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Bis[μ-2-(benzyliminomethyl)-4-chlorophenolato]bis[chloridocopper(II)]

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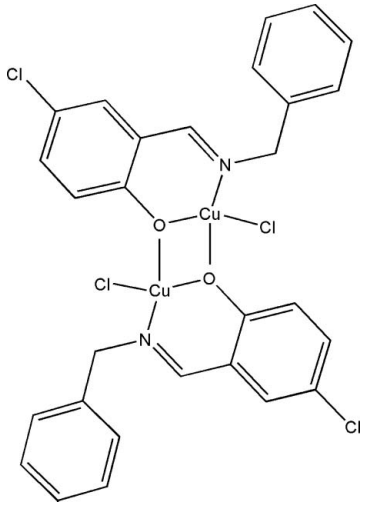
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.005 Å; R factor = 0.026; wR factor = 0.071; data-to-parameter ratio = 13.7.

The title complex, $[Cu_2(C_{14}H_{11}ClNO)_2Cl_2]$, has a centrosymmetric dinuclear structure where two symmetry-related copper(II) metal centres are bridged by the O atoms of two phenoxy groups. Each copper(II) centre displays a distorted tetrahedral coordination provided by one N atom and two O atoms from two Schiff base ligands and by one Cl atom. The Cu···Cu separation is 3.0702 (9) Å.

Related literature

For related literature, see: Bencini & Mani (1988); Jiang *et al.* (2004); Liu & Su (1996).



Experimental

Crystal data

$[Cu_2(C_{14}H_{11}ClNO)_2Cl_2]$
M_r = 687.36
Monoclinic, $C2/c$
a = 22.572 (3) Å
b = 9.3964 (13) Å
c = 16.649 (2) Å
β = 130.724 (2)°
V = 2676.2 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.02 mm^{-1}
T = 298 (2) K
0.55 × 0.43 × 0.30 mm

Data collection

Siemens SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.379, T_{max} = 0.548
6545 measured reflections
2364 independent reflections
1910 reflections with $I > 2\sigma(I)$
R_{int} = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.071
S = 1.04
2364 reflections
172 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.9334 (16)	Cu1—Cl2	2.1934 (8)
Cu1—N1	1.953 (2)		
O1—Cu1—N1	93.43 (8)	N1—Cu1—Cl2	100.42 (6)
O1—Cu1—Cl2	149.90 (6)		

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ2176).

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supporting information

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S1. Comment

During the past two decades, considerable attention has been paid to the chemistry of heterocyclic compounds and complexes with metal ions due to their chelating ability and their potentially beneficial chemical and biological activities. Dinuclear copper(II) units exist on active sites of many metalloenzymes and metalloproteins such as, for example, hemocyanin, tyrosinase and cytochrome oxidase. Schiff base complexes containing salicylaldehyde and amine derivatives have been also often reported. The complexes of salicylaldehyde with polyamines and bis(phenoxy)-bridged dinuclear copper(II) complexes are sparse. As an extension of our work on the structural characterization of Schiff base complexes, the crystal structure of a new dinuclear copper(II) compound is reported here.

The molecular structure of the title complex consists of two centrosymmetrically related $[CuL]^{2+}$ units [where *L* is 4-chloro-2-(benzylaminethyl)-phenolato], which are bridged by the oxygen atoms of two phenoxy groups in such a way as to define an $NCuO_2CuN$ core. A chloride anion completes the coordination around each Cu atom (Fig. 1), thus defining a distorted tetrahedral geometry for the metal centres, with angles subtended at the copper(II) atoms in the range 93.43 (8)–149.90 (6)° (Table 1). The Cu—N, Cu—O, Cu—Cl bond lengths of 1.953 (2), 1.9334 (16) and 2.1934 (8) Å respectively (Table 1) are comparable with those reported previously (Bencini & Mani, 1988; Jiang *et al.*, 2004; Liu & Su, 1996). The Cu···Cu separation within the dimer is 3.0702 (9) Å. The crystal packing (Fig. 2) is governed only by van der Waals interactions.

