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Study of the Effect of Structural Factors on Magnetism of Di-μ-alkoxodicopper(II) Complexes by Ab Initio MO Calculations[1)]

Makoto HANDA,† Nobuaki KOGA,† and Sigeo KIDA*
Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashi-ku, Fukuoka 812
†Institute for Molecular Science, Myodaiji, Okazaki 444[2)]
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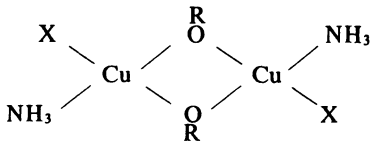
The effect of variation of structural factors on the spin-exchange interaction between copper(II) centers in dialkoxo-bridged dinuclear copper complexes were studied by the ab initio MO method with UHF formalism. The calculations were performed on di-μ-methoxotetraamminedicopper(II). The *J*-values were obtained as functions of Cu–O–Cu angle, dihedral angle between two coordination planes, planarity of bonds on the bridging oxygens, tetrahedral distortion of coordination planes, and the tilt of O–C bond from the O–O axis. The results demonstrated that the Cu–O–Cu angle most effectively affect the *J*-value but the other factors are less effective.

A great number of dinuclear copper complexes have been synthesized in the recent two decades, and their structures and magnetisms have been extensively studied.

Hodgson, Hatfield, and the co-workers first showed the relation between a structural factor and magnetic coupling of dinuclear copper(II) complexes. Based on experimental data of several dihydroxo-bridged copper complexes, they showed that there is a linear relationship between the Cu–O–Cu bond angle and the *J*-value, where $-2J$ represents the energy separation between the lowest spin-triplet and singlet states.[3)] Merz and Haase,[4)] and Nieminen[5)] pointed out that a similar relation also exists for dialkoxo-bridged copper(II) complexes based on numerous experimental results. These relations were theoretically interpreted in terms of extended Hückel MO by Hoffmann et al.,[6)] and later by Kahn.[7)] Bencini and Gatteschi[8)] applied the angular overlap approach to a two-atom-bridged dinuclear copper(II) system, and obtained a result similar to that of Hoffmann et al.[6)] However, some other structural factors such as the planarity of Cu_2O_2 entity, the dihedral angle formed by two coordination planes, and the planarity of bonds about bridging oxygen, have been claimed by several workers to be important factors to determine the spin coupling as well as or rather than the Cu–O–Cu angle.[5,7–11)] Indeed, such factors seem to have a good correlation with experimentally obtained *J*-values of dialkoxo-bridged copper(II) complexes. However, in practice, such factors are not independent of other structural factors, but are linked to each other in more or less degree. Hence, it is difficult to determine which factor is the most important one for the spin-exchange interaction from the experimental data.

Thus, theoretical approaches were attempted to see the correlation between each of structural factors and *J*-value. Bencini and Gatteschi also examined effects of various structural factors on the spin coupling by the angular overlap approach.[8)] However, there is limitation in their results, since the angular overlap approach cannot expect quantitative results. De Loth et al. calculated *J*-values by an ab initio SCF MO method on copper(II) acetate monohydrate[12)] and a μ-oxalato-dicopper(II) complex.[13)] Haase et al. applied a similar approach to di-μ-hydroxo and di-μ-methoxo-dicopper(II) complexes shown below.[14)]



They calculated *J*-values on the model complexes using ps HONDO program with pseudo potential for core electrons of copper, varying the Cu–O–Cu angle, the Cu–O distance, coordination geometry, and the planarity of bonds about the bridging oxygens, and they concluded that the magnitude of exchange coupling strongly depends on these factors. However, they did not investigate the effect of variation of the dihedral angle formed by the two coordination planes, in spite of that the importance of this factor has been pointed out by some workers.[7,11)] Furthermore, they did not discuss on which structural factor the *J* value most deeply depends.

