The Explanation of the Significant Differences in Antiferromagnetic Interactions between Two Homologous Tetranuclear Copper(II) Complexes: A Theoretical Study

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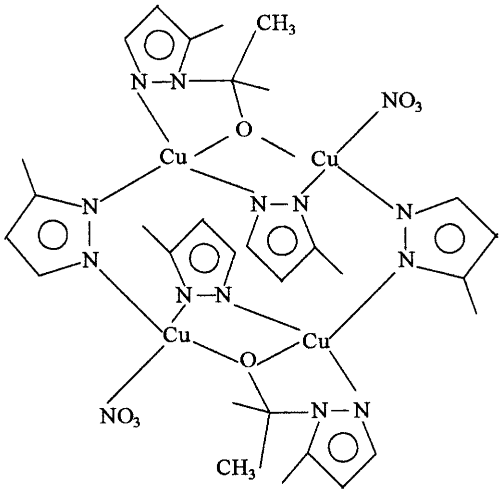
The influence of overlap interactions between the bridging ligands and the metal d orbitals on the super-exchange coupling constant has been studied by means of ab-initio Restricted Hartree-Fock molecular orbital calculations. The interaction between the magnetic d orbitals and the HOMOs of the pyrazolate nitrogens has been investigated in homologous tetranuclear copper(II) complexes which have significantly different $-2J$ values (the energy separation between the spin – triplet and spin – singlet states).

Key words: Tetranuclear Copper(II) Complex; Antiferromagnetic Coupling; Overlap Interaction; Countercomplementary Effect; Ab-initio Restricted Hartree-Fock Molecular Orbital Calculation.

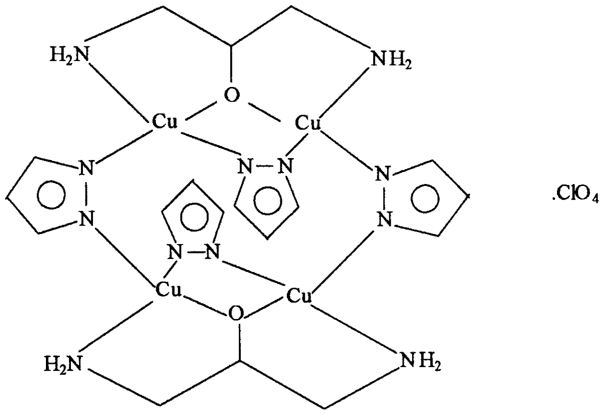
Introduction

There has been considerable interest in the properties of polynuclear copper(II) complexes in order to understand the relation between the structure and the magnetic properties [1 - 5]. In addition, copper(II) complexes are of interest because of their relevance as active site structures of metalloproteins [6, 7].

In the last two decades, dinuclear copper(II) complexes have been investigated, and several magneto-structural correlations were determined for certain types of dinuclear copper(II) complexes. In recent



Compound 1



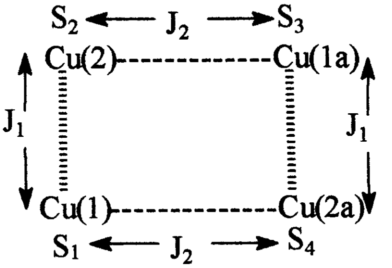
Compound 2

years, the magnetic properties of several higher nuclearity metal complexes, such as tetranuclear complexes, have been investigated, and considerable insight has been obtained [8 - 12].

Recently, Ten Hoedt et al. [13] reported the synthesis, structure and magnetic properties of a tetranuclear copper(II) compound, $[Cu_4(MPZ)_4(AcMPZ)_2(NO_3)_2]$ (**1**), [MPZ = 3(5)-Methylpyrazolato; AcMPZ = 1-(1-Ethanoyl)-5-Methypyrazolato]. Very recently we also studied the crystal structure and magnetic properties of tetranuclear copper(II) complex, $[Cu_4(PZ)_4(L)_2(ClO_4)]$ (), [LH = 1,3-diamino-2-propanol, HPZ = pyrazole] [14]. Both tetranuclear copper(II) complexes contain two dimeric units which are bridged by two pyrazolate ligands and in each dimeric moiety, two copper(II) centers are bridged by the alkoxide and pyrazolate ligands.