S2. Experimental

5-Chlorosalicylaldehyde (0.1 mmol, 15.7 mg), $CuCl_2.2H_2O$ (0.1 mmol, 17.05 mg) and benzylamine (0.1 mmol, 10.7 mg) were dissolved in methanol (10 ml). The mixture was stirred for 30 min at room temperature to give a clear brown solution. After allowing the resulting solution to stand in air for 11 d, brown block-shaped crystals of the title compound were formed on slow evaporation of the solvent. The crystals were collected, washed with methanol and dried in a vacuum desiccator using anhydrous $CaCl_2$ (yield 54%). Analysis found: C 48.88%, H 3.20%, N 4.07%; calculated for ($Cu_2C_{28}H_{22}N_2O_2Cl_4$): C48.9%, H 3.20%, N 4.08%.

S3. Refinement

All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with C—H distances in the range 0.93–0.97 Å and U_{iso}(H) = 1.2 U_{eq}(C).

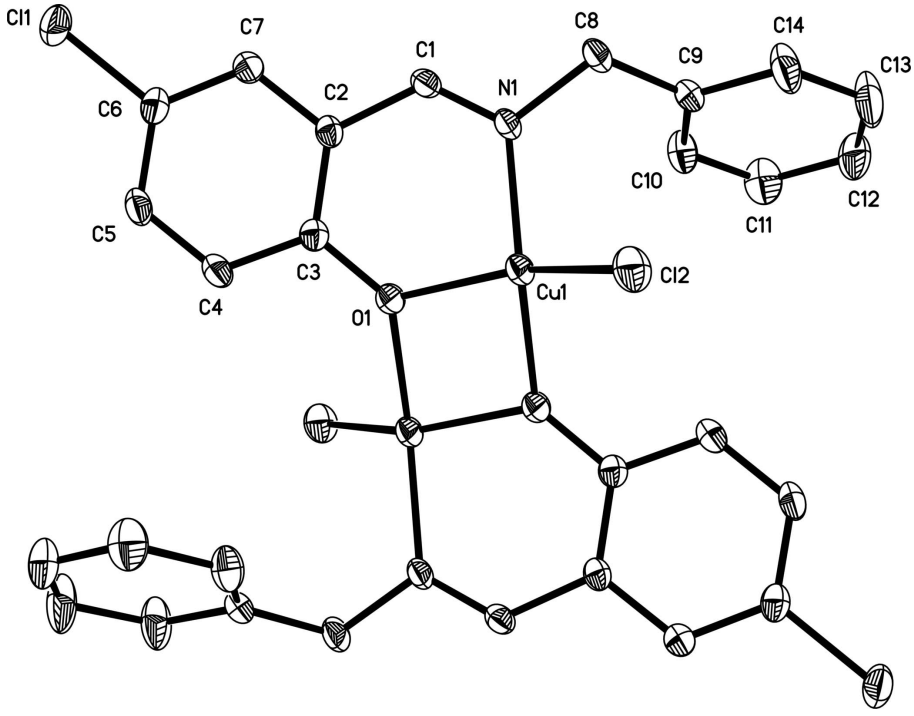

Figure 1

The structure of the title compound with 30% probability ellipsoids. H atoms are omitted for clarity. Unlabelled atoms are related to the labelled atoms by the symmetry operation (0.5 - *x*, 1.5 - *y*, -*z*).

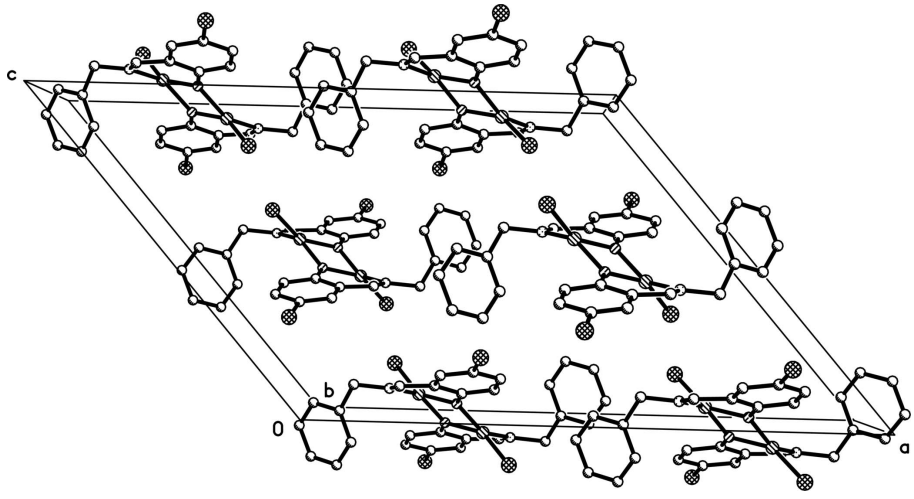

Figure 2

The crystal packing of the title compound viewed along the *b* axis. H atoms are omitted for clarity.

