

Dichloro(*O*-ethyl 3-methylpyridine-2-carboximidic acid- κ^2N,N')copper(II)

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Received 2 August 2006

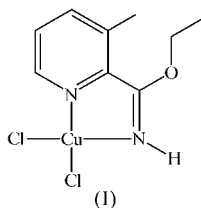
Accepted 10 October 2006

Online 10 November 2006

In the title compound, $[\text{CuCl}_2(\text{C}_9\text{H}_{12}\text{N}_2\text{O})]$, the Cu^{II} atom is coordinated by two Cl^- anions and two N atoms of one *O*-ethyl 3-methylpyridine-2-carboximidic acid molecule in a slightly distorted square-planar geometry, with Cu—N distances of 2.0483 (17) and 1.9404 (18) Å, and Cu—Cl distances of 2.2805 (10) and 2.2275 (14) Å. In addition, each Cu^{II} atom is connected by one Cl^- anion and the Cu^{II} atom from a neighbouring molecule, with Cu \cdots Cl and Cu \cdots Cu distances of 2.9098 (13) and 3.4022 (12) Å, respectively, and, therefore, a centrosymmetric dimer is formed. Adjacent molecular dimers are connected by π – π stacking interactions between pyridine rings to form a zigzag molecular chain. The molecular chains are also enforced by N—H \cdots Cl and C—H \cdots Cl interactions.

Comment

2-Cyano-3-methylpyridine is a useful intermediate in producing drugs and pesticides (Hirosh & Akimitsu, 1997), but it is usually contaminated with by-products. As 2-chloro-5-methylpyridine can be separated from its isomer by forming a complex with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Xuan *et al.* 2003), we attempted to obtain pure 2-cyano-3-methylpyridine in the same way. To our surprise, we obtained the title compound, (I), instead of the desired product.



The molecular structure of (I) is shown in Fig. 1. The pyridine ring and methyl and imidate substituent groups are almost coplanar, and their bond lengths and angles are normal. The Cu^{II} atom is coordinated by atoms N1 and N2 of one *O*-ethyl 3-methyl-2-pyridinecarboximidic acid ligand and by atoms Cl1 and Cl2 in a slightly distorted square-planar geometry (Table 1). The Cu1—N1, Cu1—N2, Cu1—Cl1 and

Cu1—Cl2 distances are 2.0480 (17), 1.9414 (18), 2.2276 (14) and 2.2805 (10) Å, respectively, which agree with the corresponding values for other Cu^{II} complexes (Ivashkevich *et al.*, 2002; Zavalij *et al.*, 2002; Xuan *et al.*, 2003). The dihedral angle between the N1/Cu1/N2 and Cl1/Cu1/Cl2 planes is 26.96 (4)°. The Cu^{II} atom is almost in the pyridine ring plane, with a Cu1—N1—C5—C4 torsion angle of 177.38 (15)°.

Analysis of the supramolecular structure of (I) shows that, just as Br does (Chakrabarty *et al.*, 2004), Cl2 also acts as a bridging atom. Each Cu^{II} atom is connected by another Cl2 anion and by a Cu^{II} atom from a neighbouring molecule (Fig. 2), with Cu1 \cdots Cl2ⁱ and Cu1 \cdots Cu1ⁱ [symmetry code: (i) $-x+1, -y, -z+2$] distances of 2.9098 (13) and 3.4022 (12) Å, respectively, and therefore a centrosymmetric dimer is formed. Because both Cu1—Cl2ⁱ and Cu1—Cu1ⁱ distances are longer than the sum of their covalent radii (2.27 and 2.56 Å, respectively; Pauling, 1960) and shorter than the sum of their van der Waals radii (4.07 and 4.64 Å, respectively; Bondi,

