

Importance of Orbital Complementarity in Spin Coupling through Two Different Bridging Groups. Synthesis, Crystal Structure, Magnetic Properties and Magneto-Structural Correlations in a Dicopper(II) Complex of Endogenous Alkoxo Bridging Ligand with Exogenous Pyrazolate

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Binuclear Copper(II) Complex, Super-Exchange Interactions, Antiferromagnetic Coupling

[Cu₂(L³)(3,5-prz)] (L³ = 1,3-bis(2-hydroxy-4-methoxybenzylideneamino)-propan-2-ol) (**3**) was synthesized and its crystal structure determined. The compound consists of discrete binuclear units, in which copper atoms are linked by the alkoxide oxygen atom of the ligand and the pyrazolate nitrogen atoms. Variable-temperature magnetic susceptibility measurements for a powdered sample of the complex were carried out in the temperature range 4.4 - 308 K and analysed to obtain values of the parameter J in the exchange Hamiltonian $\mathcal{H} = -2JS_1 \cdot S_2$. Recently, the dicopper(II) complexes [Cu₂(L¹)(3,5-prz)] (L¹ = 1,3-bis(2-hydroxy-1-naphthylideneamino)-propan-2-ol) (**1**) and [Cu₂(L²)(3,5-prz)] (L² = 1,3-bis(2-hydroxy-5-chlorosalicylideneamino)-propan-2-ol) (**2**) were reported. These compounds show antiferromagnetic behaviour ($-2J$: 444 cm⁻¹ for **1**, 164 cm⁻¹ for **2**, and 472 cm⁻¹ for **3**). The strength of the super-exchange interaction ($-2J$) of **2** is much less than that of **1** and **3**, a result which is difficult to explain in terms of structural factors on the basis of widely accepted criteria. The differences in the magnetic behaviour have been rationalized in terms of the bridging ligand orbital complementary / countercomplementary concept.

Introduction

The study of exchange-coupled polynuclear complexes is an active area of the coordination chemistry [1]. In many examples, a close dependence of the isotropic exchange parameter ($2J$) on certain structural factor has been demonstrated and understood on the basis of the orbital mechanism of exchange interaction [2]. Empirical structural/magnetic relationships (particularly involving $-\mu$ -hydroxo-bridged compounds) have shown interesting correlations. For bis(μ -hydroxo)- and bis(μ -alkoxo)-bridged binuclear copper(II) complexes, Hatfield and Hodgson [3] have observed an increase in the strength of antiferromagnetic coupling with increasing Cu-O-Cu bridge angles in the range 90 - 105°. More recently, the crystal structures of binuclear complexes in which two copper(II) ions are bridged by a single alkoxide oxygen atom with larger Cu-O-Cu bridge angles (120 - 135.5°) have

been reported [4, 5]. These complexes show strong antiferromagnetic exchange coupling and this coupling is reasonably well explained by using theories developed by Hodgson [6]. The magneto-structural properties of binuclear copper(II) complexes which contain second bridging ligands such as pyrazolate or acetate ions have also received considerable attention. Nishida and Kida [7] reported the preparation and structural characterisation of binuclear copper(II) complexes in which the copper ions are linked by alkoxide and pyrazolate nitrogen atoms. Although these complexes have large Cu-O-Cu angles, they show weak antiferromagnetic super-exchange interactions. This result seemed to be inconsistent with Hodgson's rule, and it is difficult to give a reasonable explanation in terms of the widely accepted criteria such as the bond angle of the Cu-O-Cu bridge, the planarity of the bonds around the bridging oxygen atom, or the dihedral angle between the two coordination planes [8]. According to



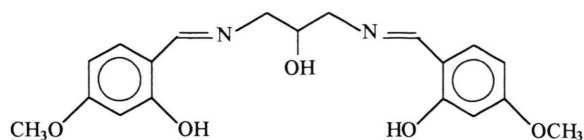


Fig. 1. Structural diagram for the ligand.

Hoffmann's theory [9] the different bridging ligands can act in a complementary or countercomplementary way to increase or decrease the strength of the super-exchange interaction as a result of differences in the symmetry of the orbitals.