As we have been much interested to clarify which structural factor is the major factor to determine the magnetic interaction in dialkoxo-bridged copper(II) complexes, in this study, we have calculated *J*-values

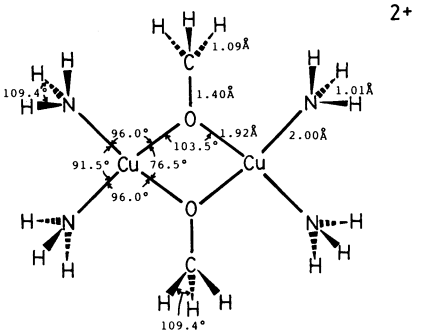


Fig. 1. Structure of the basic model.

on the model compound cited in Fig. 1 by an ab initio MO method, employing the unrestricted Hartree-Fock operator. In this calculation, in order to elucidate the effect of each structural factor on the spin coupling, we systematically varied each of various structural factors such as 1) the Cu–O–Cu angle (ϕ), 2) the dihedral angle formed by the two coordination planes (α), 3) the angle formed by the O–C vector and the Cu_2O_2 plane (θ), 4) the dihedral angle between the Cu_2O_2 plane and the plane formed by the four ammonia nitrogens (τ), and 5) the angle between the O–C and O–O vectors (δ), keeping the other factors constant as far as possible.

Calculation

The calculations were carried out by the GAUSSIAN82[15] program implemented with effective core potential code,[16a,b] the unrestricted Hartree-Fock(UHF) method being employed to estimate J value. The energies of two magnetic orbitals were calculated by the restricted Hartree-Fock (RHF) method.

The copper core electrons were described in terms of effective core potential,[16c] and the valence electrons in terms of basis function [1s1p2d] contracted from (5s2p5d).[16c] The 4-31G[16d] basis set was used for CH_3O and the STO-3G[16e] for NH_3. J values were calculated with the equation,

$$J = -(E_{TUHF} - E_{SUHF})/(\langle S^2\rangle_T - \langle S^2\rangle_S)$$

following Yamaguchi's treatment,[17] where $\langle S^2\rangle_T$ and $\langle S^2\rangle_S$ represent the spin eigenvalues of $\hat{S}^2$ for triplet and singlet states, respectively, and E_{TUHF} and E_{SUHF} are energies for the triplet and singlet states, respectively. The E_{SUHF} value was approximately represented with E_{SPUHF} which was obtained by projecting out the triplet component and using the following equation.

$$E_{SPUHF} = E_{SUHF} + \langle S^2\rangle_{SUHF}(E_{SUHF} - E_{TUHF})/(\langle S^2\rangle_{TUHF} - \langle S^2\rangle_{SUHF})$$

Results and Discussion

Throughout the calculations all bond lengths were fixed. During calculations with varying a structural parameter, all other bond angles were also fixed at the values cited in the basic model, unless there is a geometrical necessity. The results are shown diagramatically in Figs. 2—6. In each diagram the calculated J values and the energy gaps (ΔE) between the two magnetic orbitals (HOMO and LUMO) are plotted versus structural parameter. Each diagram shows that the variation of J is parallel to that of ΔE, implying that the results of the calculations by UHF and RHF are consistent with each other. The experimental data for J, ϕ, α, θ, and τ so far available are summarized in Table 1.

