

Magnetic Super-Exchange Mechanism and Crystal Structure of a Binuclear μ -Acetato-Bridged Copper(II) Complex of Pentadentate Binucleating Ligand. An Influence of Overlap Interactions to Magnetic Properties

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Z. Naturforsch. **57 b**, 323–330 (2002); received October 9, 2001

Dinuclear Copper(II) Complex, Antiferromagnetic Coupling, Overlap Interaction

$[\text{Cu}_2(\text{L})(\text{O}_2\text{CMe})] \cdot \frac{1}{2}\text{H}_2\text{O}$ (L = 1,3-bis(2-hydroxy-5-chlorosalicylideneamino)propan-2-ol) was synthesized and its crystal structure determined. $(\text{C}_{19}\text{H}_{16}\text{N}_2\text{O}_5\text{Cl}_2\text{Cu}_2) \cdot \frac{1}{2}\text{H}_2\text{O}$, monoclinic, space group $P 2_1/c$, $a = 20.660(10)$, $b = 9.618(2)$, $c = 21.810(10)$ Å, $\beta = 109.3(8)^\circ$, $V = 4090(2)$ Å³, $Z = 8$. The crystal contains two independent dicopper(II) complexes and an uncoordinated molecule of water in the asymmetric unit. In both molecules of the asymmetric unit, the two copper(II) ions are bridged by the alkoxo group of the ligand and by an acetato group. Magnetic susceptibilities of the complex in the solid state were measured over the temperature range 4.6 - 308 K. The title compound shows weak antiferromagnetic coupling with a best fit J value of -89.6 cm^{-1} , which is interpreted in terms of a compensation effects of the different bridging ligands which participate in the super-exchange interactions. *Ab initio* restricted Hartree-Fock calculations have shown that the acetato bridge and the alkoxide bridge contribute to the magnetic interaction countercomplementarily to reduce antiferromagnetic interaction.

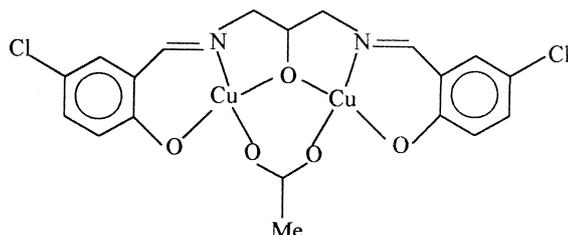
Introduction

Series of binuclear transition-metal complexes which display different physical properties have been investigated extensively in recent years. This is partly because of the use of such complexes to mimic aspects of bimetallic biosites in various proteins and enzymes [1, 2], and partly because of attempts to understand the structural factors that govern magnetic exchange phenomena [3 - 5]. A number of binuclear copper(II) species have magnetic properties which indicate considerable antiferromagnetic spin exchange between the copper ($S = 1/2$) centers. Variations of the magnitude of this exchange with the Cu-O-Cu bridging angle, the Cu...Cu distance and with the nature of the pentadentate ligand have been investigated [6 - 10].

Hatfield and Hodgson [11] have observed an increase in the strength of antiferromagnetic coupling with increasing Cu-O-Cu bridge angle in the range $90 - 105^\circ$, for bis(μ -hydroxo) and bis(μ -alkoxo)-bridged binuclear copper(II) complexes. In recent years, the structural and magnetic characterisation of binuclear copper(II) complexes in which the cop-

per ions are linked by two bridging ligands were reported by Nishida and co-workers [8, 9]. Although these complexes have large Cu-O-Cu angles, they show weaker antiferromagnetic super-exchange interactions than binuclear copper complexes in which two copper(II) ions are bridged by a single alkoxide oxygen with large Cu-O-Cu bridge angles ($120-135.5^\circ$) [12,13]. This may show that the presence of the second bridging ligand influences the strength of the antiferromagnetic interaction, depending on the second ligand. According to Hoffmann's theory [14] 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 the difference in symmetries of the magnetic orbitals.

Recently, we studied the crystal structure and magnetic properties of a μ -acetato-N,N'-bridged dicopper(II) complex of 1,3-bis(2-hydroxy-1-naphthylideneamino)propan-2-ol (**1**) [15]. In this study, we have synthesized a μ -acetato-N,N'-bridged dicopper(II) complex of 1,3-bis(2-hydroxy-5-chlorosalicylideneamino)propan-2-ol (**2**), determined its crystal structure by X-ray diffraction and



measured the magnetic susceptibilities in the temperature range 4.6 - 308 K using the Faraday method to determine the magnitude of coupling constant (J). Finally, we investigated the interaction between the magnetic d orbitals and the HOMO's of the acetate ions in order to clarify the influence of the second bridging ligand on the super-exchange interaction in compounds **1** and **2**.