In this study, preparation, crystal structure and magnetic properties of a 3,5-dimethylpyrazolate bridged binuclear copper(II) complex $[\text{Cu}_2(\text{L}^3)(3,5\text{-prz})]$ ($\text{L}^3 = 1,3\text{-bis}(2\text{-hydroxy-4-methoxybenzylideneamino)propan-2-ol}$) (**3**) are reported. In a preceding study we have described the preparation and magnetism of the dicopper(II) complexes $[\text{Cu}_2(\text{L}^1)(3,5\text{-prz})]$ ($\text{L}^1 = 1,3\text{-bis}(2\text{-hydroxy-1-naphthylideneamino)propan-2-ol}$) (**1**) and $[\text{Cu}_2(\text{L}^2)(3,5\text{-prz})]$, ($\text{L}^2 = 1,3\text{-bis}(2\text{-hydroxy-5-chlorosalicylideneamino)propan-2-ol}$) (**2**) [10, 11]. These compounds show antiferromagnetic behaviour ($-2J$: 444 cm^{-1} for **1**, 164 cm^{-1} for **2** and 472 cm^{-1} for **3**). The strength of the super-exchange interaction ($-2J$) of **2** is much less than that of **1** and **3**, a result which is difficult to explain in terms of structural factors on the basis of widely accepted criteria. In order to clarify the influence of the second bridging ligand on the super-exchange interaction we carried out molecular orbital calculations of the 3,5-dimethylpyrazolate in complex **3** by ab-initio restricted Hartree-Fock (RHF) methods and compared our results with the results for complexes **1** and **2**. We also performed extended Hückel molecular orbital (EHMO) calculations.

Experimental

Preparation

Caution: Perchlorate salts of metal complexes with organic ligands are potentially explosive. Even small amounts of material should be handled with caution.

The Schiff base ligand was prepared by reaction of 1,3-diaminopropan-2-ol (1 mmol) with 2-hydroxy-4-methoxybenzaldehyde (2 mmol) in methanol (100 ml). The yellow Schiff base precipitated from solution on cooling. The binuclear complex was obtained when a sample of the ligand (1 mmol) in methanol (50 ml) was added dropwise to a stirred mixture containing 3,5-di-

Table 1. Summary of crystallographic data for the investigated compound.

Empirical formula	$\text{C}_{24}\text{H}_{26}\text{N}_4\text{O}_5\text{Cu}_2$
Formula weight ($\text{g}\cdot\text{mol}^{-1}$)	577.57
Crystal system	monoclinic
Space group	$\text{C}2/c$
a [\AA]	10.816(1)
b [\AA]	17.506(1)
c [\AA]	12.490(1)
β [$^\circ$]	102.040(1)
V [\AA^3]	2312.9(4)
Z	4
D_{calc} ($\text{g}\cdot\text{cm}^{-3}$)	1.659
μ [cm^{-1}]	18.84
Index ranges	$0 \leq h \leq 13, 0 \leq k \leq 22,$ $-16 \leq l \leq 15$
2θ range for data collection	2.25° to 27.50°
Reflections collected	2626
Independent reflections	1584 [$R(\text{int}) = 0.034$]
Goodness-of-fit on F^2	1.106
Final R indices* [$I > 2\sigma(I)$]	$R = 0.0404, wR = 0.1059$

$$* R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|};$$

$$Rw = \left[\frac{(\sum w(|F_o| - |F_c|)^2)}{w(|F_o|^2)} \right]^{1/2}.$$

methylpyrazole (1 mmol) and copper(II) perchlorate hexahydrate (2 mmol) in methanol (25 ml). Triethylamine (3 mmol) was added to the solution. The solution was allowed to evaporate at room temperature to give green crystals, which were collected and washed with ethanol. $\text{C}_{24}\text{H}_{26}\text{N}_4\text{O}_5\text{Cu}_2$ (577.57): calcd. C 49.90, H 4.5; found: C 49.17, H 4.47.

X-ray structure determination

X-ray data collection was carried out on a RIGAKU AFC7S diffractometer [12] using a single crystal with dimensions $0.1 \times 0.02 \times 0.5$ mm, graphite monochromatized Mo- $\text{K}\alpha$ radiation ($\lambda = 0.71069\text{ \AA}$), and $\omega/2\theta$ scans. Precise unit cell dimensions were determined by least-squares refinement on the setting angles of 25 reflections ($20.19^\circ \leq \theta \leq 25.18^\circ$) carefully centered on the diffractometer. The crystallographic data and parameters used in the intensity data collection and structure refinement are listed in Table 1. Data reduction and corrections for absorption and decomposition were done using the TeXan program [13]. The structure was solved by direct methods (SHELXS-97 [14]) and refined with SHELXL-97 [15]. The relatively high residuals in the difference Fourier map can be attributed to the disorder of C1. The C1 atom was split into C1a and C1b with site occupation factors 0.47 and 0.53. C1a and C1b were refined anisotropically. The positions of the H atoms bonded to C atoms were calculated (C-H distance 0.96 \AA), and refined using a riding model, and H atom displacement parameters were

