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Magnetic Interactions in Two Heterobridged Dinuclear Copper(II) Complexes: Orbital Complementarity or Countercomplementarity?

Li-Li Wang,[†] You-Min Sun,[‡] Zhong-Nan Qi,[§] and Cheng-Bu Liu*,[†]

Institute of Theoretical Chemistry, Shandong University, Jinan 250100, P. R. China, School of Municipal and Environmental Engineering, Shandong Jianzhu University, Jinan 250101, P. R. China, and College of Chemistry and Chemical Engineering, University of Jinan, Jinan 250022, P. R. China

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The mechanisms of magnetic exchange interactions in two heterobridged μ-hydroxyl-μ-X dicopper complexes A and B (X = azaindole for A and X = pyrazole for B) are investigated by the calculations based on density functional theory combined with the broken-symmetry approach (DFT-BS). It is found that although the coordination circumstances of the copper centers in the two complexes are very similar, the magnetic magnitudes and signs are diametrically opposed. By the theoretical analyses of magnetic orbital interaction and spin distribution, it is indicated that the difference between the magnetic properties of the two complexes is due to the distinction of orbital interaction of two bridge ligands. Namely, the weak ferromagnetic coupling for complex A arises from the orbital countercomplementarity of the hydroxo and azaindole bridges while the strong antiferromagnetic coupling for complex B arises from the orbital complementarity of the hydroxo and pyrazolato bridges.

1. Introduction

In recent years, the bridged transition metal dinuclear complexes have been of interest for their simple structural and diverse magnetic properties and their ability to imitate the active sites in proteins.[1−5] Among these dinuclear metal systems, the heterodibridged dicopper compounds are attracting great attention for their flexible and novel magnetic properties. For example, in the μ-alkoxy/hydroxo-μ-X dinuclear Cu(II) complexes ($X = N_3^-$, NO_2^-, carboxylate, pyrazolate, azaindolate, etc.) the different μ-X ligands result in diverse magnetic properties.[6−9] To explain this significant phenomenon, the experimental and theoretical workers have made great efforts: the experimental chemists endeavor to develop novel heterobridged dinuclear Cu(II) complexes by changing the types and the coordinate modes of the ligands,[10−14] while the theoretical researchers focus their attention on the magnetic coupling mechanism in these complexes.[6] In general, these diverse magnetic properties of the heterobridged Cu(II) complexes are considered to be due to the cooperation effect of the different bridging ligands and this cooperation effect has been defined as orbital complementarity or countercomplementarity by McKee et al.[15,16] and Nishida et al. [17−19] However, it is still not very clear on how to explain the mechanisms of the two different cooperation effects. Herein, we chose two heterobridged μ-hydroxo-μ-azacyclo dinuclear Cu(II) complexes to investigate the cooperation interaction. Interestingly, two complexes have similar structures, but the magnetic behaviors of them are opposite. Hence, our research is focused on the different magnetic contribution of the two kinds of azacyclo bridging ligands.

2. Calculated Models

The two calculated models A and B (Figure 1) are predigested from two crystal structures, $Cu_2(L\text{-}F)(\mu\text{-azaindole})$ ($H_3L\text{-}F$ = 1,3-bis(3-fluorosalicylideneamino)-2-propanol)[20] and $\{Cu(\text{mepirizole})Br\}_2(\mu\text{-}OH)(\mu\text{-pyrazole})$,[21] respectively. The models A and B have very similar structures: the bridging ligands are both −OH and azacyclo, and the copper(II) centers are all in a square-planar four-coordinated geometry. In order to analyze independently the role of each bridging ligand, we also built single-bridged models A1, A2, B1, and B2 (Figure 1). The single-azacyclo-bridged model A1 is formed by replacing the −OH bridging ligands in model A by two −OH terminal ligands, and model B1 is formed by replacing the −OH bridging ligands in model B by two $-NH_3$ terminal ligands. The single-hydroxy-bridged models A2 and B2 are built by replacing the azacyclo bridging ligands by two $-NH_3$ terminal ligands in models A and B, respectively.

