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Di- μ -thiocyanato-bis({2,4-dichloro-6-[2-(diethylamino)ethyliminomethyl]-phenolato}copper(II))

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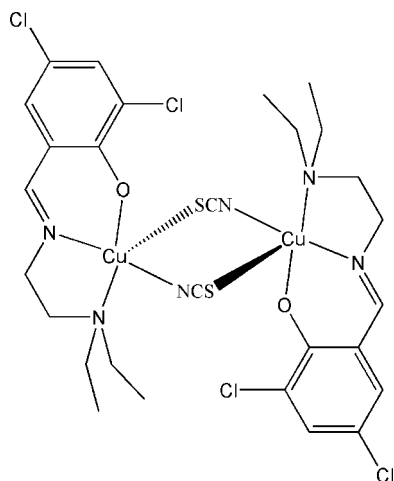
Received 17 November 2007; accepted 26 November 2007

Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.044; wR factor = 0.118; data-to-parameter ratio = 17.5.

The title compound, $[\text{Cu}_2(\text{NCS})_2(\text{C}_{13}\text{H}_{17}\text{Cl}_2\text{N}_2\text{O})_2]$, was obtained by the reaction of 3,5-dichlorosalicylaldehyde, *N,N*-diethylethane-1,2-diamine, sodium thiocyanate, and copper(II) acetate in an ethanol solution. It crystallizes as a centrosymmetric dimer with a very long $\text{Cu}\cdots\text{S}$ axial bond [2.972 (3) Å]. The Cu atom is five-coordinated by the three donor atoms of the Schiff base ligand, 2,4-dichloro-6-[2-(diethylamino)ethylimino)methyl]phenol, one N atom of a thiocyanate group, and one S atom of a symmetry-related thiocyanate group, forming a slightly distorted square-pyramidal geometry.

Related literature

For the biological activity of Schiff base compounds, see: Panneerselvam *et al.* (2005); Shi *et al.* (2007); Singh *et al.* (2006, 2007); Zhong *et al.* (2006). For related literature, see: Allen *et al.* (1987).



Experimental

Crystal data

$[\text{Cu}_2(\text{NCS})_2(\text{C}_{13}\text{H}_{17}\text{Cl}_2\text{N}_2\text{O})_2]$
 $M_r = 409.81$
 Monoclinic, $P2_1/c$
 $a = 8.632$ (2) Å
 $b = 14.115$ (3) Å
 $c = 14.002$ (3) Å
 $\beta = 90.491$ (4)°

$V = 1706.0$ (6) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 1.72$ mm⁻¹
 $T = 293$ (2) K
 $0.20 \times 0.17 \times 0.16$ mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 2004)
 $T_{\min} = 0.725$, $T_{\max} = 0.771$

13451 measured reflections
 3516 independent reflections
 3046 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.118$
 $S = 1.06$
 3516 reflections

201 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 1.34$ e Å⁻³
 $\Delta\rho_{\min} = -0.67$ e Å⁻³

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2001); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; 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: SU2031).

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supporting information

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Di- μ -thiocyanato-bis({2,4-dichloro-6-[2-(diethylamino)ethyliminomethyl]-phenolato}copper(II))

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S1. Comment

Schiff base compounds have been reported to have excellent biological activity (Shi *et al.*, 2007; Panneerselvam *et al.*, 2005). Metal complexes derived from the Schiff bases have also been shown to have excellent biological activity (Singh *et al.*, 2006, 2007; Zhong *et al.*, 2006). As part of our investigations of the structures of metal complexes derived from Schiff bases, we report herein the crystal structure of the title copper complex, (I).

Compound (I) is a centrosymmetric dinuclear copper(II) complex (Fig. 1). The Cu atom is five-coordinated by the three donor atoms (O1, N1 and N2) of the Schiff base ligand 2,4-dichloro-6-[(2-diethylaminoethylimino)methyl]phenol, one N atom of a thiocyanate group, and one S atom of the centrosymmetrically related thiocyanate group, so forming a slightly distorted square-pyramidal geometry. The Cu atom is displaced out of the best least-squares plane defined by the four basal donor atoms by 0.123 (2) Å. Apart from the long Cu...S axial bond [2.972 (3) Å], the other coordination bond distances and angles are within normal ranges (Allen *et al.*, 1987).