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$). Equivalent isotropic $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Cu1	1291(1)	1962(1)	1945(1)	29(1)
N1	1798(3)	3009(2)	1743(3)	30(1)
N2	415(3)	985(2)	2146(3)	30(1)
O1	0	2452(2)	2500	42(1)
O2	2774(3)	1538(2)	1598(2)	35(1)
O3	6786(3)	1443(2)	605(3)	50(1)
C1a	-248(3)	3227(2)	2084(3)	47(3)
C2	947(3)	3586(2)	2046(3)	45(1)
C3	2767(4)	3213(2)	1349(3)	32(1)
C4	3699(4)	2713(2)	1104(3)	31(1)
C5	4719(4)	3034(3)	713(3)	36(1)
C6	5718(4)	2611(3)	542(3)	40(1)
C7	5725(4)	1822(3)	760(3)	36(1)
C8	4731(4)	1482(3)	1093(3)	34(1)
C9	3688(4)	1911(2)	1275(3)	31(1)
C10	6884(5)	656(3)	874(4)	50(1)
C11	654(4)	251(2)	1932(3)	30(1)
C12	0	-218(3)	2500	29(1)
C13	1485(3)	22(2)	1182(3)	39(1)

restricted to be 1.2 U_{eq} of the parent atom. The final positional parameters are presented in Table 2. A perspective drawing of the molecule is shown in Fig. 2 [16]. Selected bond lengths and angles are summarised in Table 3. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-167317 [17]. E-mail: deposit@ccdc.cam.ac.uk

Susceptibility measurements

Magnetic susceptibility measurements of the powdered sample were performed on a Faraday-type magnetometer consisting of a CAHN D-200 microbalance, a Leybold Heraeus VNK 300 helium flux cryostat and a Bruker BE 25 magnet connected with a Bruker B-Mn 200/60 power supply in the temperature range 4.4 - 308 K. Details of the apparatus have already been described [18]. Diamagnetic corrections of the molar magnetic susceptibility of the compound were applied using Pascal's constants [19]. The applied field was ≈ 1.2 T. Magnetic moments were obtained from the relation $\mu_{\text{eff}} = 2.828(\chi T)^{1/2}$.

Molecular orbital calculations

Ab-initio restricted Hartree-Fock (RHF) calculations for 3,5-dimethylpyrazolate were carried out by using the GAUSSIAN-98 program [20]. STO-3G [21] minimal ba-

Table 3. Selected bond lengths [\AA] and angles [$^\circ$] characterizing the inner coordination sphere of the copper(II) centre (see Fig. 2 for labelling scheme adopted).

Cu1-O1	1.890(1)	Cu1-O2	1.898(3)
Cu1-N1	1.946(3)	Cu1-N2	1.997(3)
N2-N2	1.387(6)		
Cu1-O1-Cu1	126.0(2)	O1-Cu1-O2	170.4(1)
O1-Cu1-N1	82.5(1)	O2-Cu1-N1	93.7(1)
O1-Cu1-N2	86.4(1)	O2-Cu1-N2	98.0(1)
N1-Cu1-N2	168(1)		

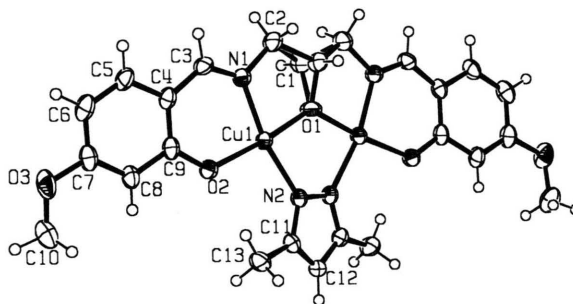


Fig. 2. View of the complex **1** showing the disorder of C1 (The numbering of the atoms corresponds to Tab. 2). Displacement ellipsoids are plotted at the 50% probability level and H atoms are presented as spheres of arbitrary radii.

sis sets were adopted for carbon and nitrogen atoms. The structural parameters as obtained from X-ray analysis were employed. Extended Hückel molecular orbital (EHMO) calculations [22, 23] were done for the dinuclear complexes using the CACAO program [24].

