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Instrumental Achievement

Crystal Structure of Dimeric [4-{(2-Oxybenzyl)imino}-2-penten-2-olato-*O*,*O*′,*N*]copper(II) Complex

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Due to the super exchange mechanism over the O atoms, dimeric copper(II) complexes with double oxygen bridges show subnormal magnetic moments.[1-3] There seems to be correlations between the magnetic properties of the systems and the dihedral angle between the bridging plane and the coordination square around copper, as well as with the Cu–O–Cu bridging angle. As a contribution of our previous work[4-7] on dimeric Cu complexes, this structure determination was performed to obtain more information about the stereochemistry around the copper atom.

The crystalline ligand 4-[(2-hydroxybenzyl)imino]-2-hydroxy-2-penten was prepared from the mixture of 2-hydroxybenzylamine (1.23 g; 0.01 mol) and acetylacetone (1.0 g; 0.01 mol) in 30 ml of hot ethanol after 24 h in air. To a solution of the ligand (0.205 g; 1 mmol) in 40 ml DMF above 130˚C, a solution of $Cu(CH_3COO)_2 \cdot H_2O$ (0.199 g; 1 mmol) in 20 ml hot methanol was added dropwise and the mixture was set aside. The crystals were obtained after allowing the solution to stand for 36 h at room temperature. The chemical reaction of the title compound is shown in Fig. 1.

The complex includes two $Cu(C_{12}H_{13}NO_2)$ structure units linked *via* phenolic O atoms (Fig. 2). The central CuOCuO bridging group is practically planar. The Cu and O atoms lie alternating 0.009 Å above and below this least squares plane. The Cu1–N1 and Cu2–N2 bond lengths are 1.906(4) and 1.925(4)Å, respectively. The average Cu–O1 [1.871(2)Å] and Cu–O2 [1.946(9)Å] bond distances could be considered equal within experimental error. The average value of the Cu–O–Cu bridging angle is 102.8(3)˚. These values are

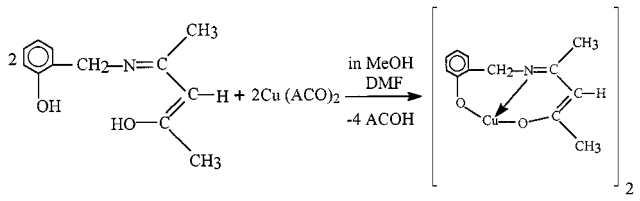

Fig. 1 Synthesis and chemical structure.

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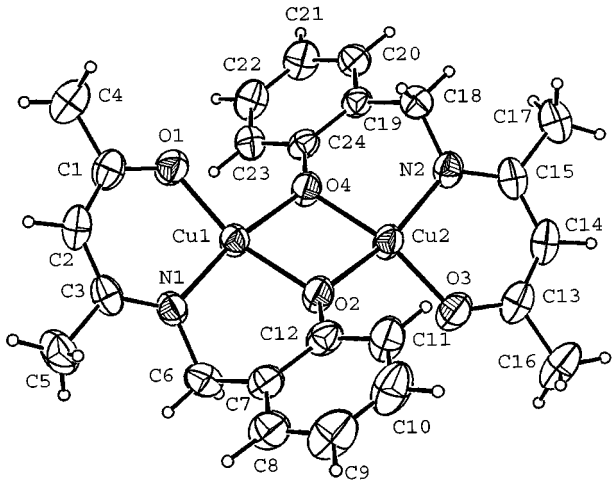

Fig. 2 The ORTEP drawing of the titled compound with atom labeling.

