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{4,4',6,6'-Tetraiodo-2,2'-[2,2-dimethylpropane-1,3-diylbis(nitrilomethanylylidene)]diphenolato}copper(II)

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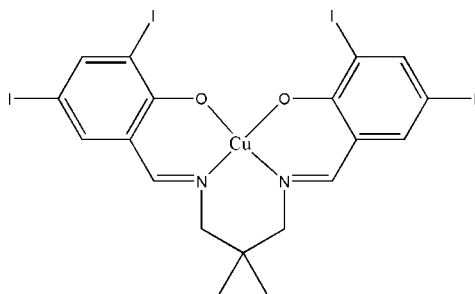
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; R factor = 0.026; wR factor = 0.059; data-to-parameter ratio = 18.0.

In the title compound, $[\text{Cu}(\text{C}_{19}\text{H}_{16}\text{I}_4\text{N}_2\text{O}_2)]$, the Cu^{II} atom and the substituted C atom of the diamine segment lie on a crystallographic twofold rotation axis. The geometry around the Cu^{II} atom is distorted square-planar, which is supported by the N_2O_2 donor atoms of the coordinated Schiff base. The dihedral angle between the symmetry-related substituted benzene rings is $29.40(19)^\circ$. In the crystal, a short $\text{I}\cdots\text{I}$ [$3.8766(6)$ Å] contact is present and links neighbouring molecules into chains propagating along the a axis.

Related literature

For applications of Schiff base ligands in coordination chemistry, see: Granovski *et al.* (1993); Blower (1998). For a related structure, see: Kargar *et al.* (2012). For standard values of bond lengths, see: Allen *et al.* (1987). For van der Waals radii, see: Bondi (1964).



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Experimental

Crystal data

$[\text{Cu}(\text{C}_{19}\text{H}_{16}\text{I}_4\text{N}_2\text{O}_2)]$
 $M_r = 875.48$
 Orthorhombic, $Pbcn$
 $a = 16.9336(10)$ Å
 $b = 15.9602(12)$ Å
 $c = 8.7041(5)$ Å
 $V = 2352.4(3)$ Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 6.20$ mm⁻¹
 $T = 296$ K
 $0.21 \times 0.12 \times 0.08$ mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2005)
 $T_{\text{min}} = 0.269$, $T_{\text{max}} = 0.551$
 9807 measured reflections
 2321 independent reflections
 1791 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.030$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.059$
 $S = 1.04$
 2321 reflections
 129 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.94$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.67$ e Å⁻³

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT (Bruker, 2005); 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: SHELXTL and PLATON (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2420).

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supporting information

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{4,4',6,6'-Tetraiodo-2,2'-[2,2-dimethylpropane-1,3-diylbis(nitrilomethanylylidene)]diphenolato}copper(II)

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S1. Comment

Schiff base complexes are one of the most important stereochemical models in transition metal coordination chemistry, owing to their ease of preparation and structural variations (Granovski *et al.*, 1993; Blower, 1998).

The asymmetric unit of the title compound, Fig. 1, comprises half of a tetradentate Schiff base ligand. Atoms Cu1 and C9 lie on a crystallographic two-fold rotation axis. The geometry around the Cu^{II} atom is distorted square-planar which is supported by the N₂O₂ donor atoms of the coordinated Schiff base. The dihedral angle between the symmetry-related substituted benzene rings is 29.40 (19)°. The bond lengths (Allen *et al.*, 1987) and angles are within the normal ranges and are comparable to those reported for a related structure (Kargar *et al.*, 2012).

