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Key indicators

Single-crystal X-ray study
T = 297 K
Mean $\sigma(\text{C}-\text{C}) = 0.007 \text{ \AA}$
R factor = 0.052
wR factor = 0.158
Data-to-parameter ratio = 16.9

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

trans-Bis(4-aminopyridine- κN)bis(succinimidato- κN)copper(II) dihydrate

The title compound, $[\text{Cu}(\text{C}_4\text{H}_4\text{NO}_2)_2(\text{C}_5\text{H}_6\text{N}_2)_2] \cdot 2\text{H}_2\text{O}$, has its metal atom in a square-planar *trans*- $[\text{CuN}_4]$ coordination environment; the Cu^{II} atom lies on a center of symmetry. Both succinimidate and 4-aminopyridine ligands behave as monodentate ligands, which coordinate through deprotonated imidate and pyridine (not amino) N atoms, respectively. The 4-aminopyridine is the first ligand in such Cu^{II} complexes containing two different N atoms to take potentially different coordination modes.

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Comment

Recently, supramolecular self-assembling metal-organic frameworks of transition-metal complexes have been studied widely (Eddaoudi *et al.*, 2001; Evans *et al.*, 2002; Yaghi *et al.*, 1998). In particular, rational design of crystals as well as molecular structures with anisotropy may be important fundamentals in the production of optical and electronic functional materials. It has been found that Cu^{II} complexes show flexible coordination geometries and electronic states (Hathaway & Billing, 1970). We have reported that the tetragonal Jahn–Teller distortion can be affected by the external temperature or light irradiation for Cu^{II} complexes with amine ligands (Akitsu & Einaga, 2003). Succinimidate ligands give rise to square-planar CuN_4 complexes, not only with four identical ligands (Akitsu, Komorita & Urushiyama, 2001) but also with mixed ligands such as *trans*-forms with two succinimidate and two monodentate amine ligands (Akitsu,

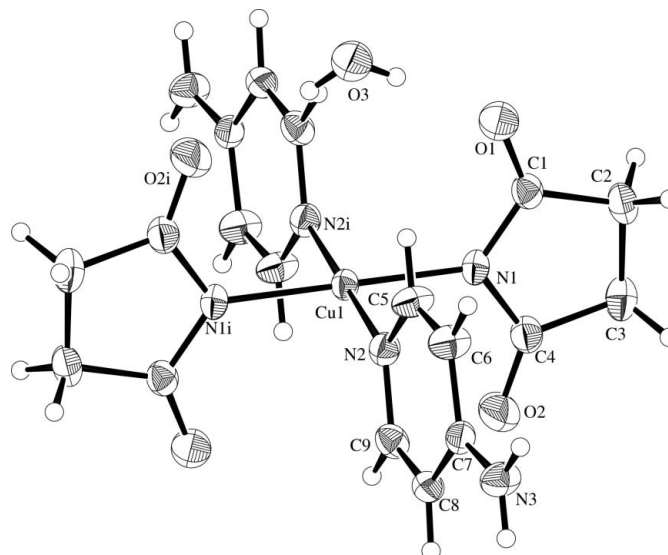
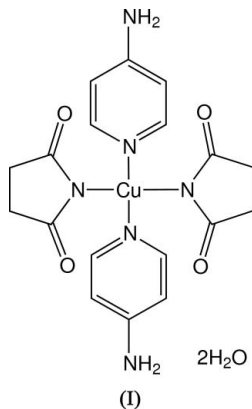


Figure 1
The molecular structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (i) $-x, -y, -z$.]

Komorita & Kushi, 2001). Furthermore, five-coordinate CuN_4O or six-coordinate CuN_4O_2 square-bipyramidal chromophores have been reported for *cis*-forms with bidentate diimine (Akitsu *et al.*, 1999) or bidentate amine (Akitsu & Komorita, 2002). However, the related Cu^{II} complexes with amine ligands containing two different coordinating N atoms have not been reported so far. Here, we report the crystal structure of the title compound, (I), incorporating 4-aminopyridine ligands with competitive amino and pyridine N-atom sites.



In (I) (Fig. 1), the Cu atom exists in a square-planar CuN_4 coordination geometry; it lies on an inversion center. Both succinimide and 4-aminopyridine ligands behave as monodentate. The Cu–N bond distances, the N–Cu–N bond angles, and other geometric parameters of the ligands (Table 1) are comparable to those of the analogous Cu^{II} complexes with pyridine derivative ligands (Latavalya & Taylor, 1975). The C1–N1–C4 angle of $110.2(4)^\circ$ indicates the sp^2 character of the deprotonated N1 atom; the O1–C1–N1 and O2–C4–N1 angles of $123.6(4)^\circ$ and $124.6(4)^\circ$, respectively, also reflect electron delocalization in the π -conjugated system, similar to the Cu^{II} complexes with 5,5-diphenylhydantoinate ligands (Akitsu & Einaga, 2004, 2005). The dihedral angle between the coordination plane [Cu1/N1/N2/N1ⁱ/N2ⁱ, symmetry code: (i) $-x, -y, -z$] and the succinimide five-membered ring (N1/C1–C4) is $80.2(2)^\circ$, and that between the coordination plane and the pyridine ring (N2/C5–C9) is $81.9(2)^\circ$. The dihedral angle between the succinimide and pyridine rings is $85.0(2)^\circ$.