3. Computational Methods

All the calculations are carried out using the density functional theory (DFT) combined with the broken-symmetry (BS) approach, proposed by Noodleman.[22−24] The magnetic coupling constants J of the systems are described by the Heisenberg model, and the Heisenberg spin Hamiltonian is defined as $\hat{H} = -2J\hat{S}_1\hat{S}_2$ where $\hat{S}_1$ and $\hat{S}_2$ present the spins at sites 1 and 2, respectively. For the copper(II) dinuclear complexes, the calculation of the J value accords with the following expression:

$$E_{HS} - E_{BS} = -2J \qquad (1)$$

where the E_{HS} and E_{BS} denote the energy values of the highest spin state and the broken-symmetry state, respectively, the positive sign of the J value shows the ferromagnetic interaction, and the negative sign of the J value indicates the antiferromagnetic interaction.

All the calculations have been performed using Amsterdam density functional (ADF) package (version 2.0.1).[25] Vosko, Wilk, and Nusair's (VWN) functional is used for local spin

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* To whom correspondence should be addressed. Phone: +86-531-88361398. Fax: +86-531-88564464. E-mail: cbliu@sdu.edu.cn.

[†] Shandong University.

[‡] Shandong Jianzhu University.

[§] University of Jinan.

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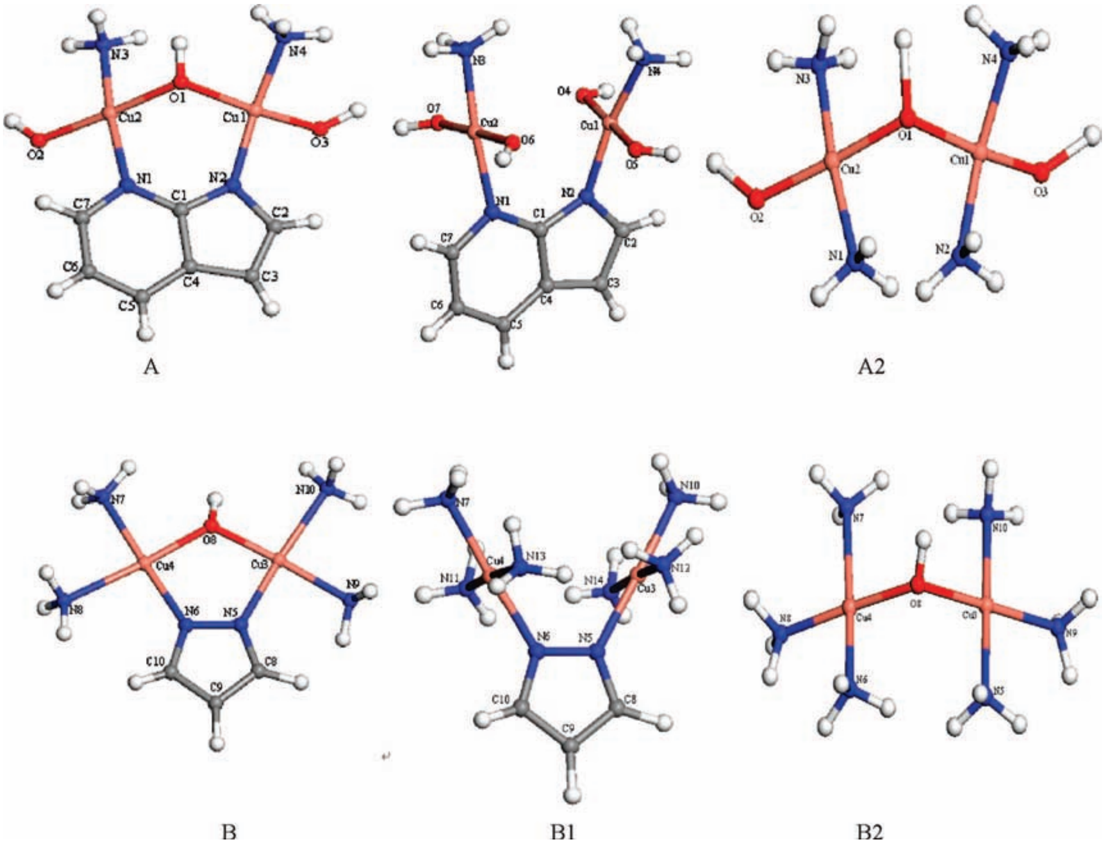


A A2

B B1 B2

Figure 1. Structures of the calculated models.

