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 magnetostructural correlations were determined for certain types of dinuclear copper(II) complexes. In recent years,
years, the magnetic properties of several higher nu-
clearity metal complexes, such as tetranuclear com-
xplexes, have been investigated, and considerable in-
sight has been obtained [8 - 12].

Recently, Ten Hoedt et al. [13] reported the syn-
thesis, structure and magnetic properties of a tetranuclear copper(II) compound, \([\text{Cu}_4(\text{MPZ})_4-(\text{AcMPZ})_2(\text{NO}_3)_2] \) (1), \([\text{MPZ} = 3(5)-\text{Methylpyrazol}
-o-\text{o})\). Very recently we also studied the crystal structure and mag-
netic properties of tetranuclear copper(II) com-
plexes, have been investigated, and considerable in-
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sight has been obtained [8 - 12].

Molecular Orbital Calculations

Ab-initio restricted Hartree-Fock (RHF) molecular orbital calculations for the pyrazolate ion were car-
ried out by using the GAUSSIAN-98 program [17].

Magnetostructural Correlations

Both tetranuclear copper(II) complexes can be con-
sidered as composed of two weakly associated pairs of
dimers. Since in compounds 1 and 2 the magnetic ex-
change interaction between only two copper(II) cen-
ters, which are bridged by alkoxide and pyrazolate lig-
ands, is considered, we can compare the tetranuclear
copper(II) compounds 1 and 2 with similar dinuclear
copper(II) complexes [2, 19 - 24]. Although the struc-
tural properties of compounds 1 and 2 are almost iden-
tical with the similar dinuclear copper(II) complexes,
the antiferromagnetic super exchange interactions of
compounds 1 and 2 are weaker than single alkox-
ide 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 ex-
change interaction. However, the reason of the weak
antiferromagnetic super exchange interaction can not
be explained by considering only the second bridg-
ing ligand, because there is a significant difference
between the \(-2J\) values of compounds 1 and 2, al-
though 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-alkoxide)-bridged dinuclear copper complexes, when the Cu-O-Cu angle is larger than 90° (120 - 135.5°), the $d_s$ overlap with $p_x$ is larger than the $d_l$ overlap with $p_y$. Consequently, $d_s$ and $d_l$ split as illustrated in Fig. 1a. Thus, $d'^s_s$ and $d'^l_l$ molecular orbitals are formed. The larger energy separation of $d'^s_s$ and $d'^l_l$ gives a strong antiferromagnetic interaction. In the presence of a second bridging ligand, according to the orbital symmetries, $d'^s_s$ and $d'^l_l$ interact with antisymmetric ($\psi^a_s$) and symmetric ($\psi^s_s$) combinations of the ligand, respectively. This interaction forms the new molecular orbitals $d'^{as}$ and $d'^{ls}$ (Fig. 1b).

In the case of the pyrazolate bridge, the separation of $d'^s_s$ and $d'^l_l$ 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

$$E_T - E_S = -2J = -2K_{ab} + \frac{[E(d'^s_s) - E(d'^l_l)]^2}{J_{aa} - J_{ab}},$$

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 ($d'^s_s$) and symmetric ($d'^l_l$) 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-
crease or decrease the strength of the super-exchange process [26].

In compound 1, since the orbital energy of \( \psi_s \) is higher than that of \( \psi_a \) 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 \( \psi_s \) overlaps more effectively with \( \psi_a \) than \( \psi_s \) with \( \psi_a \), 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 \( S(d_s, \psi_a) \) and \( S(d_a, \psi_s) \). We determined approximate values for \( S(d_s, \psi_s) \) and \( S(d_a, \psi_s) \) and calculated the difference between \( S(d_s, \psi_s) \) and \( S(d_a, \psi_s) \) 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):

\[
Psis = 0.06320\ [s(N1) + s(N2)] + 0.17457\ [p_x(N1) - p_x(N2)] + 0.26093[p_y(N1) + p_y(N2)] + (\text{terms of carbon orbitals}),
\]

\[
Psis = 0.15870\ [s(N1) - s(N2)] + 0.08615\ [p_x(N1) + p_x(N2)] + 0.13657[p_y(N1) - p_y(N2)] + (\text{terms of carbon orbitals}).
\]

The overlap integrals are given as a function of \( \alpha \) [20]. As seen in Fig. 3, \( \alpha \) 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

\[
F(\alpha) = \alpha^2 + \beta^2 + \gamma^2 + \delta^2
\]

is minimized, maximum overlapping is obtained. In (3), \( \alpha, \beta, \gamma, \delta \) are the angles formed by the coordinate bonds and the axes of d orbitals (Fig. 3).