Experimental

Preparation

The Schiff base ligand was synthesized by reaction of 1,3-diamino-2-hydroxypropane and 2-hydroxy-5-chlorosalicylaldehyde in 1:2 molar ratio at room temperature. The product was obtained as pale yellow crystals. For the preparation of the complex, 0.1 mmol ligand and 0.3 mmol triethylamine were dissolved in a methanol-water mixture (5:1, 50 ml) and a solution of 0.2 mmol $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ in 20 ml methanol was added. The solution was allowed to evaporate at room temperature to give green crystals, which were collected and washed with ethanol.

X-ray structure determination

X-ray data collection was carried out on an Enraf-Nonius CAD-4 diffractometer [16] using a single crystal with dimensions $0.30 \times 0.10 \times 0.05$ mm with graphite monochromatized $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073$ Å). Experimental conditions are summarized in Table 1. Precise unit cell dimensions were determined by least-squares refinement on the setting angles of 25 reflections ($2.15^\circ \leq \theta \leq 12.35^\circ$) carefully centered on the diffractometer. Three standard reflections (510, 020, 011) were measured every 7200 s and the orientation of the crystal was checked after every 600 reflections. These measurements (298 K) did not indicate any variations in the experimental conditions, but a decrease of 0.5% in the intensity of the standard reflections indicated a decay of the crystal. Data reduction and corrections for absorption and decomposition were achieved using the Nonius Diffractometer Control Software [16]. The structure was solved by SHELXS-97 [17] and refined with SHELXL-97 [18]. The positions of the H atoms bonded to C atoms were calculated (C-H distance 0.96 Å), and refined using a riding model, and H atom

Table 1. Crystallographic data for compound **2**.

| | |
|---|---|
| Sum formula | $\text{C}_{19}\text{H}_{16}\text{N}_2\text{O}_5\text{Cu}_2\text{Cl}_2 \cdot \frac{1}{2} \text{H}_2\text{O}$ |
| f_w ($\text{g} \cdot \text{mol}^{-1}$) | 559.33 |
| Space group | $P2_1/c$ |
| $a = 20.660(10)$ Å | $\alpha = 90.00^\circ$ |
| $b = 9.618(2)$ Å | $\beta = 109.3(8)^\circ$ |
| $c = 21.810(10)$ Å | $\gamma = 90.00^\circ$ |
| Vol [Å^3] | 4090(3) |
| Z | 8 |
| D_{calc} ($\text{g} \cdot \text{cm}^{-3}$) | 1.817 |
| μ [cm^{-1}] | 23.79 |
| $F(000)$ | 2248 |
| Index ranges | $-25 \leq h \leq 24, 0 \leq k \leq 11, 0 \leq l \leq 26$ |
| θ Range for data collection | $0.04^\circ < \theta < 26.01^\circ$ |
| Reflections collected | 8023 |
| Independent reflections | 7925 [$R(\text{int}) = 0.032$] |
| Data / restraints / params | 7925 / 0 / 550 |
| Goodness-of-fit on F^2 | 1.121 |
| Extinction coefficient | 0.0019(2) |
| Final R indices [$I > 2\sigma(I)$] | $R = 0.0428, wR = 0.0836$ |
| Final R indices (all data) | $R = 0.0468, wR = 0.0895$ |
| Largest diff. peak and hole | 0.29 and $-0.63 \text{ e} \cdot \text{Å}^{-3}$ |

displacement parameters were restricted to $1.2 U_{\text{eq}}$ of the parent atom. The hydrogen atoms of the water molecule were located in a difference electron density map and their positions were not refined. The final positional parameters are presented in Table 2. A perspective drawing of the molecule is shown in Fig. 1 [19]. 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-172041 [20].

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 4.6 - 308 K. Details of the apparatus have already been described [21]. Diamagnetic corrections of the molar magnetic susceptibility of the compound were applied using Pascal's constants [22]. 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 the acetate ion were carried out by using the GAUSSIAN-98 program [23]. STO-3G [24] minimal basis sets were adopted for the carbon and oxygen atoms.