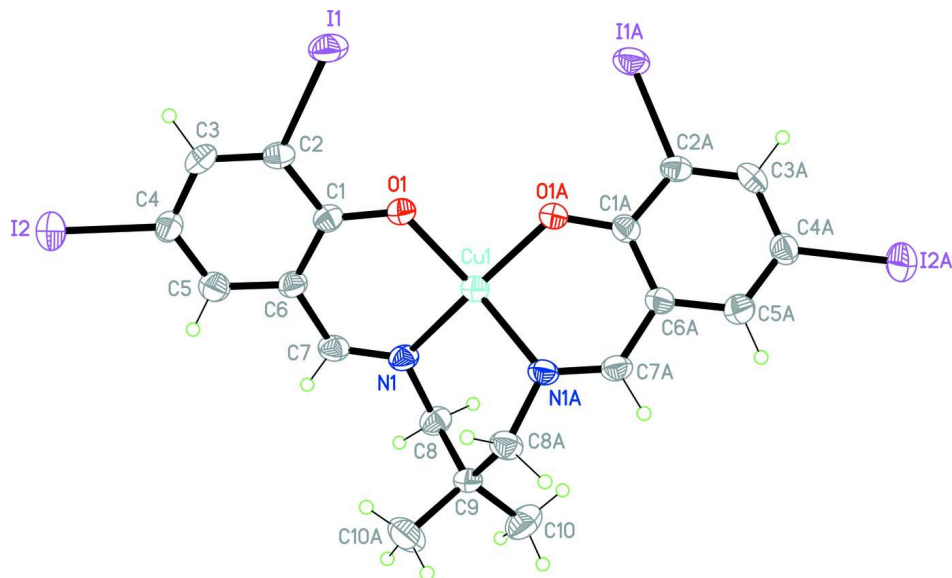
In the crystal, a short I...I [3.8766 (6) Å] contact is present, which is shorter than the sum of the van der Waals radii of I atoms [3.96 Å; Bondi, 1964]. It links neighbouring molecules along the *a* axis forming chains.

S2. Experimental

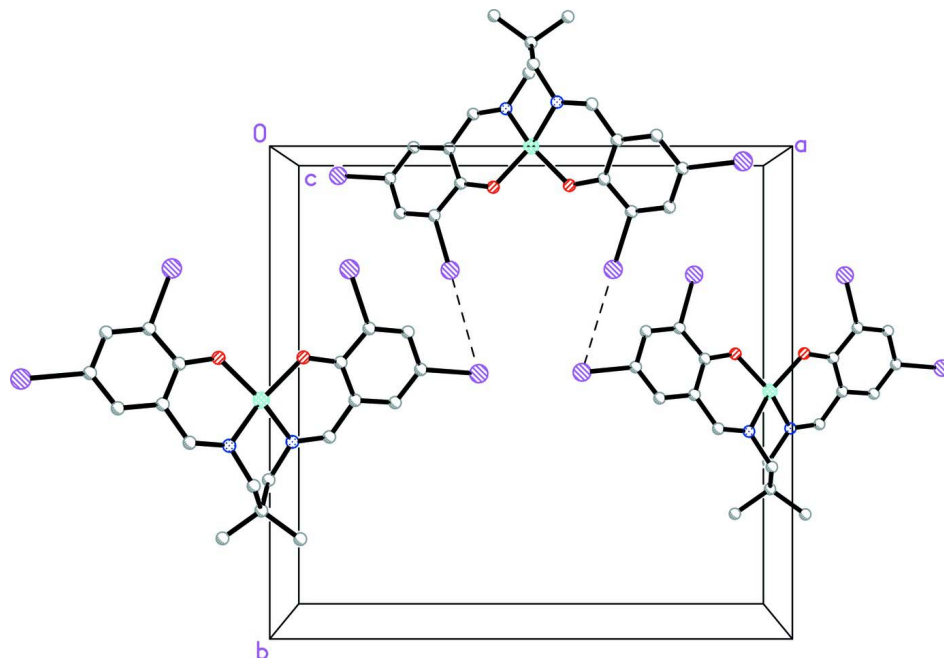
The title compound was synthesized by adding 3,5-diiodo-salicylaldehyde-2,2-dimethyl-1,3-propanediamine (2 mmol) to a solution of CuCl₂·4H₂O (2.1 mmol) in ethanol (30 ml). The mixture was refluxed with stirring for 30 min. The resultant solution was filtered. Red single crystals of the title compound, suitable for X-ray structure analysis, were obtained from ethanol by slow evaporation of the solvent at room temperature over several days.

