Crystal structure of aquadiazidobipyridylcopper(II), $Cu(H_2O)(N_3)_2(C_5H_5N)_2$

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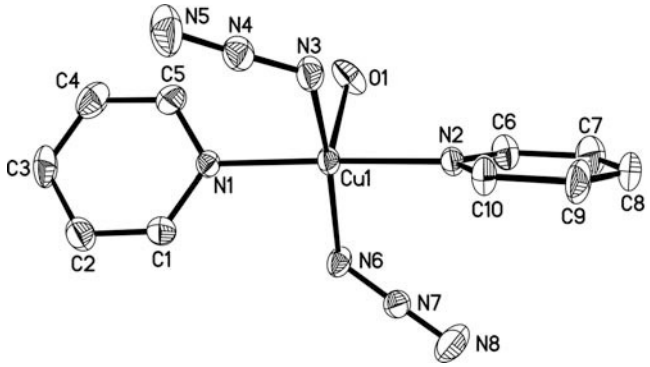

Abstract

$C_{10}H_{12}CuN_8O$, triclinic, $P\bar{1}$ (no. 2), a = 7.910(1) Å, b = 8.6502(6) Å, c = 10.865(1) Å, α = 71.126(1)°, β = 86.694(2)°, γ = 74.918(1)°, V = 678.9 Å^3, Z = 2, $R_{gt}(F)$ = 0.086, $wR_{ref}(F^2)$ = 0.229, T = 298 K.

Source of material

A solution of $CuCl_2 \cdot 2H_2O$ (430 mg, 2.5 mmol) and NaN_3 (320 mg, 5 mmol) in EtOH (50 mL) was dropped slowly into a solution of 2-amino-5-bromopyridine (870 mg, 5 mmol) dissolved in ethanol (50 mL). The mixed solution was stirred for 2 h at 40 °C and then was cooled to room temperature to brown microcrystals, which were collected by filtration, washed successively with H_2O, EtOH and dried in vacuo. The product was then dissolved in pyridine and water (1 : 1). The solution was evaporated over a period of a few days. Pale-green needle-like crystals of the title compound suitable for X-ray analysis were obtained (m.p. 103 - 105 °C). Chemical analysis — found: C, 44.68 %; H, 3.97 %; N, 34.32 %; calculated for $C_{10}H_{12}N_8OCu$: C, 44.51 %; H, 3.74 %; N, 34.60 %.

Discussion

A substantial amount of copper(II) azido complexes with neutral pyridine derivative ligands have been prepared, structurally characterized and shown to have a wide variety of compositions, solid state stereochemistry and varying degrees of oligomerization [1-4].

In the crystal structure of the title complex, the copper atom is coordinated by two pyridine molecules, two azido groups and one aqua molecule. The copper centre is penta-coordinated with four normal Cu—N distances from 1.992(5) to 2.017(5) Å and a Cu—O bond length of 2.263(4) Å. The coordination of Cu(II) ion is a distorted trigonal bipyramidal. The Addison's criterion is 0.95 for the copper moiety (1 for an ideal trigonal bipyramid and 0 for an ideal tetragonal pyramid, respectively [5]). The N3 and N6 atoms and O1 oxygen atom form the equatorial plane, while the N1 and N2 nitrogen atoms of the ligand occupy the axial positions with ∠N1–Cu1–N2 = 176.97(2)°. The dihedral angle between two pyridine rings is 61.34(2)°. O1, N3 and N6 form hydrogen bonds with N3^{i} (d(O1–H···N3^{i}) = 2.843 Å), N6^{ii} (d(O1–H···N6^{ii}) = 2.830 Å), O1^{i} (d(O1^{i}–H···N3) = 2.843 Å) and O1^{ii} (d(O1^{ii}–H···N6) = 2.830 Å) respectively, giving rise to a chain along [100] (symmetry code i: $-x$+1, $-y$+1,$-z$+2; ii: $-x$+2,$-y$+1,$-z$+2). The nitrogen atom of azido group not only coordinates to the Cu(II) center, but also forms intermolecular hydrogen bonds with the coordinated water molecules of the adjacent molecules to construct a chain. To our best knowledge, this behavior is differnt compared from previously reported [6-8]. The Cu1 further has a contact to N5^{iii} at a very long distance d(Cu1···N5^{iii}) = 3.409 Å (symmetry code iii: $-x$+1, $-y$+2,$-z$+2). The distances between Cu1···Cu1^{i}, Cu1···Cu1^{iii} and Cu1···Cu1^{ii} are 5.279, 5.484 and 5.249 Å, respectively.

Table 1. Data collection and handling.

