Crystal and Molecular Structure of an Unsubstituted Bis(phenoxo)-derivative of Copper(II), the [{$Cu(OPh)_2(en)$}$_2$]·2PhOH † Dimer, with a 'Normal' Magnetic Moment at Room Temperature

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The title compound has been shown by *X*-ray diffraction methods to be a centrosymmetric phenoxo-bridged dimer with terminal phenoxo- and ethylenediamine groups and hydrogen-bonded phenol molecules. The crystals are monoclinic, space group $P2_1/n$, and the unit cell has dimensions a = 19.000(13), b = 10.930(9), c = 8.968(5) Å, β = 89.90(2)°, U = 1 862.4 Å^3, and Z = 4. The structure was refined by three-dimensional Patterson and Fourier techniques up to a conventional R value of 0.0437. The copper atoms are five-co-ordinate and the co-ordination geometry is that of a distorted square pyramid. The Cu • • • Cu distance is 3.215 Å. The compound has a nearly normal magnetic moment at room temperature and the results of the present investigation are discussed in connection with the known magnetic and structural data for dimeric oxygen-bridged copper(II) complexes.

SOME of us have recently reported [1] the preparation of the first stable unsubstituted bis(phenoxo)-derivative of copper(II) with 2,2′-bipyridyl (bipy) and ethylenediamine (en) of formula [$Cu(OPh)_2$(bipy)] (1), and [$Cu(OPh)_2$(en)]·PhOH, (2) respectively. Monomeric structures were assigned to these compounds on the basis of spectroscopic results and the normal paramagnetic behaviour observed at room temperature.

We now report that the *X*-ray investigation of one of these compounds, (2), has revealed that it is in fact dimeric, [$Cu_2(OPh)_4(en)_2$]·2PhOH, with bridging phenoxo-groups and thus it belongs to the class of the oxygen-bridged copper(II) dimers.[2] Its structural details appear to be of general interest for co-ordination chemists, especially in connection with the 'normal' magnetic behaviour observed at room temperature.

EXPERIMENTAL

The e.s.r. spectra were measured with a Varian E-112 Century Series spectrometer, by operating in the *X*-band and by magnetic modulation at 100 kHz.

Preparation of [$Cu_2(OPh)_4(en)_2$]·2PhOH.—The title compound was prepared by a slightly modified version of the procedure already reported.[1] All solvents and reagents were carefully dried prior to use. The preparation was carried out under an atmosphere of nitrogen dried over P_4O_{10}. A solution of phenol (4.645 g, 49.3 mmol) in tetrahydrofuran (thf) (350 cm^3) was treated with sodium sand (0.73 g, 31.75 mmol) at room temperature. The resulting solution of sodium phenoxide and phenol was added to the suspension of $CuCl_2$ (2.166 g, 16.11 mmol) in diethyl ether (25 cm^3) containing ethylenediamine (0.953 g, 15.86 mmol). After *ca.* 40 h stirring, the resulting deep green solution was filtered, in order to eliminate sodium chloride. Evaporation of the solution to about one eighth its original volume under reduced pressure gave rise to the incipient precipitation of the microcrystalline complex. The precipitate was dissolved by heating briefly to *ca.* 50 °C and the resulting solution was then kept in the refrigerator overnight. The crystalline complex was filtered off and dried *in vacuo* (2.17 g, 33.3% yield). Attempts were not made to optimize the yields. The compound analyzed correctly for the formulation given. The solution of the compound in thf is extremely sensitive to moisture.

A polycrystalline sample of the compound gave the e.s.r. spectrum of Figure 1, with a main line at g = 2.09 and a very weak line at g = 4.25. From the integrated area of these signals and from the weight of the sample, by using copper(II) sulphate as standard, it was calculated that 5.8×10^{23} unpaired spins were present per mole of copper in the substance. Several measurements of the magnetic susceptibility at room temperature (Faraday method) gave values of the magnetic moment ranging from 1.7 to 1.8 B.M.‡ (diamagnetic correction = -2.94×10^{-9} m^3 mol^{-1}). A *X*-ray powder diagram (see Table 1) of the polycrystalline substance prepared as described above could be indexed with the cell parameters found for the single crystal (see below). The polycrystalline substance after exposure to air (*ca.* 2 h) had identical *X*-ray powder pattern and identical e.s.r. signals.

Crystal Data and Data Collection.—For the *X*-ray investigation, single crystals were grown from thf solution. The single crystal used for the structural determination was sealed in a Lindemann capillary under nitrogen saturated with thf. The unit-cell dimensions, originally obtained from rotation and Weissenberg photographs, were refined by a least-squares procedure on the setting angles of 17 strong reflections accurately measured on a single-crystal Siemens AED diffractometer. The crystals were found to belong to the monoclinic system. The observed extinctions of $h0l$, $h + l = 2n + l$ and $0k0$, $k = 2n + l$ uniquely determined the space group to be $P2_1/n$, a non-standard setting of $P2_1/c$ (C_{2h}^5 no. 14), that was retained because of its more nearly orthogonal β angle.

