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ORBITAL COMPLEMENTARY AND COUNTERCOMPLEMENTARY EFFECTS IN SUPEREXCHANGE INTERACTION THROUGH HETEROBRIDGES IN BINUCLEAR COPPER(II) COMPLEXES[1)]

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Low antiferromagnetism of μ-alkoxo-μ-carboxylatodicopper(II) complexes were reasonably explained in terms of the orbital countercomplementary effect based on Hoffmann's theory for superexchange interaction.

It is known that antiferromagnetic interaction between copper(II) ions in di-μ-hydroxo or di-μ-alkoxo binuclear complexes is highly dependent on the Cu-O-Cu angle,[2)] i.e., the larger the angle the larger the -2J value, where -2J denotes the energy separation between the spin-triplet and -singlet states. Recently, McKee and Smith determined the crystal structure of a binuclear copper(II) complex bridged by a single alkoxo-oxygen.[3)] Its magnetic moment was 0.6 μ_B at room temperature, indicating an operation of a strong antiferromagnetic interaction despite the single bridge. This was reasonably explained in terms of the large Cu-O-Cu angle(135.5°) based on the above rule. On the other hand, the present authors prepared a μ-alkoxo-μ-acetatodicopper(II) complex, 1(Fig. 1), and determined its crystal structure.[4)] This complex showed very weak antiferromagnetic interaction(1.64 μ_B at 295 K) in spite of its large Cu-O-Cu angle(133.3°) (O:alkoxo-oxygen atom). This result appeared to contradict the above rule. Thus, in order to elucidate this, we have in this study prepared a series of analogous binuclear copper(II) complexes, 2—5(cf. Figs. 1 and 2),[5)] and determined their crystal structures. The preparative methods were similar to that of 1.

The skeletal structures of compounds 2—4 are essentially the same as that of 1(cf. Fig. 1). The copper(II) atoms are bridged by the alkoxide and carboxylate oxygens, and the coordination planes are approximately coplanar. Their magnetic behaviours are also similar to that of 1(cf. Table 1). In the case of 5, however, the copper atoms are bridged by alkoxide only as illustrated in Fig. 2,[6)] and a strong antiferromagnetic interaction(0.74 μ_B at 295 K) was observed. Since there is no significant structural difference among the complexes(1 — 3, and 5) except the carboxylate bridge, these facts imply that the relation between antiferromagnetic interaction and the Cu-O-Cu angle established in di-μ-hydroxodicopper(II) is held in the present system, but the presence of a

