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Poly[[[*trans*-bis(3-aminopyridine)copper(**II**)]-μ_3-5-hydroxy-1,3-benzenedicarboxylato] monohydrate]

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Key indicators

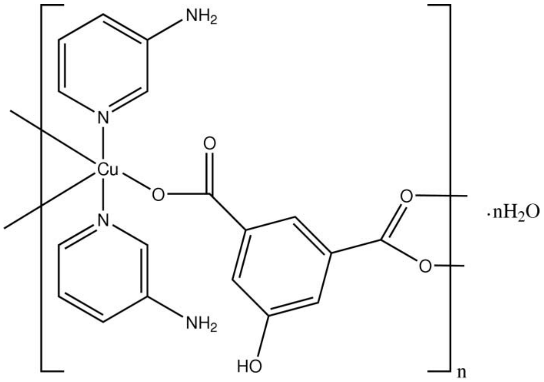
Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.006 Å
Disorder in solvent or counterion
R factor = 0.044
wR factor = 0.128
Data-to-parameter ratio = 11.7

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

In the crystal structure of the title two-dimensional complex, $\{[Cu(C_8H_4O_5)(C_5H_6N_2)_2]\cdot H_2O\}_n$, the Cu atom has a distorted square-pyramidal coordination geometry. As well as O—H···O hydrogen bonds within a two-dimensional layer, there are N—H···O hydrogen bonds which connect layers into a three-dimensional network. In addition, there are significant π–π stacking interactions between layers.

Comment

Recently, transition metal complexes with benzenedicarboxylate derivatives have received much attention due to their important potential applications as functional materials (Braun *et al.*, 2001; Rosi *et al.*, 2003; Zhu *et al.*, 2004). The ligand 5-hydroxy-1,3-benzenedicarboxylic acid (H_2hmbdc) has been used to produce many interesting complexes (Cao *et al.*, 2004; He *et al.*, 2005; Plater *et al.*, 2001; Skakle *et al.*, 2001; Xu & Li, 2004; Zakaria *et al.*, 2002). Among them, several copper–hmbdc^{2-} complexes have been synthesized and exist as monomers (Xiao *et al.*, 2005), dimers (Xiao *et al.*, 2004), polynuclear nanoballs (Abourahma *et al.*, 2001) and two-dimensional networks with a paddle-wheel motif (Ma *et al.*, 2004). As part of our systematic inverstigation of hmbdc^{2-} complexes, the structure of the title copper complex, (I), was determined.



(I)

The title complex is a two-dimensional network, in which each Cu atom has a distorted square-pyramidal geometry defined by two N-atom donors from two *trans*-arranged 3-aminopyridine ligands and three O atoms from three hmbdc^{2-} ligands (Fig. 1 and Table 1). Atoms O1, O5^{ii}, N1, and N2 occupy the basal plane, while atom O4^{i} occupies the apical position (see Table 1 for symmetry codes). Two 3-aminopyridine ligands act as terminal species. The hmbdc^{2-} ligand is a μ_3-linker, bridging three Cu atoms. Two carboxyl groups of

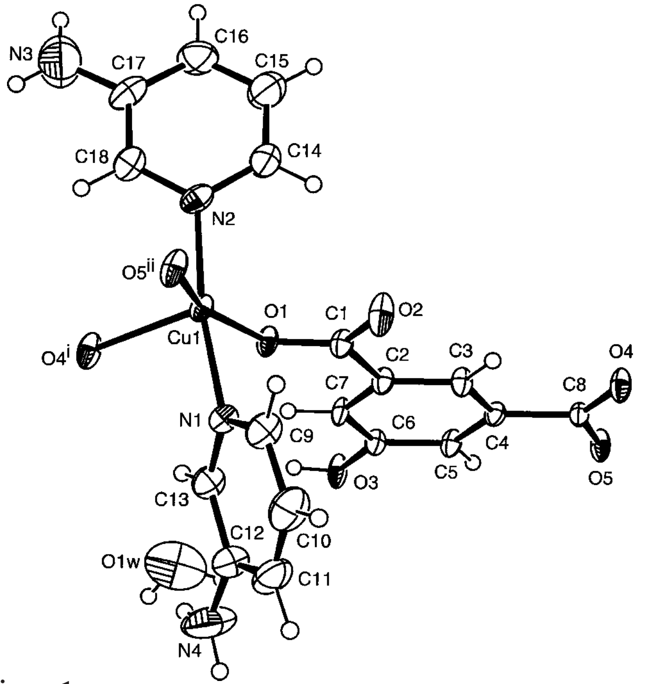


Figure 1
A view of a segment of the polymeric structure of (I). Displacement ellipsoids are drawn at the 30% probability level. The minor part of disordered water molecule has been omitted for clarity. [Symmetry codes: (i) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii): $\frac{1}{2} + x, \frac{3}{2} - y, -\frac{1}{2} + z$.]

hmbdc^{2-} have different coordination modes, one is monodentate, while the other is a bridging group separating two Cu atoms with a Cu$\cdots$Cu distance of 4.5658 (9) Å. Therefore, the μ_3 property of hmbdc^{2-} extends the structure into a two-dimensional network (Fig. 2). In addition to O—H$\cdots$O hydrogen bonds within a two-dimensional layer, there are N—H$\cdots$O hydrogen bonds which connect layers into a three-dimensional network. Significant π–π stacking interactions exist between the layers, with $Cg1\cdots Cg1(1 - x, 2 - y, -z)$ = 3.832 (3) Å and a perpendicaular distance of 3.58 Å ($Cg1$ is the centroid of atoms N2/C14–C18).

