metal-organic compounds

Dichlorobis(2-chloro-5-methyl-pyridine-κN)copper(II)

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In the crystals of the title compound, [CuCl$_2$(C$_6$H$_6$ClN)$_2$], the Cu atom lies on an inversion centre and is four-coordinated by two pyridine N atoms and two Cl atoms in *trans* positions. The coordination geometry is square planar, with Cu—N and Cu—Cl distances of 1.986 (2) and 2.2536 (11) Å, respectively. The two pyridine rings are parallel, but twist from the CuN$_2$Cl$_2$ coordination plane by about 95° in the complex molecule. There are three kinds of intermolecular C—H···Cl hydrogen bonds in the crystals. Two of these types generate two-dimensional molecular networks, viewed in the direction of the *a* axis, and the other connects adjacent molecular networks.

Comment

2-Chloro-5-methylpyridine is a very important intermediate for the preparation of biological active compounds, especially insecticides (Guenther, 1991), *e.g.* imidacloprid (Diehr, 1990), and is usually manufactured from 3-methylpyridine *N*-oxide. However, the product of the manufacturing process also contains 3-methylpyridine and its isomer 2-chloro-3-methyl-pyridine (Kaufmann *et al.*, 1991). Because the properties of the isomers are similar, it is difficult to separate them by ordinary methods, such as distillation. We have found that the crystalline complex of 2-chloro-5-methylpyridine can be formed easily when crude 2-chloro-5-methylpyridine is mixed with CuCl$_2$·2H$_2$O in absolute ethanol, and hence the complex can be isolated with over 99% purity. In order to look for specific structural features, we have performed an X-ray structural analysis of this copper complex, (I).

The molecular structure of (I) is shown in Fig. 1. The Cu atom lies on a crystallographic inversion centre so that the angles N—Cu—N and Cl2—Cu—Cl2 are 180°. The two pyridine rings are coplanar in the complex molecule because of crystallographic symmetry, but they twist from the CuN$_2$Cl$_2$ coordination plane with a torsion angle, Cl2—Cu—N—C1, of 95.2 (2)°. Bond distances Cu—N and Cu—Cl2 [1.986 (2) and

2.2536 (11) Å, respectively] agree with the corresponding values for other Cu^{II} complexes (Silva *et al.*, 2001a,b; Zavalij *et al.*, 2002). The bond lengths and angles in (I) are generally similar to those of other Cu^{II} complexes.

(I)
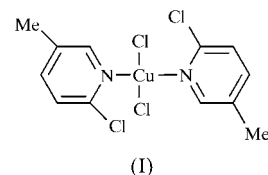
A further analysis of the short intermolecular contacts shows that there are three kinds of C—H···Cl interaction (Table 2). In the first type, the H···Cl distance is 2.76 Å, which is shorter than the sum of the van der Waals radii of these two atoms (2.95 Å). The C—H···Cl angle is 171°, which is close to 180°. These parameters indicate a hydrogen-bonding interaction (Aullon *et al.*, 1998). In the two other types of interaction, the H···Cl distances are close to 2.95 Å. If the C—H···Cl distances and angles are normalized (Jeffrey & Lewis, 1978; Taylor & Kennard, 1983), the H···Cl distances are 2.82 and 2.87 Å and the angles are 159 and 155° for the second and third types of interaction, respectively. These values suggest that the second and third types can also be considered as hydrogen-bonding interactions. Among these three kinds of interaction, the first is the strongest, the second is less strong and the third is the weakest.