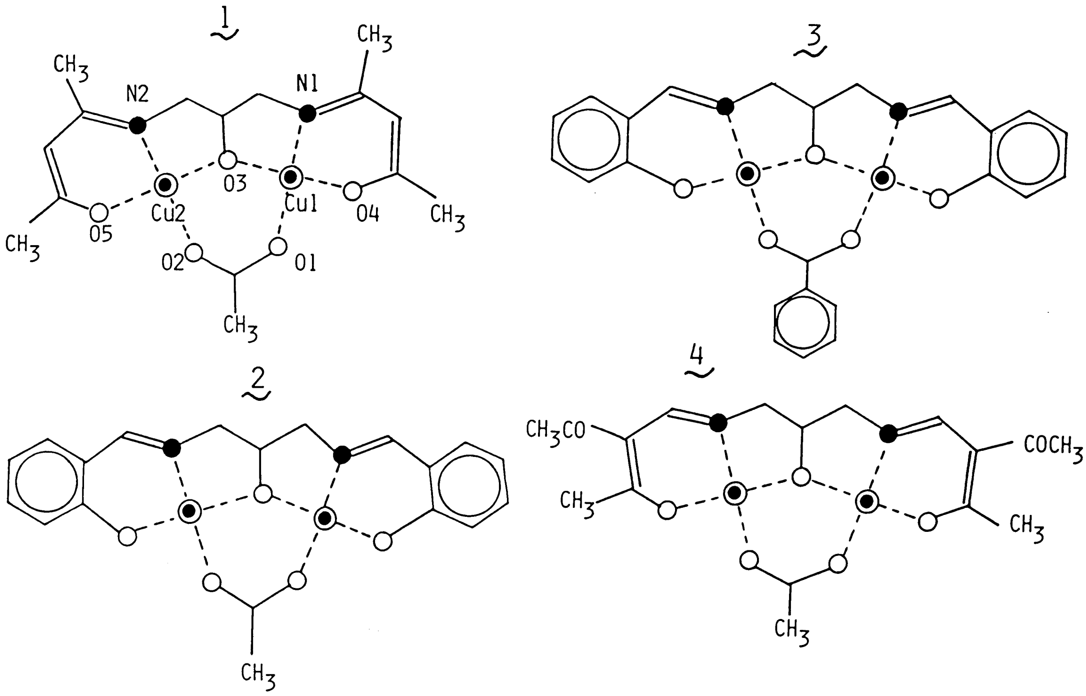

Fig. 1. Illustration of structures of compounds 1—4.

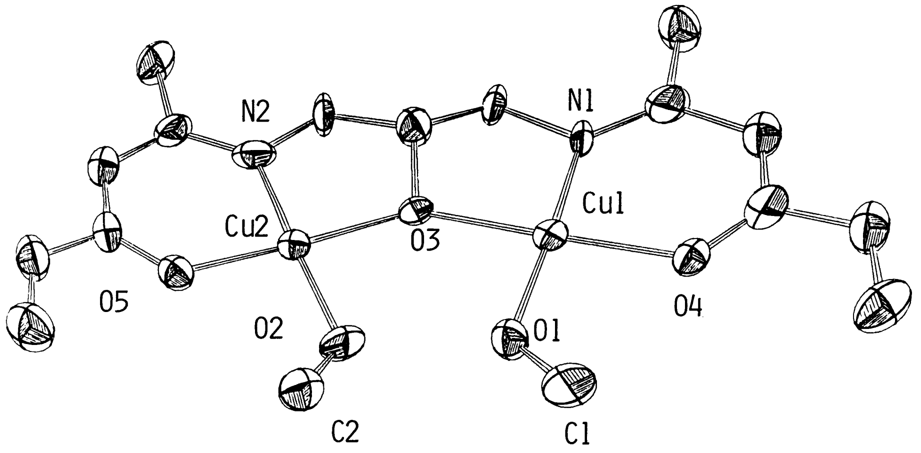

Fig. 2. ORTEP drawing of compound 5(50 % probability ellipsoids). Distances(Å): Cu1-Cu2, 3.644(2); Cu1-O3, 1.944(9); Cu1-O1, 1.914(13); Cu1-O4, 1.923(9); Cu1-N1, 1.920(9); Cu2-O3, 1.964(9); Cu2-N2, 1.897(10); Cu2-O5, 1.930(10); Cu2-O2, 1.915(9). Angle(deg): Cu1-O3-Cu2, 137.7(5)°.

Table 1. Magnetic and structural data[a)]

Compound	1	2	3	4	5
μ_{eff}(295 K)/μ_B	1.64	1.63	1.65	1.77	0.74
∠Cu1-O3-Cu2/°	133.3	134.5	132.7	109.1	137.7
Cu1-Cu2/Å	3.502	3.495	3.482	3.129	3.644
Cu1-O3/Å	1.902	1.877	1.917	1.903	1.944
Cu2-O3/Å	1.913	1.912	1.884	1.938	1.964
O1-O2/Å	2.26	2.23	2.24	2.24	2.35
τ/°[b)]	5.4	18.7	8.2	54.6	15.3
Cu1/Å	-0.017	0.010	0.027	-0.300	0.080
Cu2/Å	-0.007	0.024	-0.088	-0.399	0.085
O1/Å	0.011	-0.024	0.044	0.038	-0.026
c) O2/Å	-0.004	0.006	-0.081	0.158	-0.018
O3/Å	0.017	-0.016	0.098	0.502	-0.120
C[d)]/Å	-0.67	0.30	0.14	0.54	0.22

a) For the atomic numbering system, see the compound 1 in Fig. 1.
b) Dihedral angle(deg) between the coordination planes, (Cu1, N1, O3, O1 and O4) and (Cu2, N2, O2, O3, and O5). c) Deviations(Å) from the best plane of (Cu1, Cu2, O1, O2, and O3). d) Carbon atom which attaches to alkoxo-oxygen atom.

carboxylate bridge reduces the antiferromagnetic interaction. This appeared to be inconsistent with the well known fact that a carboxylate bridge itself can conduct a considerable antiferromagnetic interaction. In order to gain a reasonable explanation for these facts, we have considered superexchange pathways in more detail.

