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Contribution from the Laboratoire de Chimie de Coordination du CNRS,
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An Unusual μ-Olato-μ-Phenolato-Bridged Dicopper(II) Complex, $Cu_2(L\text{-}H)(L\text{-}2H)ClO_4$ [L = 2-((2-((*o*-Hydroxy-α-methylbenzylidene)amino)ethyl)amino)ethanol], with Quasi-Orthogonal Coordination Planes

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A dinuclear copper(II) complex of the new ligand 2-((2-((*o*-hydroxy-α-methylbenzylidene)amino)ethyl)amino)ethanol (L) was prepared and its crystal structure solved at room temperature. It crystallizes in the monoclinic system, space group C_{2h}^5-$P2_1/c$ with $Z = 4$. The lattice constants are $a = 16.126$ (3) Å, $b = 13.403$ (3) Å, $c = 14.004$ (3) Å, and $\beta = 115.69$ (3)°. The structure is made of dinuclear cations $[Cu_2(L\text{-}H)(L\text{-}2H)]^+$ and perchlorate anions. Within each cation, the bridging unit involves two oxygen atoms afforded by an alcoholate and a phenolate group, respectively. The two coordination planes are not far from being orthogonal to each other. Variable-temperature magnetic susceptibility measurements show that the two copper atoms are antiferromagnetically coupled in their ground state, with a weak coupling constant ($-2J = 22$ cm^{-1}).

Introduction

The widespread occurrence of binuclear copper centers in biology[1] has stimulated the synthesis and study of potential models involving either multiatoms bridging ligands such as acetate,[2] catecholate, carbonate, imidazolate, ... or single-atom bridging ligands such as halide, alkoxide, hydroxide, ... Particular interest has been given to the latter class of complexes, since a single-atom bridge likely binds the oxidized copper atoms in hemocyanine, tyrosinase, and related proteins.[1] One important characteristic of these binuclear systems is their magnetic behavior due to coupling between the two metallic centers. The attempt to relate the sign and magnitude of this magnetic coupling with structural features is one of the main research topics of the last few years. In this respect, amino alcohols and imino alcohols have been particularly valuable for designing complexes of widely differing structural types and magnetic behaviors.[4-12]

In this paper we describe the synthesis, molecular structure, and magnetic properties of a copper complex involving an amino imino alcohol as ligand. The ligand (Hapenol) represented in Figure 1 results from the condensation of *N*-(2-hydroxyethyl)ethylenediamine with 2-hydroxyacetophenone.

Experimental Section

Synthesis. Preparation of the ligand is carried on in a Dean and Stark apparatus. Stoichiometric amounts of *N*-(2-hydroxyethyl)ethylenediamine and 2-hydroxyacetophenone are dissolved in benzene. The mixture is kept boiling till the required quantity of water is collected. The solvent is then removed under reduced pressure to yield the desired product in the form of microcrystalline powder. Microanalytical data and NMR (^{1}H, ^{13}C) characteristics[13] are consistent with the expected formulation (Figure 1).

Table I. Crystal Data and Details of Data Collection and Structure Refinement

	Crystal Data
formula	$C_{24}ClCu_2H_{33}N_4O_8$
M_r	668.1
crystal system	monoclinic
space group	C_{2h}^5-$P2_1/c$
a, Å	16.126 (3)
b, Å	13.403 (3)
c, Å	14.004 (3)
β, deg	115.69 (3)
V, Å^3	2727.6
Z	4
F(000)	1376
D(calcd), g cm^{-3}	1.627
μ(Mo Kα), cm^{-1}	17.1
	Data Collection
temp, °C	20
radiation, Å	$\lambda = 0.71073$ (Mo Kα from graphite monochromator)
θ, deg: min, max	1.5, 26
scan range, deg	$1.00 + (0.35 \tan \theta)$
scan mode	θ–2θ
scan speed, deg min^{-1}	1.10 - 10.1
aperture, mm: horiz, vert	4.0, 4.0
measd reflcns	$\pm h,k,l$
ref reflcns	140, 006, $\bar{3}32$
no. of collcd data	5565
no. of unique reflcns	5348
no. of obsd data ($I > 2\sigma(I)$), *n*	3331
	Refinement
no. of refined params, *m*	352
weighting scheme	$w = 1$
minimized function	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
$R = \sum(\lvert F_o\rvert - \lvert F_c\rvert)/\sum\lvert F_o\rvert$	0.023
$R_w = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o{}^2\rvert]^{1/2}$	0.029
$S = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(n - m)]^{1/2}$	1.3

