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Bis[4-chloro-2-(iminomethyl)phenolato]-copper(II) methanol disolvate

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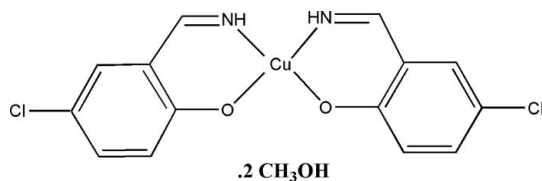
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.038; wR factor = 0.084; data-to-parameter ratio = 13.8.

The title compound, $[\text{Cu}(\text{C}_7\text{H}_5\text{ClNO})_2] \cdot 2\text{CH}_3\text{OH}$, possesses crystallographic twofold symmetry, with the twofold axis passing through the central Cu^{II} ion. The metal centre is coordinated by two O atoms and two N atoms from two symmetry-related Schiff base ligands, forming a slightly distorted *cis*- CuN_2O_2 square-planar geometry. The complex molecules are linked *via* the solvent methanol molecules by $\text{O}-\text{H} \cdots \text{O}$ and $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds, leading to the formation of chains along the b axis.

Related literature

For general background to Schiff base copper(II) complexes, see: Adsule *et al.* (2006); Erxleben & Schumacher (2001); Stewart *et al.* (1961). For related structures, see: Li & Zhang (2004); Wei *et al.* (2004).



Experimental

Crystal data

 $[\text{Cu}(\text{C}_7\text{H}_5\text{ClNO})_2] \cdot 2\text{CH}_4\text{O}$
 $M_r = 436.76$

 Monoclinic, $C2/c$
 $a = 20.603$ (2) Å

 $b = 7.639$ (1) Å
 $c = 14.6681$ (15) Å
 $\beta = 129.376$ (2)°
 $V = 1784.5$ (3) Å³
 $Z = 4$

 Mo $K\alpha$ radiation
 $\mu = 1.55$ mm⁻¹
 $T = 298$ K
 $0.15 \times 0.11 \times 0.08$ mm

Data collection

 Bruker SMART CCD area-detector diffractometer
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
 $T_{\text{min}} = 0.801$, $T_{\text{max}} = 0.886$

 4502 measured reflections
 1568 independent reflections
 1167 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.048$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.084$
 $S = 1.05$
 1568 reflections

 114 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.38$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.27$ e Å⁻³
Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{O2}-\text{H2} \cdots \text{O1}$	0.82	2.04	2.822 (3)	160
$\text{N1}-\text{H1} \cdots \text{O2}^{\dagger}$	0.86	2.20	2.986 (4)	153

Symmetry code: (i) $x, y - 1, z$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

The author thanks Xi'an Medical University for financial support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2879).

References

- Adsule, S., Barve, V., Chen, D., Ahmed, F., Dou, Q. P., Padhye, S. & Sarkar, F. H. (2006). *J. Med. Chem.* **49**, 7242–7246.
- Bruker (2000). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Erxleben, A. & Schumacher, D. (2001). *Eur. J. Inorg. Chem.* **12**, 3039–3046.
- Li, Z.-X. & Zhang, X.-L. (2004). *Acta Cryst.* **E60**, m958–m959.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Stewart, J. M., Lingafelter, E. C. & Breazeale, J. D. (1961). *Acta Cryst.* **14**, 888–891.
- Wei, Y.-B., Yuan, C.-X. & Yang, P. (2004). *Acta Cryst.* **C60**, m512–m514.

supplementary materials

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Bis[4-chloro-2-(iminomethyl)phenolato]copper(II) methanol disolvate

B. Qin

Comment

The syntheses of copper(II) complexes with Schiff base have been reported for their applications in the design and construction of new magnetic materials (Erxleben & Schumache, 2001; Stewart *et al.*, 1961). Some of these complexes also inhibit the cellular proteasome activity (Adsule *et al.*, 2006). As an extension of the work on structural characterization of mononuclear copper(II) complexes, the crystal structure of the title compound is reported.

Complex (I) is a mononuclear copper(II) compound. The central Cu^{II} atom is coordinated by two O atoms and two N atoms of the two Schiff base ligands to form a slightly distorted square-planar geometry, with angles subtended at the copper(II) atoms in the range 84.48 (12)°–172.02 (10)°. The Cu—O and Cu—N bond lengths are 1.915 (2) Å and 1.939 (2) Å, respectively, which are a little longer than the corresponding value of 1.842 (3) Å and 1.837 (3) Å observed in a similar Schiff base copper(II) complex (Li & Zhang, 2004).