Table 1 Crystal and experimental data

Formula: $C_{24}H_{26}Cu_2N_2O_4$
Formula weight=533.57
Crystal system: orthorhombic
Space group: *P*ca2$_1$ *Z*=4
a=21.885(3)Å
b=12.972(3)Å
c=8.082(2)Å
V=2294.4(8)Å^3
D_x=1.544 g/cm^3
μ(Mo K$_\alpha$)=1.890 mm^{-1}
T=295 K
Dark
F(0 0 0)=1096
Crystal size: 0.5×0.4×0.35 mm
Radiation=Mo K$_\alpha$
R=0.029
R_w=0.035
No. of reflections used=2232
No. of parameters=294
Goodness-of-fit=0.94
Measurements: Enraf Nonius CAD-4 diffractometer
Program system: CAD-4 EXPRESS Software
Structure determination: MolEN
Treatment of hydrogen atoms: geometric calculation
Refinement: full matrix least-squares (MolEN)

Table 2 Final atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms

Atom	*x*	*y*	*z*	B_{eq}/Å^2
Cu1	0.43842(2)	0.27842(3)	0.110	3.061(8)
Cu2	0.31676(2)	0.18031(4)	0.2043(1)	3.494(9)
O1	0.5185(1)	0.2338(2)	0.1486(5)	3.90(7)
O2	0.3529(1)	0.3136(2)	0.1484(5)	3.86(7)
O3	0.2358(1)	0.2226(2)	0.1759(5)	4.48(8)
O4	0.4021(1)	0.1461(2)	0.1704(4)	3.40(6)
N1	0.4588(2)	0.4114(3)	0.0262(5)	3.16(7)
N2	0.2991(2)	0.0558(3)	0.3249(5)	3.27(7)
C1	0.5660(2)	0.2922(3)	0.1342(6)	3.61(9)
C2	0.5656(2)	0.3915(4)	0.0780(7)	4.0(1)
C3	0.5142(2)	0.4495(3)	0.0259(6)	3.41(8)
C4	0.6247(2)	0.2445(4)	0.1918(9)	5.2(1)
C5	0.5270(2)	0.5604(4)	-0.0238(8)	5.0(1)
C6	0.4055(2)	0.4735(4)	-0.0265(6)	3.9(1)
C7	0.3625(2)	0.4938(3)	0.1127(7)	3.41(8)
C8	0.3466(2)	0.5933(3)	0.1603(7)	4.2(1)
C9	0.3051(2)	0.6106(4)	0.2851(9)	5.5(1)
C10	0.2794(2)	0.5277(4)	0.3651(9)	5.5(1)
C11	0.2952(2)	0.4279(4)	0.3254(8)	4.5(1)
C12	0.3358(2)	0.4103(3)	0.1948(7)	3.44(8)
C13	0.1891(2)	0.1713(4)	0.2272(7)	3.90(9)
C14	0.1910(2)	0.0792(4)	0.3090(7)	3.90(9)
C15	0.2438(2)	0.0231(3)	0.3572(6)	3.35(8)
C16	0.1284(2)	0.2201(4)	0.188(1)	5.4(1)
C17	0.2326(2)	-0.0776(4)	0.4473(7)	4.6(1)
C18	0.3536(2)	-0.0007(4)	0.3832(7)	3.63(9)
C19	0.3962(2)	-0.0299(3)	0.2448(6)	2.93(8)
C20	0.4137(2)	-0.1307(3)	0.2190(7)	3.61(9)
C21	0.4546(2)	-0.1560(3)	0.0944(8)	4.4(1)
C22	0.4779(2)	-0.0804(4)	-0.0033(7)	4.2(1)
C23	0.4613(2)	0.0221(4)	0.0194(7)	3.71(9)
C24	0.4203(2)	0.0469(3)	0.1447(5)	2.85(8)

$B_{eq}=(8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*(\boldsymbol{a}_i\cdot\boldsymbol{a}_j)$.

comparable with the corresponding values reported in the literature.[4-7] The displacement of the Cu1 and Cu2 atoms from their coordination best planes are 0.0861(1) and 0.0378(9)Å respectively. The dihedral angles between the bridging plane and the coordination planes around Cu1 and Cu2 are 9.9(3)˚ and 12.6(3)˚ respectively. The Cu–Cu separation [3.0478(6)Å] is comparable with the values found in the reported structures.[4-7] Table 1 shows the crystal and experimental data, while final atomic parameters are given in Table 2. The bond distances and angles are shown in Table 3.