In a typical preparation of the complex, a solution of $Cu(ClO_4)_2\cdot 6H_2O$ (5×10^{-3} mol) in 10 mL of methanol is added dropwise to a hot solution of the ligand (5×10^{-3} mol) and of the deprotonating agent $N(C_2H_5)_3$ (1×10^{-2} mol) in 20 mL of methanol. A blue-green precipitate readily forms. It is filtered off and washed with methanol. Evaporation of the solvent yields a second crop of complex. Crystals suitable for structural investigation are obtained by slowly cooling a hot methanolic solution.

Anal.[14] Calcd for $[Cu_2C_{24}H_{33}N_4O_4]ClO_4$: Cu, 19.0; C, 43.1; H, 5.0; N, 8.4; Cl, 5.3. Found: Cu, 18.7; Cu, 43.2; H, 4.8; N, 8.2; Cl, 5.4.

Safety Notes. The complex reported here was isolated as a perchlorate salt. We have worked with this compound in a number of organic solvents without incident, and as a solid, it seems to be reasonably stable to shock and heat. However, the unpredictable behavior of perchlorate

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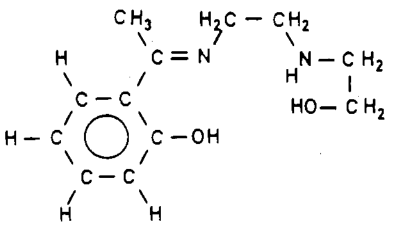

Figure 1. Schematic representation of the ligand.

Table II. Fractional Coordinates with Esd's in Parentheses

atom	x/a	y/b	z/c
Cu(1)	0.12870 (3)	0.11968 (3)	0.57824 (3)
Cu(2)	0.30375 (3)	0.19910 (3)	0.56122 (3)
O(1)	0.2531 (2)	0.0862 (2)	0.6078 (2)
N(1)	0.1735 (2)	0.1013 (3)	0.7307 (2)
N(2)	0.0099 (2)	0.1448 (2)	0.5740 (2)
O(2)	0.0821 (2)	0.0926 (2)	0.4326 (2)
O(3)	0.2218 (2)	0.1367 (2)	0.3856 (2)
N(3)	0.4022 (2)	0.1159 (2)	0.5523 (2)
N(4)	0.3802 (2)	0.3154 (2)	0.5745 (2)
O(4)	0.2049 (2)	0.2771 (2)	0.5566 (2)
C(1)	0.3054 (3)	0.0672 (3)	0.7214 (3)
C(2)	0.2726 (3)	0.1357 (4)	0.7826 (3)
C(3)	0.1148 (3)	0.1642 (4)	0.7606 (4)
C(4)	0.0148 (3)	0.1517 (3)	0.6845 (3)
C(5)	−0.0692 (3)	0.1444 (3)	0.4933 (3)
C(6)	−0.0765 (2)	0.1364 (3)	0.3859 (3)
C(7)	−0.0041 (3)	0.1101 (3)	0.3620 (3)
C(8)	−0.0203 (3)	0.0999 (3)	0.2530 (3)
C(9)	−0.1067 (3)	0.1165 (3)	0.1715 (3)
C(10)	−0.1785 (3)	0.1479 (3)	0.1935 (4)
C(11)	−0.1666 (3)	0.1553 (3)	0.2973 (3)
C(12)	−0.1595 (3)	0.1468 (3)	0.5051 (3)
C(13)	0.2787 (3)	0.0531 (3)	0.3855 (3)
C(14)	0.3775 (3)	0.0895 (3)	0.4369 (3)
C(15)	0.4864 (2)	0.1745 (3)	0.6003 (3)
C(16)	0.4682 (3)	0.2859 (3)	0.5717 (3)
C(17)	0.3650 (3)	0.4049 (3)	0.5847 (3)
C(18)	0.2773 (3)	0.4378 (3)	0.5889 (3)
C(19)	0.2045 (3)	0.3732 (3)	0.5744 (3)
C(20)	0.1244 (3)	0.4102 (3)	0.5790 (3)
C(21)	0.1194 (3)	0.5110 (3)	0.6001 (3)
C(22)	0.1913 (3)	0.5722 (4)	0.6204 (3)
C(23)	0.2680 (3)	0.5393 (3)	0.6141 (3)
C(24)	0.4272 (3)	0.4881 (4)	0.5835 (4)
Cl	0.58017 (7)	0.19116 (9)	0.37594 (8)
O(5)	0.6327 (3)	0.1981 (4)	0.4838 (4)
O(6)	0.5010 (2)	0.2517 (3)	0.3425 (3)
O(7)	0.6344 (2)	0.2150 (3)	0.3221 (3)
O(8)	0.5504 (3)	0.0924 (4)	0.3581 (4)
H(O3)	0.165 (1)	0.161 (2)	0.329 (1)