For both tetranuclear copper(II) complexes the molar magnetic susceptibility was calculated by using an isotropic (Heisenberg) exchange Hamiltonian [15]:

$$H = -2J_1(S_1 \cdot S_2 + S_3 \cdot S_4) - 2J_2(S_1 \cdot S_4 + S_2 \cdot S_3),$$



Since the compounds **1** and **2** have C_i symmetry, two different coupling constants J_1 and J_2 must be taken into account. However, these two J values cannot be determined separately by a fitting procedure. Consequently, the tetrameric complexes can be described magnetically as dimeric. The observed data of compounds **1** and **2** were therefore fitted to the Bleaney-Bowers equation [16], which is used for copper dimers. The good quality of the fits to the dimer equation showed that both tetranuclear compounds can be considered as composed of two weakly associated pairs of dimers. In addition it was found that in both tetranuclear copper(II) complexes the magnetic exchange pathway via the alkoxide and the pyrazolate bridge is possible [13, 14]. In compounds **1** and **2**, weak antiferromagnetic coupling between two copper(II) centers takes place through the alkoxide and pyrazolate bridges. In compound **1**, the distortion of the geometry around the Cu atom from square planar toward tetrahedral was considered as the main reason for the small J value [13]. On the other hand, we noticed that, although the compounds **1** and **2** have almost same bridging ligands, the antiferromagnetic interactions, which were observed for the compounds **1** and **2**, show significant differences.

In the present paper, in order to explain the significant difference in antiferromagnetic interactions between the two homologous tetranuclear copper(II) complexes **1** and **2**, we have studied the magnetostructural correlations by means of ab-initio Restricted Hartree-Fock molecular orbital calculations.

Molecular Orbital Calculations

Ab-initio restricted Hartree-Fock (RHF) molecular orbital calculations for the pyrazolate ion were carried out by using the GAUSSIAN-98 program [17]. STO-3G [18] minimal bases sets were adopted for the carbon and nitrogen atoms. The structural parameters were obtained from the x-ray analysis [13].

Magnetostructural Correlations

Both tetranuclear copper(II) complexes can be considered as composed of two weakly associated pairs of dimers. Since in compounds **1** and **2** the magnetic exchange interaction between only two copper(II) centers, which are bridged by alkoxide and pyrazolate ligands, is considered, we can compare the tetranuclear copper(II) compounds **1** and **2** with similar dinuclear copper(II) complexes [2, 19 - 24]. Although the structural properties of compounds **1** and **2** are almost identical with the similar dinuclear copper(II) complexes, the antiferromagnetic super exchange interactions of compounds **1** and **2** are weaker than single alkoxide bridged [23, 24] and other double hetero bridged [2, 19, 20] dinuclear copper(II) complexes. This may show that the presence of the second bridging ligand affects the strength of the antiferromagnetic super exchange interaction. However, the reason of the weak antiferromagnetic super exchange interaction can not be explained by considering only the second bridging ligand, because there is a significant difference between the $-2J$ values of compounds **1** and **2**, although they have almost the same second bridging ligand. In order to explain this fact, we considered overlap interactions between the metal d orbitals and the HOMO's of the pyrazolate ion in compound **1**.

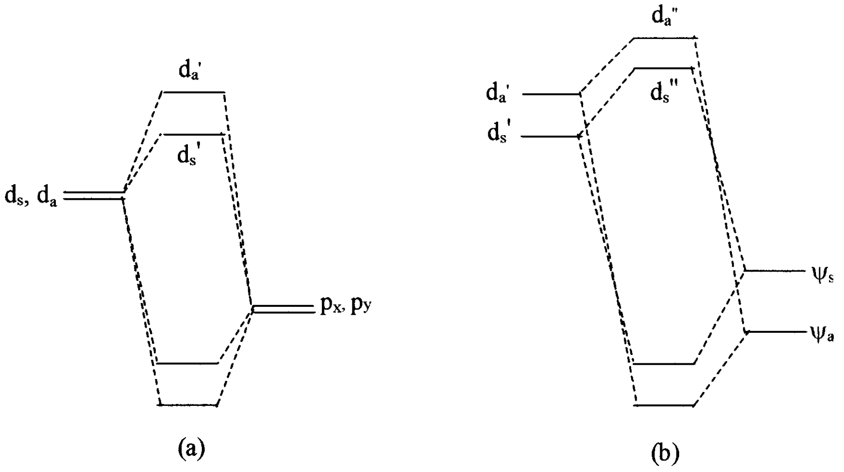


Fig. 1. Orbital energy level diagrams showing the interaction between the magnetic and bridging group orbitals (a) for a single alkoxide-bridged system; (b) for an additional bridging ligand.