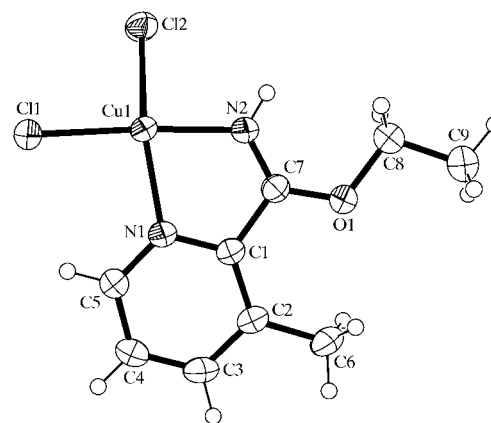


Figure 1

A view of the molecule of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

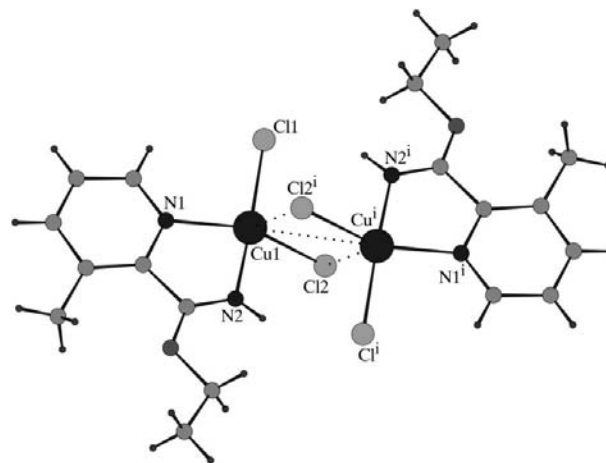


Figure 2

The dimer of compound (I), showing the interactions (dotted lines) between Cu1 and adjacent Cu1ⁱ and Cl2ⁱ atoms. [Symmetry code: (i) $-x+1, -y, -z+2$.]

1964), there should be some weak interactions between these atoms which hold them together. This kind of Cu1—Cl2ⁱ interaction can also be regarded as a coordinate bond, as observed in similar compounds (Kostakis *et al.*, 2006; Bernalte-Garcia *et al.*, 2006), with Jahn–Teller distortion causing the Cu1—Cl2ⁱ distance to be longer than Cu1—Cl1 and Cu1—Cl2. In the present dimer, atoms Cu1, Cl2ⁱ, Cu1ⁱ and Cl2 are coplanar, with Cl2—Cu1—Cl2ⁱ and Cu1—Cl2—Cu1ⁱ angles of 99.07 and 80.93°. The Cl1, Cu1, Cu1ⁱ and Cl1ⁱ atoms are in another plane. The dihedral angle between these two planes is 86.31°.

In the packing diagram, it can be readily observed that there are two parallel pyridine rings between neighbouring dimers (Fig. 3), with the latter transposed by $(-x, -y, -z + 2)$. The distance between these two ring centroids is 3.992 Å, the interplanar distance is 3.550 Å and the offset is 1.826 Å, so this may be regarded as a π – π interaction between these two rings (Cox & MacManus, 2003; Portilla *et al.*, 2005). Thus, the molecular dimers are connected by π – π interactions and generate molecular chains.

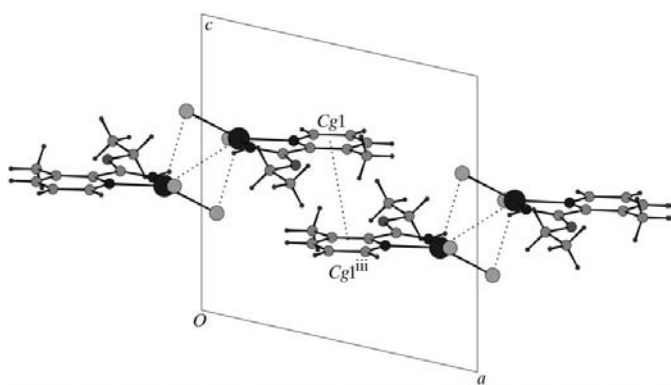


Figure 3
The molecular chain, showing π – π interactions (dotted lines) between molecular dimers. Cg1 and Cg1ⁱⁱⁱ are pyridine ring centroids. [Symmetry code: (iii) $-x, -y, -z + 2$.]

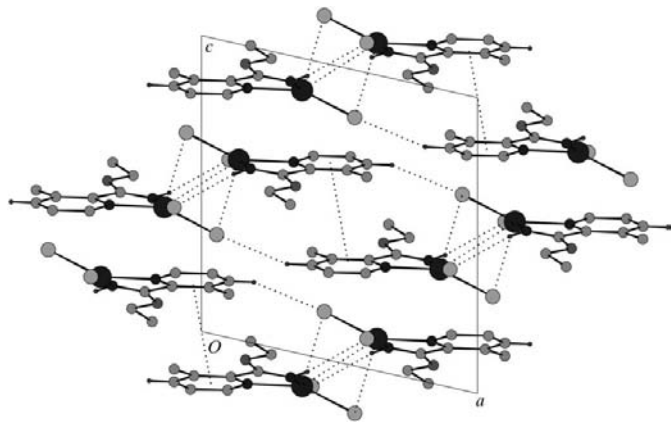


Figure 4
A packing diagram of (I). Dotted lines indicate Cu...Cu, Cu...Cl, π – π , N2–H2...Cl1($-x + 1, -y, -z + 2$) and C3–H3...Cl2($x - 1, y, z$) interactions.