A detailed analysis of the crystal packing shows that the hydrogen bonds involving the first and the third type of C—H···Cl interaction [*viz.* C2···Cl2($-x$, $y - \frac{1}{2}$, $-z + \frac{3}{2}$) and C6···Cl2(x, $-y + \frac{1}{2}$, $z - \frac{1}{2}$), respectively] generate two-dimensional networks when viewed in the direction of the *a* axis (Fig. 2). The molecular networks are stacked on top of each other. Because the centroid–centroid distances between pyridine rings in adjacent molecular networks are 5.862 Å, any intermolecular forces between these rings should be very weak (Panda *et al.*, 2001). The C5—H···Cl2($-x + 1$, $-y + 1$, $-z + 1$) interactions (Fig. 3) enforce the connection between adjacent molecular networks. Therefore, the C—H···Cl interactions are likely to be the major intermolecular forces,
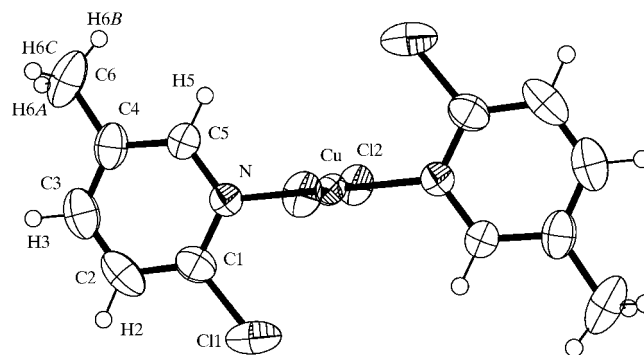

Figure 1
A view of a molecule of (I), showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms.

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causing the complex molecules to pack compactly and to be isolated from the reactant mixture.

The action of all three kinds of C—H···Cl interaction on the same pyridine ring in the complex molecule forces the pyridine ring to rotate around the N—Cu bond, so that the pyridine ring twists from the CuN_2Cl_2 coordination plane.
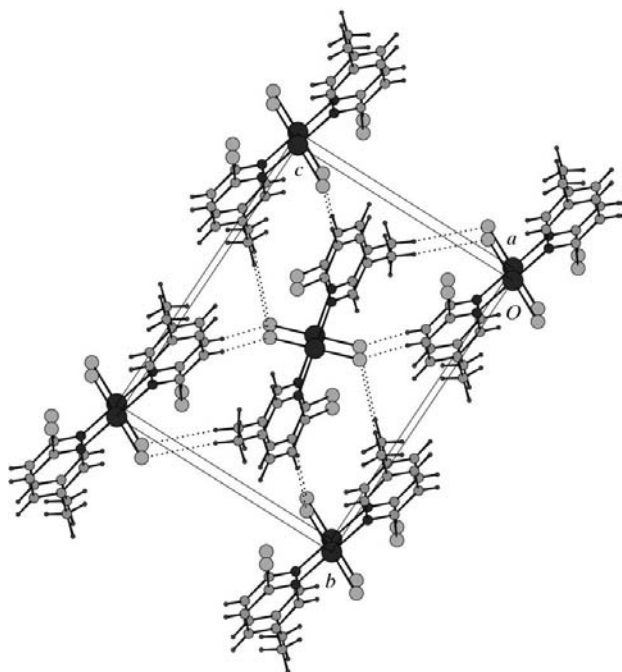

Figure 2
The packing diagram of (I), viewed along the *a* axis. C2—H2···Cl2($-x$, $y - \frac{1}{2}$, $-z + \frac{3}{2}$) and C6—H6C···Cl2(x, $-y + \frac{1}{2}$, $z - \frac{1}{2}$) interactions are indicated by dotted lines.
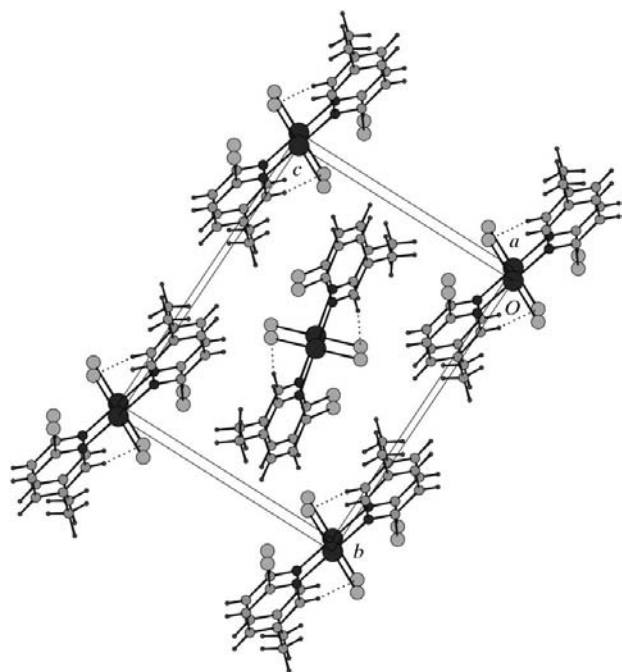