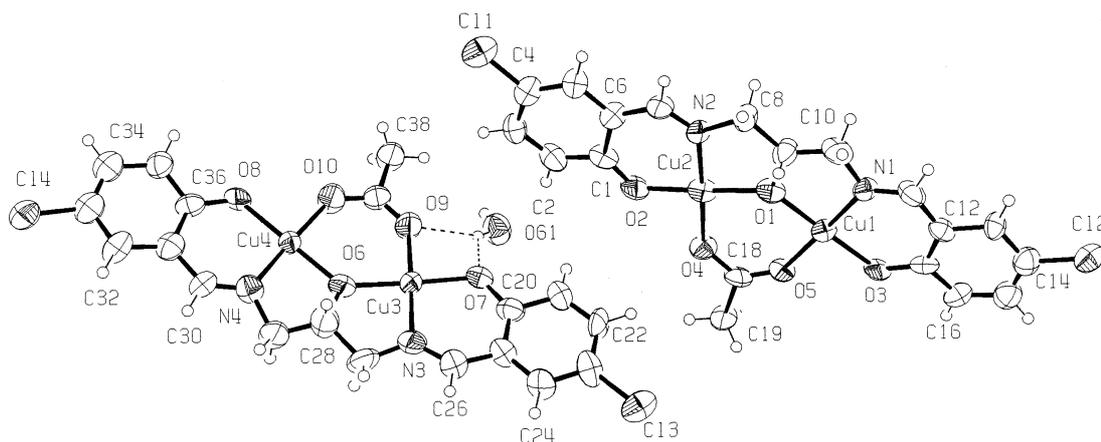


Fig. 1. View of the molecule (numbering of atoms corresponds to Table 2). Displacement ellipsoids are plotted at the 50% probability level and H atoms are presented as spheres of arbitrary radii.

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) |
|------|----------|----------|----------|---------------|
| C1 | 1638(1) | 1158(2) | 735(1) | 44(1) |
| C2 | 2230(2) | 1771(3) | 624(1) | 62(1) |
| C3 | 2861(2) | 1214(3) | 702(1) | 56(1) |
| C4 | 2913(1) | -169(3) | 902(1) | 53(1) |
| C5 | 2389(1) | -914(3) | 994(1) | 49(1) |
| C6 | 1752(1) | -277(3) | 899(1) | 47(1) |
| C7 | 1255(1) | -1091(2) | 1035(1) | 47(1) |
| C8 | 188(1) | -1652(3) | 1106(2) | 56(1) |
| C9 | -466(2) | -996(3) | 1057(2) | 67(1) |
| C10 | -1066(2) | -1591(3) | 1135(2) | 70(1) |
| C11 | -2208(1) | -1014(3) | 1032(2) | 58(1) |
| C12 | -2791(1) | -170(2) | 932(1) | 46(1) |
| C13 | -3404(1) | -817(3) | 970(1) | 47(1) |
| C14 | -4004(2) | -24(3) | 868(1) | 61(1) |
| C15 | -4023(2) | 1295(4) | 689(2) | 66(1) |
| C16 | -3463(1) | 1881(3) | 575(2) | 61(1) |
| C17 | -2837(1) | 1190(2) | 725(1) | 49(1) |
| C18 | -650(2) | 3557(3) | 545(2) | 58(1) |
| C19 | -708(2) | 5067(2) | 404(2) | 72(1) |
| N1 | -1644(1) | -648(2) | 988(1) | 46(1) |
| N2 | 649(1) | -669(2) | 957(1) | 41(1) |
| O1 | -540(1) | 407(2) | 858(1) | 51(1) |
| O2 | 1087(1) | 1831(2) | 650(1) | 60(1) |
| O3 | -2314(1) | 1864(2) | 640(1) | 47(1) |
| O4 | -74(2) | 3017(2) | 554(1) | 51(1) |
| O5 | -1185(1) | 2958(2) | 500(1) | 44(1) |
| C11 | 3706(1) | -940(1) | 1020(1) | 70(1) |
| C12 | -4678(1) | -829(1) | 1010(1) | 69(1) |
| Cu1 | -1426(2) | 1154(1) | 744(1) | 39(1) |
| Cu2 | 272(2) | 1158(1) | 757(1) | 44(1) |
| C20 | 2500(2) | 5670(3) | 1725(1) | 56(1) |
| C21 | 1840(2) | 5059(4) | 1430(2) | 74(1) |

Table 2 (continued).