S2. Experimental

The title compound was obtained by the reaction of equimolar amounts of 3,5-dichlorosalicylaldehyde, *N,N*-diethyl-ethane-1,2-diamine, sodium thiocyanate, and copper acetate in an ethanol solution. Blue block-like single crystals were obtained by slow evaporation of the filtrate in air.

S3. Refinement

H atoms were positioned geometrically and treated as riding atoms, with C—H = 0.93–0.97 Å and $U_{\text{iso}}(\text{H}) = 1.2$ (1.5 for methyl groups) times $U_{\text{eq}}(\text{C})$.

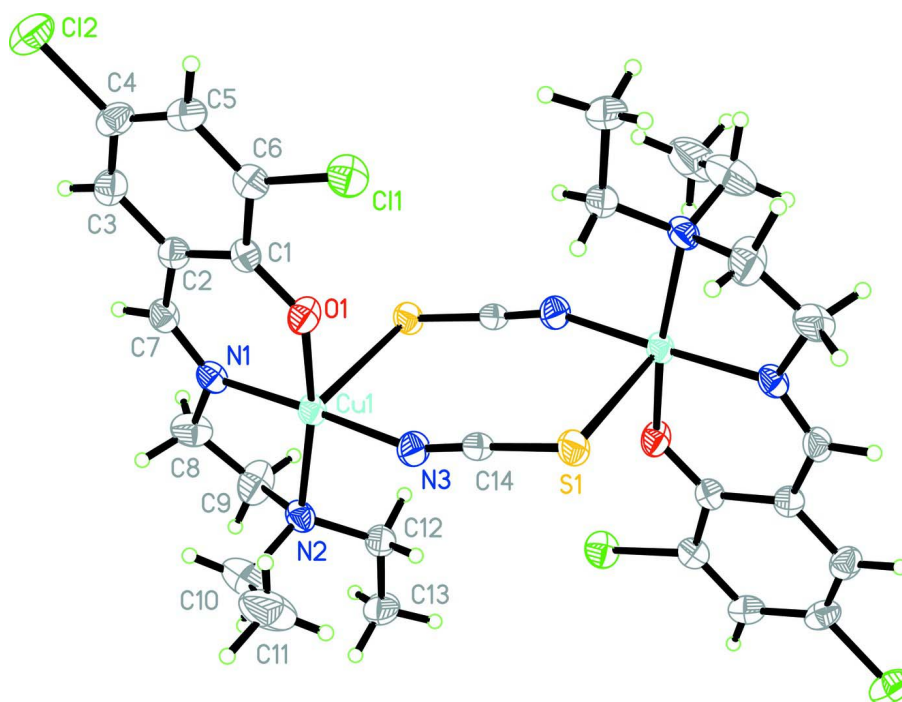


Figure 1

The molecular structure of complex (I), with atom labels and 30% probability displacement ellipsoids for non-H atoms.

Di- μ -thiocyanato-bis({2,4-dichloro-6-[2-(diethylamino)ethyliminomethyl]phenolato}copper(II))

Crystal data

$[\text{Cu}_2(\text{NCS})_2(\text{C}_{13}\text{H}_{17}\text{Cl}_2\text{N}_2\text{O})_2]$

$M_r = 409.81$

Monoclinic, $P2_1/c$

$a = 8.632(2) \text{ \AA}$

$b = 14.115(3) \text{ \AA}$

$c = 14.002(3) \text{ \AA}$

$\beta = 90.491(4)^\circ$

$V = 1706.0(6) \text{ \AA}^3$

$Z = 4$

$F(000) = 836$

$D_x = 1.596 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 6502 reflections