Effect of the Cu–O–Cu angle, ϕ. Since all the atoms

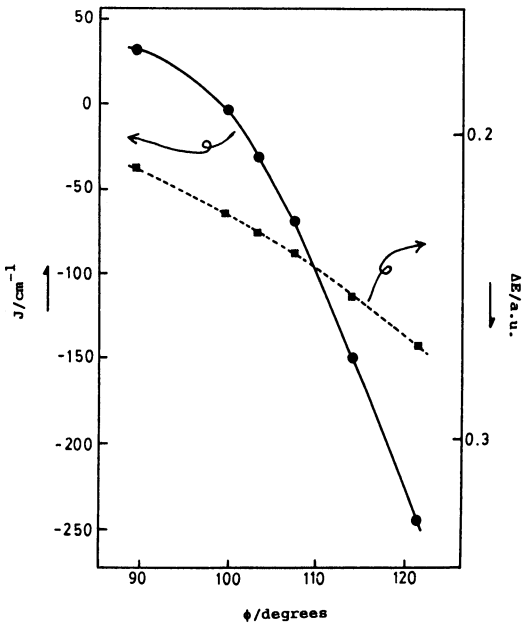


Fig. 2. Variation of the calculated J(——) and ΔE(---) with Cu–O–Cu angle ϕ. (1 a.u.= 2.62550×10^{-6} J mol^{-1}).

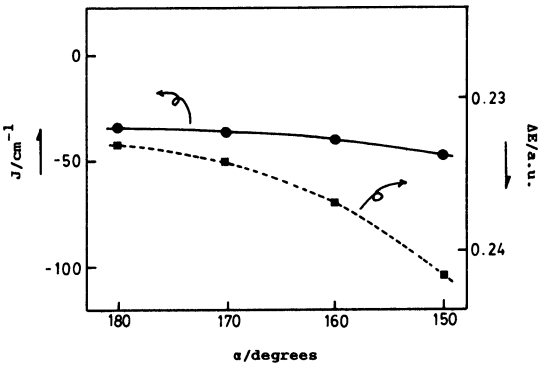


Fig. 3. Variation of the calculated J(——) and ΔE(---) with the dihedral angle formed by the two coordination planes α.

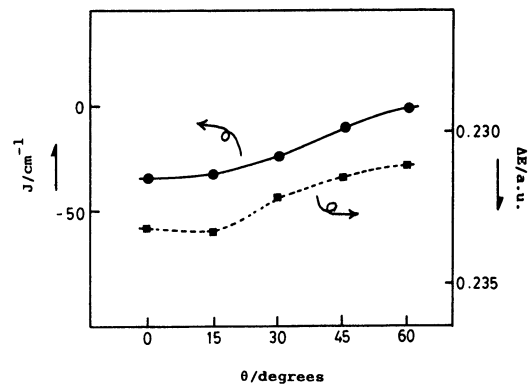


Fig. 4. Variation of the calculated J(——) and ΔE(---) with the angle formed by the O–C vector and the Cu_2O_2 planes θ.

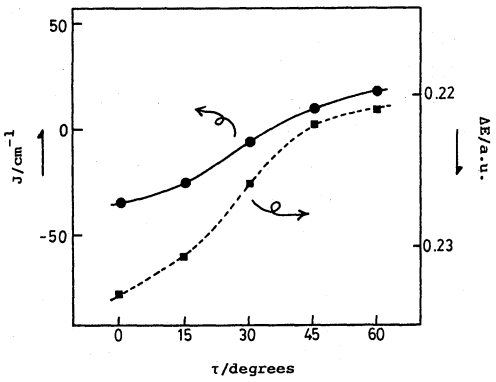


Fig. 5. Variation of the calculated J(——) and ΔE(---) with the dihedral angle between the Cu_2O_2 plane and the plane formed by the four ammonia nitrogen τ.

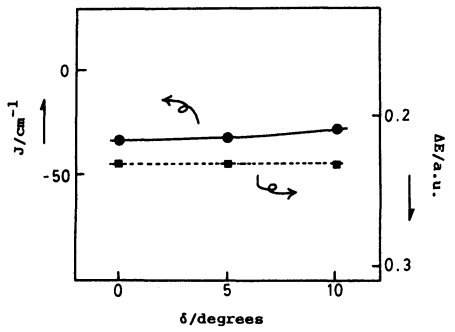


Fig. 6. Variation of the calculated J(——) and ΔE(---) with the angle between the O-C and O-O vectors δ.

are kept in a plane, the variation of ϕ is necessarily required to vary the angles about the copper atoms to keep the summation of angles around the copper atom at 360°. In order to fulfil the requirement, the necessary angle variation was equivalently portioned out on ∠OCuN, ∠NCuN, and ∠NCuO, so that the strain due to the angle variation is made minimum.

