.6	19.3	–4.5	3.3	1.7	39.8	19.9	–1.0	3.1	1.7
PBE	40.2	20.1	–4.2	3.4	1.8	41.4	20.7	–0.7	3.3	1.9
OP86	32.8	16.4	1.8	5.8	4.3	33.8	16.9	5.5	5.6	5.0
OPBE	34.2	17.1	2.6	6.6	5.1	36.0	18.0	6.2	6.4	5.1
VSXC	67.2	33.6	9.4	7.1	5.4	66.6	33.3	13.9	7.0	5.7
tau-HCTH	1.2	0.6	2.6	10.4	8.4	7.4	3.7	8.3	10.2	8.5
Exp.			–3.5[10]							

and **2-La**. In conclusion, substituting La^{III} with Y^{III} enhances the antiferromagnetic interactions between the two nearest Cu^{II} centers and these interactions in models **1** (**1-La** and **1-Y**) are always stronger than those in models **2** (**2-Y** and **2-La**), irrespective of whether the central ions are La^{III} or Y^{III}. Moreover, we find that the central ions La^{III} and Y^{III} have only a very small influence on the values of J' and J'' and can be ignored for models **1** (**1-La** and **1-Y**) and **2** (**2-Y** and **2-La**).

From the above results, we conclude that the antiferromagnetic Cu···Cu interactions increase with a decrease of the ionic radius of the diamagnetic central ion. Irrespective of whether the central ions are La^{III} or Y^{III}, the nearest Cu···Cu interactions in models **1** (**1-La** and **1-Y**) are all stronger than those in models **2** (**2-Y** and **2-La**), therefore their structures have a larger influence on the nearest Cu···Cu interactions. In the next section we will investigate the effects of the structural parameters on the nearest Cu···Cu interactions.

Effects of the Structural Parameters on the Interactions Between the Two Nearest Cu^{II} Ions

The nearest Cu···Cu distance decreases from 3.383 to 3.323 Å, the Ln···Cu distance decreases from 3.509 to 3.447 Å, and the Cu···O···Cu angle decreases from 120.7° to 118.4° on going from complex **1-La** to complex **2-Y**. In a recent paper,[43] Ruiz et al. calculated the value of J between Cu^{II} with several different Cu···O···Cu angles and Cu···Cu distances and concluded that a decrease of the Cu···O···Cu angle weakens the antiferromagnetic Cu···Cu interactions when such angles are larger than about 100° in spite of the antiferromagnetic contributions due to the decrease of the Cu···Cu distance. We can see the same from Table 2, which only gives the results calculated using the PW91 functional, namely that the decrease of the Cu···O···Cu angle weakens the antiferromagnetic Cu···Cu interactions in spite of the decrease of the Cu···Cu distance when the diamagnetic central ions are La^{III}. The same results are also obtained using the other functionals. When the central ions are Y^{III}, we obtain the same trend. The above results can also be obtained from the book written by Kahn.[44] Therefore, we can see from the calculated and experimental results in Table 1 that the absolute J values in models **1** (**1-La** and **1-Y**) are all larger than those in models **2** (**2-Y** and **2-La**).

From the calculated J' and J'' values in Table 2, the weaker Cu···Cu ferromagnetic interactions in **2-La** appear to be due to its shorter Cu···Cu distances, which enhance the antiferromagnetic interactions and therefore decrease J' and J''. The same results can also be found for **1-Y** and **2-Y**.

That the differences between the J values calculated for **1-La** and **1-Y** or **2-Y** and **2-La** are small shows that the antiferromagnetic exchange interactions between the two nearest Cu^{II} centers occur mostly through the nearest exchange pathway (Cu···O···Cu) and that the long exchange pathways via Y^{III} or La^{III} could possibly give rise to a weak antiferromagnetic component similar to the results reported in ref.[45]

Table 2. Dependence of J_{ij} values between each two Cu^{II} on d(Cu···Cu) and Cu···O···Cu for complexes **1-La** and **2-Y** using the second approach (this approach gives J_{ij} by calculating the energies of several pure spin states) with the PW91 functional.

		d(Cu···Cu) [Å]	Cu···O···Cu [°]	J_{ij} [cm^{-1}]
J	**1-La**	3.383	120.7	–22.5
	2-La	3.323	118.3	–1.0
J'	**1-La**	5.326		6.1
	2-La	5.230		3.1
J''	**1-La**	6.310		8.3
	2-La	6.197		1.7

Qualitative Analysis of the Exchange Interaction

According to the Kahn–Briatt[46,47] (KB) and Hay–Thibeault–Hoffmann[48] (HTH) models, see Equations (13) and (14), respectively.

$$(\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2)$$

$$J_{ab} = K_{ab} - S_{ab}(\Delta^2 - \delta^2)^{1/2} \quad (13)$$

$$J_{ab} = K_{ab} - \frac{(\varepsilon_1 - \varepsilon_2)^2}{2(J_{aa} - J_{ab})} \quad (14)$$