For compound 1, when the values

\[
\beta = \alpha + 0.99 - 99.0, \\
\gamma = \alpha + 180 - 99.0 - 89.6, \\
\delta = \alpha + 270 - 99.0 - 89.6 - 90.9
\]

are used in (3), \( \alpha \) is obtained as

\[
\alpha = 6.775^\circ
\]

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

\[
d_1 = (\cos(2\alpha)d_{x^2-y^2} + (\sin(2\alpha))d_{xy}.
\]

The \( \psi_1 \) and \( \psi_a \) orbitals of pyrazolate ion can be expressed as the sum of the orbitals on N1 and N2 and the neighboring carbon atoms:

\[
\psi_1 = \phi_{s1} + \phi_{s2} + \phi_{c},
\]

\[
\psi_a = \phi_{s1} + \phi_{s2} + \phi_{c}.
\]

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

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

\[
\phi_{s1} = 0.06320\ s + 0.02071\ p_x + 0.31326\ p_y.
\]

From (4) and (7) follows

\[
S(d_1, \phi_{s1}) = 0.06320(\cos(2\alpha))S(3d_1, 2s) + 0.02071(\sin(2\alpha))S(3d_1, 2p_\sigma) + 0.31326(\cos(2\alpha))S(3d_1, 2p_\sigma).
\]

Since \( d_1 = (d_1 - d_2)/21/2 \) and \( S(d_2, \phi_{s2}) = -S(d_1, \phi_{s1}) \),

\[
S(d_1, \phi_{s1}) = 2\ S(d_1, \phi_{s1})/21/2
\]

and

\[
S(d_a, \psi_a) = 0.08938(\cos(2\alpha))S(3d_a, 2s) + 0.02929(\sin(2\alpha))S(3d_a, 2p_\sigma) + 0.44302(\cos(2\alpha))S(3d_a, 2p_\sigma).
\]
In a similar way \( S(d_a, \psi_a) \) is obtained:
\[
S(d_a, \psi_a) = 0.22443(\cos(2\alpha)) - \sin(2\alpha) - 8.942.10^{-3}(\sin(2\alpha)) - S(3d, 2s)
\]
\[
+ 0.22818(\cos(2\alpha)) - S(3d, 2p).
\]

The difference between \( S(d_a, \psi_a) \) and \( S(d_s, \psi_s) \) was calculated for compound 1. The rough overlap integrals are evaluated by using data from Jaffe and Kuroda [27, 28]: \( S(3d, 2s) \approx 0.04, S(3d, 2p) \approx 0.02, S(3d, 2p) \approx 0.06 \). The difference between \( S(d_a, \psi_a) \) and \( S(d_s, \psi_s) \) is denoted by \( S(a-s) \):
\[
S(a-s) = S(d_a, \psi_a) - S(d_s, \psi_s) = -0.0073.
\]

### Discussion

At the end of our calculation we noticed that \( S(a-s) \) of the compound 1 is negative. This shows that the \( \psi_s \) overlap with \( d_s \) is more effective than the \( \psi_a \) overlap with \( d_a \):
\[
S(d_s, \psi_s) > S(d_a, \psi_a).
\]

This means that the pyrazolate bridge acts in a countercomplementary fashion with the alkoxide bridge. 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 [26]. The countercomplementary fashion of the pyrazolate bridge with alkoxide bridge reduces the energy separation between \( d^a \) and \( d^s \). For this reason the compound 1 has a weak antiferromagnetic super exchange interaction.

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 \( S(d_a, \psi_a) \) overlap for 2 is more effective, and the energy separation between \( d^a \) and \( d^s \) 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:
\[
-S(a-s)(2) > -S(a-s)(1), -J(2) < -J(1).
\]

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 calculations 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 \( S(a-s) \).

![Table 1. Comparison of the values of \( S(a-s) \) and \( J \) for the compounds 1 and 2.](image)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(-J ) (cm(^{-1}))</th>
<th>(-S(a-s) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>202</td>
<td>0.0073</td>
</tr>
<tr>
<td>2</td>
<td>98.5</td>
<td>0.0170</td>
</tr>
</tbody>
</table>