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Dichloro[2-chloro-6-(mercaptopyridin-2-yl)-pyridine]copper(II)

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The title compound, [$CuCl_2(C_{10}H_7ClN_2S)$], crystallizes as neutral $CuCl_2L$ [L = 2-chloro-6-(mercaptopyridin-2-yl)-pyridine] molecular units. The copper(II) centre adopts a distorted four-coordinate geometry comprising the two pyridinyl N atoms of the bidentate chelating ligand [Cu—N 2.012 (2) and 2.029 (2) Å] and the two chloride anions [Cu—Cl 2.2049 (6) and 2.2335 (6) Å]. The dihedral angle δ quantifying the extent of the distortion of the geometry from square planar (δ = 0°) towards tetrahedral (δ = 90°) is 36.81 (6)°. There is evidence for the formation of dimeric units *via* Cl···S interactions.

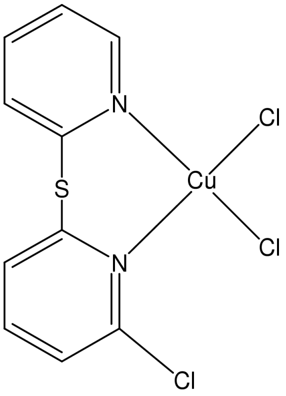
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.003 Å
R factor = 0.029
wR factor = 0.071
Data-to-parameter ratio = 19.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The structure of $CuCl_2L$ [L = 2-chloro-6-(mercaptopyridin-2-yl)pyridine], (I), is that of a neutral molecular complex (Fig. 1) in which the copper(II) centre has a distorted four-coordinate geometry comprising the two N atoms of the bidentate chelating ligand L [Cu—N 2.012 (2) and 2.029 (2) Å] and the two chloride anions [Cu—Cl 2.2049 (6) and 2.2335 (6) Å]. The coordination geometry lies between square planar and tetrahedral, with a dihedral angle (δ) between the CuN_2 and $CuCl_2$ planes of 36.81 (6)°. Distortion from planarity is unusual for copper(II) complexes. Here, it is attributed to steric repulsion between a coordinated chloride anion and the Cl atom at the 2-position of the pyridine ring [Cl···Cl 3.787 (1) Å].



(I)

There is considerable evidence for dimer formation through Cl···S interactions (Fig. 2). Not only is the Cu···Cl distance to the chloride anion involved in dimer formation [2.2335 (6) Å] significantly longer than that to the other chloride anion [2.2049 (6) Å], but also the U_{eq} value for the former [0.02691 (13) Å^2] is considerably smaller than that for the

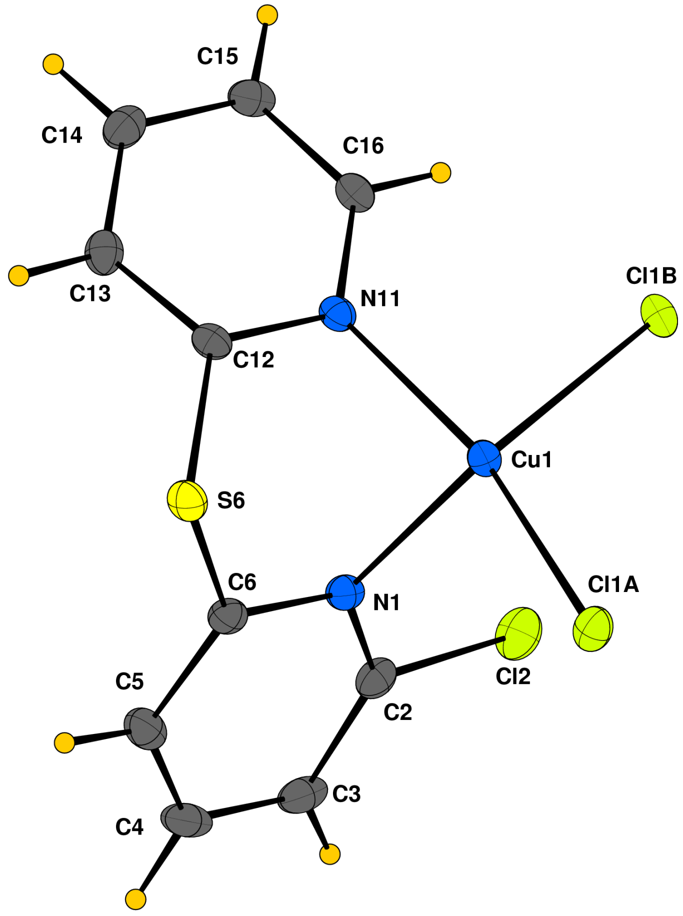


Figure 1
A view of the title compound showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

latter [0.03713 (16) Å^2]. A search of the Cambridge Structural Database (Allen & Kennard, 1993) revealed that the intra-dimer Cl$\cdots$S separation [3.4085 (9) Å] is typical for the distance separating the chloride anion of a $CuCl_2$ fragment and the S atom of either an aromatic or an aliphatic thioether.