As seen in Fig. 2, $-J$ value increases with increasing

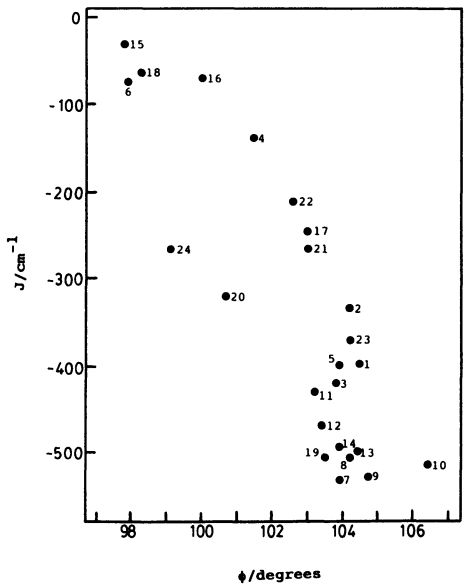


Fig. 7. A plot of experimental J versus Cu-O-Cu angle ϕ. Numbers refer to the complexes listed in Table 1.

Table 1. Experimental Data of $-2J, \phi, \alpha, \theta$, and τ

Compd.	$-2J$/cm^{-1}	ϕ/°	α/°	θ/°[a]	τ/°[a]	Ref.
1	799	104.5	180	4.5	5.2	18
2	670	104.2	180	4.5	8.5	19
3	845	103.8[b]	176.5	1.3[b,c]	—	20,21
4	279	101.5	180	26.1	20.5	22,23
5	800	103.9	180	4.5	16.7	24,25
6	149	97.9[b]	148.5	27.9[b,c]	—	26
7	1065	103.9	180	23.1	12.2	27
8	1020	104.2	180	22.8	15.0	27
9	1056	104.7	180	1.5	12.6	27
10	1030	106.4	180	0.7	0.5	28
11	863	103.2	180	23.5	5.5	29
12	940	103.4	180	12.5	6.8	29
13	1001	103.9	180	7.3	13.9	29
14	988	103.9	180	14.2	16.3	29
15	65	97.8[b]	180	40.8[b]	20.4	30
16	141	100.0	180	31.9	15.8	31
17	495	103.1	180	7.9	30.2	32
18	128	98.3	164.1	36.5[c]	—	33
19	1015	103.5	180	3.5	4.8	34
20	640	100.7[b]	167.9	27.4[b,c]	—	35
21	535	103.0	180	7.2	13.2	36
22	425	102.6	180	13.4	18.0	7
23	745	104.2	180	5.4	12.6	37
24	530	99.4[b]	164.7	23.0[b,c]	—	38,39

a) Calculated from atomic coordinates in the references except for 3 and 5 which were taken from the literature values.
b) Mean value of two angles. c) Angle formed by the O-C vector and the Cu_2 O plane.

ϕ as has been pointed out by many workers on the bases of either experimental results[3-5] or quantum mechanical approaches.[6-8,14] The experimentally obtained J values so far available were plotted versus ϕ, and shown in Fig. 7. A good agreement was obtained between our results (Fig. 2) and experimental ones (Fig. 7) in general trend with some exceptions, though the agreement in numerical values is poor. As for the exceptions, we will discuss in the later part of this paper.

Ferromagnetic interactions were observed for some hydroxo-bridged dicopper(II) complexes with small Cu-O-Cu angles,[3] and were reasonably explained in terms of Hückel MO by Hoffmann et al.[6] The present result also predicts the possibility of ferromagnetism in alkoxo-bridged copper(II) complexes with small ϕ. In fact,the complex with ϕ=97.8° bears $-2J$=65 cm^{-1} (cf. compound 15 in Table 1), suggesting that ferromagnetism may be observed for alkoxo-bridged complexes with ϕ<97°.

