Crystal Structure and Magnetic Properties of a Binuclear Copper(II) Complex Bridged by an Alkoxo-oxygen Atom and an Acetate Ion

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Dinuclear Copper(II) Complex, Super-exchange Interactions, Antiferromagnetic Coupling

$[Cu_4(L)_2(O_2CMe)_2]\cdot H_2O$ (L = 1,3-bis(5-bromo-2-hydroxybenzylidene)propan-2-ol) was synthesized and its crystal structure determined. $(C_{38}H_{34}N_4O_{10}Br_4Cu_4)\cdot H_2O$, monoclinic, space group $P2_1/c$, $a = 21.072(5)$, $b = 9.673(2)$, $c = 21.934(4)$ Å, $\beta = 109.73(2)^\circ$, $V = 4208(2)$ Å^3, $Z = 4$. The crystal structure consists of two independent binuclear copper(II) complexes and the non-coordinating water molecule in the asymetric unit. The Cu(II) ions are in a square-planar geometry and coordinated by donor atoms of the ligand (NO_3).

The average Cu···Cu distance and average Cu-O-Cu angle are 3.491(2) Å and 132.0(1)°, respectively. Temperature-dependent magnetic susceptibility measurements of the complex show an intramolecular antiferromagnetic coupling in the dimeric Cu(II) core. The fitting parameters are $-2J = 174.4$ cm^{-1}, $g = 1.98$.

Introduction

The structures and magnetic properties of binuclear Cu(II) complexes with both μ-alkoxo and μ-carboxylato bridges were studied by Nishida and Kida to determine the importance of orbital counter complementarity in spin coupling through the two different bridging groups [1]. An extensive study of the structural and magnetic properties of the di-μ-hydroxo-copper(II) dimers has yielded a linear correlative relationship between the Cu-O-Cu bridge angle and the exchange parameter 2J [2,3]. According to Hodgson, antiferromagnetic interaction becomes stronger with increasing Cu-O-Cu angle. The experimental data, including di-μ-alkoxo-dicopper(II) complexes so far reported, generally fall in line with this rule for Cu-O-Cu angles in the range of 94 - 105° [4, 5]. A quantum mechanical explanation for this rule was given by Hoffmann and other workers in terms of a super-exchange mechanism [6 - 8]. Recently, McKee and Smith prepared a binuclear complex in which two copper(II) ions were linked by a single alkoxide oxygen atom with a larger Cu-O-Cu angle (135.5°) [9]. Its magnetic moment ($\mu = 0.6$) at room temperature suggested that Hodgson's rule is held also for larger angles (~135°). This was also supported by the result on the mono-μ-hydroxo-copper(II) complexes with a large Cu-O-Cu angle [10, 11]. The magnetostructural properties of binuclear copper(II) complexes which contain second bridging ligands such as pyrazolate or acetate ions have also received considerable attention. Nishida *et al.* reported the preparation and structural characterization of a binuclear copper(II) complex in which the copper(II) ions are linked by alkoxide and acetate oxygen atoms [12]. The antiferromagnetic interaction of this complex is very weak in relation to its Cu-O-Cu angle. It is apparent that a carboxylate bridge can also conduct an antiferromagnetic interaction as verified in copper acetate and analogous compounds [13 - 15]. Accordingly, this result seemed to contradict Hodgons's rule, and if so, Hoffmann's theory should be re-examined.

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-napthylideneamino)propan-2-ol and observed a weak intramolecular antiferromagnetic super-exchange interaction in the dimeric Cu(II) core [16]. In

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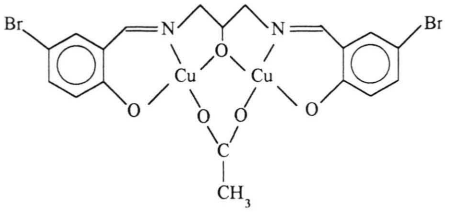

this study, we have synthesized a μ-acetato-N,N'-bridged dicopper(II) complex of 1,3-bis(5-bromo-2-hydroxybenzylidene)propan-2-ol and determined its crystal structure by X-ray diffraction. We have also measured magnetic susceptibilities in the temperature range 4.3 - 307 K using the Faraday method to investigate the relationship between the magnetic properties and the molecular structure.