$\theta = 2.4\text{--}27.7^\circ$

$\mu = 1.72 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Block, blue

$0.20 \times 0.17 \times 0.16 \text{ mm}$

Data collection

Bruker SMART 1K CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans

Absorption correction: multi-scan
(*SADABS*; Sheldrick, 2004)

$T_{\min} = 0.725$, $T_{\max} = 0.771$

13451 measured reflections

3516 independent reflections

3046 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.024$

$\theta_{\max} = 26.5^\circ$, $\theta_{\min} = 2.1^\circ$

$h = -10 \rightarrow 10$

$k = -17 \rightarrow 17$

$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.118$
 $S = 1.06$
 3516 reflections
 201 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
 $w = 1/[\sigma^2(F_o^2) + (0.058P)^2 + 2.2599P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 1.34 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.67 \text{ e } \text{\AA}^{-3}$

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.13607 (4)	0.16622 (3)	0.06969 (3)	0.03794 (14)
O1	-0.0063 (3)	0.22330 (17)	-0.01736 (16)	0.0489 (6)
N1	0.1165 (3)	0.2683 (2)	0.16144 (18)	0.0410 (6)
N2	0.3213 (3)	0.1254 (2)	0.1558 (2)	0.0444 (6)
N3	0.1658 (4)	0.0673 (2)	-0.0253 (2)	0.0477 (7)
Cl1	-0.21684 (12)	0.25400 (7)	-0.17482 (6)	0.0585 (3)
Cl2	-0.33491 (14)	0.58481 (8)	-0.00046 (9)	0.0716 (3)
S1	0.10771 (10)	-0.05935 (7)	-0.17261 (6)	0.0476 (2)
C1	-0.0792 (4)	0.3018 (2)	-0.0076 (2)	0.0396 (7)
C2	-0.0634 (4)	0.3643 (2)	0.0713 (2)	0.0419 (7)
C3	-0.1427 (4)	0.4516 (3)	0.0723 (3)	0.0498 (8)
H3	-0.1293	0.4927	0.1236	0.060*
C4	-0.2389 (4)	0.4760 (3)	-0.0013 (3)	0.0510 (9)
C5	-0.2616 (4)	0.4157 (3)	-0.0785 (3)	0.0490 (8)
H5	-0.3279	0.4327	-0.1283	0.059*
C6	-0.1850 (4)	0.3311 (2)	-0.0802 (2)	0.0435 (7)
C7	0.0343 (4)	0.3430 (2)	0.1518 (2)	0.0450 (8)
H7	0.0382	0.3872	0.2010	0.054*
C8	0.2109 (5)	0.2585 (3)	0.2480 (3)	0.0621 (11)
H8A	0.2939	0.3048	0.2477	0.075*
H8B	0.1477	0.2698	0.3038	0.075*
C9	0.2742 (7)	0.1654 (3)	0.2521 (3)	0.0741 (14)
H9A	0.1983	0.1234	0.2803	0.089*
H9B	0.3644	0.1662	0.2939	0.089*
C10	0.4629 (6)	0.1738 (4)	0.1273 (4)	0.0883 (17)