S3. Refinement

The H-atoms were included in calculated positions and treated as riding atoms: C—H = 0.93, 0.96 and 0.97 Å for CH, CH₃ and CH₂ H-atoms, respectively, with U_{iso}(H) = k x U_{eq}(C), where k = 1.5 for CH₃ H-atoms, and = 1.2 for other H-atoms.

**Figure 1**

A view of the molecular structure of the title compound, showing 40% probability displacement ellipsoids and the atomic numbering [symmetry code: (A) = $-x, y, -z+1/2$].

**Figure 2**

The crystal packing of the title compound viewed along the *c*-axis, showing how the molecules are linked via the intermolecular I...I interactions (dashed lines) to form chains along the *a* axis [the H atoms have been omitted for clarity].

{4,4',6,6'-Tetraiodo-2,2'-[2,2-dimethylpropane-1,3-diylbis(nitrilomethanylylidene)]diphenolato}copper(II)*Crystal data*[Cu(C₁₉H₁₆I₄N₂O₂)] $M_r = 875.48$ Orthorhombic, *Pbcn*

Hall symbol: -P 2n 2ab

 $a = 16.9336$ (10) Å $b = 15.9602$ (12) Å $c = 8.7041$ (5) Å $V = 2352.4$ (3) Å³ $Z = 4$ $F(000) = 1604$ $D_x = 2.472$ Mg m⁻³Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1126 reflections

 $\theta = 2.5$ – 27.5° $\mu = 6.20$ mm⁻¹ $T = 296$ K

Block, red

 $0.21 \times 0.12 \times 0.08$ mm*Data collection*Bruker SMART APEXII CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

 φ and ω scansAbsorption correction: multi-scan
(*SADABS*; Bruker, 2005) $T_{\min} = 0.269$, $T_{\max} = 0.551$

9807 measured reflections

2321 independent reflections

1791 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.030$ $\theta_{\max} = 26.0^\circ$, $\theta_{\min} = 2.4^\circ$ $h = -20 \rightarrow 20$ $k = -13 \rightarrow 19$ $l = -9 \rightarrow 10$ *Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.026$ $wR(F^2) = 0.059$ $S = 1.04$

2321 reflections

129 parameters

0 restraints

Primary atom site location: structure-invariant
direct methodsSecondary atom site location: difference Fourier
mapHydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.021P)^2 + 2.4697P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.001$ $\Delta\rho_{\max} = 0.94$ e Å⁻³ $\Delta\rho_{\min} = -0.67$ e Å⁻³*Special details*

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\sigma(F^2)$ 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 (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
I1	0.16096 (2)	0.747572 (19)	0.30639 (4)	0.04900 (11)
I2	0.39828 (2)	0.53650 (3)	0.63814 (5)	0.06704 (14)
Cu1	0.0000	0.48949 (5)	0.2500	0.03357 (18)
O1	0.07523 (17)	0.57300 (18)	0.3038 (3)	0.0384 (7)
N1	0.0505 (2)	0.4038 (2)	0.3745 (4)	0.0348 (8)

