

Poly[[copper(II)-di- μ -5-aminoisophthalato(1-)- κ^4 N:O] monohydrate]

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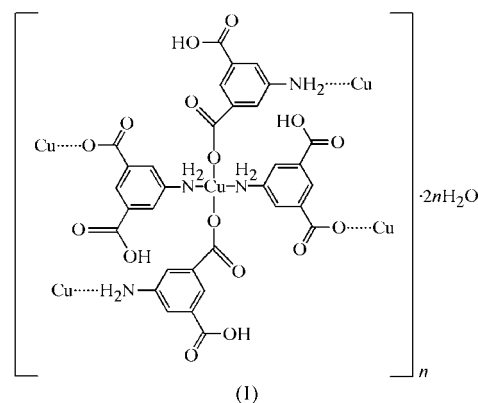
The title compound, $\{[\text{Cu}(\text{C}_8\text{H}_6\text{NO}_4)_2] \cdot \text{H}_2\text{O}\}_n$, was prepared by the hydrothermal assembly of 5-aminoisophthalic acid with copper nitrate. Single-crystal X-ray analysis shows that it has a two-dimensional layer coordination framework, in which the unique Cu atom lies on an inversion centre and adopts a square-planar geometry, coordinated to two N and two O atoms from symmetry-related ligands. The water molecule lies on a twofold axis and there are hydrogen-bonding interactions between the layers.

Comment

Through coordination bonds and non-covalent interactions, such as hydrogen bonds and/or π - π stacking interactions, the self-assembly method has proved to be a powerful tool for the construction of supramolecular structures (Batten & Robson, 1998; Moulton & Zaworotko, 2001; Kepert & Rosseinsky, 1999; Biradha & Fujita, 2000). Multi-dimensional frameworks containing large channels of various shapes and sizes (Yaghi *et al.*, 1996, 1997; Subramanian & Zaworotko, 1995; Harrison & Hannonman, 1997) and intercalating arrays (Vaccari, 1999) have recently been reported. Coordination of transition metals to multidentate ligands is one of the main design principles.

As a rigid multidentate ligand, 5-aminoisophthalic acid (AIP) has received considerable attention, owing to its variety of possible bridging modes (Wu, Lu, Yang *et al.*, 2002; Wu, Lu, Zhuang *et al.*, 2002; Xu *et al.*, 2002; Tao *et al.*, 2003; Yang *et al.*, 2003; Yang & Zheng, 2003). It can engage in three types of intermolecular interactions, namely $M-L$ bonding, hydrogen bonding and π - π stacking interactions. In order to understand its interesting chemistry, we recently studied the assembly reaction of AIP with various metal ions in solution or under hydrothermal conditions. We report here the synthesis and crystal structure of the title compound, (I), which has a two-dimensional layer network.

As illustrated in Fig. 1, the Cu^{II} atom, situated at the centre of a square plane, is coordinated by two O atoms and two N atoms from four different AIP ligands. The ligand uses its amine group and one of its carboxylate groups to coordinate two Cu^{II} moieties [$\text{Cu}-\text{N} = 2.026(4) \text{ \AA}$ and $\text{Cu}-\text{O} = 1.969(3) \text{ \AA}$]; the carboxyl group is left free. This coordination pattern of AIP is similar to that in the complex $[\text{Co}(\text{C}_8\text{H}_6\text{NO}_4)_2(\text{H}_2\text{O})]_n$ (Wu, Lu, Zhuang *et al.*, 2002), where the central Co^{II} ion adopts an octahedral geometry.



The coordination around the Cu^{II} ion in (I) leads to a two-dimensional layer network and Fig. 2 shows the packing of the complex along the a axis. There is intramolecular hydrogen bonding within these two-dimensional layers [$\text{O}2-\text{O}4(x, 1-y, z-\frac{1}{2}) = 2.554(6) \text{ \AA}$].

Fig. 3 shows the unit-cell packing diagram viewed from the b direction. Interestingly, the two-dimensional networks are packed into a three-dimensional framework *via* interlayer hydrogen-bonding interactions [$\text{N}1 \cdots \text{O}1 = 2.944(6) \text{ \AA}$]. There are also isolated water molecules between the layers,

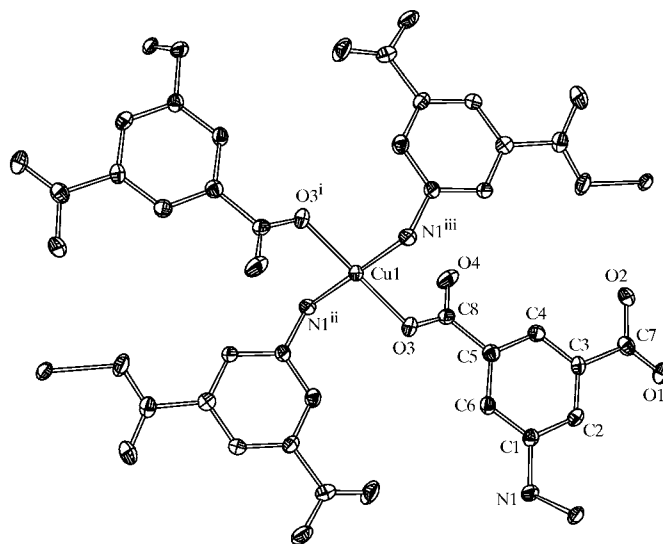


Figure 1

A view of (I), showing the atomic labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms and isolated water molecules have been omitted for clarity. [Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (ii) $x, -y, \frac{1}{2} + z$; (iii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.]