Crystal data are as follows: $C_{20}H_{24}CuN_2O_3$, M = 403.9, Monoclinic, a = 19.000(13), b = 10.930(9), c = 8.968(5) Å, β = 89.90(9)°, U = 1 862.4 Å^3, Z = 4, D_c = 1.440 g cm^{-3}, $F(000)$ = 844, Mo-K_α radiation, λ = 0.710 69 Å; μ(Mo-K_α) = 11.3 cm^{-1}.

The *X*-ray intensity data were recorded using a crystal of

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† Bis[ethylenediaminebis(phenoxo)copper(II)]—phenol (1/2).

‡ Throughout this paper: 1 B.M. = 9.274×10^{-24} A m^2.

approximate dimensions 0.18 × 0.31 × 0.52 mm sealed in a Lindemann-glass capillary and mounted with its *c* axis coincident with the ϕ axis of the Siemens diffractometer. Niobium-filtered Mo-K_α radiation and the moving-counter-moving-crystal procedure with a take-off angle of 4° were used to collect data for an octant of the reciprocal lattice. The scan rate was 2.5° min^{-1}. In this way the intensities of 3 254 symmetry-independent reflections were measured within the 2.5—25.0° range of 2 θ. The rejection criterion for the 1 103 unobservably weak reflections, which were excluded from the crystal analysis, was $I < 2\sigma(I)$, where $\sigma(I)$ is the standard deviation of the measured intensity based on counting statistics. Attenuation filters were automatically inserted between the crystal and the detector in order to stay in the linear zone of counting. Crystal and instrument stabilities were monitored throughout by remeasuring the intensity of a standard reflection every 20 measurements, without significant variation being noted. After the usual data reduction, the structure amplitudes were put on an absolute scale, first by comparison with the calculated values and then refining the scale factor for the F_0 as a variable parameter in the least-squares procedure. No absorption correction was made because of the very low absorbance of the sample ($r = 0.14$). Final atomic co-ordinates for non-hydrogen atoms are given in Table 2, those for hydrogen atoms have been deposited as Supplementary Publication No. SUP 22752 (17 pp.),* together with a list of observed and calculated structure factors and thermal parameters.

TABLE 1

X-Ray powder data of $[Cu_2(OPh)_4(en)_2]\cdot 2PhOH$

Relative intensity	$d_{obs.}$ (Å)	$d_{calc.}$ (Å) *	*hkl*
100	9.46	9.500	200
		9.500	$\bar{2}00$
		9.474	110
		9.474	$\bar{1}10$
91	8.14	8.115	101
		8.105	$\bar{1}01$
5	7.16	7.170	201
		7.170	$\bar{2}01$
23	6.93	6.933	011
32	5.60	5.604	$\bar{2}11$
		5.597	211
9	5.47	5.480	310
		5.480	$\bar{3}10$
		5.465	020
12	4.78	4.750	400
		4.750	$\bar{4}00$
27	4.69	4.679	311
		4.667	021
36	4.54	4.533	121
		4.531	$\bar{1}21$
		4.484	002
17	4.36	4.356	410
		4.356	$\bar{4}10$
8	4.14	4.148	012
		4.138	320
		4.138	$\bar{3}20$
10	4.07	4.058	202
		4.054	112
		4.052	$\bar{2}02$
		4.052	$\bar{1}12$
38	3.93	3.921	411
		3.916	$\bar{4}11$
6	3.82	3.804	212
		3.800	$\bar{2}12$
13	3.77	3.759	321
		3.755	$\bar{3}21$
29	3.61	3.589	510
		3.589	$\bar{5}10$
		3.585	420
		3.578	130

* Calculated from the crystal data obtained by the single-crystal diffractometric study.

TABLE 2

Final atomic co-ordinates of non-hydrogen atoms with their estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Cu	0.069 81(3)	0.036 62(6)	0.408 75(6)
O(1)	0.088 0(2)	0.203 8(3)	0.473 0(4)
O(2)	0.049 3(2)	−0.034 9(3)	0.600 2(3)
O(3)	0.127 5(2)	0.344 8(4)	0.259 0(4)
N(1)	0.086 0(3)	0.088 6(4)	0.194 8(5)
N(2)	0.092 4(3)	−0.132 6(4)	0.328 1(5)
C(1)	0.071 7(2)	0.257 1(4)	0.602 7(5)
C(2)	0.105 2(3)	0.224 1(5)	0.733 6(6)
C(3)	0.090 6(4)	0.282 6(6)	0.863 8(7)
C(4)	0.042 7(4)	0.373 7(7)	0.807 9(8)
C(5)	0.008 8(4)	0.407 9(7)	0.743 8(9)
C(6)	0.023 3(3)	0.351 2(6)	0.612 3(8)
C(7)	0.097 5(3)	−0.106 1(5)	0.666 6(5)
C(8)	0.167 9(3)	−0.076 3(6)	0.665 3(7)
C(9)	0.216 1(4)	−0.146 0(8)	0.740 5(8)
C(10)	0.197 4(4)	−0.247 6(8)	0.815 5(7)
C(11)	0.128 7(5)	−0.281 5(7)	0.814 2(7)
C(12)	0.078 4(3)	−0.212 8(6)	0.739 8(6)
C(13)	0.164 9(3)	0.446 7(5)	0.291 5(6)
C(14)	0.173 8(3)	0.487 8(6)	0.434 3(7)
C(15)	0.210 4(4)	0.595 0(7)	0.461 2(7)
C(16)	0.237 0(4)	0.660 6(6)	0.346 8(8)
C(17)	0.228 9(4)	0.620 3(6)	0.203 2(8)
C(18)	0.193 0(3)	0.514 1(6)	0.174 0(7)
C(19)	0.091 4(7)	−0.021 4(7)	0.101 5(8)
C(20)	0.108 9(7)	−0.126 2(8)	0.170 0(9)