C1	0.1415 (2)	0.5623 (3)	0.3769 (4)	0.0332 (10)
C2	0.1945 (3)	0.6301 (3)	0.3943 (4)	0.0350 (10)
C3	0.2653 (2)	0.6228 (3)	0.4678 (4)	0.0384 (11)
H3	0.2985	0.6691	0.4758	0.046*
C4	0.2882 (2)	0.5464 (3)	0.5306 (5)	0.0394 (10)
C5	0.2393 (3)	0.4793 (3)	0.5191 (5)	0.0417 (11)
H5	0.2547	0.4283	0.5613	0.050*
C6	0.1657 (2)	0.4854 (3)	0.4444 (5)	0.0348 (10)
C7	0.1168 (2)	0.4116 (3)	0.4443 (5)	0.0364 (10)
H7	0.1349	0.3656	0.4997	0.044*
C8	0.0045 (3)	0.3268 (3)	0.3955 (4)	0.0401 (10)
H8A	-0.0486	0.3416	0.4270	0.048*
H8B	0.0281	0.2941	0.4776	0.048*
C9	0.0000	0.2724 (4)	0.2500	0.0369 (14)
C10	-0.0730 (3)	0.2171 (3)	0.2632 (6)	0.0599 (14)
H10A	-0.0709	0.1862	0.3578	0.090*
H10B	-0.0745	0.1787	0.1783	0.090*
H10C	-0.1195	0.2515	0.2618	0.090*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.0663 (2)	0.03097 (18)	0.04979 (18)	-0.00876 (16)	-0.00490 (15)	0.00638 (14)
I2	0.04541 (19)	0.0625 (3)	0.0932 (3)	0.00148 (19)	-0.02547 (19)	-0.0029 (2)
Cu1	0.0359 (4)	0.0272 (4)	0.0376 (4)	0.000	-0.0041 (3)	0.000
O1	0.0396 (16)	0.0278 (16)	0.0478 (17)	-0.0031 (14)	-0.0093 (14)	0.0029 (14)
N1	0.041 (2)	0.027 (2)	0.0359 (18)	-0.0058 (17)	-0.0016 (16)	0.0042 (16)
C1	0.037 (2)	0.032 (2)	0.031 (2)	-0.003 (2)	-0.0005 (18)	-0.0022 (19)
C2	0.042 (2)	0.028 (2)	0.035 (2)	-0.004 (2)	0.0031 (19)	0.0039 (19)
C3	0.038 (2)	0.037 (3)	0.041 (2)	-0.012 (2)	0.0025 (19)	-0.007 (2)
C4	0.033 (2)	0.041 (3)	0.045 (2)	-0.003 (2)	-0.002 (2)	-0.003 (2)
C5	0.045 (3)	0.037 (3)	0.043 (3)	0.003 (2)	-0.005 (2)	-0.001 (2)
C6	0.038 (2)	0.029 (2)	0.037 (2)	-0.0042 (19)	-0.0026 (19)	0.0021 (19)
C7	0.046 (3)	0.028 (2)	0.036 (2)	0.000 (2)	-0.002 (2)	0.0057 (19)
C8	0.048 (3)	0.035 (3)	0.036 (2)	-0.008 (2)	-0.0007 (19)	0.004 (2)
C9	0.041 (3)	0.024 (3)	0.045 (3)	0.000	-0.007 (3)	0.000
C10	0.063 (3)	0.050 (3)	0.066 (3)	-0.022 (3)	-0.006 (3)	-0.002 (3)

Geometric parameters (Å, °)

I1—C2	2.103 (4)	C4—C5	1.358 (6)
I2—C4	2.092 (4)	C5—C6	1.409 (6)
Cu1—O1	1.902 (3)	C5—H5	0.9300
Cu1—O1 ⁱ	1.902 (3)	C6—C7	1.439 (6)
Cu1—N1 ⁱ	1.944 (3)	C7—H7	0.9300
Cu1—N1	1.944 (3)	C8—C9	1.538 (5)
O1—C1	1.301 (5)	C8—H8A	0.9700
N1—C7	1.283 (5)	C8—H8B	0.9700