Figure 3
The packing diagram of (I), viewed along the *a* axis. C5—H5···Cl2($-x + 1$, $-y + 1$, $-z + 1$) interactions are indicated by dotted lines.

The crystal-packing diagrams (Figs. 2 and 3) also show that, although each Cl atom in a Cu—Cl interaction can form all three kinds of C—H···Cl connection, the interaction does not fully fit the concept of a hydrogen bond. Moreover, the H···Cl distances in the second and third C—H···Cl interactions, before normalizing, are 2.96 and 2.99 Å, respectively, which are a little longer than 2.95 Å. It would be better to describe these three kinds of C—H···Cl interaction as hydrogen bridges (Desiraju, 2002). The complex molecules form a supramolecular structure in the crystals *via* these hydrogen bridges.

Experimental

Crystal data

$[CuCl_2(C_6H_6ClN)_2]$	$D_x = 1.676$ Mg m^{-3}
$M_r = 389.58$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25
$a = 5.8620\ (10)$ Å	reflections
$b = 12.941\ (4)$ Å	$\theta = 2.6$–$30.2°$
$c = 10.538\ (4)$ Å	$\mu = 2.09$ mm^{-1}
$\beta = 105.12\ (3)°$	$T = 293\ (2)$ K
$V = 771.7\ (4)$ Å^3	Prism, dark violet
$Z = 2$	$0.35 \times 0.30 \times 0.20$ mm

Data collection

Enraf–Nonius CAD-4	$R_{int} = 0.028$
diffractometer	$\theta_{max} = 30.2°$
$\omega/2\theta$ scans	$h = -8 \to 8$
Absorption correction: empirical	$k = -1 \to 18$
(North *et al.*, 1968)	$l = 0 \to 14$
$T_{min} = 0.528$, $T_{max} = 0.680$	3 standard reflections
2585 measured reflections	every 100 reflections
2284 independent reflections	frequency: 60 min
1352 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0684P)^2$
$R(F) = 0.037$	$+ 0.0962P]$
$wR(F^2) = 0.116$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.98$	$(\Delta/\sigma)_{max} = 0.023$
2284 reflections	$\Delta\rho_{max} = 0.54$ e Å^{-3}
90 parameters	$\Delta\rho_{min} = -0.64$ e Å^{-3}
H-atom parameters constrained	Extinction correction: *SHELXL*97
	Extinction coefficient: 0.053 (4)

Table 1
Selected geometric parameters (Å, °).

Cu—N	1.986 (2)	Cu—Cl2	2.2536 (11)
Cl2—Cu—N—C1	95.2 (2)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C2—H2$\cdots$Cl2[i]	0.93	2.76	3.685 (4)	171
C5—H5$\cdots$Cl2[ii]	0.93	2.96	3.850 (3)	160
C6—H6$C\cdots$Cl2[iii]	0.96	2.99	3.885 (4)	156

Symmetry codes: (i) $-x, y - \frac{1}{2}, \frac{3}{2} - z$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $x, \frac{1}{2} - y, z - \frac{1}{2}$.

H atoms were added at calculated positions, refined using a riding model and given U_{iso} parameters equal to 1.2 (or 1.5 for methyl H atoms) times the U_{eq} parameters of their parent atoms. C—H distances were restrained to 0.98 Å for methyl H atoms and 0.95 Å for H atoms bonded to C2, C3 and C5.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *DATARED* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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