Further analysis of the short contacts present in (I) shows that there are also N2–H2...Cl1ⁱ and C3–H3...Cl2ⁱⁱ [symmetry code: (ii) $x - 1, y, z$] interactions in the same molecular chain, because both the H2...Cl1ⁱ and H3...Cl2ⁱⁱ distances are shorter than 2.95 Å, and the N2–H2...Cl1ⁱ and C3–H3...Cl2ⁱⁱ angles are larger than 140° (Brammer *et al.*, 2001; Steiner, 1998; Aullon *et al.*, 1998), and these enforce the molecular chain (Fig. 4 and Table 2).

Experimental

2-Cyano-3-methylpyridine 0.2362 g (0.20 mmol) in absolute ethanol (5 ml) was mixed with a solution of CuCl₂·2H₂O (0.3409 g, 0.20 mmol) in absolute ethanol (5 ml) in a round-bottomed flask. The solution was heated under reflux for 10 min and then cooled to room temperature. Single crystals of (I) were obtained after 3 d.

Crystal data

[CuCl ₂ (C ₉ H ₁₂ N ₂ O)]	$Z = 2$
$M_r = 597.29$	$D_x = 1.706 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 10.531 (5) \text{ \AA}$	$\mu = 2.31 \text{ mm}^{-1}$
$b = 10.274 (6) \text{ \AA}$	$T = 293 (2) \text{ K}$
$c = 11.012 (5) \text{ \AA}$	Prism, blue
$\beta = 102.654 (15)^\circ$	$0.47 \times 0.32 \times 0.27 \text{ mm}$
$V = 1162.5 (10) \text{ \AA}^3$	

Data collection

Rigaku R-Axis RAPID diffractometer	11146 measured reflections
ω scans	2644 independent reflections
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	2378 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.417, T_{\max} = 0.539$	$R_{\text{int}} = 0.022$
	$\theta_{\max} = 27.5^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0251P)^2 + 0.5469P]$
$R[F^2 > 2\sigma(F^2)] = 0.023$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.058$	$(\Delta/\sigma)_{\max} = 0.001$
$S = 1.05$	$\Delta\rho_{\max} = 0.28 \text{ e \AA}^{-3}$
2644 reflections	$\Delta\rho_{\min} = -0.42 \text{ e \AA}^{-3}$
142 parameters	Extinction correction: SHELXL97 (Sheldrick, 1997)
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.0080 (6)

Table 1

Selected geometric parameters (Å, °).

Cu1—N1	2.0480 (17)	Cu1—Cl1	2.2276 (14)
Cu1—N2	1.9414 (18)	Cu1—Cl2	2.2805 (10)
N1—Cu1—Cl1	96.71 (4)	N2—Cu1—Cl1	169.71 (5)
N1—Cu1—Cl2	152.39 (5)	N2—Cu1—Cl2	90.78 (5)
N2—Cu1—N1	79.48 (6)	Cl1—Cu1—Cl2	96.73 (3)
Cu1—N1—C5—C4	177.38 (15)		

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2...Cl1 ⁱ	0.835 (16)	2.634 (18)	3.4038 (19)	154 (2)
C3—H3...Cl2 ⁱⁱ	0.93	2.89	3.766 (2)	158

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

All H atoms were found in a difference Fourier map. The H atom bonded to atom N2 was refined with a bond-length restraint of 0.835 (16) Å. The other H atoms were treated using a riding model, fixing the bond lengths at 0.96, 0.97 and 0.93 Å for methyl, methylene and aromatic H atoms, respectively. The displacement parameters of the H atoms were constrained to $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for methylene and aromatic H atoms and to $1.5U_{\text{eq}}(\text{C})$ for methyl H atoms.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO* (Rigaku, 1998); data reduction: *CrystalStructure* (Rigaku/MSK, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3037). Services for accessing these data are described at the back of the journal.

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