Bis[μ-2-(benzyliminomethyl)-4-chlorophenolato]bis[chloridocopper(II)]

Crystal data

$[Cu_2(C_{14}H_{11}ClNO)_2Cl_2]$
M_r = 687.36
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc

a = 22.572 (3) Å
b = 9.3964 (13) Å
c = 16.649 (2) Å
β = 130.724 (2)°

V = 2676.2 (6) Å^3
Z = 4
F(000) = 1384
D_x = 1.706 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3416 reflections

θ = 2.4–27.9°
μ = 2.02 mm^{-1}
T = 298 K
Block, brown
0.55 × 0.43 × 0.30 mm

Data collection

Siemens SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.379, T_{max} = 0.548

6545 measured reflections
2364 independent reflections
1910 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 25.0°, θ_{min} = 2.4°
h = −26→25
k = −11→11
l = −12→19

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.071
S = 1.04
2364 reflections
172 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0314P)^2 + 2.8567P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Cu1	0.219816 (18)	0.74677 (3)	0.06012 (3)	0.03095 (12)
Cl1	0.39728 (5)	0.05623 (8)	0.19873 (7)	0.0525 (2)
Cl2	0.21728 (4)	0.90619 (8)	0.15408 (6)	0.0452 (2)
N1	0.17933 (12)	0.5810 (2)	0.08161 (17)	0.0312 (5)
O1	0.27824 (11)	0.63270 (18)	0.03605 (15)	0.0349 (4)
C1	0.20487 (14)	0.4550 (3)	0.09374 (19)	0.0300 (6)
H1	0.1797	0.3831	0.0998	0.036*
C2	0.26936 (14)	0.4117 (3)	0.09912 (19)	0.0277 (5)
C3	0.30487 (14)	0.5008 (3)	0.0735 (2)	0.0287 (6)
C4	0.37020 (15)	0.4504 (3)	0.0898 (2)	0.0350 (6)
H4	0.3950	0.5090	0.0747	0.042*