TABLE 1: Calculated Values of *J* for All the Models and Experimental Values of *J* for Models A and B

	model					
J, cm^{-1}	A	A1	A2	B	B1	B2
J_{cal}	10.49	4.47	−321.02	−556.50	−115.08	−316.64
J_{exp}	26.00[a]			−770.00[b]		

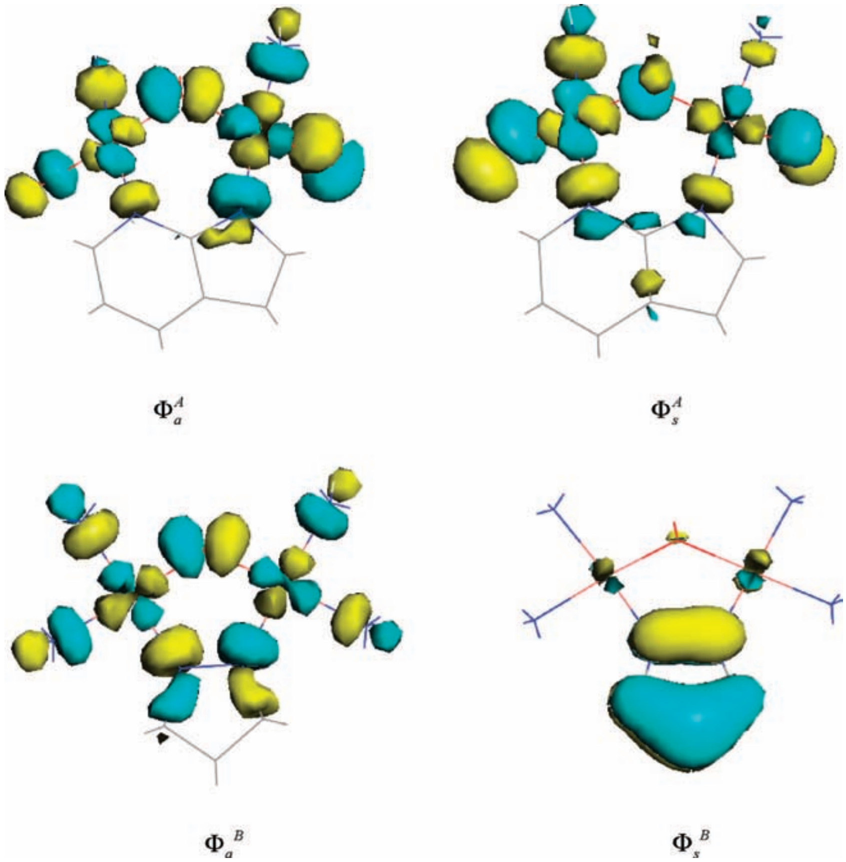
[a] Data from the ref 20. [b] Data from the ref 21.

density approximation (LSDA).[26] Generalized gradient correlations are introduced by using the Becke exchange functional[27] and the Perdew correlation functional.[28] IV basis sets in ADF containing triple-ζ basis sets and a polarization function from H to Ar are used for all atoms in the systems. The frozen core (FC) approximation for the inner core electrons is employed. The orbitals up to 2p for Cu atoms and 1s for C, N, and O atoms are kept frozen. The scalar relativistic effect is taken into account. The convergence criterion of SCF is 10^{-6}. The numerical integration procedure applied for the calculation is the polyhedron method developed by Velde and co-worker.[29] All the calculations have been done on an SGI O2100 server.