Experimental

Preparation

The Schiff base ligand was prepared by reaction of 1,3-diamino-2-propanol and 5-bromo-salicylidene in a 1:2 molar ratio at room temperature. The yellow Schiff base ligand was obtained from the solution on cooling. For the preparation of the binuclear Cu(II) complex, the Schiff base ligand (0.5 mmol, 0.236 g) was dissolved in a hot methanol-water mixture (5:1, 50 ml) and a solution of $Cu(CH_3COO)_2 \cdot H_2O$ (1 mmol, 0.2 g) in 40 ml of methanol was added. The solution was allowed to evaporate at room temperature to give prismatic blue crystals, which were collected and washed with cold ethanol.

Table 1. Crystallographic data for the investigated compound.

Sum formula	$C_{38}H_{34}N_4O_{10}Br_4Cu_4 \cdot H_2O$
f_w (g·mol^{-1})	1296.49
Space group	$P2_1/c$
a [Å]	21.072(5)
b [Å]	9.673(2)
c [Å]	21.934(4)
α [°]	109.73(2)
Vol [Å^3]	4208.3(15)
Z	4
D_{calc} [g·cm^{-3}]	2.046
μ [cm^{-1}]	5.856
$F(000)$	2536
Index ranges	$-25 \leq h \leq 24$, $0 \leq k \leq 10$, $0 \leq l \leq 26$
Reflections collected	8319
Independent reflections	8019 [R(int) = 0.016]
Data / restraints / params	8012 / 0 / 550
Goodness-of-fit on F^2	1.202
Final R indices [$I > 2\sigma(I)$]	$R = 0.0384$, $wR = 0.1504$
Largest diff. peak and hole	0.367 and –0.956 e·Å^{-3}

Table 2. Atomic coordinates and equivalent isotropic displacement parameters.

Atom	x	y	z	U(eq)
Cu1	0.472661(16)	0.87689(4)	0.424777(17)	0.04880(13)
Cu2	0.639842(16)	0.87952(4)	0.42885(2)	0.04440(14)
Br1	0.12799(2)	1.08727(6)	0.39460(3)	0.08052(17)
Br2	0.96580(2)	1.07979(5)	0.40152(2)	0.07582(16)
N1	0.43593(14)	1.0614(3)	0.40410(13)	0.0464(6)
N2	0.66149(13)	1.0595(2)	0.40621(11)	0.0417(5)
O1	0.39380(12)	0.8076(2)	0.43568(11)	0.0509(5)
O2	0.72632(13)	0.8080(2)	0.44018(14)	0.0595(6)
O3	0.55331(11)	0.95534(19)	0.41711(11)	0.0469(5)
O4	0.51009(12)	0.6922(2)	0.44421(11)	0.0511(5)
O5	0.61780(11)	0.70007(18)	0.45121(10)	0.0464(5)
C1	0.33668(17)	0.8770(3)	0.42873(12)	0.0422(6)
C2	0.28350(19)	0.8094(4)	0.44017(18)	0.0622(9)
C3	0.22313(18)	0.8649(4)	0.43090(16)	0.0554(8)
C4	0.21302(16)	1.0020(4)	0.40967(13)	0.0542(8)
C5	0.26496(17)	1.0786(4)	0.40012(14)	0.0500(7)
C6	0.32663(16)	1.0153(3)	0.40923(13)	0.0469(6)
C7	0.37813(17)	1.1034(3)	0.40002(16)	0.0476(7)
C8	0.48594(18)	1.1561(4)	0.3980(2)	0.0574(8)
C9	0.5422(2)	1.0858(4)	0.3884(3)	0.0672(11)
C10	0.60829(19)	1.1585(4)	0.3946(2)	0.0689(10)
C11	0.71703(19)	1.1010(3)	0.39888(19)	0.0568(8)
C12	0.77516(16)	1.0129(3)	0.41038(13)	0.0451(6)
C14	0.88763(19)	0.9923(4)	0.41288(16)	0.0603(8)
C13	0.83114(16)	1.0756(3)	0.40124(15)	0.0485(7)
C15	0.8922(2)	0.8596(5)	0.43306(19)	0.0674(10)
C16	0.83628(18)	0.8006(4)	0.44244(19)	0.0607(8)
C17	0.77764(18)	0.8742(3)	0.42999(15)	0.0486(7)
C18	0.56591(19)	0.6404(3)	0.44938(19)	0.0569(8)

