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Crystal structure of bis(6-aminopyridine-2-carboxylato- $\kappa^2 O,N$)-copper(II), $C_{12}H_{10}O_6N_4Cu$

Table 1: Data collection and handling.

Crystal:	Green block
Size:	0.30 × 0.25 × 0.22 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.89 mm ⁻¹
Diffractometer, scan mode:	EosS2, ω
$\theta_{\max}$, completeness:	25.5°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	4327, 1086, 0.030
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1016
$N(\text{param})_{\text{refined}}$:	97
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], Olex2 [4]

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Abstract

$C_{12}H_{10}O_6N_4Cu$, monoclinic, $P2_1/c$ (no. 14), $a = 3.7015(2)$ Å, $b = 7.3920(4)$ Å, $c = 21.3535(12)$ Å, $\beta = 91.060(5)^\circ$, $Z = 2$, $V = 584.16(6)$ Å³, $R_{\text{gt}}(F) = 0.0319$, $wR_{\text{ref}}(F^2) = 0.0769$, $T = 293$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

All chemicals were used without further purification. The title compound was prepared under the hydrothermal conditions. A mixture of $Cu(OAc)_2 \cdot H_2O$ (20.0 mg, 0.1 mmol), 6-aminopyridine-2-carboxylic acid (13.8 mg, 0.1 mmol) and 8 mL distilled water in a 20 mL Teflon-lined autoclave was kept under autogenous pressure at 353 K for 2 days. After cooling to room temperature at a rate of 5 K h⁻¹, green

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.5000	0.5000	0.5000	0.02190(18)
O1	0.8102(6)	0.6781(3)	0.53906(9)	0.0308(5)
O2	1.0079(6)	0.7760(3)	0.63203(9)	0.0312(5)
N1	0.5479(6)	0.3779(3)	0.58390(10)	0.0166(5)
N2	0.2922(7)	0.0955(3)	0.56337(11)	0.0273(6)
H2A	0.2599	0.1255	0.5248	0.033*
H2B	0.2266	−0.0097	0.5761	0.033*
C1	0.8531(7)	0.6635(3)	0.59926(12)	0.0201(6)
C2	0.7119(7)	0.4909(3)	0.62650(12)	0.0167(5)
C3	0.7606(7)	0.4500(4)	0.68811(12)	0.0200(6)
H3	0.8660	0.5328	0.7157	0.024*
C4	0.6477(7)	0.2795(4)	0.70897(12)	0.0214(6)
H4	0.6745	0.2479	0.7510	0.026*
C5	0.4991(7)	0.1610(4)	0.66742(12)	0.0216(6)
H5	0.4328	0.0460	0.6806	0.026*
C6	0.4444(7)	0.2123(3)	0.60363(12)	0.0173(5)

crystals were collected by filtration and washed with distilled water in 32% yield. Elemental analysis calculated for $C_{12}H_{10}O_6N_4Cu$: C 42.63, H 2.96, O 28.42%; found C 42.79, H 3.08, O 27.9%.

Experimental details

Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms.

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Comment

Recently, compounds constructed from joining metal centers and organic linkers have developed rapidly due to their wide applications in numerous areas [5–7]. As it is well known, there is still limited understanding concerning many complicated factors that determine their synthesis and the resulting structure. Among, the design of suitable organic ligands and the reasonable selection of joining metal centers are crucial to the construction and structural tuning of the resulting complexes [8–10]. In contrast to the plentiful research based on bridging aromatic polycarboxylates or pyridyl ligands in the past decade, the multidentate ligands containing N and O atoms are very limited on nicotinic acid, isonicotinic acid and pyridinedicarboxylic acids [11–14]. In this work, we report a compound based on central Cu(II) ions and 6-aminopyridine-2-carboxylate (L^-) (L) ligand under hydrothermal conditions. From the point of view of structural chemistry, HL/L^- is an efficient ligand, which contains a number of N or O coordination sites and rich coordination modes. Whereas, compounds based on HL are still rare [15].

X-ray diffraction analysis reveals that the title compound crystallizes in the space group $P2_1/c$ with $Z = 2$ and the asymmetric unit of the crystal structure consists of half of a Cu(II) center located on a crystallographic inversion center and one L^- anion. The Cu(II) center is in a distorted square-planar geometry finished by two carboxylate oxygen atoms and two pyridyl nitrogen atoms from L^- anions. The distances of Cu–O bonds are 1.9268(18) Å and the distance of Cu–N bond is 2.011(2) Å, respectively. The bond angles about the Cu(II) centers range from 83.06(8)° to 180°. These values match with the previously reported Cu(II) compounds [16]. In contrast to the expectation of a multidentate ligand, L^- ligands coordinate with a N,O chelating mode to form a discrete Cu(L)₂ structure [17]. The Cu(L)₂ molecule as a whole is nearly planar. In addition, there are obviously face-to-face π – π stacking interactions between the L^- anions contributing to the formation of the three-dimensional architecture.

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