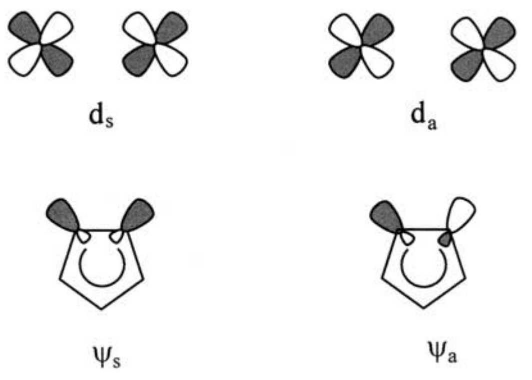


Fig. 2. Orbital symmetry combinations of metal d orbitals and pyrazolate HOMO's.

Results

In order to explain the significant difference in the antiferromagnetic interactions between compounds **1** and **2**, we considered the same theoretical model which was used in our former papers [5, 14, 25].

Theoretical Model

Bridging ligands between the metal ions influence the sign and magnitude of the coupling constant depending on the various types of overlap interactions between the metal d orbitals and the ligand orbitals. In the single (μ-alkoxo)-bridged dinuclear copper complexes, when the Cu-O-Cu angle is larger than 90° (120 - 135.5°), the d_a overlap with p_x is larger than the d_s overlap with p_y. Consequently, d_a and d_s split as illustrated in Fig. 1a. Thus, d_a' and d_s' molecular orbitals are formed. The larger energy separation of d_a' and d_s' gives a strong antiferromagnetic interaction. In the presence of a second bridging ligand, according to the orbital symmetries, d_a' and d_s' interact with antisymmetric (ψ_a) and symmetric (ψ_s) combinations of the ligand, respectively. This interaction forms the new molecular orbitals d_a'' and d_s'' (Fig. 1b).

In the case of the pyrazolate bridge, the seperation of d_a'' and d_s'' is effected by the highest occupied molecular orbital (HOMO) of the pyrazolate ion as shown in Figure 2.

The coupling constant is expressed according to Hoffmann [26] as

$$E_\mathrm{T} - E_\mathrm{S} = -2J = -2K_\mathrm{ab} + \frac{[E(d_\mathrm{a}'') - E(d_\mathrm{s}'')]^2}{J_\mathrm{aa} - J_\mathrm{ab}},$$

where K_ab, J_aa, and J_ab are the exchange integral and one-center and two-center Coulomb repulsion integrals, respectively. When the bridging ligands are all similar, K_ab, J_aa, and J_ab may be regarded as nearly constant. Consequently, the energy difference between the antisymmetric (d_a'') and symmetric (d_s'') combinations of the magnetic orbitals is the determining factor for the magnitude of the coupling constant.

Ab-Initio Restricted Hartree-Fock Molecular Orbital Calculations

We want to determine the effect of the presence of the second bridging ligand on the antiferromagnetic super exchange interaction. In dinuclear copper(II) complexes which contain two different bridging ligands, the bridging units may act in a complementary or countercomplementary fashion to in-

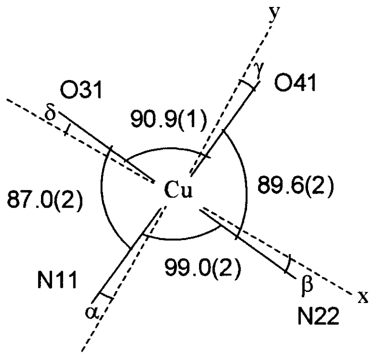


Fig. 3. Projection of Cu and donor atoms onto the best plane formed by these atoms (The broken lines are the axes of the magnetic d orbital) for **1**.

crease or decrease the strength of the super-exchange process [26].

In compound **1**, since the orbital energy of ψ_s is higher than that of ψ_a by 0.212 eV, the energies of the interacting orbitals cause the pyrazolate bridge to work in a countercomplementary fashion with the alkoxide bridge [20]. According to Nishida [20] , if ψ_s overlaps more effectively with d_s than ψ_a with d_a, the overlap integrals of the interacting orbitals may affect the pyrazolate bridge to work in a countercomplementary fashion with the alkoxide bridge again.