Results and Discussion

X-ray crystal structure

The complex consists of binuclear molecules in which each copper ion is surrounded by two O and two N atoms in a square planar coordination. The Cu-N and Cu-O bond lengths are comparable with the bond lengths reported in other binuclear copper(II) complexes [25 - 28]. The distance between the two copper(II) centers is 3.368(1) \AA and the Cu-O-Cu bridging angle is 126.0(2) $^\circ$ which is in the range of similar binuclear copper(II) complexes [7, 8, 29, 30]. The dihedral angle formed by the two coordination planes is 178.6 $^\circ$, and the whole molecule therefore is nearly planar (Fig. 3). The sum of the bond angles around the bridging oxygen atom is 355.6 $^\circ$, indicating that the three bonds are essentially planar.

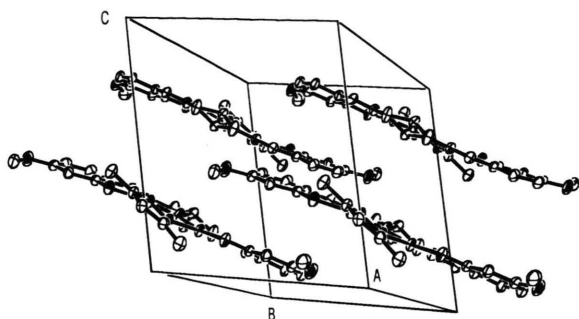


Fig. 3. View of the unit cell packing.

Two molecules are partially stacked in the crystal as illustrated in Fig. 3. The shortest intermolecular Cu...Cu distance is 9.158(1) Å, and the Cu-O distance is 3.445(4) Å ($i = -x, y, 1/2 - z$).

Magnetic properties

The magnetic susceptibilities of the complex are shown as a function of temperature in Fig. 4 (top) and the magnetic moments are shown as a function of temperature in Fig. 4 (bottom). The variable-temperature data were fitted to the modified Bleaney-Bowers equation [31] (eq. (1)).

$$\chi = \frac{Ng^2\mu_B^2}{3kT} \left[1 + \frac{1}{3} \exp(-2J/kT) \right]^{-1} (1 - x_p) \quad (1)$$

$$+ \frac{Ng^2\mu_B^2}{4kT} x_p + N_\alpha$$

using the isotropic Heisenberg - Dirac - Van Vleck Hamiltonian

$$\mathcal{H} = -2JS_1 \cdot S_2$$

for two interacting $S = 1/2$ centers, where $-2J$ is the energy difference between spin-singlet and -triplet states. N_α is the temperature-independent paramagnetism and its value is $6 \cdot 10^{-5} \text{ cm}^3/\text{mol}$ for each copper atom. x_p is the fraction of a monomeric impurity. Least squares fitting of the data leads to $J = -236 \text{ cm}^{-1}$, $g = 2.25$, $x_p = 0.38\%$. Fig. 4 (top) shows a broad maximum at a temperature of *ca.* 300 K indicative of an antiferromagnetically coupled system. The rapid increase in magnetic susceptibility at low temperatures is due to the presence of a small amount of a mononuclear impurity. The magnetic moments were obtained from the relation

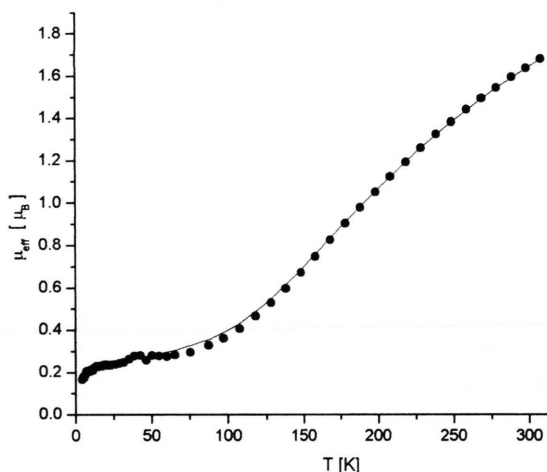
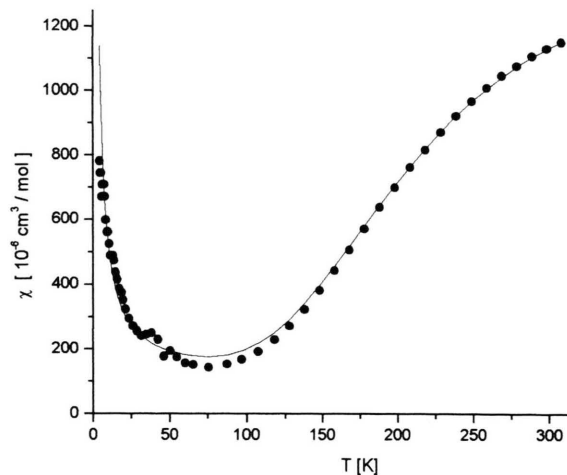


