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Key indicators

# Acetatoaqua(di-2-pyridylamine)isothiocyanatocopper(II)

In the structure of the title complex, $[Cu(C_2H_3O_2)(NCS)(C_{10}H_9N_3)(H_2O)]$, the Cu^{II} atom displays a square-pyramidal geometry, coordinated by two N atoms of the di-2-pyridylamine ligand, the N atom from the isothiocyanate ligand and two O atoms from the acetate group and the water molecule. The structure displays intermolecular hydrogen bonding.

## Comment

Copper(II) complexes are known to display a large variety of non-regular stereochemistries (Hathaway, 1987). A large number of $[Cu(chelate)(OXO)(OYO)]^+$ cations, where the chelate is 2,2′-bipyridyl (bpy), 1,10-phenanthroline (phen) or di-2-pyridylamine (dpyam) and OXO and OYO are monovalent oxyanions, e.g. ONO^-, HCO_2^-, $CH_3CO_2^-$ or $CH_3CH_2CO_2^-$, are well known and have been characterized as having distorted octahedral stereochemistry (Youngme et al., 1998). However, very few complexes containing mixed pseudohalide and carboxylate ligands have been reported in the literature. In this study, we present the five-coordinate copper(II) complex acetatoaqua(di-2-pyridylamine)isothiocyanatocopper(II), (I).

(I)
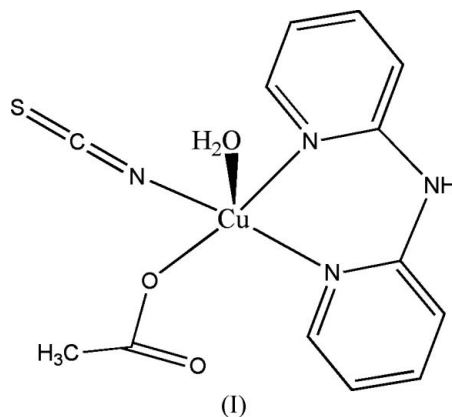
The molecular structure of (I) is shown in Fig. 1. The coordination geometry around the Cu^{II} atom is distorted square pyramidal with a CuN_3O_2 chromophore ($\tau = 0.19$). The structure index is defined as $\tau = (\beta–\alpha)/60$, where β and α are the largest coordination angles; $\tau = 0$ for square pyramidal (SP) and $\tau = 1$ for trigonal bipyramidal (TBP) geometry (Addison et al., 1984). The four shorter bonds in the basal plane involve two N atoms of the dpyam ligand, an O atom from an acetate anion and an N atom from an isothiocyanate anion. A coordinated water molecule occupies the axial positions with a longer Cu—O bond distance (Table 1). The Cu atom is displaced 0.166 (1) Å from its basal plane. The
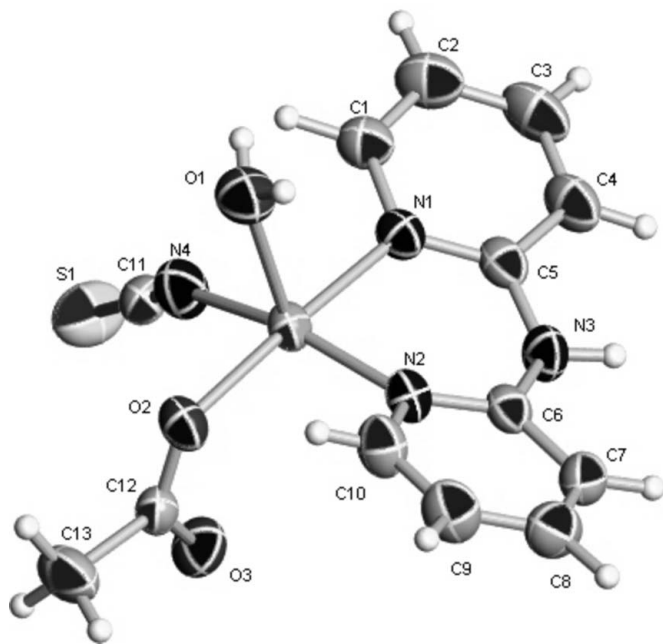
Figure 1
The molecular structure of (I) with 50% probability displacement ellipsoids (arbitrary spheres for H atoms).

dihedral angle between the pyridine rings is 20.4 (1)°, and that between the N1—Cu—N2 and N4—Cu—O3 planes is 15.7 (1)°.