Structure Determination and Refinement.—The structure was solved by three-dimensional Patterson and Fourier techniques, with successive addition of atom positions to improve the phasing for all the non-hydrogen atoms. Full-matrix least-squares refinement, in which $\Sigma w(F_o - F_c)^2$ was minimized, led to $R = 9.64\%$, which fell to 5.53% when anisotropic thermal parameters were introduced. At this stage all the hydrogen atoms, except those belonging to the ethylenediamine ligand, were located in their expected

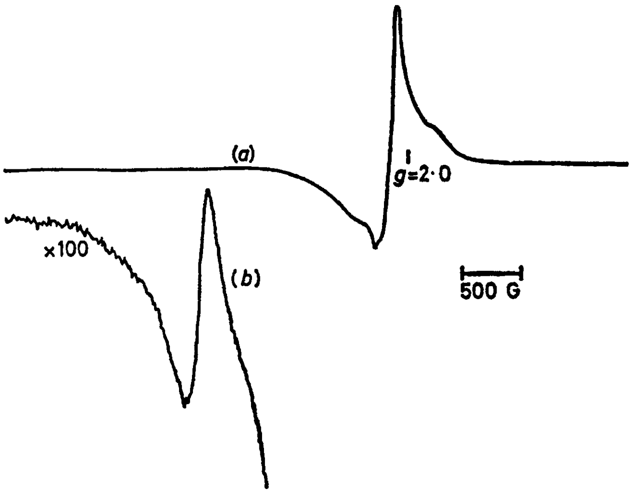

FIGURE 1 (*a*) Room-temperature e.s.r. spectrum of a polycrystalline sample of $[Cu_2(OPh)_4(en)_2]\cdot 2$ PhOH obtained at H_0 = 3 400 G. The microwave frequency was 9.525 GHz. (*b*) The same spectrum, 100 times magnified, to show the very weak line at $g = 4.25$