salts[15] necessitates that only small amounts of material should be prepared and they should be handled with extreme caution.

Magnetic Measurements. Magnetic susceptibility data were collected on powdered samples with use of a Faraday type magnetometer fitted with a helium continuous-flow cryostat. Mercury tetrakis(thiocyanato)cobaltate (susceptibility at 20 °C: 16.44 × 10^{-6} cgsu) was used as a susceptibility standard. All data were corrected for diamagnetism (estimated at −249.3 × 10^{-6} cgsu)[16] and TIP (taken as 60 × 10^{-6} cgsu/copper atom). EPR spectra were recorded at X-band frequencies (9.4–9.6 GHz) with a Bruker 200 TT spectrometer.

Collection and Reduction of X-ray Data. Crystals belong to the monoclinic system, space group C_{2h}^5-$P2_1/c$. The selected crystal was a dark blue prism (section 0.075 × 0.150 × 0.075 mm, height 0.3 mm). The crystal was sealed on a glass fiber and mounted on an Enraf-Nonius CAD4 diffractometer. Cell constants were obtained from a least-squares fit of the setting angles of 25 reflections. The crystal data and details of the data collection and structure refinement are summarized in Table I. The intensities of three reflections were monitored every 2 h of X-ray exposure time. Standards showed only random, statistical fluctuations. Intensity data were corrected for Lorentz and polarization effects by using the SDP package.[17] The empirical absorption correction[18] was applied (μ = 17.1 cm^{-1}, minimum and maximum corrections 0.88 and 1.00).

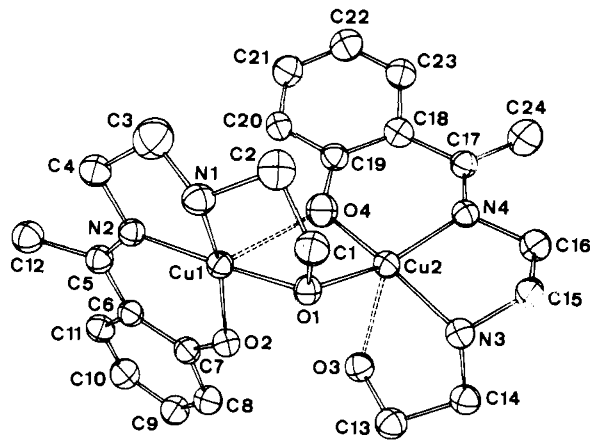

Figure 2. Dimeric unit of the compex showing the atom-labeling scheme.