The overlap integrals between the interacting orbitals are expressed as $S(d_a, \psi_a)$ and $S(d_s, \psi_s)$. We determined approximate values for $S(d_a, \psi_a)$ and $S(d_s, \psi_s)$ and calculated the difference between $S(d_a,\psi_a)$ and $S(d_s, \psi_s)$ for compound **1**.

We obtained the HOMO's of the pyrazolate ions of compound **1** by using the GAUSSIAN-98 program [17]. The HOMO's for compound **1** are expressed in terms of LCAO's in (1) and (2):

$$\begin{aligned}\psi_s = {} & 0.06320\,[s(N1) + s(N2)] \\ & + 0.17457\,[p_x(N1) - p_x(N2)] \\ & + 0.26093[p_y(N1) + p_y(N2)] \\ & + \text{(terms of carbon orbitals)},\end{aligned} \tag{1}$$

$$\begin{aligned}\psi_a = {} & 0.15870\,[s(N1) - s(N2)] \\ & + 0.08615\,[p_x(N1) + p_x(N2)] \\ & + 0.13657[p_y(N1) - p_y(N2)] \\ & + \text{(terms of carbon orbitals)}.\end{aligned} \tag{2}$$

The overlap integrals are given as a function of α [20]. As seen in Fig. 3, α is the angle between the Cu-pyrazolate N bond vector and the nearest lobe of the local magnetic d orbital.

We determined the orientation of magnetic d orbitals in order to attain maximum overlapping. When the function

$$F(\alpha) = \alpha^2 + \beta^2 + \gamma^2 + \delta^2 \tag{3}$$

is minimized, maximum overlapping is obtained. In (3), α, β, γ and δ are the angles formed by the coordination bonds and the axes of d orbitals (Fig. 3).

For compound **1**, when the values

$$\begin{aligned}\beta &= \alpha + 90 - 99.0, \\ \gamma &= \alpha + 180 - 99.0 - 89.6, \\ \delta &= \alpha + 270 - 99.0 - 89.6 - 90.9\end{aligned}$$

are used in (3), α is obtained as

$$\alpha = 6.775°$$

When the x and y axes in Fig. 3 are rotated by α, the d_1 orbital is expressed in terms of the new coordinate system as

$$d_1 = (\cos(2\alpha))d_{x^2-y^2} + (\sin(2\alpha))d_{xy}. \tag{4}$$

The ψ_s and ψ_a orbitals of pyrazolate ion can be expressed as the sum of the orbitals on N1 and N2 and the neighboring carbon atoms:

$$\psi_s = \phi_{s1} + \phi_{s2} + \phi_{sC}, \tag{5}$$

$$\psi_a = \phi_{a1} + \phi_{a2} + \phi_{aC}. \tag{6}$$

These orbitals can be expressed in terms of a new coordinate system in which the y axis is on the Cu-N1 bond:

$$\begin{aligned}\phi_{s1} = {} & 0.06320\,s + 0.17457\,[(\cos 30)\,p_x + (\sin 30)\,p_y] \\ & + 0.26093\,[-(\cos 60)\,p_x + (\sin 60)p_y],\end{aligned}$$

$$\phi_{s1} = 0.06320\,s + 0.02071\,p_x + 0.31326\,p_y]. \tag{7}$$

From (4) and (7) follows

$$\begin{aligned}S(d_1, \phi_{s1}) = {} & 0.06320(\cos(2\alpha))\cdot S(3d, 2s) \\ & + 0.02071\,(\sin(2\alpha))\cdot S(3d_\pi, 2p_\pi) \\ & + 0.31326\,(\cos(2\alpha))\cdot S(3d_\sigma, 2p_\sigma).\end{aligned} \tag{8}$$

Since $d_s = (d_1 - d_2)/2^{1/2}$ and $S(d_2,\phi_{s2}) = - S(d_1,\phi_{s1})$,

$$S(d_s,\psi_s) = 2\,S(d_1, \phi_{s1})/2^{1/2} \tag{9}$$

and

$$\begin{aligned}S(d_s, \psi_s) = {} & 0.08938(\cos(2\alpha))\cdot S(3d, 2s) \\ & + 0.02929(\sin(2\alpha))\cdot S(3d_\pi, 2p_\pi) \\ & + 0.44302\,(\cos(2\alpha))\cdot S(3d_\sigma, 2p_\sigma).\end{aligned} \tag{10}$$