4. Results and Discussion

4.1. Correlation of the Two Bridging Ligands. The calculated magnetic coupling constants J of the models A and B along with the experimental values are listed in Table 1. It is found that the calculated J values of models A and B are smaller than the experimental datas. The errors of J values between the calculated and the experimental results are mainly due to the modeling of experimental structures. In addition, the intermolecular interaction and the influence of counterions on magnetic coupling are also not considered. However, the calculated magnetic properties of both models are in agreement with the experimental results, which reveal that model A shows a weak ferromagnetic behavior while model B shows a strong antiferromagnetic behavior. Structurally, model A and model B are very similar. However, the magnetic interactions of them are opposite to each other.

In order to elucidate the different magnetic properties of models A and B, the magnetic coupling constants of the single-bridged models A1, A2, B1, B2 (see Figure 1) are also calculated. The detail values are also summarized in Table 1. For the single-azacyclo-bridged models A1 and B1, the J values are calculated to be 4.47 and −115.08 cm^{-1}, respectively. Obviously, there are significant differences of the magnetic magnitudes and properties between the two single-azacyclo-bridged models. However, the calculated J values of the single-hydroxyl-bridged models A2 and B2 are very close (−321.02 and −316.64 cm^{-1}, respectively). In other words, in models A and B, the magnetic contributions of the hydroxyl bridging ligands are similar while the contributions of the azacyclo bridging ligands are diametrically opposed: one is weakly ferromagnetic coupling and the other is strong antiferromagnetic interaction. Furthermore, for model A, although the ferromagnetic contribution of the azaindole bridge is very small and the antiferromagnetic contribution of the hydroxyl bridge is large, the magnetic interaction is dominated by ferromagnetic interaction. This indicates that there may be counteraction between the two bridging ligands in model A. In model B, both the contributions of the hydroxyl and pyrazole bridging ligands are antiferromagnetic, and the J value of model B is larger than that of single-bridged models B1 and B2. Therefore, it is indicated that there exists cooperation between two bridging ligands in model B. In order to get the essential reason for the difference between the magnetic properties of model A and



Φ_a^A Φ_s^A

Φ_a^B Φ_s^B

Figure 2. Diagrams of the magnetic orbitals for the models A and B.

model B, we have made the molecular orbital analysis and spin density distribution analysis.

4.2. Molecular Orbital Analysis. According to the active-electron approximation,[6] in the bridged dinuclear magnetic systems it can be assumed that the coupling interaction is mainly associated with the overlaps between the magnetic orbitals of the metal centers and the highest occupied molecular orbitals (HOMO) of the bridging ligands. For the square-planar four-coordinate geometry of the Cu(II) centers of the two crystal structures, it is obvious that the unpaired electrons of Cu(II) centers occupy the $d_{x^2-y^2}$ orbitals of models A and B. According to Hoffmann's approach,[30] the two singly occupied d orbitals of the Cu(II) centers can form a symmetric magnetic orbital (ϕ_s) and an antisymmetric magnetic orbital (ϕ_a). The ϕ_s and ϕ_a can be expressed as eq 2.

$$\begin{aligned}\phi_s &= d_{x^2-y^2}(1) + d_{x^2-y^2}(2)\\ \phi_a &= d_{x^2-y^2}(1) - d_{x^2-y^2}(2)\end{aligned} \tag{2}$$

The magnetic orbitals of model A and model B are named as ϕ_a^A, ϕ_s^A, ϕ_a^B, and ϕ_s^B, respectively. Hoffmann's theory also suggests that the energy gap $\Delta = |\varepsilon_a - \varepsilon_s|$ (ε_a and ε_s are the energy of two singly occupied molecular orbitals) is the dominant factor in antiferromagnetic interactions:

$$2J = 2K_{ab} - \frac{|\varepsilon_a - \varepsilon_s|^2}{J_{aa} - J_{ab}} \tag{3}$$

The larger the energy gap ($\Delta = |\varepsilon_a - \varepsilon_s|$) is, the stronger the antiferromagnetic coupling interaction between the two Cu(II) centers is. On the other hand, when $\varepsilon_a = \varepsilon_s$ or the energy gap $\Delta = |\varepsilon_a - \varepsilon_s|$ is small enough to result in $2K_{ab} > |\varepsilon_a - \varepsilon_s|^2/(J_{aa} - J_{ab})$, the magnetic coupling interaction between the two Cu(II) centers is ferromagnetic.