| Atom | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> (eq) |
|------|----------|----------|----------|---------------|
| C22 | 1346(1) | 5209(3) | 1740(2) | 63(1) |
| C23 | 1468(2) | 6067(3) | 2299(1) | 63(1) |
| C24 | 2114(1) | 6670(3) | 2617(1) | 59(1) |
| C25 | 2610(1) | 6422(3) | 2313(1) | 51(1) |
| C26 | 3282(1) | 6930(3) | 2632(1) | 55(1) |
| C27 | 4468(2) | 7555(4) | 2785(2) | 77(1) |
| C28 | 5064(2) | 6920(4) | 2662(2) | 77(1) |
| C29 | 5681(2) | 7677(4) | 2790(1) | 70(1) |
| C30 | 6715(1) | 7038(3) | 2639(1) | 57(1) |
| C31 | 7201(2) | 6524(3) | 2358(1) | 59(1) |
| C32 | 7931(1) | 6742(3) | 2669(1) | 57(1) |
| C33 | 8357(2) | 6193(3) | 2341(2) | 66(1) |
| C34 | 8162(2) | 5259(2) | 1861(2) | 66(1) |
| C35 | 7460(1) | 4954(3) | 1609(2) | 59(1) |
| C36 | 6965(1) | 5690(3) | 1780(1) | 52(1) |
| C37 | 4335(1) | 4637(3) | 703(1) | 52(1) |
| C38 | 4147(2) | 3853(4) | 80(1) | 68(1) |
| N3 | 3825(1) | 6892(2) | 2433(1) | 59(1) |
| N4 | 6071(1) | 6878(3) | 2473(1) | 57(1) |
| O6 | 4795(1) | 6375(2) | 1986(1) | 68(1) |
| O7 | 2922(1) | 5318(2) | 1412(1) | 67(1) |
| O8 | 6326(1) | 5274(2) | 1526(1) | 49(1) |
| O9 | 3883(1) | 4969(2) | 922(1) | 67(1) |
| O10 | 4981(1) | 4892(3) | 958(1) | 68(1) |
| C13 | 827(1) | 6339(1) | 2635(1) | 71(1) |
| C14 | 9218(1) | 6649(1) | 2716(1) | 69(1) |
| Cu3 | 3846(1) | 5913(1) | 1675(1) | 46(1) |
| Cu4 | 5547(1) | 5883(1) | 1711(1) | 45(1) |
| O61 | 2432(1) | 5088(3) | -38(1) | 74(1) |

The structural parameters obtained by X-ray analysis were employed. Extended Hückel molecular orbital (EHMO) calculations [25,26] were done for the dinuclear complex using the CACAO program [27].

Table 3. Selected bond lengths [Å] and angles [°] characterizing the inner coordination sphere of the copper(II) centre in **2** (see Fig. 1 for labelling scheme adopted).

| | | | |
|------------|----------|------------|----------|
| Cu1-O3 | 1.900(3) | Cu1-N1 | 1.910(3) |
| Cu1-O1 | 1.904(4) | Cu1-O5 | 1.928(2) |
| Cu2-O2 | 1.889(3) | Cu2-O1 | 1.905(3) |
| Cu2-N2 | 1.913(3) | Cu2-O4 | 1.922(3) |
| Cu2-O1-Cu1 | 133.4(1) | O3-Cu1-O1 | 178.7(1) |
| O3-Cu1-N1 | 93.0(2) | O1-Cu1-N1 | 85.8(2) |
| O3-Cu1-O5 | 88.3(2) | O1-Cu1-O5 | 92.9(2) |
| N1-Cu1-O5 | 178.7(1) | O2-Cu2-O1 | 177.7(1) |
| O2-Cu2-N2 | 91.8(1) | O1-Cu2-N2 | 86.2(1) |
| O2-Cu2-O4 | 86.0(1) | O1-Cu2-O4 | 96.0(1) |
| N2-Cu2-O4 | 177.8(1) | | |
| Cu3-O7 | 1.891(8) | Cu3-O9 | 1.900(2) |
| Cu3-O6 | 1.903(9) | Cu3-N3 | 1.916(3) |
| Cu4-O8 | 1.876(5) | Cu4-O6 | 1.903(7) |
| Cu4-N4 | 1.914(1) | Cu4-O10 | 1.924(1) |
| Cu3-O6-Cu4 | 133.1(2) | O7-Cu3-O9 | 85.3(6) |
| O7-Cu3-O6 | 175.1(1) | O9-Cu3-O6 | 95.1(6) |
| O7-Cu3-N3 | 95.8(6) | O9-Cu3-N3 | 178.7(1) |
| O6-Cu3-N3 | 83.8(6) | O8-Cu4-O6 | 173.5(1) |
| O8-Cu4-N4 | 93.7(5) | O6-Cu4-N4 | 83.6(4) |
| O8-Cu4-O10 | 89.1(5) | O6-Cu4-O10 | 93.6(4) |
| N4-Cu4-O10 | 177.1(1) | | |