C5	0.39847 (15)	0.3151 (3)	0.1281 (2)	0.0374 (6)
H5	0.4422	0.2829	0.1390	0.045*
C6	0.36163 (16)	0.2276 (3)	0.1502 (2)	0.0345 (6)
C7	0.29761 (15)	0.2734 (3)	0.1358 (2)	0.0303 (6)
H7	0.2731	0.2128	0.1503	0.036*
C8	0.11883 (16)	0.6011 (3)	0.0906 (2)	0.0401 (7)
H8A	0.1424	0.6477	0.1575	0.048*
H8B	0.1005	0.5084	0.0918	0.048*
C9	0.04988 (15)	0.6876 (3)	0.0021 (2)	0.0327 (6)
C10	0.02317 (17)	0.6889 (3)	−0.0990 (2)	0.0433 (7)
H10	0.0490	0.6354	−0.1150	0.052*
C11	−0.04162 (19)	0.7684 (3)	−0.1780 (3)	0.0541 (9)
H11	−0.0583	0.7693	−0.2459	0.065*
C12	−0.08114 (18)	0.8456 (3)	−0.1565 (3)	0.0550 (8)
H12	−0.1249	0.8988	−0.2094	0.066*
C13	−0.0555 (2)	0.8436 (4)	−0.0561 (3)	0.0708 (11)
H13	−0.0824	0.8948	−0.0409	0.085*
C14	0.0098 (2)	0.7667 (4)	0.0228 (3)	0.0599 (10)
H14	0.0271	0.7681	0.0910	0.072*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0324 (2)	0.0343 (2)	0.0364 (2)	0.00520 (14)	0.02696 (18)	0.00292 (15)
Cl1	0.0578 (5)	0.0436 (4)	0.0659 (5)	0.0233 (4)	0.0447 (5)	0.0165 (4)
Cl2	0.0497 (4)	0.0505 (4)	0.0440 (4)	0.0045 (4)	0.0343 (4)	−0.0057 (4)
N1	0.0265 (11)	0.0389 (13)	0.0367 (13)	0.0068 (10)	0.0243 (11)	0.0070 (10)
O1	0.0424 (11)	0.0340 (10)	0.0467 (11)	0.0088 (9)	0.0371 (10)	0.0076 (9)
C1	0.0253 (13)	0.0392 (15)	0.0290 (14)	0.0019 (12)	0.0192 (13)	0.0055 (12)
C2	0.0226 (13)	0.0338 (14)	0.0243 (13)	0.0034 (11)	0.0142 (12)	0.0009 (11)
C3	0.0279 (14)	0.0315 (14)	0.0261 (14)	0.0026 (11)	0.0174 (12)	0.0002 (11)
C4	0.0305 (14)	0.0419 (16)	0.0402 (16)	0.0016 (12)	0.0264 (14)	0.0000 (13)
C5	0.0297 (14)	0.0448 (16)	0.0422 (17)	0.0096 (13)	0.0255 (14)	0.0030 (14)
C6	0.0326 (15)	0.0370 (15)	0.0294 (14)	0.0096 (12)	0.0182 (13)	0.0036 (12)
C7	0.0283 (14)	0.0358 (15)	0.0268 (14)	0.0014 (11)	0.0179 (13)	0.0011 (11)
C8	0.0368 (16)	0.0508 (17)	0.0495 (18)	0.0126 (13)	0.0356 (16)	0.0127 (15)
C9	0.0264 (14)	0.0370 (15)	0.0395 (16)	0.0010 (12)	0.0236 (13)	0.0011 (13)
C10	0.0376 (17)	0.0505 (18)	0.0401 (17)	0.0081 (14)	0.0246 (16)	−0.0061 (14)
C11	0.0461 (19)	0.069 (2)	0.0340 (17)	0.0097 (17)	0.0205 (17)	−0.0007 (16)
C12	0.0373 (17)	0.062 (2)	0.049 (2)	0.0210 (16)	0.0207 (17)	0.0115 (17)
C13	0.065 (2)	0.094 (3)	0.067 (2)	0.047 (2)	0.049 (2)	0.020 (2)
C14	0.057 (2)	0.090 (3)	0.051 (2)	0.0372 (19)	0.0432 (19)	0.0196 (18)

Geometric parameters (Å, º)

Cu1—O1	1.9334 (16)	C5—H5	0.9300
Cu1—N1	1.953 (2)	C6—C7	1.371 (4)
Cu1—O1^{i}	1.9850 (17)	C7—H7	0.9300

Cu1—Cl2	2.1934 (8)	C8—C9	1.504 (4)
Cl1—C6	1.746 (3)	C8—H8A	0.9700
N1—C1	1.274 (3)	C8—H8B	0.9700
N1—C8	1.480 (3)	C9—C10	1.369 (4)
O1—C3	1.341 (3)	C9—C14	1.376 (4)
O1—Cu1^{i}	1.9850 (17)	C10—C11	1.385 (4)
C1—C2	1.457 (3)	C10—H10	0.9300
C1—H1	0.9300	C11—C12	1.367 (4)
C2—C7	1.401 (3)	C11—H11	0.9300
C2—C3	1.404 (3)	C12—C13	1.367 (5)
C3—C4	1.396 (3)	C12—H12	0.9300
C4—C5	1.378 (4)	C13—C14	1.376 (5)
C4—H4	0.9300	C13—H13	0.9300
C5—C6	1.379 (4)	C14—H14	0.9300