X-ray structure determination

A crystal of dimension 0.30×0.20×0.05 mm was mounted on an Enraf-Nonius CAD-4 diffractometer [17] equipped with a graphite monochromatized Mo-K_α radiation source (λ = 0.71093 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 ($2.32^\circ \leq \theta \leq 9.20^\circ$) carefully centered on the diffractometer. The standard reflections ($\bar{1}$12, 200, 040) were measured every 7200 s and the orientation of the crystal was checked after every 600 reflections. A total of 8319 reflections were recorded, with Miller indices $h_{\min} = -25$, $h_{\max} = 24$, $k_{\min} = 0$, $k_{\max} = 10$, $l_{\min} = 0$, $l_{\max} = 26$. Data reduction and corrections for absorption and decomposition were achieved using the Nonius Diffractometer Control Software [17]. The structure was solved by SHELXS-97 [18] and refined with SHELXL-97 [19]. 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 displacement parameters were restricted to be 1.2 U_{eq} of the parent atom. The parameters of the hydrogen atoms

Table 2 (continued).

Atom	x	y	z	U(eq)
C19	0.5676(2)	0.4847(3)	0.4555(3)	0.0763(13)
Cu3	–0.053186(18)	0.40688(4)	0.328170(18)	0.04515(13)
Cu4	0.113630(19)	0.40273(4)	0.332057(18)	0.04618(14)
Br3	–0.42093(2)	0.31559(6)	0.22777(2)	0.07560(16)
Br4	0.41628(2)	0.34863(6)	0.23636(3)	0.08406(18)
N3	–0.10679(17)	0.3045(3)	0.25216(16)	0.0591(7)
N4	0.11669(15)	0.3088(3)	0.25508(13)	0.0560(7)
O6	–0.12884(13)	0.4722(3)	0.34639(14)	0.0679(7)
O7	0.20407(13)	0.4630(3)	0.35631(14)	0.0675(7)
O8	0.01981(11)	0.3565(2)	0.29979(9)	0.0488(5)
O9	0.00228(13)	0.5064(3)	0.40362(13)	0.0674(7)
O10	0.11035(13)	0.4969(3)	0.40697(12)	0.0679(7)
C20	–0.19248(19)	0.4322(4)	0.32048(17)	0.0557(8)
C21	–0.2398(2)	0.4883(5)	0.3426(2)	0.0753(11)
C22	–0.30745(18)	0.4538(5)	0.31562(19)	0.0634(9)
C23	–0.32884(19)	0.3657(4)	0.26324(17)	0.0636(10)
C24	–0.28470(18)	0.3144(4)	0.23565(13)	0.0587(9)
C25	–0.21448(17)	0.3451(4)	0.26418(13)	0.0509(7)
C26	–0.17244(18)	0.2851(4)	0.23372(14)	0.0545(7)
C27	–0.0659(2)	0.2352(5)	0.2210(2)	0.0779(12)
C28	–0.0011(2)	0.3026(6)	0.2377(2)	0.0780(13)
C29	0.05422(19)	0.2385(5)	0.21981(17)	0.0701(10)
C30	0.17055(18)	0.2979(4)	0.23742(18)	0.0572(8)
C31	0.23306(19)	0.3568(4)	0.27030(18)	0.0594(8)
C32	0.28393(18)	0.3305(4)	0.24145(14)	0.0579(9)
C33	0.3476(2)	0.3877(4)	0.27242(19)	0.0660(9)
C34	0.36205(16)	0.4645(4)	0.3269(2)	0.0624(9)
C35	0.31289(17)	0.4863(4)	0.35519(19)	0.0588(8)
C36	0.24776(19)	0.4295(4)	0.32715(15)	0.0511(7)
C37	0.06326(17)	0.5297(4)	0.42983(14)	0.0524(7)
C38	0.0827(2)	0.6096(5)	0.49107(18)	0.0692(11)
O11	0.25520(15)	0.0084(4)	0.00663(14)	0.0772(8)

of the water molecule were not refined. The final positional parameters are presented in Table 2. A perspective drawing of the molecule is shown in Fig. 1 [20]. Selected bond lengths and angles are summarized in Table 3. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, e-mail: deposit@cam.ac.uk as supplementary publication no. CCDC 147885 [21].