Table 3 Bond distances (Å) and angles (˚)

Cu1 - O1	1.872(3)	C3 - C5	1.520(7)
Cu1 - O2	1.952(3)	C6 - C7	1.490(8)
Cu1 - O4	1.954(3)	C7 - C8	1.391(7)
Cu1 - N1	1.906(4)	C7 - C12	1.397(7)
Cu2 - O2	1.954(3)	C8 - C9	1.376(9)
Cu2 - O3	1.869(3)	C9 - C10	1.374(9)
Cu2 - O4	1.939(3)	C10 - C11	1.378(8)
Cu2 - N2	1.925(4)	C11 - C12	1.399(8)
O1 - C1	1.291(5)	C13 - C14	1.366(8)
O2 - C12	1.361(5)	C13 - C16	1.504(7)
O3 - C13	1.289(6)	C14 - C15	1.420(8)
O4 - C24	1.363(5)	C15 - C17	1.516(7)
N1 - C3	1.309(6)	C18 - C19	1.505(7)
N1 - C6	1.481(6)	C19 - C20	1.378(6)
N2 - C15	1.309(7)	C19 - C24	1.387(6)
N2 - C18	1.476(6)	C20 - C21	1.387(8)
C1 - C2	1.366(7)	C21 - C22	1.358(8)
C1 - C4	1.500(7)	C22 - C23	1.390(7)
C2 - C3	1.418(7)	C23 - C24	1.390(7)
O1 - Cu1 - O2	160.7(2)	N1 - C3 - C5	121.9(5)
O1 - Cu1 - O4	93.9(1)	C2 - C3 - C5	115.8(5)
O1 - Cu1 - N1	96.9(2)	N1 - C6 - C7	112.1(4)
O2 - Cu1 - O4	77.0(1)	C6 - C7 - C8	122.0(5)
O2 - Cu1 - N1	94.0(1)	C6 - C7 - C12	119.0(4)
O4 - Cu1 - N1	168.3(2)	C8 - C7 - C12	118.9(5)
O2 - Cu2 - O3	95.5(1)	C7 - C8 - C9	121.2(5)
O2 - Cu2 - O4	77.3(1)	C8 - C9 - C10	119.2(5)
O2 - Cu2 - N2	160.1(2)	C9 - C10 - C11	121.5(6)
O3 - Cu2 - O4	164.4(2)	C10 - C11 - C12	119.3(6)
O3 - Cu2 - N2	96.8(2)	O2 - C12 - C7	118.0(5)
O4 - Cu2 - N2	94.1(1)	O2 - C12 - C11	122.2(5)
Cu1 - O1 - C1	123.9(3)	C7 - C12 - C11	119.8(4)
Cu1 - O2 - Cu2	102.6(1)	O3 - C13 - C14	125.6(4)
Cu1 - O2 - C12	121.5(3)	O3 - C13 - C16	114.6(5)
Cu2 - O2 - C12	129.9(3)	C14 - C13 - C16	119.8(5)
Cu2 - O3 - C13	124.2(3)	C13 - C14 - C15	127.3(4)
Cu1 - O4 - Cu2	103.0(1)	N2 - C15 - C14	122.1(4)
Cu1 - O4 - C24	132.2(3)	N2 - C15 - C17	121.7(5)
Cu2 - O4 - C24	121.3(2)	C14 - C15 - C17	116.2(5)
Cu1 - N1 - C3	124.0(3)	N2 - C18 - C19	112.8(5)
Cu1 - N1 - C6	114.2(3)	C18 - C19 - C20	121.6(4)
C3 - N1 - C6	121.6(4)	C18 - C19 - C24	119.2(4)
Cu2 - N2 - C15	123.9(4)	C20 - C19 - C24	119.2(4)
Cu2 - N2 - C18	114.6(3)	C19 - C20 - C21	120.9(5)
C15 - N2 - C18	121.4(4)	C20 - C21 - C22	119.6(4)
O1 - C1 - C2	125.3(4)	C21 - C22 - C23	121.0(5)
O1 - C1 - C4	114.8(5)	C22 - C23 - C24	119.1(5)
C2 - C1 - C4	119.8(4)	O4 - C24 - C19	118.5(4)
C1 - C2 - C3	127.2(4)	O4 - C24 - C23	121.2(4)
N1 - C3 - C2	122.3(4)	C19 - C24 - C23	120.2(4)

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