An intermolecular hydrogen-bonding network is present in the crystal structure of (I) (Table 2).

Experimental

The title complex was obtained as a side product in the preparation of [Cu₄(dpyam)₄(μ-NCS)₆(OOCCH₃)] by adding a warm solution of di-2-pyridylamine (0.171 g, 1.0 mmol) in methanol (20 ml) to a hot aqueous solution (10 ml) of Cu(CH₃COO)₂ (0.182 g, 1.0 mmol) and KSCN (0.041 g, 0.5 mmol). An aqueous solution (5 ml) of NaOH (0.021 g, 0.5 mmol) was then added. The resulting green solution was allowed to evaporate slowly at room temperature. After several days, blue crystals of (I) formed. The crystals were filtered off, washed with mother liquor and dried in air.

Crystal data

$[Cu(C_2H_3O_2)(NCS)(C_{10}H_9N_3)$ $(H_2O)]$	$Z = 4$
$M_r = 369.88$	$D_x = 1.555$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 6.97420$ (10) Å	$\mu = 1.53$ mm^{-1}
$b = 13.2883$ (1) Å	$T = 273$ (2) K
$c = 17.0472$ (2) Å	Rod, blue
$V = 1579.85$ (3) Å^3	$0.48 \times 0.30 \times 0.23$ mm

Data collection

Siemens SMART CCD area-detector diffractometer	11607 measured reflections
	4384 independent reflections
ω scans	4133 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 2000a)	$R_{int} = 0.016$
$T_{min} = 0.596$, $T_{max} = 0.709$	$\theta_{max} = 30.4°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0328P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.020$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.051$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.05$	$\Delta\rho_{max} = 0.24$ e Å^{-3}
4384 reflections	$\Delta\rho_{min} = -0.27$ e Å^{-3}
255 parameters	Absolute structure: Flack (1983),
H atoms treated by a mixture of independent and constrained refinement	1666 Friedel pairs
	Flack parameter: 0.20 (2)

Table 1
Selected geometric parameters (Å, °).

O1—Cu1	1.9615 (10)	O3—Cu1	2.2937 (13)
N4—C11	1.153 (2)	Cu1—N1	2.0129 (12)
N4—Cu1	1.9794 (14)	Cu1—N2	2.0141 (12)
C11—S1	1.6237 (16)		
O1—Cu1—N4	88.74 (6)	N1—Cu1—N2	89.39 (5)
O1—Cu1—N1	90.41 (5)	O1—Cu1—O3	90.07 (5)
N4—Cu1—N1	164.83 (6)	N4—Cu1—O3	97.81 (7)
O1—Cu1—N2	176.11 (5)	N1—Cu1—O3	97.34 (6)
N4—Cu1—N2	90.43 (6)	N2—Cu1—O3	93.81 (5)

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

D—H$\cdots$$A$	D—H	H$\cdots$$A$	$D\cdots A$	D—H$\cdots$$A$
O3—H12$W$$\cdots$O2^i	0.81 (3)	1.98 (3)	2.782 (3)	171 (4)
O3—H11$W$$\cdots$S1^i	0.77 (3)	2.72 (2)	3.436 (3)	166 (4)
N3—H5$\cdots$O2^{ii}	0.87 (1)	1.96 (1)	2.831 (2)	176 (1)
C8—H8$\cdots$O1^{iii}	0.93 (1)	2.52 (1)	3.378 (1)	155 (1)

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

The H atoms of the dpyam ligand and coordinated water molecule were located in a difference Fourier map and refined isotropically, while the methyl H atoms were positioned geometrically, with C—H = 0.96 Å, and the torsion angle was refined to fit the electron density, $U_{iso}(H) = 1.5U_{eq}(C)$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2000b); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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