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 4.3 - 307 K. Details of the apparatus have already been described [22]. Diamagnetic corrections of the molar magnetic susceptibility of the compound were applied using Pascal's constants [23]. The applied field was ≈ 1.2 T. Magnetic moments were obtained from the relation $\mu_{\text{eff}} = 2.828(\chi T)^{1/2}$.

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

Cu1-O1	1.880(2)	Cu3-O6	1.879(3)
Cu1-O3	1.920(2)	Cu3-O8	1.907(2)
Cu1-N1	1.937(3)	Cu3-O9	1.930(3)
Cu1-O4	1.941(2)	Cu3-N3	1.940(3)
Cu2-O2	1.885(3)	Cu4-O7	1.890(3)
Cu2-O3	1.900(2)	Cu4-O10	1.901(3)
Cu2-O5	1.904(2)	Cu4-O8	1.914(2)
Cu2-N2	1.907(2)	Cu4-N4	1.937(3)
Cu1-O3-Cu2	132.3(1)		
O1-Cu1-O3	176.8(1)	O2-Cu2-O3	178.8(1)
O1-Cu1-N1	93.3(1)	O2-Cu2-O5	86.6(1)
O3-Cu1-N1	84.9(1)	O3-Cu2-O5	94.6(1)
O1-Cu1-O4	87.4(1)	O2-Cu2-N2	93.7(1)
O3-Cu1-O4	94.4(1)	O3-Cu2-N2	85.2(1)
N1-Cu1-O4	178.0(1)	O5-Cu2-N2	179.7(1)
Cu3-O8-Cu4	131.7(1)		
O6-Cu3-O8	172.3(1)	O7-Cu4-O10	86.3(1)
O6-Cu3-O9	87.8(1)	O7-Cu4-O8	173.6(1)
O8-Cu3-O9	94.9(1)	O10-Cu4-O8	95.6(1)
O6-Cu3-N3	93.7(1)	O7-Cu4-N4	93.6(1)
O8-Cu3-N3	83.6(1)	O10-Cu4-N4	179.3(1)
O9-Cu3-N3	178.5(1)	O8-Cu4-N4	84.4(1)

Discussion

X-ray crystal structure

The complex consists of dinuclear molecules in which two copper atoms are linked by the alkoxide and acetate oxygen atoms. There are two dinuclear molecules and a non-coordinating water molecule in the asymmetric unit. Each copper ion is coordinated by one nitrogen and three oxygen atoms forming a coordination plane. The atoms with the greatest deviation from the coordination planes Cu1, N1, O1, O3, O4 and Cu2, N2, O2, O3, O5 are O1 atom at 0.031(3) Å and O5 atom at 0.002(3) Å. In the other molecule, the atoms with the greatest deviation from the coordination planes Cu3, N3, O6, O8, O9 and Cu4, N4, O7, O8, O10 are O8 atom at –0.075(4) Å and O7 atom at –0.056(4) Å.

The average distance Cu-N 1.922(2) Å in the first molecule is slightly smaller than the comparable distances of 1.939(3) Å (average Cu-N) in the other molecule. The average Cu-O distance is 1.905(2) Å while in the other molecule, the average Cu-O distance is 1.904(3) Å, respectively. These