In a similar way $S(\mathrm{d_a}, \psi_\mathrm{a})$ is obtained:

$$\begin{aligned} S(\mathrm{d_a}, \psi_\mathrm{a}) = {} & 0.22443(\cos(2\alpha))\cdot S(3\mathrm{d}, 2\mathrm{s}) \\ & + 8.942.10^{-3}\,(\sin(2\alpha))\cdot S(3\mathrm{d}_\pi, 2\mathrm{p}_\pi) \quad (11) \\ & + 0.22818\,(\cos(2\alpha))\cdot S(3\mathrm{d}_\sigma, 2\mathrm{p}_\sigma). \end{aligned}$$

The difference between $S(\mathrm{d_a}, \psi_\mathrm{a})$ and $S(\mathrm{d_s}, \psi_\mathrm{s})$ was calculated for compound **1**. The rough overlap integrals are evaluated by using data from Jaffe and Kuroda [27, 28]: $S(3\mathrm{d}, 2\mathrm{s}) \approx 0.04$, $S(3\mathrm{d}_\pi, 2\mathrm{p}_\pi) \approx 0.02$, $S(3\mathrm{d}_\sigma, 2\mathrm{p}_\sigma) \approx 0.06$. The difference between $S(\mathrm{d_a}, \psi_\mathrm{a})$ and $S(\mathrm{d_s}, \psi_\mathrm{s})$ is denoted by S(a-s):

$$S(\text{a-s}) = S(\mathrm{d_a}, \psi_\mathrm{a}) - S(\mathrm{d_s}, \psi_\mathrm{s}) = -0.0073.$$

Discussion

At the end of our calculation we noticed that S(a-s) of the compound **1** is negative. This shows that the ψ_s overlap with $\mathrm{d_s}$ is more effective than the ψ_a overlap with $\mathrm{d_a}$:

$$S(\mathrm{d_s}, \psi_\mathrm{s}) > S(\mathrm{d_a}, \psi_\mathrm{a}).$$

This means that the pyrazolate bridge acts in a countercomplementary fashion with the alkoxide bridge. The energy difference between the antisymmetric ($\mathrm{d_a''}$) and symmetric ($\mathrm{d_s''}$) combinations of the magnetic orbitals is the determining factor for the magnitude of the coupling constant [26]. The countercomplementary fashion of the pyrazolate bridge with alkoxide bridge reduces the energy separation between $\mathrm{d_a''}$ and $\mathrm{d_s''}$. For this reason the compound **1** has a weak antiferromagnetic super exchange interaction.

Table 1. Comparison of the values of S(a-s) and J for the compounds **1** and **2**.

Compound	$-J$ (cm^{-1})	$-S$(a-s)
1	202	0.0073
2	98.5	0.0170

A natural question arises from the above explanation. Although the compounds **1** and **2** have almost the same bridging ligands, why is there significant difference between their antiferromagnetic super exchange coupling constants? The answer can be easily found from Table 1 in which the S(a-s) values of both compounds are compared. As seen in Table 1, the S(a-s) value of compound **2** is also negative and the $-S$(a-s) value of compound **2** is bigger than that of **1**. This indicates that the $S(\mathrm{d_s}, \psi_\mathrm{s})$ overlap for **2** is more effective, and the energy seperation between $\mathrm{d_a''}$ and $\mathrm{d_s''}$ is smaller. For compound **2**, therefore, a weaker antiferromagnetic coupling is observed. Consequently, the bigger the value of $-S$(a-s), the weaker is the antiferromagnetic interaction:

$$-S(\text{a-s})(\mathbf{2}) > -S(\text{a-s})(\mathbf{1}),\ -J(\mathbf{2}) < -J(\mathbf{1}).$$

The calculations show that the values of S(a-s) correlate very well with the J values.

Conclusion

The reason of the weak antiferromagnetic coupling of the tetranuclear copper(II) complexes **1** and **2** is explained by the countercomplementary fashion of the pyrazolate bridge. On the other hand, our calculatins show that there is a significant difference in the J values of compounds **1** and **2**, because of the significant difference in their values of S(a-s).

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