Fig. 4. Plot of the molar susceptibility χ_M (top) and the effective magnetic moment μ_{eff} (bottom) versus temperature. The solid line represents the least squares fitting of the data.

$\mu_{\text{eff}} = 2.828 (\chi T)^{1/2}$. From Fig. 4 (bottom) it is clear that the observed and calculated magnetic moments μ_{eff} decrease from $1.68 \mu_B$ at 308 K to $0.2 \mu_B$ at 4.6 K.

Magneto-Structural Correlation

Some interesting correlations between structural and magnetic parameters emerge from the data in Table 4.

In general, binuclear copper(II) complexes have several structural features to affect the strength of exchange coupling interactions, such as the dihedral angle between the two coordination planes, the planarity of the bonds around the bridging oxygen atom, the length of the copper-oxygen bridging

Table 4. Structural and magnetic data for a series of related compounds.

Compound	Cu...Cu [\AA]	Cu-O-Cu [$^\circ$]	$\langle\text{Cu-O}\rangle^a$ [\AA]	ϕ [$^\circ$] ^b	θ ^c	$-2J$ [cm^{-1}]
1	3.365(1)	125.7(1)	1.901	165.0	359.0	444
2	3.355(1)	124.7(2)	1.898	166.8	355.3	164
3	3.368(1)	126.0(2)	1.894	178.6	355.6	472
4	3.359(4)	125.1(7)	1.897	176.2	359.9	240
5	3.349	121.7	1.894	172.6	343.0	310
6	3.360	121.8	1.916	164.2	359.6	540
7	3.644	137.7	1.940	164.7	353.8	635

1: $[\text{Cu}_2(\text{L}^1)(3,5\text{-prz})]$ (Kara *et al.* [11]); **2**: $[\text{Cu}_2(\text{L}^2)(3,5\text{-prz})]$ (Kara *et al.* [10]); **3**: present work; **4**: $[\text{Cu}_2(\text{L}^1)(\text{prz})\cdot\text{H}_2\text{O}]$ (Mazurek *et al.* [8]); **5**: $[\text{Cu}_2(\text{L}^1)(\text{prz})]$ (Nishida and Kida [7]); **6**: $[\text{Cu}_2(\text{L})(\text{prz})]$ (Doman *et al.* [30]); **7**: $[\text{Cu}_2(\text{L}^1)\text{OCH}_3(\text{CH}_3\text{OH})]$ (Nishida and Kida [41]); ^a $\langle\text{Cu-O}\rangle$ is the average distance between the copper and the bridging O atoms; ^b dihedral angle between coordination planes; ^c sum of angles around the oxygen atom.

bonds, and the Cu-O-Cu bridging angle. The most widely accepted factor correlating structure and magnetism is the Cu-O-Cu bridging angle [32 - 37]. According to Hatfield, the antiferromagnetic interaction becomes stronger with increasing Cu-O-Cu angle in bis(μ -hydroxo)- and bis(μ -alkoxo)-bridged copper(II) complexes [3]. Although the Cu-O-Cu angle of the complex **6** is almost identical with that in complex **5**, the antiferromagnetic super-exchange interaction is stronger. It is clear that there is no simple correlation of the Cu-O-Cu bridge angle with the strength of the exchange interaction. Planarity of the bonds around the bridging oxygen atom also has been cited as a factor affecting the nature of the super-exchange interaction [30]. In the case of complex **4** the sum of the bond angles around the O1 atom is 359.9° indicating almost complete planarity. Although the value is almost identical with that of complex **6**, the strength of the super-exchange interaction ($-2J$) is completely different. This indicates that this factor does not affect the strength of the exchange interaction by itself. The Cu-O bridging distance may also be a structural feature which determines the magnetic orbital overlaps leading to the size of the singlet-triplet separation, $-2J$ [38]. The average Cu-O distances of dinuclear copper(II) complexes in Table 4 are quite similar ($\approx 1.9 \text{ \AA}$), but the $-2J$ values show significant differences. This factor thus also fails to account for the variation in $-2J$ values in the compounds. The dihedral angle between the two coordination planes is considered to be a key factor in determining the spin-exchange interaction between the two copper ions. The larger the dihedral angle, the greater the strength of the exchange coupling. The dihedral angle decreases in