H10A	0.4497	0.2409	0.1395	0.106*
H10B	0.5466	0.1518	0.1683	0.106*
C11	0.5099 (6)	0.1626 (5)	0.0307 (4)	0.114 (3)
H11A	0.5219	0.0964	0.0168	0.171*
H11B	0.6069	0.1945	0.0214	0.171*
H11C	0.4328	0.1893	-0.0111	0.171*
C12	0.3232 (5)	0.0217 (3)	0.1662 (3)	0.0581 (10)
H12A	0.3370	-0.0057	0.1034	0.070*
H12B	0.2221	0.0020	0.1886	0.070*
C13	0.4448 (5)	-0.0206 (3)	0.2326 (3)	0.0661 (11)
H13A	0.5456	0.0009	0.2140	0.099*
H13B	0.4406	-0.0884	0.2288	0.099*
H13C	0.4249	-0.0010	0.2970	0.099*
C14	0.1388 (3)	0.0159 (2)	-0.0861 (2)	0.0361 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0441 (2)	0.0384 (2)	0.0312 (2)	-0.00149 (16)	-0.00774 (16)	-0.00402 (15)
O1	0.0670 (16)	0.0426 (13)	0.0368 (12)	0.0082 (11)	-0.0161 (11)	-0.0057 (10)
N1	0.0423 (15)	0.0514 (16)	0.0293 (13)	-0.0062 (12)	-0.0044 (11)	-0.0049 (11)
N2	0.0438 (15)	0.0452 (16)	0.0441 (15)	-0.0062 (12)	-0.0110 (12)	0.0016 (12)
N3	0.0522 (17)	0.0497 (17)	0.0410 (15)	0.0019 (13)	-0.0060 (13)	-0.0096 (13)
C11	0.0706 (6)	0.0653 (6)	0.0392 (5)	0.0004 (5)	-0.0145 (4)	0.0011 (4)
C12	0.0714 (7)	0.0571 (6)	0.0867 (8)	0.0217 (5)	0.0217 (6)	0.0136 (5)
S1	0.0468 (5)	0.0543 (5)	0.0417 (5)	-0.0034 (4)	0.0008 (4)	-0.0165 (4)
C1	0.0425 (17)	0.0404 (17)	0.0358 (16)	-0.0053 (14)	0.0011 (13)	0.0028 (13)
C2	0.0423 (17)	0.0428 (17)	0.0406 (17)	-0.0016 (14)	0.0037 (13)	0.0003 (14)
C3	0.052 (2)	0.048 (2)	0.050 (2)	0.0001 (16)	0.0146 (16)	-0.0041 (16)
C4	0.0471 (19)	0.047 (2)	0.059 (2)	0.0088 (15)	0.0167 (17)	0.0094 (17)
C5	0.0420 (18)	0.056 (2)	0.049 (2)	0.0045 (15)	0.0060 (15)	0.0153 (16)
C6	0.0444 (17)	0.050 (2)	0.0359 (16)	-0.0046 (14)	0.0023 (13)	0.0064 (14)
C7	0.0479 (19)	0.049 (2)	0.0379 (17)	-0.0054 (15)	0.0026 (14)	-0.0117 (14)
C8	0.056 (2)	0.094 (3)	0.0361 (18)	0.006 (2)	-0.0135 (16)	-0.0129 (19)
C9	0.111 (4)	0.066 (3)	0.045 (2)	0.014 (2)	-0.031 (2)	-0.0106 (19)
C10	0.057 (3)	0.117 (5)	0.091 (4)	-0.022 (3)	-0.014 (3)	0.028 (3)
C11	0.057 (3)	0.187 (7)	0.100 (5)	-0.016 (4)	0.020 (3)	-0.061 (5)
C12	0.052 (2)	0.045 (2)	0.077 (3)	0.0055 (16)	-0.0224 (19)	-0.0060 (19)
C13	0.058 (2)	0.061 (2)	0.079 (3)	0.015 (2)	-0.020 (2)	0.000 (2)
C14	0.0315 (15)	0.0419 (17)	0.0350 (15)	0.0029 (12)	-0.0002 (12)	-0.0001 (13)

Geometric parameters (Å, °)

Cu1—O1	1.903 (2)	C4—C5	1.389 (6)
Cu1—N1	1.939 (3)	C5—C6	1.365 (5)
Cu1—N3	1.947 (3)	C5—H5	0.9300
Cu1—N2	2.076 (3)	C7—H7	0.9300
Cu1—S1 ⁱ	2.972 (3)	C8—C9	1.423 (6)