Discussion

X-ray crystal structure

The crystals of title compound contain two independent binuclear molecules in which two copper atoms are linked by the alkoxide oxygen atom of the pentafunctional chelate ligand and the oxygen atoms of the acetato ligand and a non-coordinating water molecule in the asymmetric unit. The coordination geometry of the copper(II) centers is square planar and each copper ion is surrounded by one N and three O atoms. The dihedral angles between the two coordination planes for the molecules in the asymmetric unit are 3.4(8)° and 9.9(8)°. The intramolecular Cu(1)⋯Cu(2) and Cu(3)⋯Cu(4) distances are 3.498(2) and 3.491(2) Å, respectively. These distances are in the range of similar binuclear copper(II) complexes [28, 29]. The Cu(1)-O(1)-Cu(2) and Cu(3)-O(6)-Cu(4) angles are 133.4(1)° and 133.1(2)°. The Cu-N and Cu-O bond distances are close to values of those of conventional Schiff base and alkoxide-bridged copper(II) complexes of square planar coordination [8, 9, 15]. The sum of the bond angles around the bridging oxygen atoms O1 and O6 are 359.9° and 357.8°, respectively, indicating planarity. One complex is engaged in weak bifurcated intermolecular (O-H⋯O) hydrogen bonds

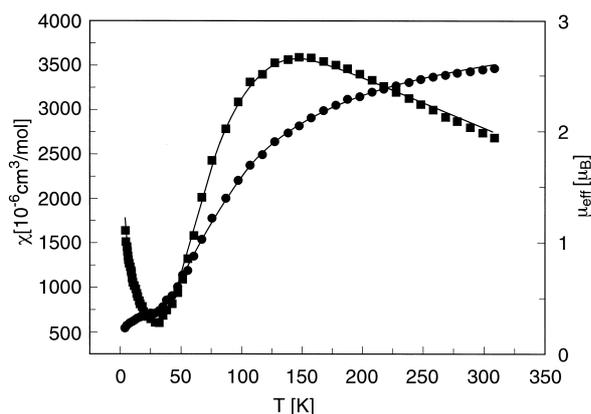


Fig. 2. Molar susceptibility (■) and effective magnetic moment (●) per copper(II) vs. temperature.

O61-H611⋯O7 [2.993(2) Å] and O61-H611⋯O9 [3.039(3) Å].

Magnetic properties

Magnetic susceptibility measurements for a powdered sample of the complex were performed by the Faraday method in the temperature range 4.6 - 308 K. The molar magnetic susceptibility is calculated by using the isotropic Heisenberg - Dirac - Van Vleck exchange Hamiltonian

$$H = -2J\vec{S}_1 \cdot \vec{S}_2 \quad (1)$$

which was first used by Kambe for this purpose [30]. The observed data were fitted by the least-squares methods to the Bleaney-Bowers equation by allowing for the presence of monomer impurity [31]:

$$\chi = \frac{N_L g^2 \mu_B^2}{3kT} \left[1 + \frac{1}{3} \exp\left(\frac{-2J}{kT}\right) \right]^{-1} (1 - x_p) + \frac{N_L g^2 \mu_B^2}{4kT} x_p + N_\alpha \quad (2)$$

A fixed value of $60 \times 10^{-6} \text{ cm}^3/\text{mol}$ per Cu atom was employed for the temperature-independent paramagnetism (N_α) contribution. x_p is the molar fraction of a monomeric impurity. Least squares fitting of the data leads to $J = -89.6 \text{ cm}^{-1}$, $g = 2.18$, $x_p = 0.7\%$. The magnetic susceptibilities and effective magnetic moments per copper(II) as a function of temperature are given in Fig. 2. The title compound shows a maximum in magnetic susceptibility at *ca.*

Table 4. Structural and magnetic data of reference compounds.

| Compound | Cu...Cu [\AA] | Cu-O-Cu [$^\circ$] | $\langle\text{Cu-O}\rangle^f$ [\AA] | θ^g [$^\circ$] | $-2J$ [cm^{-1}] |
|----------|--------------------------|----------------------|--|-------------------------|----------------------------|
| a | 3.331 | 129.1 | 1.873 | – | 586 |
| b | 3.384 | 132.2 | 1.850 | – | 820 |
| c | 3.642 | 143.7 | 1.916 | – | 1000 |
| d | 3.401 | 121.3 | 1.929 | 356.6 | 595 |
| e | 3.360 | 121.8 | 1.912 | 359.6 | 540 |
| 1 | 3.492(2) | 133.5(1) | 1.910 | 356.9 | 163.6 |
| 2 | 3.495(2) | 133.3(2) | 1.904 | 358.9 | 179.2 |