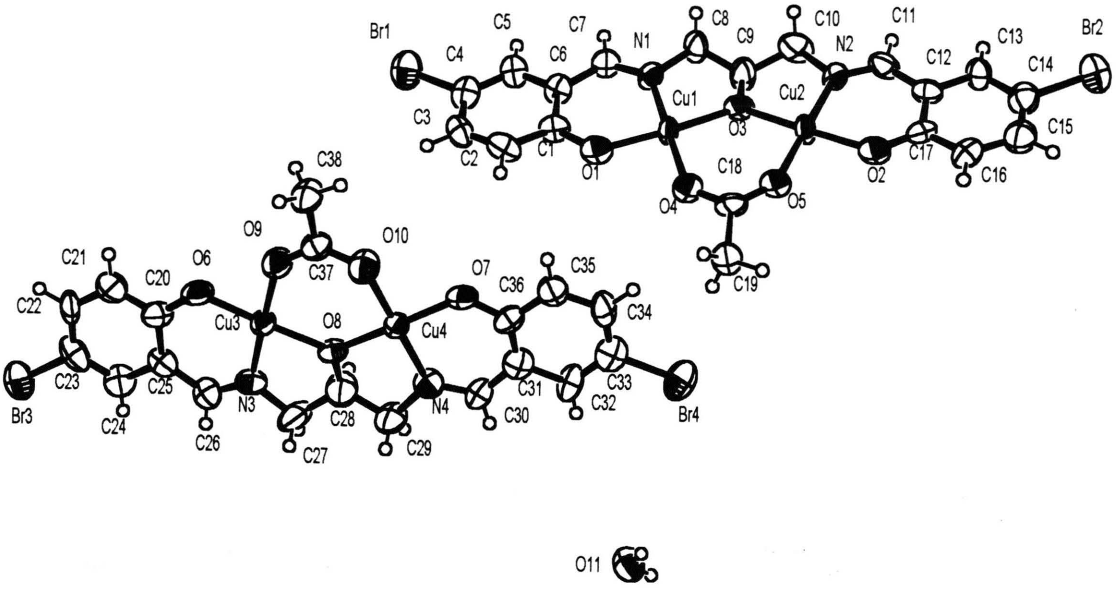

Fig. 1. View of the molecule (numbering of atoms corresponds to Table 2). Displacement ellipsoids are plotted at the 50% probability level and H atoms are presented as spheres of arbitrary radii.

distances are in the range of those of conventional Schiff-base and alk-oxide-bridged copper(II) complexes of square-planar coordination [1, 12, 16, 24]. The distances Cu1-Cu2 and Cu3-Cu4 are 3.494(2) and 3.487(2) Å, respectively. The Cu1-O3-Cu2 and the Cu2-O8-Cu4 bridging angles are 132.3(1) and 131.7(1)° which are in the range of similar binuclear complexes [23 - 26].

The least-squares planes through the mononuclear units are inclined at an angle of 1.2(1)° for the first molecule and 10.4(1)° for the other dinuclear molecule. The unique half of the Schiff base ligands of the complexes are reasonably planar. In the first molecule, the maximum deviation from the plane defined by atoms O1, O3, N1, C1-C8 and Br1 is –0.093(7) Å for the atom C8, while for and O2, O3, N2, C10-C17 and Br2 it is 0.060(8) Å for the atom C10. In the other molecule, the maximum deviation from the plane defined by atoms O6, O8, N3, C20-C27 and Br3 is –0.048(8) Å for the atom C24, and for O7, O8, N4, C29-C36 and Br4 it is 0.070(5) Å for the atom O8.

Magnetic properties

Magnetic susceptibilities for a powdered sample of the complex were measured by the Faraday method over the temperature range 4.3 - 307 K. The magnetic susceptibilities of the complex are shown as a function of temperature in Fig. 2 (top), and the magnetic moments are shown as a function of temperature in Fig. 2 (bottom). The data were fitted using the Bleaney-Bowers equation [27]

$$\chi = \frac{N_L g^2 \mu_B^2}{3k(T-\theta)} \cdot \frac{1-x_p}{1+\frac{1}{3}\exp(-2J/kT)} + \frac{N_L g^2 \mu_B^2}{4kT} x_p + N_\alpha \qquad (1)$$

and the isotropic (Heisenberg) exchange Hamiltonian $\mathbf{H} = -2J\,\mathbf{S}_1 \cdot \mathbf{S}_2$ where –2J corresponds to the energy separation between spin-singlet and -triplet states, for two interacting $S = 1/2$ centers. N_α is the temperature-independent paramagnetism, and its value is $6 \cdot 10^{-5}$ cm^3/mol for each copper atom. x_p is the molar fraction of a monomeric impurity. Least squares fitting of the data leads to $J = -87.2$ cm^{-1}, $g = 1.98$, $x_p = 0.6\%$. Magnetic moments were obtained from the relation $\mu_{\text{eff}} = 2.828\,(\chi T)^{1/2}$. The magnetic moment at 307 K is about 2.4 B.M., and 0.6 B.M. at 4.3 K.