Intermolecular O—H...O and N—H...O hydrogen bonds involving atoms O1 and N1 from the Schiff base and O2 from the methanol (Table 1) link the molecules to form chains along the *b* axis. From Fig. 2, it can be seen that benzene rings from neighbouring complexes are parallel but the distance between their centroids is 3.852 (2) Å, which is longer than the distance (3.4 Å) between neighbouring base pairs in DNA (Wei *et al.*, 2004), indicating no $\pi\cdots\pi$ packing interactions.

Experimental

All chemicals were of reagent grade and commercially available from the Beijing Chemical Reagents Company of China, and were used without further purification. 5-Chloro-2-hydroxybenzaldehyde (0.2 mmol, 31.32 mg), isopropylamine (0.2 mmol, 11.8 mg) and Cu(Ac)₂ (0.1 mmol 18.2 mg) were dissolved in methanol (10 ml). The mixture was stirred at room temperature for 30 min and then filtered. The filtrate was allowed to stand in air for 7 d, after which time yellow block-shaped crystals of the title compound were formed by slow evaporation of the solvent.

Refinement

H atoms attached to C and N atoms were placed in geometrically idealized positions (N-H = 0.86 Å and C-H = 0.93–0.96 Å) and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$. H atoms attached to O atoms (water) were located in difference Fourier maps and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$.

Figures

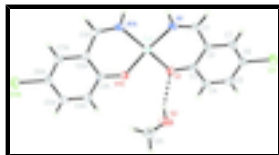


Fig. 1. The asymmetric unit of (I), showing 30% probability displacement ellipsoids. The dashed line indicates a hydrogen bond; symmetry code: (A) 1 -x, y, 3/2 - z.

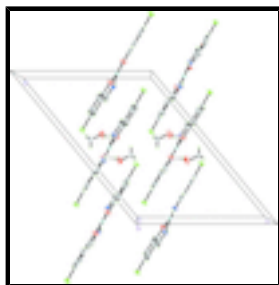


Fig. 2. Part of the crystal packing of (I), viewed along the *b* axis. Hydrogen bonds are shown as dashed lines.

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Crystal data

[Cu(C₇H₅ClNO)₂]₂·2CH₄O

M_r = 436.76

Monoclinic, *C*2/*c*

Hall symbol: -C 2yc

a = 20.603 (2) Å

b = 7.639 (1) Å

c = 14.6681 (15) Å

β = 129.376 (2)°

V = 1784.5 (3) Å³

Z = 4

*F*₀₀₀ = 892

D_x = 1.626 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 1362 reflections

θ = 2.6–27.5°

μ = 1.55 mm⁻¹

T = 298 K

Block, yellow

0.15 × 0.11 × 0.08 mm

Data collection

Bruker SMART CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

T = 298 K

φ and ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

*T*_{min} = 0.801, *T*_{max} = 0.886

4502 measured reflections

1568 independent reflections

1167 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.048

θ_{max} = 25.0°

θ_{min} = 2.6°

h = -24→20

k = -9→7

l = -15→17

Refinement

Refinement on *F*²

Secondary atom site location: difference Fourier map

Least-squares matrix: full

$$R[F^2 > 2\sigma(F^2)] = 0.038$$

$$wR(F^2) = 0.084$$

$$S = 1.05$$

1568 reflections

114 parameters

Primary atom site location: structure-invariant direct methods

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0346P)^2]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.001$$

$$\Delta\rho_{\max} = 0.38 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.26 \text{ e } \text{\AA}^{-3}$$