Table III. Copper Atom Environments: Bond Lengths (Å) and Angles (deg)

	Lengths		
Cu(1)–O(1)	1.917 (3)	Cu(2)–O(1)	1.961 (3)
Cu(1)–O(2)	1.878 (2)	Cu(2)–O(4)	1.884 (3)
Cu(1)–N(1)	1.950 (3)	Cu(2)–N(3)	1.987 (3)
Cu(1)–N(2)	1.921 (3)	Cu(2)–N(4)	1.945 (3)
Cu(1)–O(4)	2.524 (3)	Cu(2)–O(3)	2.383 (3)
Cu(1)–Cu(2)	3.121 (9)		
	Angles		
O(1)–Cu(1)–O(2)	94.4 (1)	O(1)–Cu(2)–O(4)	88.3 (1)
O(1)–Cu(1)–N(1)	83.0 (1)	O(1)–Cu(2)–N(3)	92.7 (1)
O(1)–Cu(1)–N(2)	169.7 (1)	O(1)–Cu(2)–N(4)	157.6 (1)
O(2)–Cu(1)–N(1)	161.5 (1)	O(4)–Cu(2)–N(3)	175.0 (1)
O(2)–Cu(1)–N(2)	94.4 (1)	O(4)–Cu(2)–N(4)	92.9 (1)
N(1)–Cu(1)–N(2)	86.9 (1)	N(3)–Cu(2)–N(4)	88.0 (1)
O(4)–Cu(1)–O(1)	72.8 (1)	O(3)–Cu(2)–O(1)	87.0 (1)
O(4)–Cu(1)–O(2)	91.0 (1)	O(3)–Cu(2)–O(4)	94.4 (1)
O(4)–Cu(1)–N(1)	105.6 (1)	O(3)–Cu(2)–N(3)	80.7 (1)
O(4)–Cu(1)–N(2)	112.4 (1)	O(3)–Cu(2)–N(4)	115.1 (1)
Cu(1)–O(1)–Cu(2)	107.2 (1)	Cu(1)–O(4)–Cu(2)	88.9 (1)

Table IV. Ligand Geometry: Bond Lengths (Å)

O(1)–C(1)	1.464 (4)	O(3)–C(13)	1.448 (5)
C(1)–C(2)	1.501 (7)	C(13)–C(14)	1.516 (5)
C(2)–N(1)	1.513 (5)	C(14)–N(3)	1.530 (5)
N(1)–C(3)	1.459 (7)	N(3)–C(15)	1.457 (5)
C(3)–C(4)	1.508 (6)	C(15)–C(16)	1.541 (6)
C(4)–N(2)	1.517 (6)	C(16)–N(4)	1.489 (6)
N(2)–C(5)	1.287 (4)	N(4)–C(17)	1.245 (5)
C(5)–C(6)	1.461 (6)	C(17)–C(18)	1.508 (6)
C(5)–C(12)	1.535 (7)	C(17)–C(24)	1.505 (7)
C(7)–O(2)	1.333 (4)	C(19)–O(4)	1.313 (5)
C(6)–C(7)	1.392 (6)	C(18)–C(19)	1.402 (6)
C(7)–C(8)	1.439 (6)	C(19)–C(20)	1.410 (6)
C(8)–C(9)	1.384 (5)	C(20)–C(21)	1.393 (6)
C(9)–C(10)	1.384 (8)	C(21)–C(22)	1.345 (7)
C(10)–C(11)	1.386 (7)	C(22)–C(23)	1.351 (7)
C(11)–C(6)	1.467 (5)	C(23)–C(18)	1.429 (6)

Structure Solution. The structure was solved by the heavy-atom method and refined by full-matrix least squares.[19] All non-hydrogen atoms were refined anisotropically with the atomic scattering factors proposed by Cromer and Waber[20] including anomalous dispersion effects.[21]

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Table V. Perchlorate Geometry: Bond lengths (Å) and Angles (deg)