O1—Cu1—N1	93.43 (8)	C5—C6—Cl1	119.8 (2)
O1—Cu1—O1^{i}	76.82 (8)	C6—C7—C2	119.7 (2)
N1—Cu1—O1^{i}	149.53 (9)	C6—C7—H7	120.2
O1—Cu1—Cl2	149.90 (6)	C2—C7—H7	120.2
N1—Cu1—Cl2	100.42 (6)	N1—C8—C9	113.7 (2)
O1^{i}—Cu1—Cl2	102.14 (6)	N1—C8—H8A	108.8
C1—N1—C8	117.0 (2)	C9—C8—H8A	108.8
C1—N1—Cu1	123.55 (16)	N1—C8—H8B	108.8
C8—N1—Cu1	119.34 (17)	C9—C8—H8B	108.8
C3—O1—Cu1	125.16 (14)	H8A—C8—H8B	107.7
C3—O1—Cu1^{i}	131.55 (14)	C10—C9—C14	118.0 (3)
Cu1—O1—Cu1^{i}	103.18 (8)	C10—C9—C8	123.6 (2)
N1—C1—C2	126.9 (2)	C14—C9—C8	118.4 (2)
N1—C1—H1	116.6	C9—C10—C11	121.1 (3)
C2—C1—H1	116.6	C9—C10—H10	119.4
C7—C2—C3	119.8 (2)	C11—C10—H10	119.4
C7—C2—C1	116.0 (2)	C12—C11—C10	120.2 (3)
C3—C2—C1	124.1 (2)	C12—C11—H11	119.9
O1—C3—C4	120.0 (2)	C10—C11—H11	119.9
O1—C3—C2	121.4 (2)	C13—C12—C11	119.0 (3)
C4—C3—C2	118.6 (2)	C13—C12—H12	120.5
C5—C4—C3	121.0 (2)	C11—C12—H12	120.5
C5—C4—H4	119.5	C12—C13—C14	120.6 (3)
C3—C4—H4	119.5	C12—C13—H13	119.7
C4—C5—C6	119.7 (2)	C14—C13—H13	119.7
C4—C5—H5	120.2	C13—C14—C9	121.0 (3)
C6—C5—H5	120.2	C13—C14—H14	119.5
C7—C6—C5	121.1 (2)	C9—C14—H14	119.5
C7—C6—Cl1	119.0 (2)		

O1—Cu1—N1—C1	11.7 (2)	C1—C2—C3—C4	175.0 (2)
O1^{i}—Cu1—N1—C1	81.3 (3)	O1—C3—C4—C5	−179.9 (2)
Cl2—Cu1—N1—C1	−141.5 (2)	C2—C3—C4—C5	1.4 (4)

O1—Cu1—N1—C8	−171.9 (2)	C3—C4—C5—C6	0.3 (4)
O1^{i}—Cu1—N1—C8	−102.3 (2)	C4—C5—C6—C7	−0.7 (4)
Cl2—Cu1—N1—C8	34.9 (2)	C4—C5—C6—Cl1	−180.0 (2)
N1—Cu1—O1—C3	−25.7 (2)	C5—C6—C7—C2	−0.7 (4)
O1^{i}—Cu1—O1—C3	−176.5 (2)	Cl1—C6—C7—C2	178.58 (19)
Cl2—Cu1—O1—C3	92.0 (2)	C3—C2—C7—C6	2.4 (4)
N1—Cu1—O1—Cu1^{i}	150.78 (10)	C1—C2—C7—C6	−175.6 (2)
O1^{i}—Cu1—O1—Cu1^{i}	0.0	C1—N1—C8—C9	−132.1 (3)
Cl2—Cu1—O1—Cu1^{i}	−91.53 (12)	Cu1—N1—C8—C9	51.3 (3)
C8—N1—C1—C2	−173.3 (2)	N1—C8—C9—C10	31.3 (4)
Cu1—N1—C1—C2	3.2 (4)	N1—C8—C9—C14	−150.8 (3)
N1—C1—C2—C7	166.4 (3)	C14—C9—C10—C11	0.7 (5)
N1—C1—C2—C3	−11.5 (4)	C8—C9—C10—C11	178.7 (3)
Cu1—O1—C3—C4	−154.0 (2)	C9—C10—C11—C12	−1.2 (5)
Cu1^{i}—O1—C3—C4	30.6 (4)	C10—C11—C12—C13	0.4 (5)
Cu1—O1—C3—C2	24.7 (3)	C11—C12—C13—C14	0.9 (6)
Cu1^{i}—O1—C3—C2	−150.76 (19)	C12—C13—C14—C9	−1.3 (6)
C7—C2—C3—O1	178.6 (2)	C10—C9—C14—C13	0.5 (5)
C1—C2—C3—O1	−3.6 (4)	C8—C9—C14—C13	−177.5 (3)
C7—C2—C3—C4	−2.8 (4)		

Symmetry code: (i) −*x*+1/2, −*y*+3/2, −*z*.