In general, several structural features of binuclear copper(II) complexes are thought to regulate the strength of exchange coupling interactions: (i) the

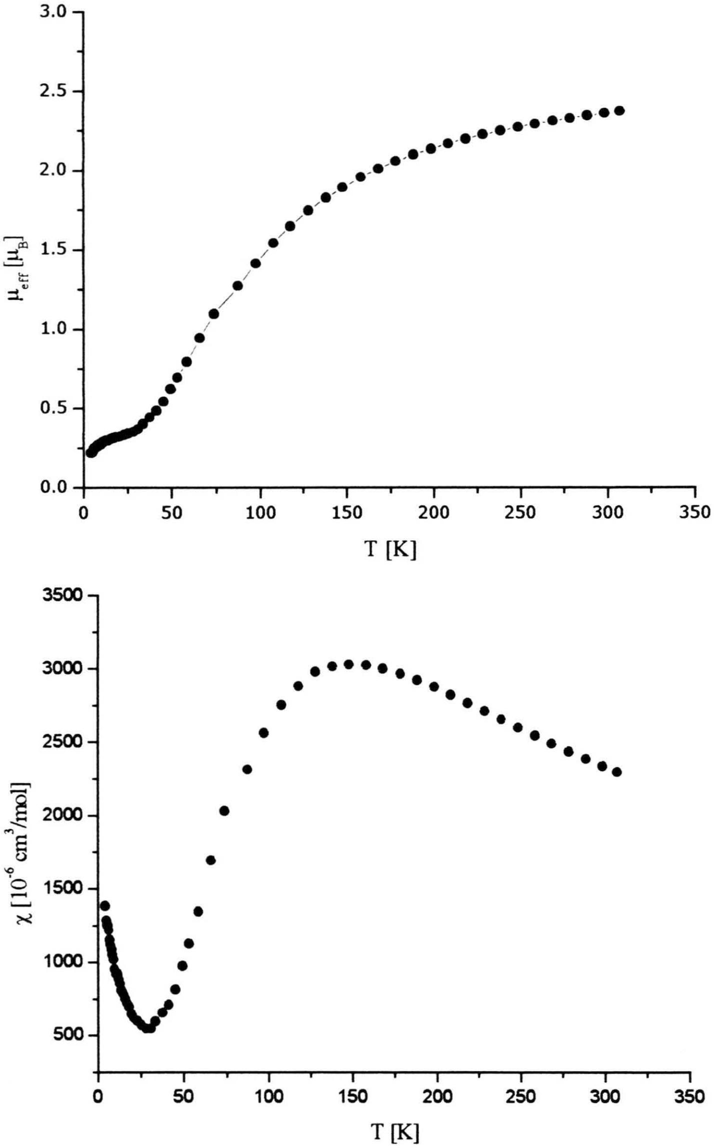

Fig. 2. *Top:* Molar susceptibility per copper(II) *vs.* temperature curve. *Bottom:* Magnetic moment per copper(II) *vs.* temperature curve.

dihedral angle between the two coordination planes, (ii) planarity of the bonds around the bridging atom, and (iii) the Cu-O-Cu bridging angle [28, 29]. The dihedral angle between the two coordination planes is considered to be a key factor in determining the magnitude of the spin-exchange coupling. However, as shown in Table 4, the dihedral angle decreases in the order b > c > d > e > a , while –2J decreases in the order e > b > a > d > c. This indicates that the dihedral angle of the coordination sphere of unsymmetric doubly bridged complexes may play only a minor role in determining the exchange interaction.

Planarity of the bonds about the bridging oxygen atom also has been cited as a factor influencing the nature of the spin-exchange interaction [30 - 32]. Curiously, for the title compound the sum of the angles about the bridging oxygen atoms are 359.2° for O3 and 358.4° for O8, which is close to the idealized 360° angle expected for complete planarity. Again, this criterion by itself does not accurately predict the trend in the –2J values. Perhaps the most widely accepted criterion for correlating structure and magnetism is the Cu-O-Cu bridging angle [30 - 33]. This factor has been invaluable in

Table 4. Structural and magnetic data of reference compounds.

Compound	Cu···[Å]	Cu-O-Cu [°]	⟨Cu-O⟩[f] [Å]	ϕ[g] [°]	θ[h] [°]	–2J [cm^{-1}]
[a]	3.502(2)	133.3(3)	1.908	5.4	352.8	165
[b]	3.495(3)	134.5(5)	1.895	18.7	358.1	170
[c]	3.482(2)	132.7(3)	1.900	8.2	360.0	160
[d]	3.492(2)	133.5(8)	1.910	6.3	356.9	163.6
[e]	3.491(2)	132.0(1)	1.905	5.8	358.8	174.4