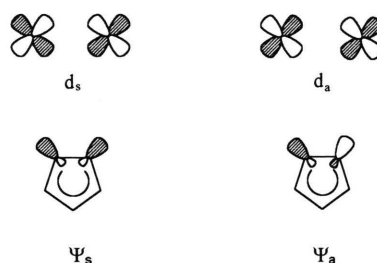


Fig. 5. Metal - 3,5-dimethylpyrazolate orbital symmetry combinations.

the order $\mathbf{3} > \mathbf{4} > \mathbf{5} > \mathbf{2} > \mathbf{1} > \mathbf{7} > \mathbf{6}$ while $-2J$ decreases in the order $\mathbf{7} > \mathbf{6} > \mathbf{3} > \mathbf{1} > \mathbf{5} > \mathbf{4} > \mathbf{2}$. This indicates that the dihedral angle of unsymmetrically doubly bridged complexes plays only a minor role in determining the exchange interaction. Thus, all the criteria so far widely accepted have failed to account for the experimental results. Accordingly, we have examined the orbitals contributing to the superexchange interaction in more detail.

Orbitals contributing to superexchange interaction

The difference in magnitude of the coupling constant of the single alkoxide bridged and doubly hetero-bridged dinuclear copper complexes may be explained by the metal-ligand orbital overlap. The single μ -alkoxo-bridged dinuclear copper complexes are antiferromagnetically coupled [5, 6]. When the Cu-O-Cu angle is larger than 90° ($120 - 135.5^\circ$) the d_a overlap with p_x is larger than of d_s with p_y , so d_a and d_s split as illustrated in Fig. 6a to give the d'_a and d'_s molecular orbitals. A large energy separation of d'_a and d'_s leads to a stronger antiferromagnetic interaction. In the presence of a second

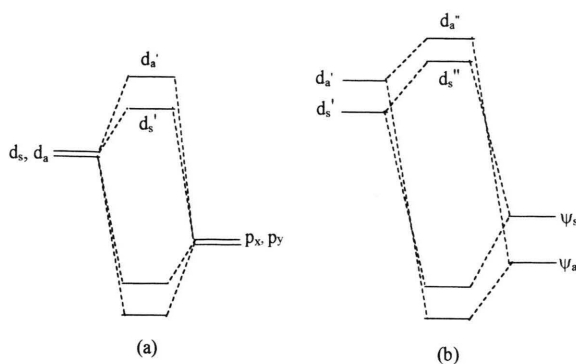


Fig. 6. Orbital Energy diagrams illustrating the interacting between bridging-group orbitals and metal magnetic orbitals. (a) Single alkoxide bridged system. (b) Further interaction due to the additional of 3,5-dimethylpyrazolate bridge to (a). d_s = symmetric orbitals on Cu(1) and Cu(2) (symmetric with respect to the plane perpendicular to the N-N bond); d_a = antisymmetric combination; p_x and p_y : orbitals of the bridging oxygen atom; ψ_s and ψ_a : symmetric and antisymmetric orbitals of the bridging ligand, respectively.

bridging ligand (Fig. 6b), either a complementary or countercomplementary effect on the spin exchange interaction may arise due to further interactions of the ligand symmetric (ψ_s) and antisymmetric (ψ_a) combinations with the d_a'' and d_s'' MO's. This interaction results in the formation of d_a'' and d_s'' . The magnitude of the magnetic exchange parameter, J , may be determined according to Hoffmann's expression [9],

$$J = J_F + J_{AF} = -2K_{12} + \frac{[E(d_a'') - E(d_s'')]^2}{J_{11} - J_{12}}. \quad (2)$$

In this expression, J_{11} , J_{12} and K_{12} are Coulomb and exchange integrals, respectively, and $E(d_a'')$ and $E(d_s'')$ are the energy levels of the HOMO and LUMO. J can be written as the sum of two terms: J_F , being the term defined by the exchange integral between the two localised molecular orbitals, which is always ferromagnetic, and J_{AF} , comprising the difference in energy between the two molecular orbitals $[E(d_a'') - E(d_s'')]^2$. The interaction of the metal-ligand orbitals thus affects the $d_a'' - d_s''$ energy and determines whether the magnetic exchange process results in overall antiferromagnetism or ferromagnetism.

