

Bis[3,6-bis(6-methyl-2-pyridyl)pyridazine- κ^2N^2,N^3]chlorocopper(II) perchlorate

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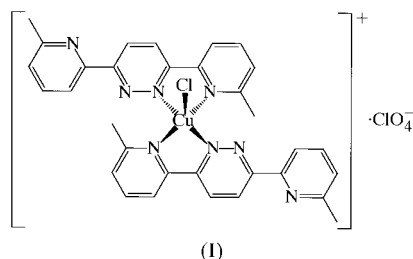
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The title compound, $[\text{CuCl}(\text{C}_{16}\text{H}_{14}\text{N}_4)_2]\text{ClO}_4$, consists of a mononuclear complex cation and a perchlorate anion. The coordination of the copper(II) ion exhibits a trigonal bipyramidal geometry, where the equatorial plane is composed of the Cl atom and two N atoms of the two pyridazine rings, and the axial positions are occupied by the N atoms of two methylpyridine rings.

Comment

The existence of a dinuclear complex with two 3,6-bis(6-methyl-2-pyridyl)pyridazine ligands is not thought to be possible, due to intermolecular steric hindrance between the 6-methyl groups on the pyridyl rings. The most interesting feature of the title compound, (I), is an unusual penta-coordination of the Cu atom by the organic ligands, which showed reasonable hydrolysis reactivity for phosphodiester and DNA model compounds (Sung *et al.*, 2000).



The crystal structure of (I) can be best described as having a pseudo-trigonal bipyramidal geometry, with the two N atoms (N4 and N5) of the two methylpyridine rings in the axial positions and one Cl and two N atoms (Cl1, N3 and N6) in the equatorial plane. The interaxial N4—Cu—N5 angle of $173.6(2)^\circ$ is nearly linear. The Cu atom deviates slightly from the basal N_2Cl plane by $0.044(3) \text{ \AA}$, shifted toward the axially coordinated N4 atom.

The geometry is somewhat distorted from a perfect trigonal bipyramid, as is apparent from the observed τ value of 0.70 (values of 0 and 1 are indicative of idealized square-pyramidal and trigonal-bipyramidal geometries, respectively; Addison *et al.*, 1984). The axial Cu—N bond distances [$2.021(4)$ and $2.030(4) \text{ \AA}$] are considerably longer than those in chlorobis[3,6-di(2-pyridyl)pyridazine]copper(II) chloride pentahydrate [$1.970(5)$ and $1.976(5) \text{ \AA}$; Manotti Lanfredi *et al.*, 1982]. These long axial Cu—N distances may be due to steric hindrance between the 6-methyl groups and the pyridazine rings. The axial Cu—N bonds are not perfectly perpendicular to the CuN_2Cl plane, with N—Cu—N and N—Cu—Cl angles ranging from $79.5(2)$ to $131.6(1)^\circ$. All atoms in each of the two ligands are planar to within $0.572(6) \text{ \AA}$ and the dihedral angle between the two ligands is $52.47(6)^\circ$.

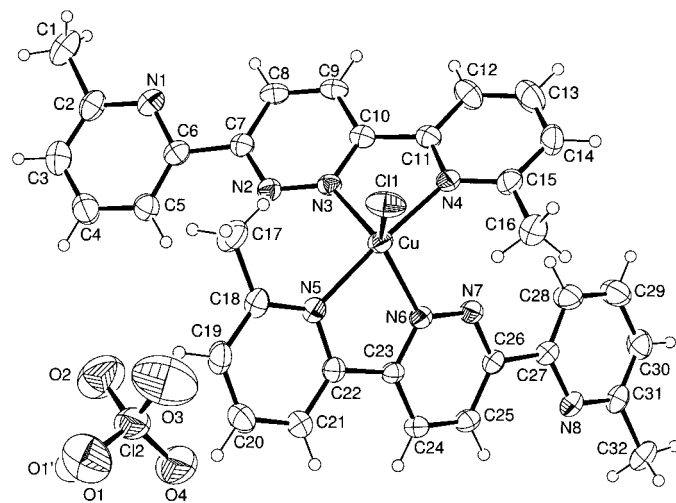


Figure 1
ORTEP-3 (Farrugia, 1997) diagram of (I) showing 35% probability displacement ellipsoids. H atoms are drawn as small spheres of arbitrary radii.