O1—C1	1.282 (4)	C8—H8A	0.9700
N1—C7	1.278 (4)	C8—H8B	0.9700
N1—C8	1.461 (4)	C9—H9A	0.9700
N2—C10	1.459 (5)	C9—H9B	0.9700
N2—C12	1.470 (5)	C10—C11	1.424 (8)
N2—C9	1.520 (5)	C10—H10A	0.9700
N3—C14	1.141 (4)	C10—H10B	0.9700
C11—C6	1.734 (4)	C11—H11A	0.9600
C12—C4	1.745 (4)	C11—H11B	0.9600
S1—C14	1.632 (3)	C11—H11C	0.9600
C1—C2	1.420 (5)	C12—C13	1.518 (5)
C1—C6	1.422 (5)	C12—H12A	0.9700
C2—C3	1.410 (5)	C12—H12B	0.9700
C2—C7	1.434 (5)	C13—H13A	0.9600
C3—C4	1.362 (5)	C13—H13B	0.9600
C3—H3	0.9300	C13—H13C	0.9600
O1—Cu1—N1	92.89 (11)	N1—C7—H7	117.3
O1—Cu1—N3	87.38 (11)	C2—C7—H7	117.3
N1—Cu1—N3	176.78 (12)	C9—C8—N1	109.4 (3)
O1—Cu1—N2	168.48 (11)	C9—C8—H8A	109.8
N1—Cu1—N2	83.82 (12)	N1—C8—H8A	109.8
N3—Cu1—N2	95.29 (12)	C9—C8—H8B	109.8
O1—Cu1—S1 ⁱ	93.98 (12)	N1—C8—H8B	109.8
N1—Cu1—S1 ⁱ	89.43 (12)	H8A—C8—H8B	108.2
N2—Cu1—S1 ⁱ	97.02 (12)	C8—C9—N2	114.4 (4)
N3—Cu1—S1 ⁱ	93.75 (12)	C8—C9—H9A	108.7
C1—O1—Cu1	127.8 (2)	N2—C9—H9A	108.7
C7—N1—C8	118.1 (3)	C8—C9—H9B	108.7
C7—N1—Cu1	126.5 (2)	N2—C9—H9B	108.7
C8—N1—Cu1	115.4 (2)	H9A—C9—H9B	107.6
C10—N2—C12	119.0 (4)	C11—C10—N2	117.0 (5)
C10—N2—C9	107.4 (4)	C11—C10—H10A	108.0
C12—N2—C9	106.6 (3)	N2—C10—H10A	108.0
C10—N2—Cu1	110.7 (3)	C11—C10—H10B	108.0
C12—N2—Cu1	110.0 (2)	N2—C10—H10B	108.0
C9—N2—Cu1	101.6 (2)	H10A—C10—H10B	107.3
C14—N3—Cu1	159.8 (3)	C10—C11—H11A	109.5
O1—C1—C2	125.2 (3)	C10—C11—H11B	109.5
O1—C1—C6	119.2 (3)	H11A—C11—H11B	109.5
C2—C1—C6	115.6 (3)	C10—C11—H11C	109.5
C3—C2—C1	120.5 (3)	H11A—C11—H11C	109.5
C3—C2—C7	117.2 (3)	H11B—C11—H11C	109.5
C1—C2—C7	122.3 (3)	N2—C12—C13	117.3 (3)
C4—C3—C2	120.4 (3)	N2—C12—H12A	108.0
C4—C3—H3	119.8	C13—C12—H12A	108.0
C2—C3—H3	119.8	N2—C12—H12B	108.0
C3—C4—C5	121.0 (3)	C13—C12—H12B	108.0

C3—C4—C12	120.3 (3)	H12A—C12—H12B	107.2
C5—C4—C12	118.7 (3)	C12—C13—H13A	109.5
C6—C5—C4	119.0 (3)	C12—C13—H13B	109.5
C6—C5—H5	120.5	H13A—C13—H13B	109.5
C4—C5—H5	120.5	C12—C13—H13C	109.5
C5—C6—C1	123.4 (3)	H13A—C13—H13C	109.5
C5—C6—C11	119.2 (3)	H13B—C13—H13C	109.5
C1—C6—C11	117.4 (3)	N3—C14—S1	177.6 (3)
N1—C7—C2	125.3 (3)		

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