Some authors[49,50] have recently shown that magnetic orbitals **a** and **b** are well represented by the localized orbitals of the broken-symmetry solution (called the BS-OMSO[51]). As usual, the changes in the J_{AF} term are more important and these contributions will usually control the magnetostructural correlations, especially those whose intramolecular interactions are antiferromagnetic. Hence, we have only considered the changes in the J_{AF} term. The J_{AF} term is associated with the overlap integral S_{ab} in the broken-symmetry spin solution between the two e_g magnetic orbitals ($d_{x^2-y^2}$) (KB model) or the square of the energy gap $(\varepsilon_1 - \varepsilon_2)^2$ in the high-spin solution between the orbitals bearing the unpaired electrons (HTH model). The S_{ab} and $(\varepsilon_1 - \varepsilon_2)^2$ values calculated using the first approach with the PW91 functional are shown in Table 3, where it can be seen that the values for models **1-La** and **1-Y** are almost the same, but larger than those of models **2-La** and **2-Y**. The above results show that the different diamagnetic central ions essentially do not influence the overlap integrals S_{ab} and the $(\varepsilon_1 - \varepsilon_2)^2$ values, although the structures of models **1** (**1-La** and **1-Y**) and **2** (**2-La** and **2-Y**) do have an influence on them. On going from the structures of models **1** to those of **2**, the Cu···O···Cu angles decrease from 120.7° to 118.4°. According to Kahn's investigations,[44] a decrease of the Cu···O···Cu angle will bring the magnetic orbitals closer to orthogonality and so the S_{ab} values for models **1** are larger than those for **2**. The stronger antiferromagnetic interactions in models **1** corresponding to the larger S_{ab} values show that the direct overlap between Cu^{II} orbitals also plays a major role.

Table 3. Calculated S_{ab} (a and b denote the magnetic orbitals occupied by the unpaired electrons on two Cu^{II} centers in the broken-symmetry spin solutions), $(\varepsilon_1 - \varepsilon_2)^2$ (eV^2) (ε_1 and ε_2 denote the energies of the orbitals bearing the unpaired electrons in the high-spin solutions), and $-(\rho^2_{HS} - \rho^2_{BS})$ values for models **1** (**1-La** and **1-Y**) and **2** (**2-La** and **2-Y**) obtained using the first approach (BS-DFT) with the PW91 functional.

	1-La	1-Y	2-Y	2-La
S_{ab}	0.021	0.023	0.008	0.008
$(\varepsilon_1 - \varepsilon_2)^2$ [eV^2]	0.6464	0.6544	0.1764	0.1789
$\rho^2_{HS} - \rho^2_{BS}$	0.0092	0.0089	0.0027	0.0028

Blanchet-Boiteux and Mouesca[50,52] have proposed that the antiferromagnetic part of the exchange coupling constant in di-μ-oxo-bridged binuclear Cu^{II} complexes can be split into two terms, one associated with the metal d orbitals, which is always positive, and the other representing the contribution of the bridging ligand. The second term can be related to the copper spin population through the analytical expression given in Equation (15), derived from a Mulliken population analysis.[53]

$$J \propto -(\rho^2_{HS} - \rho^2_{BS}) \quad (15)$$

Bi et al.[54] have found that the J values are almost linearly related to $-(\rho^2_{HS} - \rho^2_{BS})$ for a series of oxamidocopper complexes. We have also used Equation (15) to evaluate binuclear Mo^{III} complexes and also found that the J values are almost linearly related to $-(\rho^2_{HS} - \rho^2_{BS})$.[55] The spin populations were obtained by PW91 calculations on the basis of a Mulliken population analysis[53] using the first approach. Due to the symmetry of the structures, we only give the results for one of the Cu^{II} ions (Table 3). The stronger antiferromagnetic interactions in models **1** (**1-La** and **1-Y**), which correspond to larger $(\rho^2_{HS} - \rho^2_{BS})$ values, show that Equation (15) is also valid for the systems studied here, although it cannot differentiate the relative strengths of **1-La** and **1-Y** or **2-La** and **2-Y**.

Conclusions

From the above calculations, we conclude that the strength of the nearest Cu···Cu antiferromagnetic interactions increase with a decrease of the ionic radius of the diamagnetic central ion. However, this influence of the central ion on the exchange coupling interactions is small compared to the influence of the variation of the Cu···O···Cu angle. The weaker Cu···Cu antiferromagnetic interactions in models **2** (**2-La** and **2-Y**) compared to those in models **1** (**1-La** and **1-Y**) are because of the smaller Cu···O···Cu angles corresponding to the smaller S_{ab} and $(\varepsilon_1 - \varepsilon_2)^2$ values in models **2**. KB and HTH models have been used to demonstrate that the antiferromagnetic contributions of the direct overlap between the two nearest Cu^{II} centers also plays a major role and that the influence of the diamagnetic central ion on the direct overlap can be ignored.

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