Lengths			
Cl–O(5)	1.378 (4)	Cl–O(7)	1.416 (5)
Cl–O(6)	1.411 (4)	Cl–O(8)	1.393 (5)
Angles			
O(5)–Cl–O(6)	111.3 (3)	O(6)–Cl–O(7)	111.9 (2)
O(5)–Cl–O(7)	109.9 (3)	O(6)–Cl–O(8)	107.2 (3)
O(5)–Cl–O(8)	105.1 (3)	O(7)–Cl–O(8)	111.3 (3)

All hydrogen atoms were located on a difference Fourier map and introduced in calculations in constrained geometry, with temperature factors kept fixed, $U_H = 0.06$ Å^2. H(O3) was allowed to vary at a distance of 0.97 Å from O(3). Their scattering factors were those of Stewart et al.[22]

The final atomic coordinates, with their estimated standard deviations as derived from the inverse matrix of the last cycle of least-squares refinement, are given in Table II.

Results and Discussion

Description of the Structure. As suggested by microanalytical data and charge balance considerations, the complex consists of $[(L\text{-}H)(L\text{-}2H)Cu_2]^+$ cations, (L-H) and (L-2H) standing for the mono- and dideprotonated forms of the ligand (L), respectively. They are well separated from the perchlorate anions. The structure does not include any solvent molecule.

A view of the binuclear cation is given in Figure 2. The relevant distances and angles are listed in Tables III–V.

For both copper atoms the geometry may be approximately described as square pyramidal, but for Cu(2) it is more distorted. The main departure from ideal square-pyramidal coordination arises from nonplanarity of the atoms defining the basal planes of the pyramids. Atoms O(1), O(2), N(1), and N(2) lie between 0.09 and 0.17 Å from the calculated least-squares plane, and Cu(1) sits 0.1816 Å out of this plane toward O(4). Higher deviations (from 0.17 to 0.26 Å) are observed for the atoms O(1), O(4), N(3), and N(4) bonded to Cu(2). However, it may be recognized that the values of the angles around Cu(2) do not support a trigonal-bipyramidal coordination. The differences in the geometries of the two mononuclear units likely originate in the fact that the two ligands have different protonation states and different coordination modes. The ligand bonded to Cu(1) is twice deprotonated, at the phenolic O(2) and alcoholic O(1) oxygens whereas the ligand bonded to Cu(2) is deprotonated at the phenolic oxygen O(4) only. There is a short distance of 2.673 (4) Å between the protonated O(3) and the deprotonated O(2) oxygens. However, the values of the O(3)–H(O3)···O(2) angle and the O(2)···H(O3) separation, i.e. 87 (2)° and 2.54 (4) Å, respectively, are not consistent with the occurrence of a hydrogen bond between the two ligands. In both units three equatorial positions are similarly occupied by two nitrogen atoms and a phenolic oxygen. The fourth position, which is shared by the two coordination spheres, is occupied by the alkoxo oxygen of the (L-2H) ligand. The corresponding O(3) atom of the (L-H) ligand is only involved in axial bonding to Cu(2). As previously mentioned, the two phenolic oxygen atoms, O(2) and O(4), are basal to Cu(1) and Cu(2), respectively, but in addition, O(4) is weakly linked to Cu(1) in the axial position. The neat result is that the two coordination planes are not far from being orthogonal, with a dihedral angle of 94.8°.

The binuclear center Cu(1)O(1)Cu(2)O(4) is unsymmetrical with three short basal bonds, Cu(1)–O(1), Cu(2)–O(1),and Cu(2)–O(4), and one long axial bond, Cu(1)–O(4). The short Cu–O distances are comparable to those observed in other complexes whereas the axial bond is abnormally long, as previously noted. The bridging angles Cu(1)–O(1)–Cu(2) and Cu(1)–O(4)–Cu(2), which are equal to 107.2 and 88.9°, respectively, are also markedly different. The angle involved in the Cu–O(1)–Cu bridge is more acute than those usually found for monohydroxo[23-28] and monoalkoxo complexes.[6,29] However, some monohydroxo complexes with acute Cu–O–Cu angles have been recently reported,[30] but in these compounds the two copper(II) centers are bridged by three groups. As a whole, the bridging unit Cu(1)O(1)O(4)Cu(2) is roof-shaped, with a dihedral angle of 163.3° between the planes Cu(1)–O(1)–O(4) and Cu(2)–O(1)–O(4). A similar shape has been previously observed for a dihydroxo complex[31] that shows however a more acute dihedral angle of 147.5°.