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

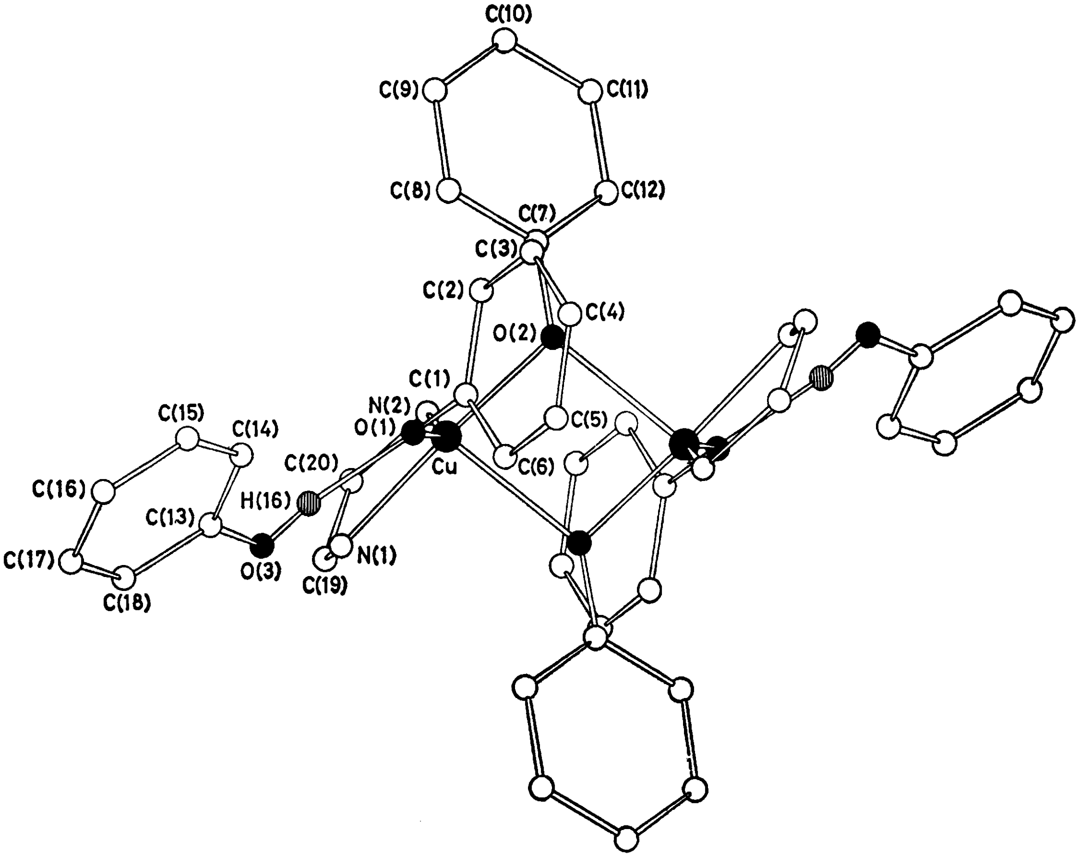


FIGURE 2 Molecular Structure of $[Cu_2(OPh)_4(en)]\cdot 2$ PhOH

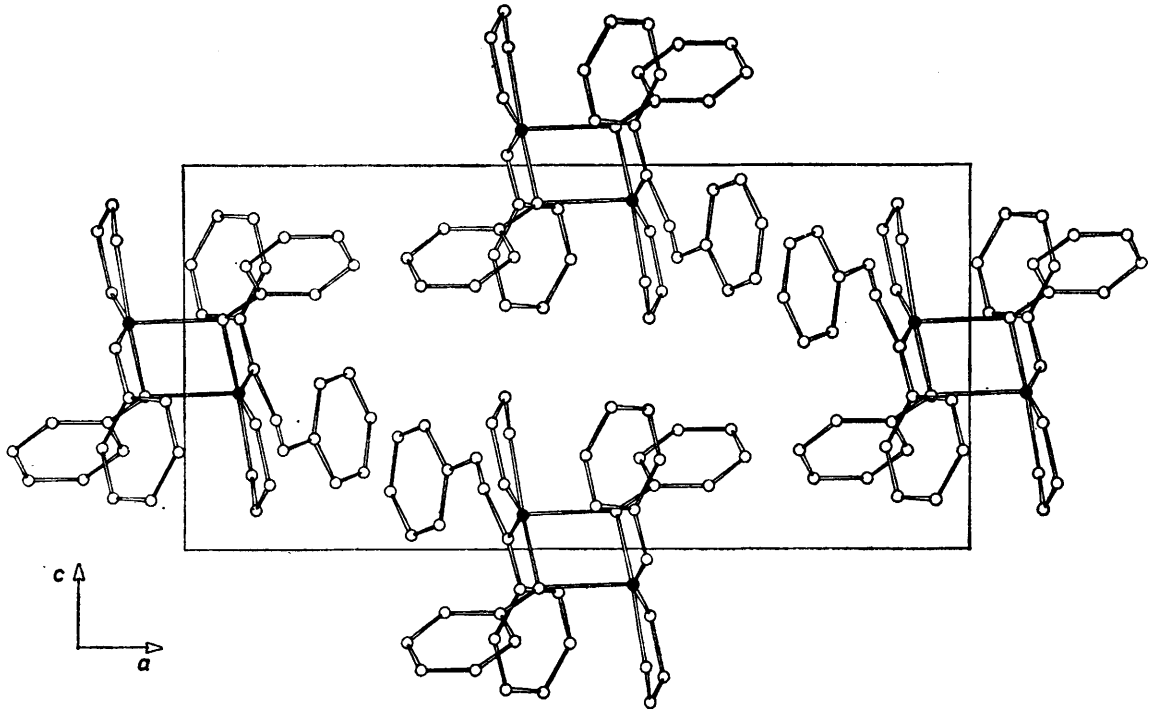


FIGURE 3 Crystal packing of $[Cu_2(OPh)_4(en)_2]\cdot 2$ PhOH, viewed along the *b* axis

positions from a difference synthesis and included in the refinement with isotropic thermal parameters. In the final stages of refinement each reflection was assigned a weight according to $w = 1/[\sigma^2(F_o) + 0.005\ F_o^2]$, chosen to minimize the variation of $w(\Delta F)^2$ with $|F_o|$ and the final residuals were $R = 4.37$ and $R' = 4.74\%$. A final difference synthesis showed no peaks higher than 0.28 e Å^{-3}. At the end of refinement the shifts of the atomic parameters were negligible, all being well below the corresponding estimated standard deviations. Scattering factors for neutral atoms and correction terms for anomalous dispersion for non-hydrogen atoms[3] and for hydrogen atoms[4] were taken from the literature. All calculations were carried out with the programs SHELX 76[5] on a Cyber 76 computer.