Extinction correction: none

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.5000	0.17304 (7)	0.7500	0.0365 (2)
Cl1	0.11369 (5)	0.33974 (13)	0.15757 (7)	0.0592 (3)
N1	0.41857 (15)	-0.0028 (3)	0.6418 (2)	0.0413 (7)
H1	0.4297	-0.1088	0.6674	0.050*
O1	0.43140 (12)	0.3587 (2)	0.64243 (18)	0.0417 (6)
O2	0.41114 (18)	0.6573 (3)	0.7355 (2)	0.0727 (8)
H2	0.4284	0.5693	0.7249	0.109*
C1	0.3505 (2)	0.0205 (4)	0.5374 (3)	0.0407 (8)
H1A	0.3177	-0.0776	0.4964	0.049*
C2	0.32026 (18)	0.1865 (4)	0.4774 (3)	0.0342 (7)
C3	0.36158 (18)	0.3465 (4)	0.5328 (3)	0.0343 (7)
C4	0.32418 (18)	0.5002 (4)	0.4667 (3)	0.0414 (8)
H4	0.3504	0.6069	0.5010	0.050*
C5	0.25007 (19)	0.4981 (5)	0.3530 (3)	0.0439 (8)
H5	0.2269	0.6020	0.3110	0.053*
C6	0.21020 (18)	0.3407 (4)	0.3012 (3)	0.0408 (8)
C7	0.24355 (19)	0.1877 (4)	0.3604 (3)	0.0411 (8)
H7	0.2159	0.0829	0.3240	0.049*
C20	0.4423 (2)	0.6610 (5)	0.8525 (3)	0.0618 (10)
H20A	0.5025	0.6544	0.9048	0.093*
H20B	0.4204	0.5632	0.8665	0.093*
H20C	0.4254	0.7680	0.8666	0.093*

supplementary materials

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0396 (3)	0.0265 (3)	0.0406 (3)	0.000	0.0241 (3)	0.000
Cl1	0.0508 (5)	0.0672 (7)	0.0368 (5)	0.0024 (5)	0.0170 (4)	-0.0017 (4)
N1	0.0480 (16)	0.0252 (14)	0.0447 (16)	-0.0017 (13)	0.0266 (14)	-0.0018 (12)
O1	0.0385 (12)	0.0252 (12)	0.0398 (13)	-0.0011 (9)	0.0147 (11)	0.0018 (9)
O2	0.118 (2)	0.0396 (15)	0.0717 (19)	0.0145 (15)	0.0654 (18)	0.0053 (13)
C1	0.0474 (19)	0.0295 (17)	0.049 (2)	-0.0093 (15)	0.0324 (18)	-0.0109 (15)
C2	0.0352 (16)	0.0332 (17)	0.0381 (17)	0.0000 (15)	0.0251 (15)	-0.0016 (14)
C3	0.0362 (17)	0.0296 (18)	0.0398 (18)	0.0007 (14)	0.0253 (16)	0.0008 (14)
C4	0.0429 (18)	0.0338 (18)	0.0427 (19)	-0.0015 (15)	0.0248 (16)	0.0013 (15)
C5	0.050 (2)	0.0404 (19)	0.045 (2)	0.0080 (17)	0.0314 (17)	0.0103 (16)
C6	0.0379 (18)	0.050 (2)	0.0327 (17)	0.0020 (16)	0.0214 (15)	-0.0004 (15)
C7	0.0457 (19)	0.0416 (19)	0.0409 (19)	-0.0048 (17)	0.0299 (17)	-0.0087 (16)
C20	0.068 (3)	0.054 (2)	0.062 (3)	0.002 (2)	0.040 (2)	-0.001 (2)

Geometric parameters (\AA , $^\circ$)

Cu1—O1 ⁱ	1.9152 (19)	C2—C3	1.414 (4)
Cu1—O1	1.9152 (19)	C2—C7	1.415 (4)
Cu1—N1	1.939 (2)	C3—C4	1.402 (4)
Cu1—N1 ⁱ	1.939 (2)	C4—C5	1.372 (4)
Cl1—C6	1.754 (3)	C4—H4	0.93
N1—C1	1.272 (4)	C5—C6	1.380 (4)
N1—H1	0.86	C5—H5	0.93
O1—C3	1.315 (3)	C6—C7	1.355 (4)
O2—C20	1.400 (4)	C7—H7	0.93
O2—H2	0.82	C20—H20A	0.96
C1—C2	1.440 (4)	C20—H20B	0.96
C1—H1A	0.93	C20—H20C	0.96
O1 ⁱ —Cu1—O1	84.48 (12)	C4—C3—C2	117.4 (3)
O1 ⁱ —Cu1—N1	172.02 (10)	C5—C4—C3	122.0 (3)
O1—Cu1—N1	92.03 (9)	C5—C4—H4	119.0
O1 ⁱ —Cu1—N1 ⁱ	92.03 (9)	C3—C4—H4	119.0
O1—Cu1—N1 ⁱ	172.02 (10)	C4—C5—C6	119.6 (3)
N1—Cu1—N1 ⁱ	92.31 (15)	C4—C5—H5	120.2
C1—N1—Cu1	127.5 (2)	C6—C5—H5	120.2
C1—N1—H1	116.2	C7—C6—C5	121.1 (3)
Cu1—N1—H1	116.2	C7—C6—Cl1	119.6 (3)
C3—O1—Cu1	128.18 (18)	C5—C6—Cl1	119.3 (2)
C20—O2—H2	109.5	C6—C7—C2	120.3 (3)
N1—C1—C2	125.3 (3)	C6—C7—H7	119.8
N1—C1—H1A	117.3	C2—C7—H7	119.8
C2—C1—H1A	117.3	O2—C20—H20A	109.5
C3—C2—C7	119.6 (3)	O2—C20—H20B	109.5