The perchlorate anions are not coordinated to copper atoms. The shortest distance is observed between N(3) and the perchlorate

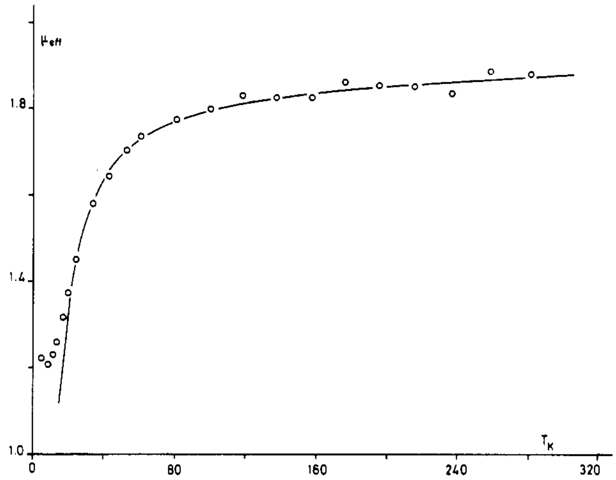

Figure 3. Plot of the effective magnetic moment per copper atom as a function of temperature. The solid line was calculated as described in the text.

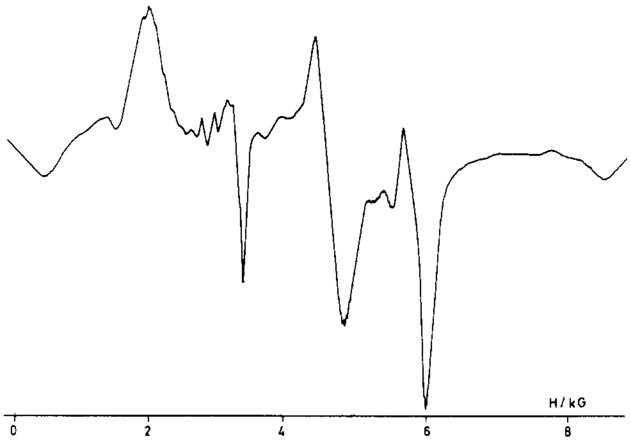

Figure 4. Polycrystalline-powder EPR spectrum of the complex at X-band frequency.

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oxygen O(8), suggesting a hydrogen bond with an N(3)–HN(3)–O(8) angle of 161.3 (4)°.

Magnetic Properties. Magnetic susceptibility was determined as a function of temperature in the range 4.5–280 K. The experimental data corrected for diamagnetism are illustrated in Figure 3 in the form of μ_{eff}/Cu atom vs. T.

The variation of χ_M^{-1} vs. T is well fit by a Curie–Weiss law with $C = 0.46$ and $\Theta = -15.04$ K in the temperature range of 25–280 K. From the small negative value of Θ is can be estimated that the complex is slightly antiferromagnetic. Analysis of the experimental data in terms of the Bleaney and Bowers equation[32] yields $\bar{g} = 2.15$ and $2J = -22$ cm^{-1}. In Figure 3, the best fit curves are represented by solid lines, and it can be seen that the fit to experimental data is good in the range 25–280 K. Below 25 K, significant deviations are observed between the two sets of values. Inclusion of additional terms in the Bleaney and Bowers equation to account for the occurrence of a paramagnetic impurity and interdimer interaction does not substantially improve the fit. Therefore, the deviations are probably due to a zero-field-splitting effect.