^a $[\text{Cu}_2(\text{L}_1)(\text{pyd})]\text{BF}_4 \cdot \text{H}_2\text{O}$ (Li *et al.* [10]); ^b $[\{\text{Cu}(\text{II})\dots(\text{OH})\dots\text{Cu}(\text{II})\}](\text{BF}_4)_3$ (Burk, Osborn and Youinou [13]); ^c $[\text{Cu}_2(\text{OH})-(\text{ClO}_4)_2 \cdot \text{A}](\text{ClO}_4)_2 \cdot \text{CHCl}_3$ (A: binucleating macrocycle) (Coughlin, Lippard [12]); ^d $[\text{Cu}_2(\text{L}^2)(\text{prz})]$ (Nishida and Kida [36]); ^e $[\text{LCu}_2(\text{prz})]$ (Doman *et al.* [35]); ^f $\langle\text{Cu-O}\rangle$ is the average distance between the copper and the bridging O atoms; ^g Solid angle around the bridging oxygen atom.

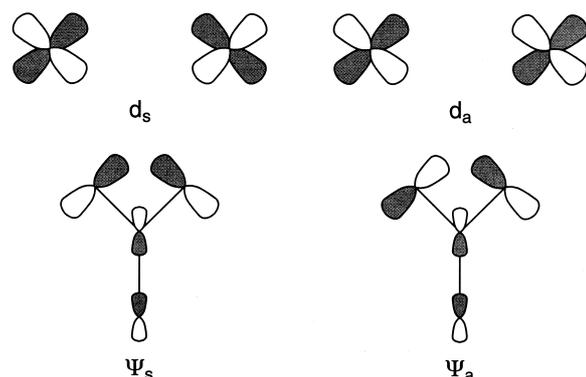


Fig. 3. Orbital symmetry combinations of metal d orbitals and acetate HOMO's.

150 K which is typical of antiferromagnetic behaviour. The rapid increase in magnetic susceptibility at low temperatures is due to the presence of a small amount of monomeric impurity (0.7%) as commonly encountered in such systems [32]. From Fig. 2, it is clear that the observed and calculated magnetic moments ($\mu_{\text{eff}} = 2.828 (\chi T)^{1/2}$) decrease from a value of 2.57 B. M. at 308 K to 0.25 B. M. at 4.6 K, indicating a moderate intramolecular antiferromagnetic exchange interaction.

Correlation of structural and magnetic properties

Magnetostructural correlations have been established for many dinuclear copper(II) complexes in the last two decades [33, 34]. Although many factors influence the value of $-2J$, the Cu-O-Cu bridging angle is the most widely accepted factor correlating structure and magnetism [11]. When we considered single alkoxide bridged and double hetero bridged complexes (pyrazolate or pyridazine instead of the acetato bridge), we noticed that although the Cu-

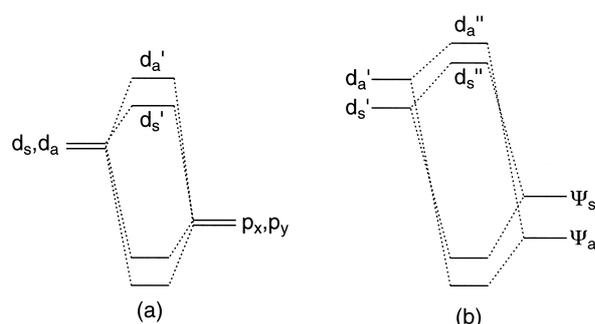


Fig. 4. The orbital energy level diagrams showing the interaction between the magnetic orbitals and bridging group orbitals (a) for single-alkoxide-bridged system; (b) for an additional bridging ligand.

O-Cu bridge angles of the compounds **1** and **2** are almost identical with those of reference complexes [10, 12, 13, 35, 36], their antiferromagnetic super-exchange interactions are weaker (Table 4). This may indicate that the presence of the second bridging ligand affects the strength of the antiferromagnetic super-exchange interaction. Since it is difficult to explain this fact in terms of structural factors, we considered overlap interactions between the metal d orbitals and the HOMO's of the acetate ion (Fig. 3).