Angle Formed by Two Coordination Planes, α. The variation of α necessitates to vary the O-O distance in order to keep the Cu-O-Cu angle at the value of the basic structure (Fig. 1).

As seen in Fig. 3, the variation of J per degree is very small compared with that in the case of ϕ, especially, J is practically constant in the range 180—170°, inspite of that some workers[11] regarded this angle as an important factor to determine the spin coupling. According to Bencini and Gatteschi's calculations by angular overlap approach[8] $-J$ increases when α decreases from 180°. On the other hand, Kahn[7] reported the opposite trend based on the Hückel MO calculations. Kahn's result may be due to that the O-O distance was kept constant in his calculations so that the Cu-O-Cu angle also decreases with decreasing α. Such feature has been often observed in practical examples, hence in such cases the decrease in antiferromagnetic interaction should be attributed not to the change in α but to the change in ϕ which is usually linked to α.

Angle between the Cu_2O_2 Plane and O-C Vector, θ. This angle can be varied without any change of the other factors.

As seen in Fig. 4, $-J$ gradually decreases with increasing θ. Figure 4 implies that there is the transition point from antiferro- to ferromagnetic interaction at about θ=60°. However, the extent of the effect of θ on J is much small compared with that of ϕ.

Dihedral Angle between the Cu_2O_2 Plane and the Plane Formed by the Four Ammonia Nitrogens, τ. This parameter was first proposed by Sinn to represent the extent of terahedral distorsion of the coordination plane.[9] He considered this angle an important factor to determine the spin coupling.

As seen in Fig. 5, $-J$ decreases with increasing τ, and there is the antiferro—ferro transition point at about τ=35°. According to Bencini and Gatteschi's calculations the transition point exsists at about 60°.[8] However, in practical examples the variations of τ all fall in the range of 0—20°(cf. Table 1), and Fig. 5 shows that the variation of J/degree is relatively small in this range. Accordingly, the effect of τ on J value would be minor compared with that of ϕ.

Angle between O-O and O-C Vectors, δ. This angle represents the deviation of the O-C bond from the O-O axis due to the strain of chelate ring formation.

Figure 6 shows that the effect of δ on J is very small at least in the range of δ=0—10° which covers whole range of δ for practical compounds.

Concluding Remarks

J-values of dialkoxo-bridged dinuclear copper(II) complexes were obtained as functions of each of five structural parameters by ab initio MO calculations using the unrestricted Hartree-Fock method. Each parameter was varied in keeping the other ones unchanged unless there is any geometrical requirement. The results revealed that the Cu-O-Cu angle is the major factor to determine J value, and the other factors bring only minor effects on J value. This is readily seen in Table 2, in which $|\Delta J|$/degree for each parameter is summarized in the third column. Further, taking into consideration the practical range of the parameters, we have compared effects of variation of these parameters in the last column of Table 2, which shows that the Cu-O-Cu angle is still the major factor to determine J value. However, it should be noted that these structural parameters are not independent, but linked to each other. Therefore, one must be careful to discuss the variation of J as a function of a single parameter. Thus, the existence of exceptions observed in Fig. 7 may be ascribed to the above mentioned reason, i.e., J varies linking to other

Table 2. $|\Delta J|$/degree and $|\Delta J|$/(the pratically variable range of each parameter)

Structural parameter	Practically[a] variable range/°	$\|\Delta J\|$/degree[b]/cm^{-1}	$\|\Delta J\|$/range/cm^{-1}
ϕ	97—107	7.4	74
α	180—150	0.41	12
θ	0—40	0.48	19
τ	0—30	0.96	29
δ	0—10	0.12	1.2

a) Estimated from the data in Table 1. b) Averaged value of $|\Delta J|$/degree in the variable range.

structural parameters in practical compounds, though it is difficult to assign which factor plays the major role to cause deviation from the general rule at present.

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1) This work was partly presented at 37th Symposium on Coordination Chemistry, Tokyo (1987).

2) This work was mainly carried out at the Institute for Molecular Science and partly at Kyushu University.

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