Crystal:	pale-green block, size 0.40 × 0.48 × 0.49 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	16.18 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	50.02°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3474, 2339
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1998
$N(param)_{refined}$:	185
Programs:	SHELXS-97 [9], SHELXL-97 [10], SHELXTL [11]

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

Atom	Site	x	y	z	U_{iso}
H(1)	2*i*	0.8797	0.9328	1.0210	0.049
H(2)	2*i*	0.9967	0.9523	1.1992	0.061
H(3)	2*i*	0.9893	0.7505	1.4005	0.069
H(4)	2*i*	0.8674	0.5309	1.4092	0.074
H(5)	2*i*	0.7511	0.5212	1.2265	0.055
H(6)	2*i*	0.7227	0.5142	0.7669	0.055
H(7)	2*i*	0.5998	0.5270	0.5763	0.075
H(8)	2*i*	0.3781	0.7585	0.4719	0.078
H(9)	2*i*	0.2764	0.9676	0.5654	0.067
H(10)	2*i*	0.4061	0.9467	0.7589	0.052
H(1A)	2*i*	0.7076	0.3623	1.0110	0.04(2)
H(1B)	2*i*	0.8600	0.3832	1.0540	0.13(5)

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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)	2*i*	0.69325(8)	0.71951(8)	0.94374(6)	0.0303(6)	0.0416(6)	0.0284(5)	–0.0109(3)	–0.0040(3)	–0.0138(3)
N(1)	2*i*	0.8055(6)	0.7243(6)	1.1041(5)	0.024(2)	0.041(3)	0.028(2)	–0.009(2)	–0.002(2)	–0.012(2)
N(2)	2*i*	0.5766(6)	0.7281(6)	0.7807(5)	0.032(3)	0.041(3)	0.030(2)	–0.012(2)	–0.001(2)	–0.015(2)
N(3)	2*i*	0.4559(7)	0.7659(8)	1.0180(5)	0.032(3)	0.068(4)	0.042(3)	–0.015(3)	0.002(2)	–0.029(3)
N(4)	2*i*	0.4229(7)	0.8123(7)	1.1107(5)	0.035(3)	0.057(3)	0.045(3)	–0.013(2)	–0.002(2)	–0.020(3)
N(5)	2*i*	0.3883(9)	0.854(1)	1.2019(8)	0.058(4)	0.115(6)	0.082(5)	–0.018(4)	0.009(4)	–0.074(5)
N(6)	2*i*	0.9140(7)	0.7470(7)	0.8516(5)	0.029(3)	0.061(3)	0.028(3)	–0.011(2)	–0.002(2)	–0.014(2)
N(7)	2*i*	0.9240(7)	0.7888(7)	0.7349(5)	0.034(3)	0.048(3)	0.035(3)	–0.014(2)	–0.004(2)	–0.008(2)
N(8)	2*i*	0.939(1)	0.821(1)	0.6254(6)	0.069(5)	0.128(7)	0.034(4)	–0.038(5)	0.001(3)	–0.005(4)
O(1)	2*i*	0.7599(6)	0.4337(6)	1.0175(5)	0.048(3)	0.037(2)	0.081(4)	–0.011(2)	–0.026(3)	–0.013(2)
C(1)	2*i*	0.8775(9)	0.8501(8)	1.1006(6)	0.047(4)	0.038(3)	0.038(3)	–0.014(3)	0.000(3)	–0.010(3)
C(2)	2*i*	0.947(1)	0.863(1)	1.2069(7)	0.050(4)	0.057(4)	0.054(4)	–0.020(3)	–0.001(3)	–0.025(3)
C(3)	2*i*	0.944(1)	0.744(1)	1.3258(7)	0.057(4)	0.081(5)	0.043(4)	–0.012(4)	–0.016(3)	–0.032(4)
C(4)	2*i*	0.870(1)	0.615(1)	1.3304(7)	0.069(5)	0.071(5)	0.032(4)	–0.013(4)	–0.007(3)	–0.004(3)
C(5)	2*i*	0.8021(9)	0.6088(9)	1.2205(6)	0.053(4)	0.047(4)	0.035(3)	–0.016(3)	–0.001(3)	–0.005(3)
C(6)	2*i*	0.6318(9)	0.6071(9)	0.7261(7)	0.045(4)	0.051(4)	0.047(4)	–0.009(3)	–0.003(3)	–0.026(3)
C(7)	2*i*	0.559(1)	0.614(1)	0.6114(8)	0.079(6)	0.070(5)	0.053(4)	–0.021(4)	0.002(4)	–0.038(4)
C(8)	2*i*	0.427(1)	0.751(1)	0.5502(7)	0.083(6)	0.094(6)	0.031(4)	–0.046(5)	–0.012(4)	–0.016(4)
C(9)	2*i*	0.368(1)	0.875(1)	0.6050(7)	0.062(5)	0.066(5)	0.034(3)	–0.010(4)	–0.025(3)	–0.008(3)
C(10)	2*i*	0.4459(9)	0.8614(8)	0.7217(6)	0.049(4)	0.050(4)	0.034(3)	–0.011(3)	–0.009(3)	–0.019(3)

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