According to Hoffmann,7) strong antiferromagnetism is caused in binuclear complexes when the energy separation of the symmetric(ϕ_s) and antisymmetric(ϕ_a) combination of the two magnetic orbitals(Fig. 3) is large, irrespective of that which combination is lower in energy. In the case of an alkoxide bridge the intervening oxygen p_x orbital interacts with the ϕ_a orbital to raise its energy (cf. Fig. 3).7) The energy of ϕ_s orbital is raised in the case of an acetate bridge, because the highest occupied orbital of an acetate ion is a_1(assuming C_{2v} symmetry) orbital7) mainly composed of oxygen 2p character, and this orbital interacts with ϕ_s orbital. Thus, the acetate bridge reduces the energy separation between ϕ_a and ϕ_s orbitals caused by the interaction through alkoxide bridge only, thereby diminishing the antiferromagnetic interaction.

The present results demonstrate that it is important for magnetic interaction through heterobridges that which combination is brought higher in energy by the respective bridge. When both bridging groups interact with the same combination of magnetic orbitals to raise the orbital energy, the superexchange interaction through the two bridges operate complementarily, and the total of antiferromagnetism will be sum of that caused through each bridging group. Reed proposed to call this effect "orbital complementary effect".[8] A typical example is the μ-alkoxo-μ-azidodicopper(II) complex which is diamagnetic.[9] When one of the bridging group interacts with the ϕ_s orbital and the other with the ϕ_a orbital to raise each of the orbital energies, the superexchange interaction through the bridges operate counter-complementarily to reduce the total antiferromagnetism significantly. In this case, "countercomplementary effect" is operating. This is the case of μ-alkoxo-μ-carboxylatodicopper(II) complexes shown here.

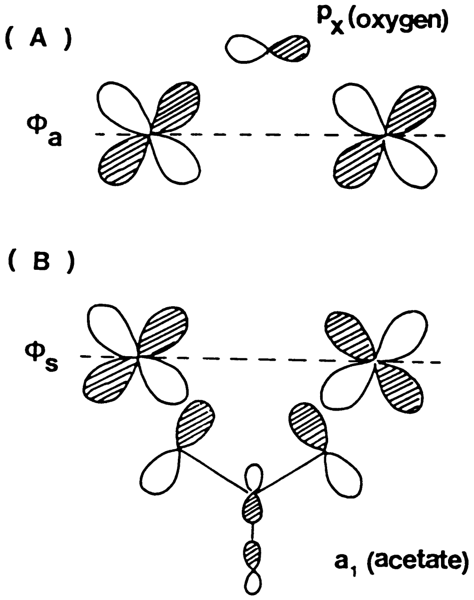

Fig. 3. Symmetric and antisymmetric combinations of metal and ligand orbitals.

References

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3) V. McKee and J. Smith, J. Chem. Soc., Chem. Commun., 1983, 1465.
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5) New copper(II) complexes prepared in this study are **2**, $[Cu_2(L_a)CH_3COO]$; **3**, $[Cu_2(L_a)C_6H_5COO]$; **4**, $[Cu_2(L_b)CH_3COO]$; and **5**, $[Cu_2(L_c)OCH_3(OHCH_3)]$; where $H_3(L_a)$, $H_3(L_b)$ and $H_3(L_c)$ are the Schiff bases derived from 1,3-diamino-2-propanol and salicylaldehyde, 3-ethoxymethylene-2,4-pentanedione, and methylacetoacetate, respectively. Satisfactory elemental analyses(C, H, and N) were obtained for these complexes. The absence of acetate group in **5** was also confirmed by its infrared spectrum.
6) Crystal data: **2**, space group Pbca, a=18.196(5), b=22.636(5), c=9.731(1) Å, R=0.097. **3**, space group $P2_1/c$, a=18.234(2), b=11.478(2), c=10.327(1) Å, β=100.09(1)°, R=0.064. **4**, space group $P\bar{1}$, a=13.398(8), b=16.024(5), c=11.691(3) Å, α=111.92(2), β=116.50(2), γ=64.09(3)°, R=0.046. **5**, space group $P2_1/a$, a=28.45(1), b=6.952(4), c=10.128(8) Å, β=110.96(4)°, R=0.082.
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