[a] $[Cu_2(L^1)(O_2CMe)] \cdot H_2O$ (Nishida *et al.* [12]); [b] $[Cu_2(L^5)(O_2CMe)] \cdot MeOH$ (Nishida *et al.* [12]); [c] $[Cu_2(L^5)(O_2CPh)] \cdot H_2O$ (Nishida *et al.* [12]); [d] $[Cu_2(L)(O_2CMe)] \cdot H_2O$ (Kavlakoglu *et al.* [16]); [e] this work, average values of two independent complexes in the asymetric unit; [f] ⟨Cu-O⟩ is the average distance between the copper and the bridging O atoms; [g] dihedral angle between coordination planes; [h] sum of angles around the oxygen atom.

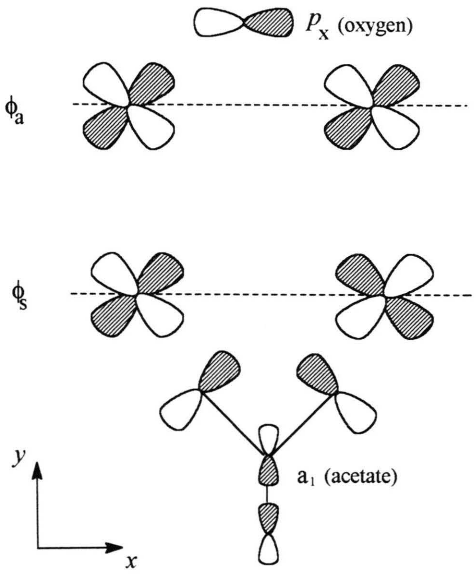

Fig. 3. Symmetric (ϕ_s) and antisymmetric (ϕ_a) combinations of metal and ligand orbitals.

systematically correlating the degree of interaction in both singly and doubly alkoxide (or hydroxide) bridged copper complexes [2, 33]. The Cu-O-Cu bridging angle decreases in the order b > d > a > c > e while the value of –2J does not decrease in the same order. But, in the symmetric bridged Cu(II) binuclear complexes, for small values of Cu-O-Cu bridging angles (95° - 105°), Ruiz and co-workers observed that the Cu-O-Cu angle decreases in the same order with the value of –2J [34].

Clearly, the variation of the strength of the super-exchange interaction cannot be explained completely by the structural features of binuclear copper(II) complexes. A different approach must be discussed to clarify the origin of the super-exchange mechanism of this system. To gain a reasonable explanation for these facts we examined the super-exchange mechanism of this system in terms of Hoffman's theory [6]. In planar copper(II) complexes, an unpaired electron resides in a d_{xy} orbital, and the symmetric and antisymmetric combinations of these orbitals are expressed as in equations (2) and (3) (for the definition of x and y coordinates, see Fig. 3).

$$\phi_s = d_x + d'_{xy} \tag{2}$$

$$\phi_a = d_x - d'_{xy} \tag{3}$$

According to Hoffman [6] in bimetallic complexes strong antiferromagnetism is observed if the energy separation of the symmetric (ϕ_s) and antisymmetric (ϕ_a) combination of the two magnetic orbitals is large (Fig. 3), irrespective of the fact which combination is lower in energy. Spin exchange interaction in binuclear copper(II) complexes in which two copper(II) ions are linked by alkoxide and acetate oxygens thus can be explained in the following manner. The p_x orbital of the alkoxide oxygen atom interacts with the ϕ_a orbital to raise its energy. In the case of an acetate bridge the energy of the ϕ_s orbital is raised, because the highest occupied molecular orbital (h.o.m.o) of an acetate ion has mainly oxygen 2p character and this orbital interacts with the ϕ_s orbital. Consequently, the presence of the acetate bridge reduces the energy separation between ϕ_a and ϕ_s orbitals caused by the interaction through the alkoxide bridge only, and decreases the strength of the antiferromagnetic interaction. If both bridging ligands interact with the same combination of "magnetic orbitals" to raise the orbital energy, the super-exchange interaction through the two bridges work in a complementary fashion and the antiferromagnetic exchange interaction is enhanced. Conversely, if one of the bridging ligand interacts with an ϕ_s orbital and the other with an ϕ_a orbital to raise each of the orbital energies, the super-exchange interactions through the bridges work in a countercomplementary fashion and the antiferromagnetic exchange interactions attenuate.

As a result, in binuclear 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.

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