The molecular orbital diagrams (HOMO and HOMO−1, transforming as Φ_a andΦ_s) of models A and B are schematized in Figure 2. For model A, the interactions between the p orbitals of the two bridging ligands and magnetic orbital ϕ_a^A of the Cu(II) centers both occur through the σ pathway, which is the most effective pathway to get the largest overlap of the orbitals. Hence, the interactions between the p orbitals of the two bridging ligands and the ϕ_a^A are both strong, which results in that the energy of Φ_a^A is raised. Whereas the overlaps between the p orbital of the hydroxyl bridging ligand and ϕ_s^A of Cu(II) centers occur through the π pathway, the overlaps between the p orbitals of the azaindole bridging ligand and ϕ_s^A occur through the σ pathway. As a result, the energy of the Φ_s^A is raised slightly by the contribution of the hydroxyl bridging ligand but is raised greatly by the contribution of the azaindole bridging ligand. Consequently, the energy gap of $\Delta = |\varepsilon_a - \varepsilon_s|$ becomes small ($\Delta = 1117$ cm^{-1}), which leads to the weak ferromagnetic coupling interaction in model A. Hence, it is proved that there exists orbital countercomplementarity of the bridging ligands in model A.

In the diagram of magnetic orbital of model B, the overlaps between the p orbitals of the two bridging ligands and the magnetic orbital ϕ_a^B and ϕ_s^B are both very large. For the antisymmetric magnetic orbital ϕ_a^B, the p orbital of the hydroxyl bridging ligand and the p orbital of the pyrazole bridging ligand both interact with ϕ_a^B by the σ pathway; hence, the energy of Φ_a^B is greatly raised. However, for the symmetric magnetic orbital ϕ_s^B, the p orbitals of the bridging ligands both interact with ϕ_s^B by the π pathway, so the energy of Φ_s^B is slightly affected. The calculated energy gap $\Delta = |\varepsilon_a - \varepsilon_s|$ is raised to 3983 cm^{-1}, which results in a strong antiferromagnetic interaction of model B. It reveals that there is orbital complementarity of the bridging ligands in model B.

Comparing the orbital diagrams of A and B, we find that the diagrams of Φ_a are very similar while the diagrams of Φ_s are much different. First, we make a comparison of the magnetic contribution of hydroxyl bridging ligands in the diagrams of Φ_s. From the diagram of the Φ_s of the two models, it is found that although both of the p orbitals of the −OH bridging ligands interact with ϕ_s of the Cu centers through the π pathway, the overlap of p orbital of the −OH bridging ligand and the ϕ_s in model A is much larger than that in model B. Second, the p orbitals of two azacyclo bridging ligands interact with ϕ_s through different pathways: σ pathway and π pathway for A and B, respectively. In addition, in model A and model B the interactions between the p orbitals of the azacyclo bridging ligands and ϕ_s are both much greater than that between the p orbitals of the −OH bridging ligands and ϕ_s, which reveals that the magnetic coupling interactions in the two heterobridged dicopper(II) models are both mainly determined by the azacyclo bridging ligands. This point can also explain the calculated result of analysis of the ligands correlation above: although the ferromagnetic coupling contribution of azaindole bridging ligand is very weak, the magnetic property of model A is determined by the azaindole bridging ligand.

According to the orbital analyses above, it can be concluded that the opposite magnetic coupling interactions in the two models are due to the different pathways of the interactions between the p orbitals of the bridging ligands and the magnetic orbitals of the Cu(II) centers; namely, one is orbital anticomplementarity of the bridging ligands (for model A), and the other is orbital complementarity of the bridging ligands (for model B).