RESULTS AND DISCUSSION

The *X*-ray investigation has shown that the bis(phenoxo)-derivative of copper(II) with ethylenediamine as additional ligand is dimeric with bridging phenoxo-groups, see Figure 2. The packing of the molecule in the unit cell is shown in Figure 3. The structure consists of discrete dimeric molecules with no relevant intermolecular interactions. The dimeric molecule contains a second type of phenoxo-ligands, namely the terminal ones, one for each copper atom. In addition, two phenol groups, which do not take part in the co-ordination to the central metal atom, are hydrogen-bonded to the terminal phenoxo-groups. The O(1) · · · O(3) contact between the oxygen atoms involved in the hydrogen bonding (see Table 3) is 2.572 Å, which is 0.23 Å shorter than the sum of the van der Waals oxygen radii.[6] The copper atoms are five-co-ordinate, the set of donor atoms being of the N_2O_3 type, the two nitrogens being from the ethylenediamine, two oxygens from the bridging phenoxo-groups, and the third oxygen from the terminal phenoxo-group. The dimeric molecule possesses a centre of inversion, thus implying that the Cu_2O_2 bridging system is strictly planar. However, the two Cu–O(bridging) distances are markedly different (2.265 and 1.926 Å, see Table 3), a fact frequently observed in binuclear copper(II) complexes with bridging oxygens. Another phenoxo-derivative is known[7] to contain phenol in its formula: however, in this case the phenol was found to be co-ordinated to the central metal atom of $Ti_2(OPh)_8{\cdot}2PhOH$ at a Ti–O distance of 2.200 Å. As far as the bonding situation around the three-co-ordinated bridging oxygen is concerned stronger deviations from a *sp*^{2} hybridisation are observed (see Tables 3 and 4), as compared with the similar cases of a molybdenum(V)[8] and of two titanium(IV)[7,9] complexes. Phenoxo-bridged thallium(III) complexes have also been studied crystallographically.[10]

As shown by the data of Tables 4 and 5, the co-ordination geometry around copper is neither trigonal

TABLE 3

Main intramolecular distances (Å) and angles (°)

(*a*) Bond distances

Cu–O(1)	1.947(4)	Cu–N(1)	2.025(5)
Cu–O(2)	1.926(3)	Cu–N(2)	2.032(5)
Cu–O(2′)	2.265(4)		
O(1)–C(1)	1.337(6)	C(2)–C(3)	1.359(8)
O(1)–H(16)	1.76(7)	C(3)–C(4)	1.350(10)
C(1)–C(2)	1.384(7)	C(4)–C(5)	1.363(11)
C(1)–C(6)	1.382(7)	C(5)–C(6)	1.360(11)
O(2)–C(7)	1.342(6)	C(9)–C(10)	1.346(12)
C(7)–C(8)	1.377(8)	C(10)–C(11)	1.357(12)
C(7)–C(12)	1.386(8)	C(11)–C(12)	1.387(10)
C(8)–C(9)	1.370(10)		
O(3)–C(13)	1.353(7)	C(14)–C(15)	1.384(10)
O(3)–H(16)	0.84(7)	C(15)–C(16)	1.349(10)
C(13)–C(14)	1.368(8)	C(16)–C(17)	1.370(10)
C(13)–C(18)	1.391(8)	C(17)–C(18)	1.372(9)
N(1)–C(19)	1.469(9)	C(19)–C(20)	1.342(12)
N(2)–C(20)	1.453(9)		

(*b*) Bond angles

O(2)–Cu–O(2′)	80.1(3)	O(2′)–Cu–N(1)	96.8(3)
O(2)–Cu–N(1)	171.6(4)	O(2′)–Cu–N(2)	101.0(3)
O(2)–Cu–N(2)	89.4(3)	N(1)–Cu–N(2)	83.5(3)
O(2)–Cu–O(1)	98.8(3)	N(1)–Cu–O(1)	89.4(3)
O(2′)–Cu–O(1)	101.3(3)	N(2)–Cu–O(1)	157.2(4)
Cu–O(1)–C(1)	128.7(6)	O(1)–H(16)–O(3)	164(7)
Cu–O(1)–H(16)	118(6)	H(16)–O(3)–C(13)	108(8)
H(16)–O(1)–C(1)	113(6)		
Cu–O(2)–Cu′	99.9(2)	Cu–O(2)–C(7)	119.6(6)
Cu′–O(2)–C(7)	134.0(8)		
Cu–N(1)–C(19)	108.7(6)	Cu–N(2)–C(20)	110.5(7)

(*c*) Non-bonding distances

Cu · · · Cu′	3.215(3)
O(1) · · · O(3)	2.572(5)

Primes refer to the co-ordinate transformation $-x$, $-y$, $1 - z$.