Experimental

The title complex was synthesized by the layer method using three solutions in a narrow tube. The upper layer solution was 5 ml of CH_3OH containing 0.06 mol l^{-1} 3-aminopyridine and 0.03 mol l^{-1} 5-hydroxy-1,3-benzenedicarboxylic acid. The bottom layer was 5 ml of an aqueous solution containing 0.035 mol l^{-1} $Cu(CH_3COO)_2\cdot H_2O$. The middle layer was 5 ml of CH_3OH–H_2O (1:1 (*v*/*v*) mixed-solvent system. After standing for three weeks, blue block-shaped crystals were obtained and collected by suction filtration.

Crystal data

$[Cu(C_8H_4O_5)(C_5H_6N_2)_2]\cdot H_2O$
M_r = 449.90
Monoclinic, $P2_1/n$
a = 10.3222 (9) Å
b = 11.5993 (10) Å
c = 16.0222 (14) Å
β = 101.197 (2)°
V = 1881.8 (3) Å^3
Z = 4
D_x = 1.588 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2213 reflections
θ = 2.2–23.9°
μ = 1.21 mm^{-1}
T = 295 (2) K
Block, blue
0.25 × 0.25 × 0.19 mm

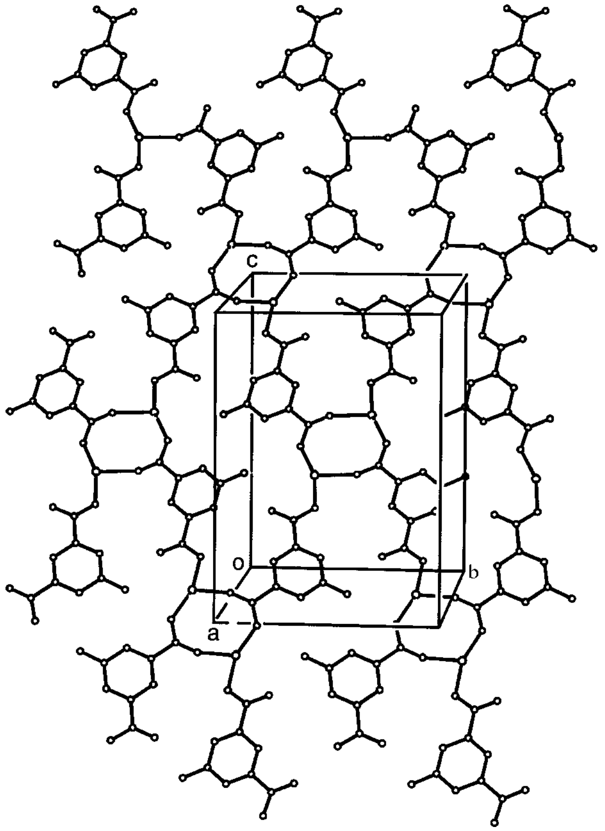


Figure 2
The minor component of a two-dimensional layer constructed by [Cu(hmbdc)] units in (I), with the 3-aminopyridine ligands and the H atoms omitted for clarity.

Data collection

Bruker APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.753, T_{max} = 0.803
9360 measured reflections
3313 independent reflections
2556 reflections with $I > 2\sigma(I)$
R_{int} = 0.070
θ_{max} = 25.0°
$h = -11 \rightarrow 12$
$k = -13 \rightarrow 13$
$l = -19 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.128
S = 1.01
3313 reflections
284 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0656P)^2 5]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.96 e Å^{-3}
$\Delta\rho_{min}$ = −0.54 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O5^i	1.940 (2)	Cu1—N1	2.025 (3)
Cu1—O1	1.966 (2)	Cu1—O4^{ii}	2.216 (3)
Cu1—N2	2.020 (3)		
O5^i—Cu1—O1	158.15 (11)	N2—Cu1—N1	171.87 (14)
O5^i—Cu1—N2	92.38 (12)	O5^i—Cu1—O4^{ii}	107.16 (11)
O1—Cu1—N2	89.71 (12)	O1—Cu1—O4^{ii}	94.20 (10)
O5^i—Cu1—N1	88.88 (12)	N2—Cu1—O4^{ii}	96.29 (13)
O1—Cu1—N1	86.18 (11)	N1—Cu1—O4^{ii}	91.01 (12)

Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$; (ii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O2$^{\text{ii}}$	0.82	1.88	2.693 (4)	171
N4—H4A···O3$^{\text{iii}}$	0.86	2.40	3.172 (5)	150
N4—H4B···O1W	0.86	2.14	2.947 (8)	155
N4—H4B···O1W'	0.86	2.57	3.05 (3)	116
O1W—H1A···O2$^{\text{ii}}$	0.87 (1)	2.17 (1)	3.023 (6)	168 (3)

Symmetry codes: (ii) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x+2, -y+2, -z+1$.

All aromatic H atoms were positioned geometrically and refined as riding atoms, with C—H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The water H atoms were located in difference Fourier maps and refined with a distance restraint of O—H = 0.85 (1) Å and fixed isotropic displacement parameters of $U_{\text{iso}}(\text{H})$ = 0.08 Å^2. The amino and hydroxy H atoms were positioned geometrically and refined as riding atoms, with N—H = 0.86 Å and O—H = 0.82 Å, and $U_{\text{iso}}(\text{H})$ = 0.08 Å^2 and $1.5U_{\text{eq}}(\text{O})$, respectively. The water O atom is disordered over two sites, with a ratio of 0.791 (8):0.209 (8) for O1w and O1w', respectively. The N atoms of the terminal amino groups have larger displacement parameters due to their librational freedom.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3* for Windows (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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