4.3. Spin Density Distribution Analysis. In order to further explain the magnetic coupling mechanisms of model A and model B, the spin density distribution is analyzed. According to the molecular orbital (MO) theory, the spin delocalization is the result of the electron transferring from the magnetic center to the ligand atoms while the spin polarization is due to the electron exchange effect and the Coulomb effect that result in the alternate distribution of the spin on the ligand atoms. Generally, for the dinuclear metal complexes, the spin delocalization favors the antiferromagnetic coupling interaction and the spin polarization favors the ferromagnetic coupling interaction. Experimentally, the spin density distribution can be provided by the polarized neutron diffraction (PND). Herein, we calculated the spin density distribution by DFT approach. The calculated spin densities on the selected atoms for models A and B in the ground state (high-spin state (HS) for A and broken-symmetry state (BS) for B are summarized in Table 2, where positive and negative signs denote α and β spin states, respectively.

For model A, the spin densities on the two Cu(II) ions both have the α spin values close to 0.5. It is obvious that the unpaired electrons are mainly localized on each Cu(II) ion, which indicates that the two Cu(II) centers are indeed the magnetic centers. The spin densities on the terminal ligand atoms and the bridging ligand atoms have the same sign as that on the Cu(II) centers, which indicates that the spin delocalization has taken place for the unpaired electrons on Cu(II) ions. Whereas the spin densities on the atoms N1, C4, C5, C6, and C7 have alternate signs, so in the azaindole bridging ligand there exists spin polarization. This point is very important to explain the mechanism of the magnetic coupling in model A. The cooperation of the spin delocalization from the Cu(II) centers and the spin polarization in the azaindole bridging ligand leads to a weak ferromagnetic coupling interaction of model A. The different forms of the spin density distribution for the two bridging ligands further demonstrate again the existence of the orbital countercomplementarity of the bridging ligands. As a result, model A shows the ferromagnetic behavior that is mainly determined by the contribution of azaindole bridging ligand.

TABLE 2: Spin Density Distribution of Model A and Model B in Their Ground States

model A		model B	
atom	HS	atom	BS
Cu1	0.5015	Cu3	−0.4453
Cu2	0.4993	Cu4	0.4583
N1	0.0991	O8	0.0113
N2	0.1037	N5	−0.1238
N3	0.0833	N6	0.0900
N4	0.0785	N7	0.0671
O1	0.1558	N8	0.1025
O2	0.1990	N9	−0.0893
O3	0.2112	N10	−0.0702
C1	0.0074	C8	−0.0018
C2	0.0016	C9	−0.0022
C3	0.0036	C10	0.0009
C4	0.0130		
C5	−0.0030		
C6	0.0065		
C7	−0.0017		

For model B, in the BS the spin densities on the two Cu(II) centers have the opposite signs and the close absolute values: Cu3 atom is mainly populated by the unpaired electron with β spin (−0.4453) and Cu4 with α spin (0.4583). The terminal ligand atoms bonding to the Cu(II) centers and the nitrogen atoms of the pyrazole bridging ligand have the spin densities with the same signs as the Cu(II) atoms they bond to. The bridging oxygen atom O2 has a α spin (0.0113) with small value that is due to the spin delocalization from the two Cu(II) centers simultaneously. The sign of the spin density on O2 is same as that on Cu4, so it can be considered that O2 is mainly affected by the β spin delocalization from Cu4. In addition, the spin densities on the N5 (−0.1238), N6 (0.0900), C8 (−0.0018), C9 (−0.0022), and C10 (0.0009) show that there is only spin delocalization in the pyrazole bridging ligand. Eventually, both the spin density distributions of the pyrazole and hydroxyl bridging ligands lead to antiferromagnetic contribution to the magnetic interaction of model B which shows the orbital complementarity of the heterobridging ligands.

5. Conclusion

The calculations of the magnetic coupling constants based on the DFT-BS method show that in the μ-hydroxyl-μ-azaindole dicopper complex A there exits weak ferromangnetic coupling interaction and in the μ-hydroxyl-μ-pyrazole dicopper complex B there is strong antiferromagnetic coupling interaction between the two Cu(II) centers. The absolutely different magnetic characteries of A and B are due to the orbital countercomplementary effect and orbital complementary effect of the two bridging ligands in A and B, respectively, which is proven by the analyses of the molecular orbitals and the spin density.

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