TABLE 4

Selected least-squares planes through groups of atoms and deviations (Å) from them in parentheses

Plane 1: Cu, Cu′, O(2), O(2′)

$$-0.412x + 9.963y + 3.683z = 1.841$$

[O(1) 1.895, N(1) −0.277, N(2) −1.992, C(7) −0.485]

Plane 2: O(1), O(2), N(1), N(2)

$$18.687x - 0.497y + 1.584z = 2.091$$

[Cu −0.158, O(1) 0.201, O(2) −0.202, N(1) −0.220, N(2) 0.221]

Plane 3: Cu, Cu′, C(7)

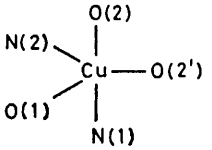
$$1.595x + 9.123y + 4.882z = 2.441$$

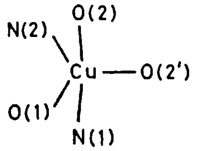
[O(2) 0.249]

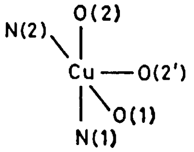
Primes refer to the co-ordinate transformation $-x$, $-y$, $1 - z$. The angle between planes 1 and 2 is 89.5°.

TABLE 5

Co-ordination geometry around copper in $[Cu_2(OPh)_4(en)_2]{\cdot}2PhOH$ as related to the theoretical bond angles for square-pyramidal and trigonal-bipyramidal geometries







	Trigonal bipyramid	Our case	Square pyramid *
O(2)–Cu–O(2′)	90	80.1	90
O(2)–Cu–N(2)	90	89.4	90
O(2)–Cu–O(1)	90	98.8	90
N(1)–Cu–O(1)	90	89.4	90
N(1)–Cu–N(2)	90	83.5	90
N(1)–Cu–O(2′)	90	96.8	90
O(1)–Cu–O(2′)	120	101.3	90
O(2′)–Cu–N(2)	120	101.0	90
N(2)–Cu–O(1)	120	157.2	180
N(1)–Cu–O(2)	180	171.6	180

* The metal is in the basal plane.

bipyramidal nor square pyramidal. With its large anisotropy, the e.s.r. spectrum supports both these geometries and it does not allow a decision to be made in favour of either one, at least in a straightforward way. The e.s.r parameters (see Figure 1) are in close agreement with those reported for the copper(II) chelate of kojic acid [11] and are consistent with the dimeric structure determined for the single crystal. Concerning the geometry around copper, by taking into account (see Table 5) the theoretical internal bond angles for the trigonal-bipyramidal and the square-pyramidal geometries and by comparing them with the observed values, we can conclude that the geometry around copper can be described as distorted square pyramidal or very distorted trigonal bipyramidal.

The compound reported in this paper has a very normal magnetic moment at room temperature. This was confirmed by the quantitative evaluation of the e.s.r. signal. The *X*-ray powder diagram on polycrystalline samples of the compound was consistent with the cell data obtained on the single crystal. *This established conclusively that the magnetic moment and the crystallographic data pertained to the same substance.*

The normal magnetic moment at room temperature found for our compound is somewhat unusual for binuclear copper(II) complexes. By considering (see Table 6) the oxygen-bridged complexes, which are of more direct interest for the case under discussion, we can see that most of them have reduced magnetic moments at room temperature; a few cases are known of ferromagnetic behaviour, whereas 'normal' magnetic moments are seldom encountered. If copper is four-co-ordinate, the geometry of the dimer is frequently centrosymmetric and it can be represented by two basal-edged squares shown in the idealised structure (I) of Figure 4. If copper in the dimer is five-co-ordinate, and by taking into consideration the fact that the more frequently encountered geometry is that of a distorted

TABLE 6

Structural and magnetic data for some binuclear oxygen-bridged copper(II) complexes