Experimental

The title compound, (I), was obtained as a green lath-shaped crystal in the midst of a crop of green acicular crystals. Both had been produced by vapour phase diffusion of diethyl ether into a methanol solution of the product of the reaction between a methanol solution (10 ml) of copper(II) chloride dihydrate (0.199 g, 0.704 mmol) and a methanol solution (20 ml) of 2-(3,5-dimethylpyrazol-1-yl)-6-(mercaptopyridin-2-yl)pyridine (0.198 g, 0.701 mmol). This last ligand had been previously prepared by treatment of 2-chloro-6-(mercaptopyridin-2-yl)pyridine with 3,5-dimethylpyrazole in the presence of sodium hydride. Mass spectrometric (electrospray), IR and analytical studies of the bulk product suggested that it comprised dichloro[2-(3,5-dimethylpyrazol-1-yl)-6-(mercaptopyridin-2-yl)pyridine]copper(II) (yield: 0.123 g, 0.290 mmol, 42%). It is assumed that the lath-shaped crystal was a rogue crystal resulting from the presence of a small amount of unreacted 2-chloro-6-(mercaptopyridin-2-yl)pyridine in the sample of 2-(3,5-dimethylpyrazol-1-yl)-6-(mercaptopyridin-2-yl)pyridine.

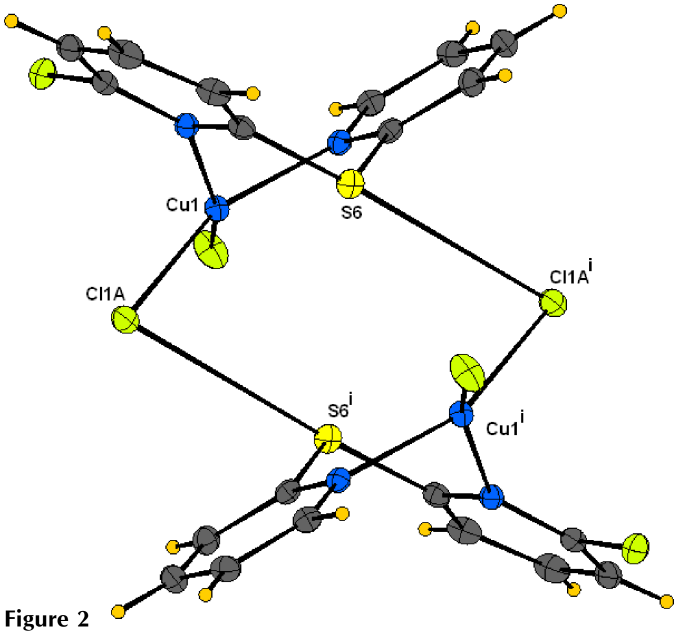


Figure 2
A view of the structure showing the pairwise centrosymmetric Cl$\cdots$S interactions leading to dimer formation. Displacement ellipsoids are drawn at the 30% probablility level. [Symmetry code (i): 3/2 $-x$, 1/2$-y$, 1$-z$.]

Crystal data

$C_{10}H_7Cl_3CuN_2S$
$M_r = 357.13$
Monoclinic, $C2/c$
$a = 13.1739$ (12) Å
$b = 9.6928$ (9) Å
$c = 21.137$ (2) Å
$\beta = 104.510$ (2)°
$V = 2612.9$ (4) Å^3
$Z = 8$
$D_x = 1.816$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3638 reflections
$\theta = 2.7$–26.8°
$\mu = 2.42$ mm^{-1}
$T = 150$ (2) K
Lath, green
0.36 × 0.11 × 0.06 mm

Data collection

Bruker SMART APEX area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
$T_{\min} = 0.782$, $T_{\max} = 0.870$
12577 measured reflections
3191 independent reflections
2709 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.026$
$\theta_{\max} = 28.2$°
$h = -16 \rightarrow 17$
$k = -12 \rightarrow 12$
$l = -25 \rightarrow 26$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.071$
$S = 1.04$
3019 reflections
154 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.035P)^2 + 3.807P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.42$ e Å^{-3}
$\Delta\rho_{\min} = -0.25$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—Cl1*A*	2.2335 (6)	Cu1—N1	2.029 (2)
Cu1—Cl1*B*	2.2049 (6)	Cu1—N11	2.012 (2)
Cl1*A*—Cu1—Cl1*B*	97.73 (2)	N1—Cu1—N11	87.58 (7)
Cl1*A*—Cu1—N1	90.65 (5)	C2—N1—Cu1	121.67 (15)
Cl1*A*—Cu1—N11	152.02 (5)	C6—N1—Cu1	119.37 (14)
Cl1*B*—Cu1—N11	95.96 (5)	C12—N11—Cu1	118.91 (14)
Cl1*B*—Cu1—N1	154.01 (5)	C16—N11—Cu1	123.11 (15)

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After location from ΔF syntheses, the aromatic H atoms were placed geometrically and refined with a riding model in which the C—H distance was constrained to be 0.93 Å and $U_{\rm iso}(H) = 1.2U_{\rm eq}(C)$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT* and *SHELXTL/*PC (Bruker, 1997); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *SHELXL*97 and *PLATON* (Spek, 2001).

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