Crystal structure of two dimensional polymeric poly[bis(μ_3-chloro)-(μ_2-2-aminopyrimidine-κ^2N,N')-dicopper(I)], $C_8H_{10}Cl_4Cu_4N_6$

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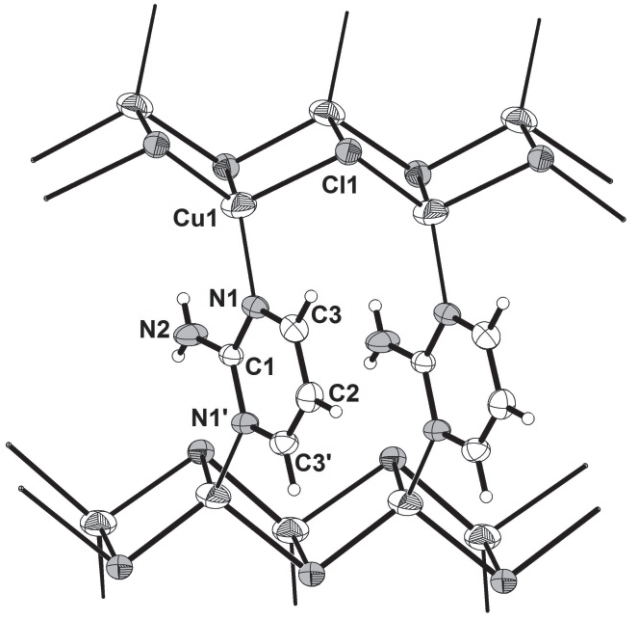

Abstract

$C_8H_{10}Cl_4Cu_4N_6$, orthorhombic, *Pnma* (no. 62), a = 14.054(1) Å, b = 14.501(1) Å, c = 3.7751(4) Å, V = 769.3 Å^3, Z = 2, $R_{gt}(F)$ = 0.0331, $wR_{ref}(F^2)$ = 0.0885, T = 296 K.

Table 1. Data collection and handling.

Crystal:	light brown rods, size 0.03×0.04×0.31 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	61.48 cm^{-1}
Diffractometer, scan mode:	Bruker P4, ω
$2\theta_{max}$:	56.46°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5018, 978
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 712
$N(param)_{refined}$:	59
Programs:	SHELX, DIAMOND [12, 13]

Source of material

The title complex was synthesized from a mixture of CuCl (0.297 g, 3.0 mmol), fumaric acid (0.116 g, 1.0 mmol), 2-amino-pyrimidine (0.095 g, 1 mmol) and ethanol (1.0 mL), which was sealed under vacuum in a Pyrex tube and heated to 140 °C for 3 days, followed by cooling to room temperature at 20 °C/h. The solid products were recovered by vacuum filtration and washed with distilled water. Light brown, thin, rod-shaped crystals suitable for X-ray diffraction analysis were obtained with unidentified blue and green powder. The product was stable in air. The yield of the compound was about 32% based on copper.

Discussion

Copper halide complexes adopt a wide variety of stoichiometries in the formation of neutral and anionic oligomers or polymers. Numerous structural motifs such as rhomboid Cu_2X_2 dimers, cubane Cu_4X_4 tetramers, double-stranded $[CuX]_n$ ladders, and several types of chains are found in copper halide complexes [1–10]. Double-stranded ladders are one of the important building units in constructing coordination complexes with other organic ligands [6–10]. The title structure is an isotype to the corresponding bromide [11]. The crystal structure of the title compound is built of two-dimensional layers. One crystallographically distinct copper atom is coordinated by three chlorine atoms and one nitrogen atom from a 2-aminopyridmidine group to form the distorted tetrahedral geometry that has a Cu–N distance of 2.003(2) Å and Cu–Cl distances in the range of 2.3175(9)–2.477(1) Å. The bond valence sum calculation for Cu gives a value of +1.01, indicating an oxidation state of +1. Each copper atom is coordinated by three μ_3-chlorine atoms, and each chlorine atom is coordinated to three copper atoms, forming infinite [CuCl] chains in the [001] direction [see the figure (' = x, 1.5–y, z)]. Neighboring [CuCl] chains are further bridged by 2-aminopyrimidine ligands in the [010] direction to form a puckered layer parallel to the *bc*-plane. The terminal NH_2 groups in 2-aminopyrimidine are weakly H-bonded to neighboring chlorine atoms of the CuCl chains, [d(N–H···Cl) = 3.3877(3) Å].

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1)	8*d*	0.273(3)	0.710(3)	0.34(1)	0.04(1)
H(2)	4*c*	–0.0693	¾	–0.2963	0.042
H(3)	8*d*	0.0074	0.6133	–0.1610	0.038

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	8*d*	0.18093(4)	0.54483(3)	0.1503(1)	0.0641(4)	0.0256(3)	0.0568(4)	0.0002(2)	–0.0060(2)	0.0040(2)
Cl(1)	8*d*	0.14295(6)	0.45141(5)	–0.3721(2)	0.0331(4)	0.0281(4)	0.0306(4)	–0.0042(3)	–0.0012(3)	0.0007(3)
N(1)	8*d*	0.1211(2)	0.6677(2)	0.0550(7)	0.030(1)	0.020(1)	0.032(1)	–0.002(1)	0.002(1)	–0.002(1)
N(2)	4*c*	0.2443(3)	¾	0.303(1)	0.042(3)	0.020(2)	0.056(3)	0	–0.016(2)	0
C(1)	4*c*	0.1611(3)	¾	0.134(1)	0.028(2)	0.021(2)	0.026(2)	0	0.003(2)	0
C(2)	4*c*	–0.0098(3)	¾	–0.188(1)	0.028(2)	0.042(3)	0.034(2)	0	–0.002(2)	0
C(3)	8*d*	0.0364(2)	0.6690(2)	–0.1044(8)	0.031(2)	0.030(2)	0.035(2)	–0.007(1)	0.005(2)	–0.002(1)

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