C3—C2—C1	122.7 (3)	H20A—C20—H20B	109.5
C7—C2—C1	117.6 (3)	O2—C20—H20C	109.5
O1—C3—C4	118.8 (3)	H20A—C20—H20C	109.5
O1—C3—C2	123.8 (3)	H20B—C20—H20C	109.5
O1—Cu1—N1—C1	4.2 (3)	C7—C2—C3—C4	-1.0 (4)
N1 ⁱ —Cu1—N1—C1	-169.1 (3)	C1—C2—C3—C4	-177.5 (3)
O1 ⁱ —Cu1—O1—C3	179.9 (3)	O1—C3—C4—C5	-178.1 (3)
N1—Cu1—O1—C3	-7.3 (3)	C2—C3—C4—C5	0.5 (5)
Cu1—N1—C1—C2	0.4 (5)	C3—C4—C5—C6	0.4 (5)
N1—C1—C2—C3	-4.3 (5)	C4—C5—C6—C7	-0.8 (5)
N1—C1—C2—C7	179.2 (3)	C4—C5—C6—C11	177.9 (2)
Cu1—O1—C3—C4	-175.7 (2)	C5—C6—C7—C2	0.3 (5)
Cu1—O1—C3—C2	5.8 (4)	C11—C6—C7—C2	-178.4 (2)
C7—C2—C3—O1	177.5 (3)	C3—C2—C7—C6	0.7 (5)
C1—C2—C3—O1	1.1 (5)	C1—C2—C7—C6	177.3 (3)

Symmetry codes: (i) $-x+1, y, -z+3/2$.

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O2—H2 \cdots O1	0.82	2.04	2.822 (3)	160
N1—H1 \cdots O2 ⁱⁱ	0.86	2.20	2.986 (4)	153

Symmetry codes: (ii) $x, y-1, z$.

Fig. 1

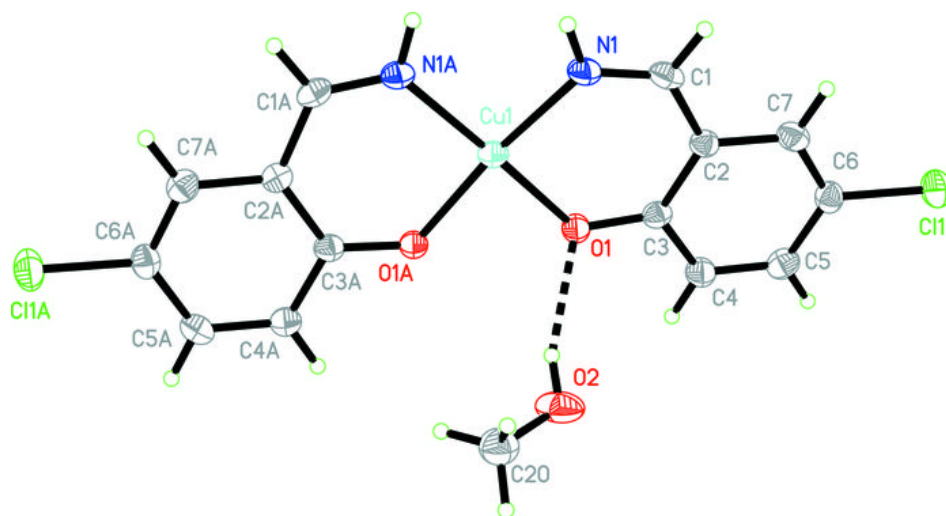


Fig. 2