The polycrystalline-powder EPR spectrum of the title complex (X-band, 4.5 K) is shown in Figure 4. In the 0–12 000 G range, at least five features at ca. 490, 2035, 4530, 6000, and 8500 G are attributable to the dinuclear species, the signal around 3200 G being most likely due to a mononuclear copper(II) impurity. The analysis of the triplet-state spectrum appears to be difficult, since it may be inferred from the structural determination that the magnetic tensors are actually misaligned. We prefer to delay this detailed analysis to a time when single crystals suitable for recording EPR spectra are available.

The proper conclusion is that the two copper atoms of the title complex are antiferromagnetically coupled in their ground state. However, the weakness of the algebraic value of the coupling constant contrasts with the high $|J|$ values generally reported for μ-alkoxo complexes. For instance, J values of ca. −300 to −500 cm^{-1} are currently observed for dicopper complexes of amino alcohols.[33] Much weaker antiferromagnetic interactions have been recently reported,[34] but in these compounds, pairs or eventually trimers of copper polyhedra are held together via hydrogen bonds.

In the present complex, the magnetic orbitals around Cu(1) and Cu(2) that point toward the equatorial donors, O(1)N(1)N(2)O(3) and O(1)N(3)N(4)O(4), respectively, lie on planes that are roughly orthogonal to each other. This geometry and the long Cu(1)···O(4) distance cause the overlap density at the O(4) oxygen to be small. Therefore, the phenoxo bridge, Cu(1)O(4)Cu(2), is unlikely to mediate a significant interaction and the coupling must be essentially determined by the O(1) bridge atom.

Experimental and theoretical studies support the view that in bis(μ-oxo) copper(II) dimers, the value of the bridging angle (ϕ) plays the key role in the sign and magnitude of the singlet–triplet energy gap ($2J$).[35] A linear relationship between J and ϕ has been found for bis(μ-hydroxo) complexes with a planar or nearly planar Cu_2O_2 network. The antiferromagnetic contribution becomes greater as ϕ increases above ca. 98°, which is the crossover point from ferromagnetic to antiferromagnetic behavior. Assuming that a similar trend holds for μ-alkoxo complexes and considering that a $-J$ value of 500 cm^{-1} has been reported for a complex with a briding angle (ϕ) of 103.2°,[33] one could predict that, due to its larger angle ($\phi = 107.2°$), the title complex could exhibit a larger antiferromagnetic interaction, i.e. $-J > 500$ cm^{-1}. If one oxo bridge is only half as good as two oxo bridges for determining the magnitude of the interaction, the expected value would be $-J > 250$ cm^{-1}, which is still much larger than the observed value ($-J = 11$ cm^{-1}). The discrepancy points to the importance of the other structural factor, since the overall geometry of our complex differs widely from that of the reference complex,[33] which is nearly perfectly planar.

Indeed, structural distortions are known to alter significantly the magnitude of the interaction. From previous works,[23a,27,28,35a] it may be inferred that the quasi-orthogonality of the principal ligand planes, the distortion from planar toward tetrahedral stereochemistry for the copper(II) ions, the weakening of one metal–oxygen bond in the bridge, ..., which characterize the present complex are responsible for its magnetic behavior.

A weak antiferromagnetic coupling ($J = -53$ cm^{-1}) has been recently reported[25b] for a dinuclear copper(II) complex that is presumed to contain a single methoxo bridge. However, the lack of structural data precludes any further comparison with the title complex.

Due to its structural particularities, the complex is interesting from a conceptual viewpoint related to relationship between structure and magnetic properties in the ground and excited states. The latter topic is of major importance due to the interest recently given to the anisotropic and antisymmetric exchanges.[36-38] To our knowledge, the related studies are yet restricted to planar or nearly planar complexes and do not include low-symmetry species.

A more detailed analysis would require the structural knowledge of an extended series of compounds followed by susceptibility measurements and single-crystal EPR study. Works are in progress to extend this investigation to copper(II) complexes involving ligands derived from other keto precursors such as acetylacetone.

Supplementary Material Available: Listings of anisotropic thermal parameters, hydrogen parameters, and least-squares plane equations (3 pages); tables of calculated and observed structure factors (16 pages). Ordering information is given on any current masthead page.

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