N1—C8	1.466 (5)	C9—C10	1.522 (6)
C1—C2	1.414 (6)	C9—C10 ⁱ	1.522 (6)
C1—C6	1.422 (6)	C9—C8 ⁱ	1.538 (5)
C2—C3	1.364 (6)	C10—H10A	0.9600
C3—C4	1.391 (6)	C10—H10B	0.9600
C3—H3	0.9300	C10—H10C	0.9600
O1—Cu1—O1 ⁱ	91.04 (17)	C5—C6—C1	120.4 (4)
O1—Cu1—N1 ⁱ	157.69 (13)	C5—C6—C7	116.9 (4)
O1 ⁱ —Cu1—N1 ⁱ	93.51 (13)	C1—C6—C7	122.7 (4)
O1—Cu1—N1	93.51 (13)	N1—C7—C6	125.7 (4)
O1 ⁱ —Cu1—N1	157.69 (13)	N1—C7—H7	117.2
N1 ⁱ —Cu1—N1	90.5 (2)	C6—C7—H7	117.2
C1—O1—Cu1	127.3 (3)	N1—C8—C9	113.4 (3)
C7—N1—C8	119.2 (4)	N1—C8—H8A	108.9
C7—N1—Cu1	125.5 (3)	C9—C8—H8A	108.9
C8—N1—Cu1	115.2 (3)	N1—C8—H8B	108.9
O1—C1—C2	120.0 (4)	C9—C8—H8B	108.9
O1—C1—C6	124.3 (4)	H8A—C8—H8B	107.7
C2—C1—C6	115.7 (4)	C10—C9—C10 ⁱ	109.2 (6)
C3—C2—C1	122.9 (4)	C10—C9—C8	107.8 (3)
C3—C2—I1	119.0 (3)	C10 ⁱ —C9—C8	110.4 (3)
C1—C2—I1	118.1 (3)	C10—C9—C8 ⁱ	110.4 (3)
C2—C3—C4	120.2 (4)	C10 ⁱ —C9—C8 ⁱ	107.8 (3)
C2—C3—H3	119.9	C8—C9—C8 ⁱ	111.2 (5)
C4—C3—H3	119.9	C9—C10—H10A	109.5
C5—C4—C3	119.6 (4)	C9—C10—H10B	109.5
C5—C4—I2	121.1 (3)	H10A—C10—H10B	109.5
C3—C4—I2	119.3 (3)	C9—C10—H10C	109.5
C4—C5—C6	121.3 (4)	H10A—C10—H10C	109.5
C4—C5—H5	119.4	H10B—C10—H10C	109.5
C6—C5—H5	119.4		
O1 ⁱ —Cu1—O1—C1	168.3 (4)	C2—C3—C4—I2	178.6 (3)
N1 ⁱ —Cu1—O1—C1	-89.9 (5)	C3—C4—C5—C6	0.1 (7)
N1—Cu1—O1—C1	10.1 (3)	I2—C4—C5—C6	-178.9 (3)
O1—Cu1—N1—C7	-7.0 (4)	C4—C5—C6—C1	1.0 (6)
O1 ⁱ —Cu1—N1—C7	-108.3 (4)	C4—C5—C6—C7	-177.3 (4)
N1 ⁱ —Cu1—N1—C7	151.1 (4)	O1—C1—C6—C5	178.8 (4)
O1—Cu1—N1—C8	168.9 (3)	C2—C1—C6—C5	-1.6 (6)
O1 ⁱ —Cu1—N1—C8	67.5 (5)	O1—C1—C6—C7	-3.0 (6)
N1 ⁱ —Cu1—N1—C8	-33.1 (2)	C2—C1—C6—C7	176.6 (4)
Cu1—O1—C1—C2	173.7 (3)	C8—N1—C7—C6	-175.1 (4)
Cu1—O1—C1—C6	-6.8 (6)	Cu1—N1—C7—C6	0.5 (6)
O1—C1—C2—C3	-179.1 (4)	C5—C6—C7—N1	-175.5 (4)
C6—C1—C2—C3	1.3 (6)	C1—C6—C7—N1	6.2 (7)
O1—C1—C2—I1	2.2 (5)	C7—N1—C8—C9	-111.6 (4)
C6—C1—C2—I1	-177.3 (3)	Cu1—N1—C8—C9	72.3 (4)

C1—C2—C3—C4	-0.4 (6)	N1—C8—C9—C10	-157.0 (4)
I1—C2—C3—C4	178.3 (3)	N1—C8—C9—C10 ⁱ	83.8 (5)
C2—C3—C4—C5	-0.4 (6)	N1—C8—C9—C8 ⁱ	-35.9 (2)

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