Nishida *et al.* [7] have shown that the energies of d_a'' and d_s'' depend on two factors, (i) the energy

differences between the interacting orbitals, $E(d_a)$ and $E(\Psi_a)$, $E(d_s)$ and $E(\Psi_s)$, (ii) the overlap integrals between the interacting orbitals, $S(d_a, \Psi_a)$ and $S(d_s, \Psi_s)$. Molecular orbitals of the 3,5-dimethylpyrazolate ion have been calculated by the ab-initio restricted Hartree-Fock method. Since the orbital energy of Ψ_s is higher than that of Ψ_a by 0.15 eV, factor (i) of the above discussion should be decreasing for the energy gap of d_a'' and d_s'' , and hence work countercomplementary with the alkoxide bridge diminishing antiferromagnetic interaction. The overlap integrals of interacting orbitals are an important factor to increase or decrease the energy separation of d_a'' and d_s'' . If ψ_a overlaps more effectively with d_a than ψ_s with d_s , the overlap integrals of the interacting orbitals may affect the 3,5-dimethylpyrazolate bridge to act in a complementary fashion with the alkoxide bridge. 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 **3**. The rigorous definition and the process of the calculation are cited in the Appendix. In a preceding study, we have also determined these values for compounds **1** and **2** [11].

We have found the following results from our calculations;

$$S(a-s)(\mathbf{3}) > S(a-s)(\mathbf{1}) > S(a-s)(\mathbf{2}) \quad (3)$$

This clearly indicates that the effect of factor ii for **2** is weak compared with that for **1** and **3**. As a result, the energy separation of d_a'' and d_s'' for **3** is reduced as compared with that for **1** and **2**; in other words, in the case of **2** the 3,5-dimethylpyrazolate bridge exerts a countercomplementary effect on the antiferromagnetic interaction caused by the alkoxide bridge. This effect may be taken as the main factor for the smaller $-2J$ value of **2** compared with that of **1** and **3**.

In addition to above calculation, we also have carried out extended Hückel Molecular Orbital (EHMO) calculations which have shown that the HOMO and LUMO are separated by 0.22 eV, 0.19 eV and 0.23 for **1**, **2** and **3**, respectively. The smaller value of **2** compared with those of **1** and **3** is entirely consistent with these magnetic properties.

Conclusion

In dinuclear copper(II) complexes which contain two different bridging ligands, the bridging units

may act in a complementary or countercomplementary fashion to increase or decrease the strength of the super-exchange process. When two copper ions are doubly bridged with alkoxide oxygen and μ -pyrazolate nitrogen atoms, as in the cases of **1**, **2**, **3**, **4**, **5** and **6**, the μ -pyrazolate bridge will increase or decrease the energy separation between d_a and d_s depending on the relative degree of interaction between d_a and Ψ_a and between d_s and ψ_s .

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Appendix

Determination of the Orientation of the Magnetic d Orbitals

Fig. 7. shows the projection of CuI and the donor atoms onto the coordination plane together with the axes of the magnetic d orbital (broken lines). The angles formed by the coordinative bonds and the axes of the d orbital are denoted as α , β , γ , and δ . In order to fulfil the requirement of maximum overlap, the following function was minimised:

$$\begin{aligned}
 F(\alpha) &= \alpha^2 + \beta^2 + \gamma^2 + \delta^2 & (A1) \\
 &= \alpha^2 + (\alpha + 90 - 82.43)^2 \\
 &\quad + (\alpha + 180 - 82.43 - 86.42)^2 \\
 &\quad + (\alpha + 270 - 82.43 - 86.42 - 98.01)^2 \\
 &= 4\alpha^2 - 43.72\alpha + 191.48.
 \end{aligned}$$

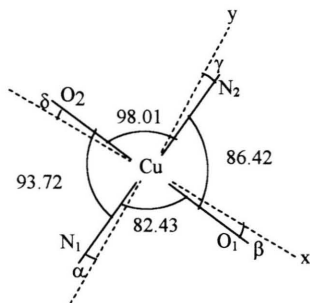


Fig. 7. Projection of CuI and the donor atoms in the best plane formed by these atoms. (The broken lines are the axes of the d orbitals.)