The single μ -alkoxo-bridged dinuclear copper complexes are antiferromagnetically coupled [12, 13]. When the Cu-O-Cu angle is larger than 90° ($120 - 135.5^\circ$), in such systems the d_a (antisymmetric combinations of d orbitals) overlap with p_x is larger than the d_s (symmetric combinations of d orbitals) overlap with p_y , so d_a and d_s split as illustrated in Fig. 4a for the d'_a and d'_s molecular orbitals. The larger energy separation of d'_a and d'_s gives a stronger antiferromagnetic interaction. In the

presence of a second bridging ligand, d'_a and d'_s interact with antisymmetric (ψ_a) and symmetric (ψ_s) combinations of this ligand, respectively, to form new molecular orbitals d''_a and d''_s (Fig. 4b). The energy separation between these two new molecular orbitals is expected to determine the super exchange coupling constant. According to the theoretical analysis by Hoffmann and co-workers [14], the coupling constant is expressed as

$$E_T - E_S = -2J = -2K_{ab} \frac{[E(d''_a) - E(d''_s)]^2}{J_{aa} - J_{bb}}, \quad (3)$$

where K_{ab} , J_{aa} and J_{ab} are the exchange integral and the one-center and two-center Coulomb repulsion integrals, respectively, and $E(d''_a)$ and $E(d''_s)$ are the orbital energies of d''_a and d''_s , respectively. Since the denominator of the second term varies very little and K_{ab} is approximately constant for similar compounds where the bridging structures are all similar, the energy difference between these two new molecular orbitals (d''_a and d''_s) determines the magnitude of the $-2J$ value. Nishida *et al.* [36] have shown that the energies of d''_a and d''_s depend on two factors: (i) the energies of the interacting orbitals and (ii) the overlap integrals between the interacting orbitals, $S(d_a, \psi_a)$ and $S(d_s, \psi_s)$.

Ab-initio and extended Hückel molecular orbital calculations

In complexes **1** and **2**, since the orbital energy of ψ_s is higher than that of ψ_a by 0.203 eV, the energies of the interacting orbitals cause the acetate bridge to work in a countercomplementary fashion with the alkoxide bridge. If ψ_s overlaps more effectively with d_s than ψ_a with d_a , the overlap integrals of the interacting orbitals, the acetate bridge may act in a countercomplementary fashion with the alkoxide bridge again. 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 compounds **1** and **2** (Appendix). The difference between $S(d_a, \psi_a)$ and $S(d_s, \psi_s)$ is denoted $S(a-s)$. In both cases $S(a-s)$ is negative:

$$S(d_s, \psi_s) > S(d_a, \psi_a).$$

According to factor (ii) the acetate bridge acts in a countercomplementary fashion to reduce the energy

separation between d''_a and d''_s . The value of $S(a-s)$ for **2** was found to be larger than the value of **1**.

In addition to the above calculations we have carried out extended Hückel molecular orbital (EHMO) calculations for **1** and **2** which have shown that the d''_a and d''_s orbitals are separated by 0.605 and 0.645 eV, respectively. The smaller value of **1** compared with that of **2** is entirely consistent with an antiferromagnetic coupling of **1** weaker than of **2**.

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. In the title compound, the weak antiferromagnetic coupling is explained by the countercomplementary behaviour of the bridging carboxylate oxygen atoms which participate in the super-exchange interaction.

Acknowledgements

We thank Prof. Dr. W. Haase to give us the opportunity for magnetic susceptibility measurements. This work was supported by the Research Fund of the University of Ankara under grant number 98-25-00-03. A. Elmali is grateful to the Scientific and Technical Research Council of Turkey (TÜBİTAK) and the Deutsche Forschungsgemeinschaft (DFG) for financial support.

Appendix

Determination of the orientation of magnetic d orbitals

Fig. 5 shows the projection of Cu1 and donor atoms onto the coordination plane together with the axes of the magnetic d orbital (broken lines). In order to fulfill the

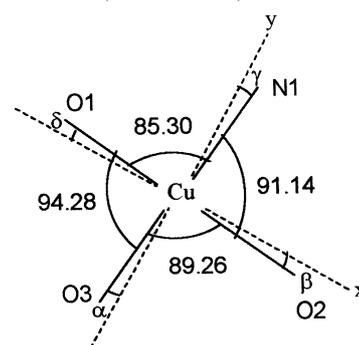


Fig. 5. Projection of Cu1 and donor atoms onto the best plane formed by these atoms. (The broken lines are the axes of the magnetic d orbital) for **1**.

requirement of maximum overlap, the function

$$F(\alpha) = \alpha^2 + \beta^2 + \gamma^2 + \delta^2 \quad (\text{A1})$$

was minimized. α , β , γ and δ are the angles formed by the coordination bonds and the axes of the d orbitals (Fig. 5). For compound **1** and **2**, the value of α is obtained as -1.16° and -2.13° , respectively.