Experimental

The 3,6-bis(6-methyl-2-pyridyl)pyridazine ligand was prepared as described previously by Sung *et al.* (2000). The green Cu^{II} complex, (I), was prepared by mixing the free ligand and $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$ in the ratio 1:2 in acetone solution and then adding NaClO_4 (1 equivalent). The final solution was left in a refrigerator for one week, after which time green crystals of (I) had formed. The crystals were washed with absolute ethanol and dried at room temperature.

Crystal data

$[\text{CuCl}(\text{C}_{16}\text{H}_{14}\text{N}_4)_2]\text{ClO}_4$
 $M_r = 723.06$
Triclinic, $P1$
 $a = 7.3928(18) \text{ \AA}$
 $b = 14.1176(11) \text{ \AA}$
 $c = 15.7262(16) \text{ \AA}$
 $\alpha = 92.439(8)^\circ$
 $\beta = 96.573(14)^\circ$
 $\gamma = 104.249(11)^\circ$
 $V = 1576.1(4) \text{ \AA}^3$

$Z = 2$
 $D_x = 1.524 \text{ Mg m}^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
 $\theta = 11.43\text{--}14.29^\circ$
 $\mu = 0.915 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
Plate, green
 $0.53 \times 0.25 \times 0.01 \text{ mm}$

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.041$
Non-profiled $\omega/2\theta$ scans	$\theta_{\text{max}} = 25.47^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$h = -8 \rightarrow 8$
$T_{\text{min}} = 0.666$, $T_{\text{max}} = 0.987$	$k = -17 \rightarrow 17$
6050 measured reflections	$l = 0 \rightarrow 19$
5821 independent reflections	3 standard reflections
3839 reflections with $I > 2\sigma(I)$	frequency: 300 min
	intensity decay: 8%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0632P)^2 + 1.2920P]$
$R[F^2 > 2\sigma(F^2)] = 0.060$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.153$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.019$	$\Delta\rho_{\text{max}} = 0.58 \text{ e } \text{\AA}^{-3}$
5821 reflections	$\Delta\rho_{\text{min}} = -0.38 \text{ e } \text{\AA}^{-3}$
424 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (\AA , $^\circ$).

Cu–N5	2.021 (4)	Cu–N3	2.122 (4)
Cu–N4	2.030 (4)	Cu–Cl1	2.2912 (16)
Cu–N6	2.052 (4)		
N5–Cu–N4	173.63 (15)	N6–Cu–N3	112.91 (15)
N5–Cu–N6	80.37 (15)	N5–Cu–Cl1	94.40 (11)
N4–Cu–N6	93.88 (14)	N4–Cu–Cl1	91.47 (12)
N5–Cu–N3	100.18 (15)	N6–Cu–Cl1	131.55 (12)
N4–Cu–N3	79.46 (15)	N3–Cu–Cl1	115.41 (11)

The perchlorate O1 atom is disordered over two positions and the two split atoms, designated as O1 and O1', were refined isotropically using *PART* (Sheldrick, 1997). The final occupancy factors of O1 and O1' are 0.54 (3) and 0.46 (3), respectively. The positional parameters of all H atoms were calculated geometrically and constrained to ride

on their attached atoms (C–H = 0.96 \AA for methyl H atoms and 0.93 \AA for the remaining H atoms), with isotropic displacement parameters fixed at 1.2 or 1.5 (for methyl groups) times the equivalent isotropic displacement parameters of their parent atoms. The highest peak and deepest hole in the final difference density map are 0.58 $\text{e } \text{\AA}^{-3}$ at 1.57 \AA from O4 and $-0.38 \text{ e } \text{\AA}^{-3}$ at 1.22 \AA from the Cu atom.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1109). Services for accessing these data are described at the back of the journal.

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