If $dF(\alpha)/d\alpha = 0$, then $\alpha = 5.465^\circ$. The same value was obtained for α about the coordination plane of Cu2.

Determination of Overlap Integrals between d_s and ψ_s and between d_a and ψ_a

When the x and y axes in Fig. 7 are rotated by α , the d_1 orbital is expressed in terms of the new coordinate system as

$$d_1 = (\cos(2\alpha))d_{x^2-y^2} + (\sin(2\alpha))d_{xy}. \quad (A2)$$

The ψ_s and ψ_a orbitals of the 3,5-dimethylpyrazolate ion can be expressed as the sum of the orbitals on N1 and N2 and the neighbouring carbon atoms:

$$\psi_s = \phi_{s1} + \phi_{s2} + \phi_{sC}, \quad (A3)$$

$$\psi_a = \phi_{a1} + \phi_{a2} + \phi_{aC}. \quad (A4)$$

These orbitals can be expressed in terms of the new coordinate system in which the y -axis is on the Cu1-N1 bond:

$$\begin{aligned}
 \phi_{s1} &= 0.01352s + 0.26662((\cos 30)p_x + (\sin 30)p_y) \\
 &\quad + 0.06713(-(\cos 60)p_x + (\sin 60)p_y), \\
 \phi_{s1} &= 0.01352s + 0.19733p_x + 0.191446p_y. & (A5)
 \end{aligned}$$

From (A2) and (A5):

$$\begin{aligned}
 S(d_1, \phi_{s1}) &= 0.01352(\cos(2\alpha))S(3d, 2s) \\
 &\quad + 0.19144(\cos(2\alpha))S(3d_\sigma, 2p_\sigma) \\
 &\quad + 0.19733(\sin(2\alpha))S(3d_\pi, 2p_\pi).
 \end{aligned}$$

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

$$\begin{aligned}
 S(d_s, \psi_s) &= 2S(d_1, \phi_{s1})/2^{1/2}, \\
 S(d_s, \Psi_s) &= 0.0191(\cos(2\alpha))S(3d, 2s) & (A6) \\
 &\quad + 0.2707(\cos(2\alpha))S(3d_\sigma, 2p_\sigma) \\
 &\quad + 0.2790(\sin(2\alpha))S(3d_\pi, 2p_\pi).
 \end{aligned}$$

In a similar way, $S(d_a, \psi_a)$ is obtained:

$$\begin{aligned}
 S(d_a, \Psi_a) &= 0.0081(\cos(2\alpha))S(3d, 2s) & (A7) \\
 &\quad + 0.5333(\cos(2\alpha))S(3d_\sigma, 2p_\sigma) \\
 &\quad - 0.2918(\sin(2\alpha))S(3d_\pi, 2p_\pi).
 \end{aligned}$$

From (A6) and (A7) for compound **3**:

$$\begin{aligned}
 S(a-s) &= S(d_a, \Psi_a) - S(d_s, \Psi_s) \\
 &= -0.0109(\cos(2\alpha))S(3d, 2s) \\
 &\quad + 0.26259(\cos(2\alpha))S(3d_\sigma, 2p_\sigma) \\
 &\quad - 0.57084(\sin(2\alpha))S(3d_\pi, 2p_\pi).
 \end{aligned}
 \tag{A8}$$

Rough values of the overlap integrals for the present complexes can be estimated from the tables of Jaffe *et al.* [39] and Kuruda and Ito [40]; $S(3d, 2s) \approx 0.04$, $S(3d_\sigma, 2p_\sigma) \approx 0.06$, $S(3d_\pi, 2p_\pi) \approx 0.02$. Considering

these values with (A8), one can conclude that $S(a-s)$ is definitely larger than zero in the case of **3**. In the case of **3**, $\alpha = 5.465^\circ$, hence

$$S(a-s) = 0.01296. \tag{A9}$$

For **1** and **2**, overlap integrals are also obtained by the same principle [11]: In the case of **1**, $\alpha = 6.125^\circ$, hence

$$S(a-s) = 0.01074. \tag{A10}$$

In the case of **2**, $\alpha = 6.46^\circ$, hence

$$S(a-s) = 0.00419. \tag{A11}$$

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