Determination of overlap integrals between d_s and ψ_s and between d_a and ψ_a

The HOMO's are expressed in terms of LCAO's in (A2) and (A3) for compound **1**:

$$\begin{aligned} \psi_s = & 0.0005 [s(\text{O1}) + s(\text{O2})] + 0.7086 [p_x(\text{O1}) - p_x(\text{O2})] \\ & + 0.0046 [p_y(\text{O1}) + p_y(\text{O2})] \\ & + 0.0194 [p_x(\text{C1})] + 0.0002 [p_y(\text{C1})], \end{aligned} \quad (\text{A2})$$

$$\begin{aligned} \psi_a = & 0.00011 [s(\text{O1}) - s(\text{O2})] + 0.2991 [p_x(\text{O1}) + p_x(\text{O2})] \\ & + 0.0055 [p_y(\text{O1}) - p_y(\text{O2})] \\ & + 0.0171 [p_x(\text{C1})] + 0.0003 [p_y(\text{C1})], \end{aligned} \quad (\text{A3})$$

and in (A4) and (A5) for compound **2**:

$$\begin{aligned} \psi_s = & 0.00036 [s(\text{O1}) + s(\text{O2})] + 0.7027 [p_x(\text{O1}) - p_x(\text{O2})] \\ & + 0.0016 [p_y(\text{O1}) + p_y(\text{O2})] \\ & + 0.0308 [p_x(\text{C1})] + 0.00001 [p_y(\text{C1})], \end{aligned} \quad (\text{A4})$$

$$\begin{aligned} \psi_a = & 0.00008 [s(\text{O1}) - s(\text{O2})] + 0.3038 [p_x(\text{O1}) + p_x(\text{O2})] \\ & + 0.0022 [p_y(\text{O1}) - p_y(\text{O2})] \\ & + 0.0169 [p_x(\text{C1})] + 0.0006 [p_y(\text{C1})]. \end{aligned} \quad (\text{A5})$$

Overlap integrals of compound **1** and **2** have been calculated according to Nishida's method [36]. Thus we have obtained for compound **1**:

$$\begin{aligned} S(d_s, \psi_s) = & 7.07 \times 10^{-4} (\cos(2\alpha)) \cdot S(3d, 2s) \\ & + 0.8645 (\sin(2\alpha)) \cdot S(3d_\pi, 2p_\pi) \\ & + 0.5067 ((\cos(2\alpha)) \cdot S(3d_\sigma, 2p_\sigma), \end{aligned} \quad (\text{A6})$$

$$\begin{aligned} S(d_a, \psi_a) = & 1.56 \times 10^{-4} (\cos(2\alpha)) \cdot S(3d, 2s) \\ & + 0.3625 (\sin(2\alpha)) \cdot S(3d_\pi, 2p_\pi) \\ & + 0.2182 ((\cos(2\alpha)) \cdot S(3d_\sigma, 2p_\sigma), \end{aligned} \quad (\text{A7})$$

and for compound **2**:

$$\begin{aligned} S(d_s, \psi_s) = & 5.02 \times 10^{-4} (\cos(2\alpha)) \cdot S(3d, 2s) \\ & + 0.8596 (\sin(2\alpha)) \cdot S(3d_\pi, 2p_\pi) \\ & + 0.4988 ((\cos(2\alpha)) \cdot S(3d_\sigma, 2p_\sigma), \end{aligned} \quad (\text{A8})$$

$$\begin{aligned} S(d_a, \psi_a) = & 1.13 \times 10^{-4} (\cos(2\alpha)) \cdot S(3d, 2s) \\ & + 0.3705 (\sin(2\alpha)) \cdot S(3d_\pi, 2p_\pi) \\ & + 0.2175 ((\cos(2\alpha)) \cdot S(3d_\sigma, 2p_\sigma). \end{aligned} \quad (\text{A9})$$

The difference between $S(d_a, \psi_a)$ and $S(d_s, \psi_s)$ is calculated for **1** and **2**. The rough overlap integrals are evaluated by using data from Jaffe and Kuroda [37, 38]: $S(3d, 2s) \approx 0.04$, $S(3d_\pi, 2p_\pi) \approx 0.02$, $S(3d_\sigma, 2p_\sigma) \approx 0.06$. In the case of **1**, $\alpha = -1.16^\circ$,

$$S(a-s) = S(d_a, \psi_a) - S(d_s, \psi_s) = -0.0169.$$

In the case of **2**, $\alpha = -2.13^\circ$ and $S(a-s) = -0.0161$.

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