Compound	Co-ordination number	Idealised geometry [a]	Cu–O–Cu (°)	Cu–Cu (Å)	μ (B.M.)	Notes	Ref.
$[Cu_2(teen)_2(OH)_2]^{2+}$	4	(I)	103.0	2.978	1.38		*b, c*
$[Cu_2(tmen)_2(OH)_2]^{2+}$	4	(I)	104.1	3.000	1.4		*d, e*
$[Cu_2Br_2(bhbim)_2]$	4	(I)	101.2	3.019	1.14		*f*
$[Cu_2(pap)_2(OH_2)_2]$	5	(II)	98.3	2.948	1.48	δ [g] = 164.2°, O–Cu–O =80.4°	*h*
$[Cu_2(tfacp)_2(OH_2)_2]\cdot H_2O$	5	(II)	103.7	3.064	0.84	Weak interaction between couples of dimers	*i*
β-$[\{Cu(dmaep)(OH)\}_2]^{2+}$	5	(III)	100.4	2.935	1.49 [j]		*k, l*
$[\{Cu(hpbim)Cl\}_2]$	5	(III)	110.3	3.294	1.1		*m*
$[\{Cu(OH)(eaep)\}_2]^{2+}$	5	(III)	98.8 99.5	2.917	1.63 [j]	δ [g] = 178.6°, O–Cu–O =80.2, 81.5°	*n, o*
$Cu_2(OH)_2(SO_4)(OH_2)(bipy)_2$	5	(III)	97.0	2.893	1.94	δ [g] = 173.9°, ferromagnetic coupling, O–Cu–O =84, 83°	*p*
$[\{Cu(het)(py)\}_2]$	5	(III)	103.0	3.051	0.64		*q*
$[\{Cu(phbim)(NO_3)\}_2]$	5	(III)	100.1	3.027			*r*
$[Cu_2(bzpd)_2(py)_2]\cdot 2\ py$	5	(III)	103.5	3.055	0.5		*i*
γ-$[\{Cu(mebim)_2\}_2]$	5	(IV)	101.0 98.8	3.358 [j]			*g*
$[Cu_2(pyo)_4(NO_3)_4]$	5	(IV)	102.9	3.548	1.90		*t, u*
$[\{Cu(hipp)_2(OH_2)_2\}_2]$	5	(IV)	101.0	3.33	1.9		*v, w*
$[\{Cu(hfpd)(metbim)\}_2]$	5	(IV)	95.4	3.119	1.79		*r, x*
$[\{CuH_2(bzpd)_2(en)\}_2]$	5	(IV)	95.7	3.38	1.86		*i*
$[Cu(OPh)_4(en)_2]\cdot 2\ PhOH$	5	(IV)	99.9	3.215	1.75		This work

Ligand abbreviations: teen = *NNN'N'*-tetraethylethylenediamine, tmen = *NNN'N'*-tetramethylethylenediamine, bhbim = *N*-butyl-5-chloro-α-phenyl-2-hydroxybenzylideneiminate, pap = *N*-picolinoyl-3-aminopropoxy, tfacp = 2,5-bis(trifluoroacetyl)-cyclopentanate, dmaep = 2-(2'-dimethylaminoethyl)pyridine, hpbim = *N*-(2-hydroxypropyl)benzylideneiminate, eaep = 2-(2'-ethylaminoethyl)pyridine, het = heptan-2,4,6-trionate, phbim = *N*-n-propyl-2-hydroxybenzylideneiminate, bzpd = benzoylpentan-2,4-dionate, mebim = *N*-methyl-benzylideneiminate, pyo = pyridine-*N*-oxide, hipp = hippurate, hfpd = 1,1,1,5,5,5-hexafluoropentan-2,4-dionate, metbim = *N*-(2'-methylethyl)-2-hydroxybenzylideneiminate.

[a] Reference should be made to Figure 4. [b] W. E. Hatfield, T. S. Piper, and U. Klabunde, *Inorg. Chem.*, 1963, **2**, 629. [c] E. D. Estes, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, 1974, **13**, 1654. [d] J. R. Wasson, T. P. Mitchell, and W. H. Bernard, *J. Inorg. Nuclear Chem.*, 1968, **30**, 2865. [e] T. P. Mitchell, W. H. Bernard, and J. R. Wasson, *Acta Cryst.*, 1970, **B26**, 2096. [f] P. Gluvchinski, G. M. Mockler, P. C. Healy, and E. Sinn, *J.C.S. Dalton*, 1974, 1156. [g] Dihedral angle along the O · · · O vector of the Cu_2O_2 bridging system. [h] J. A. Bertrand, E. Fujita, and P. G. Eller, *Inorg. Chem.*, 1974, **13**, 2067. [i] Ref. 13. [j] Recalculated from the reference data. [k] R. Krähmer, M. Maaser, K. Staiger, and E. Uhlig, *Z. anorg. Chem.*, 1967, **354**, 242. [l] D. L. Lewis, K. T. McGregor, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, 1974, **13**, 1013. [m] J. A. Bertrand, J. A. Kelley, and J. L. Breece, *Inorg. Chim. Acta*, 1970, **4**, 247. [n] D. Y. Jeter, D. L. Lewis, J. C. Hempel, D. J. Hodgson, and W. E. Hatfield, *Inorg. Chem.*, 1972, **11**, 1958. [o] D. L. Lewis, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, 1972, **11**, 2216. [p] A. T. Casey, B. F. Hoskins, and F. D. Whillans, *Chem. Comm.*, 1970, 904. [q] A. B. Blake and L. R. Fraser, *J.C.S. Dalton*, 1974, 2554. [r] E. Sinn, *Inorg. Chem.*, 1976, **15**, 2698. [s] D. Hall, S. V. Sheat, and T. N. Waters, *J. Chem. Soc.* (*A*), 1968, 460. [t] S. Ščavničar and B. Matković, *Acta Cryst.*, 1969, **B25**, 2046. [u] W. E. Hatfield, J. A. Barnes, D. Y. Jeter, R. Whyman, and E. R. Jones, *J. Amer. Chem. Soc.*, 1970, **92**, 4982. [v] J. N. Brown and L. M. Trefonas, *Inorg. Chem.*, 1973, **12**, 1730. [w] J. N. Brown, H. R. Eichelberger, E. Schaeffer, M. L. Good, and L. M. Trefonas, *J. Amer. Chem. Soc.*, 1971, **93**, 6290. [x] H. Yokoi and M. Chikira, *J. Amer. Chem. Soc.*, 1975, **97**, 3975.