As seen from Fig. 1, there is a water molecule of crystallization (together with an inversion-related one) near the Cu complex to form the O1 \cdots H3E–O3–H3F \cdots O2ⁱ hydrogen-bonding linkage (Table 2). There are also N–H \cdots O intermolecular hydrogen bonds involving the amino groups.

Experimental

Treatment of copper(II) acetate (0.226 g, 1.25 mmol), succinimide (0.495 g, 5.00 mmol), and 4-aminopyridine (0.235 g, 2.50 mmol) in ethanol (50 ml) at 318 K for 2 h gave rise to a deep blue solution. Brown microcrystals (anhydrous) were obtained from the resulting

solution. Yield 0.0752 g (13.2%). IR (KBr): 1618 cm^{-1} (amide I). UV (reflectance spectra): 16700 cm^{-1} [*sh*, $F(R_d) = 1.44$], 21000 cm^{-1} [$F(R_d) = 2.36$]. Anal. Found: C 44.42, H 5.12, N 17.21%; calcd. for $\text{C}_{18}\text{H}_{24}\text{N}_6\text{CuO}_6$: C 44.67, H 5.00, N 17.36%. m.p. 559 K (decomposition). Brown crystals of (I) suitable for X-ray analysis were obtained from a methanol solution over a period of several days. The water solvent molecules came from undried methanol.

Crystal data

$[\text{Cu}(\text{C}_4\text{H}_4\text{NO}_2)_2(\text{C}_5\text{H}_6\text{N}_2)_2]\cdot 2\text{H}_2\text{O}$	$Z = 1$
$M_r = 483.98$	$D_x = 1.521\text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.945(2)\text{ \AA}$	Cell parameters from 20 reflections
$b = 8.729(3)\text{ \AA}$	$\theta = 10.1\text{--}13.7^\circ$
$c = 9.161(3)\text{ \AA}$	$\mu = 1.08\text{ mm}^{-1}$
$\alpha = 65.04(2)^\circ$	$T = 297(2)\text{ K}$
$\beta = 86.86(3)^\circ$	Prism, brown
$\gamma = 67.59(2)^\circ$	$0.20 \times 0.20 \times 0.20\text{ mm}$
$V = 528.2(3)\text{ \AA}^3$	

Data collection

Rigaku AFC-7R diffractometer	$R_{\text{int}} = 0.058$
ω - 2θ scans	$\theta_{\text{max}} = 27.5^\circ$
Absorption correction: ψ scan	$h = -11 \rightarrow 10$
(North <i>et al.</i> , 1968)	$k = -11 \rightarrow 11$
$T_{\text{min}} = 0.696, T_{\text{max}} = 0.807$	$l = -4 \rightarrow 10$
2736 measured reflections	3 standard reflections
2430 independent reflections	every 150 reflections
1771 reflections with $I > 2\sigma(I)$	intensity decay: 0.4%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0697P)^2 + 0.5544P]$
$R[F^2 > 2\sigma(F^2)] = 0.052$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.158$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.58\text{ e \AA}^{-3}$
2430 reflections	$\Delta\rho_{\text{min}} = -0.54\text{ e \AA}^{-3}$
144 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters ($\text{\AA}, ^\circ$).

Cu1–N1	1.971 (3)	N1–C1	1.349 (6)
Cu1–N2	2.011 (4)	N1–C4	1.371 (6)
O1–C1	1.235 (6)	N2–C5	1.339 (6)
O2–C4	1.214 (6)	N2–C9	1.342 (6)
N1–Cu1–N2	89.93 (14)	C5–N2–C9	116.2 (4)
C1–N1–C4	110.2 (4)	C5–N2–Cu1	121.5 (3)
C1–N1–Cu1	127.0 (3)	C9–N2–Cu1	122.0 (3)
C4–N1–Cu1	122.8 (3)		

Table 2
Hydrogen-bond geometry ($\text{\AA}, ^\circ$).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
O3–H3E \cdots O1	0.73 (3)	2.13 (2)	2.827 (5)	161 (2)
O3–H3F \cdots O2 ⁱ	0.79 (3)	1.99 (2)	2.770 (7)	168 (2)
N3–H3C \cdots O1 ⁱⁱ	0.86	2.20	3.016 (5)	158
N3–H3D \cdots O3 ⁱⁱⁱ	0.86	2.08	2.917 (6)	164

Symmetry codes: (i) $-x, -y, -z$; (ii) $-x + 1, -y - 1, -z$; (iii) $x, y - 1, z + 1$.

The water H atoms were located in difference Fourier maps and their positions were refined with $U_{\text{iso}} = 0.064 \text{ \AA}^2$. H atoms bonded to C and N atoms were placed in calculated positions, with C–H and N–H = 0.93–0.97 and 0.86 Å, respectively, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$.

Data collection: *WinAFC Diffractometer Control Software* (Rigaku, 1999); cell refinement: *WinAFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1989); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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