square pyramid, the joining of the square pyramid can ideally be obtained in one of the manners shown in Figure 4, namely, basal-edged square pyramids, (II), centrosymmetrical basal-edged square pyramids, (III), and, finally, centrosymmetric axial- and basal-edged square pyramids, (IV). Our compound belongs to this last category, as may be clearly seen from some typical parameters, namely the very different Cu–O distances within the Cu_2O_2 bridge and the almost exact orthogonality (see Table 4) of the Cu_2O_2 plane with the mean basal plane of the copper ' square pyramid '.

Several mechanisms have been proposed for the magnetic interactions in binuclear copper(II) complexes.[2,12] The situation concerning magnetic exchange in binuclear oxygen-bridged copper(II) complexes can be summarised as follows. The following structural parameters have been considered, among others, to be responsible for the observed phenomenon: (*a*) within complexes of four-co-ordinate copper, the angle at the oxygen atom of the Cu_2O_2 bridging system; (*b*) the angle at the copper within the non-planar Cu_2O_2 bridging systems; (*c*) the dihedral angle along the $O \cdots O$ vector of the Cu_2O_2 bridging system; and (*d*) the orientation of the copper co-ordination polyhedron with respect to the Cu_2O_2 bridging system. It has also been observed by some authors[2,13] that binuclear systems belonging to the class denoted as (IV) in Figure 4 usually have a low degree of magnetic interaction, if any. It is therefore not surprising that our compound, belonging to that idealised geometry has a normal magnetic moment, probably due to incorrect orientation of the metal orbitals to interact with the oxygen *p* orbitals or, better, with themselves.

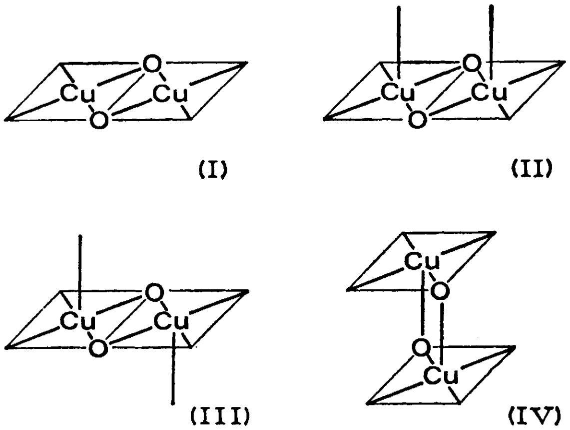


FIGURE 4 Idealised geometrical arrangements in binuclear oxygen-bridged complexes of four- and five-co-ordinate copper: (I), basal-edged squares; (II), basal-edged square pyramids; (III), centrosymmetric basal-edged pyramids; and (IV), centrosymmetric axial- and basal-edged square pyramids

It should also be considered that, beside the geometrical factors, dynamic electronic exchange processes between the copper centres can influence the total paramagnetism of the molecule. With the aim of clarifying this point, work is now in progress to measure the e.s.r. spectra and magnetic susceptibility data at various temperatures. The results of this investigation will be reported later.[14]

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REFERENCES

[1] F. Calderazzo and G. Dell'Amico, *J.C.S. Dalton*, 1979, 1238.

[2] D. J. Hodgson, *Progr. Inorg. Chem.*, 1975, **19**, 173.

[3] ' International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, pp. 99 and 149.

[4] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[5] G. M. Sheldrick, SHELX-76, A Program for Crystal Structure Determination, Cambridge, 1975.

[6] L. Pauling, ' The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960, p. 260.

[7] G. W. Svetich and A. A. Voge, *Acta Cryst.*, 1972, **B28**, 1760.

[8] B. Kamenar and M. Penavic, *J.C.S. Dalton*, 1977, 356.

[9] K. Watenpaugh and C. N. Caughlan, *Inorg. Chem.*, 1966, **5**, 1782.

[10] P. J. Burke, L. A. Gray, P. J. C. Hayward, R. W. Matthews, M. McPartlin, and D. G. Gillies, *J. Organometallic Chem.*, 1977, **136**, C7.

[11] A. D. Toy and T. D. Smith, *J. Amer. Chem. Soc.*, 1971, **93**, 3049.

[12] A. Bencini and D. Gatteschi, *Inorg. Chim. Acta*, 1978, **31**, 11, and refs. therein.

[13] R. L. Lintvedt, M. D. Glick, B. K. Tomlonovic, D. P. Gavel, and J. M. Kuszaj, *Inorg. Chem.*, 1976, **15**, 1633.

[14] F. Calderazzo, A. Colligiani, and F. Marchetti, unpublished work.