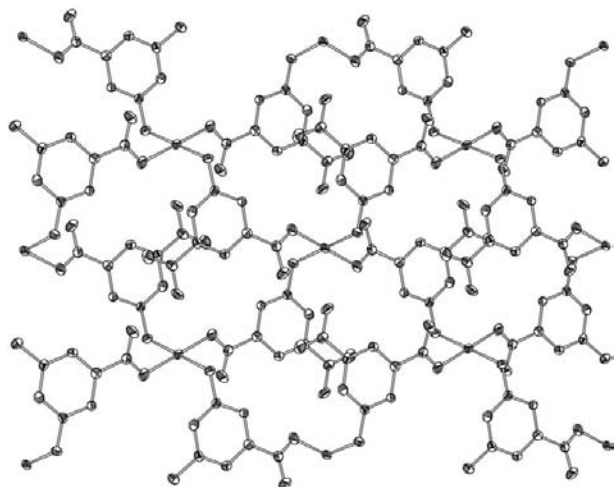


Figure 2
The extended two-dimensional lamellar structure of (I), viewed along the *a* direction. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

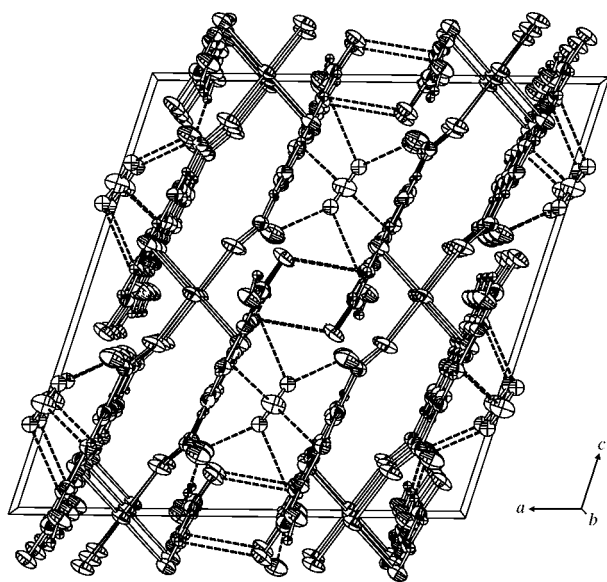


Figure 3
A unit-cell packing diagram of (I), viewed along the *b* direction, showing the interlayer hydrogen bonding connecting the two-dimensional layers into a three-dimensional framework. Displacement ellipsoids are drawn at the 50% probability level and hydrogen bonds are depicted by dashed lines.

which form hydrogen bonds with the two-dimensional layers; details are given in Table 2.

Experimental

A mixture of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (2 mmol) and 5-aminoisophthalic acid (1 mmol) in water (15 ml) was sealed in a 25 ml Teflon-lined stainless steel reactor and heated to 413 K for 6 d under autogenous pressure. After slow cooling of the reaction solution to room temperature, black prism-shaped crystals of (I) suitable for X-ray analysis were obtained. Elemental analyses were performed on an EL III CHNOS

Elemental Analyzer. Analysis found: C 43.87, H 2.48, N 6.24%; calculated: C 43.50, H 3.19, N 6.34%.

Crystal data

$[\text{Cu}(\text{C}_8\text{H}_6\text{NO}_4)_2] \cdot \text{H}_2\text{O}$
 $M_r = 441.83$
 Monoclinic, $C2/c$
 $a = 13.2692$ (11) Å
 $b = 9.1898$ (8) Å
 $c = 13.5155$ (11) Å
 $\beta = 107.542$ (2)°
 $V = 1571.5$ (2) Å³
 $Z = 4$

$D_x = 1.868$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 1257 reflections
 $\theta = 2.7\text{--}25.0^\circ$
 $\mu = 1.45$ mm⁻¹
 $T = 293$ (2) K
 Prism, black
 $0.36 \times 0.20 \times 0.20$ mm

Data collection

Siemens SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: empirical (SADABS; Sheldrick, 1996)
 $T_{\text{min}} = 0.723$, $T_{\text{max}} = 0.748$
 2289 measured reflections

1359 independent reflections
 1117 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.029$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -15 \rightarrow 12$
 $k = -10 \rightarrow 8$
 $l = -16 \rightarrow 13$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.053$
 $wR(F^2) = 0.136$
 $S = 1.06$
 1359 reflections
 137 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0601P)^2 + 12.8787P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.002$
 $\Delta\rho_{\text{max}} = 0.68$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.83$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cu1—O3	1.970 (3)	Cu1—N1 ⁱⁱ	2.041 (4)
Cu1—O3 ⁱ	1.970 (3)	Cu1—N1 ⁱⁱⁱ	2.041 (4)
O3—Cu1—N1 ⁱⁱ	91.53 (16)		

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

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1A...O3 ⁱ	0.86	2.24	2.874 (5)	130
N1—H1A...O1 ⁱⁱ	0.86	2.53	2.944 (6)	110
N1—H1B...OW1 ⁱⁱⁱ	0.86	2.32	2.923 (6)	127
N1—H1B...O3 ^{iv}	0.86	2.35	2.798 (6)	113
OW1—HW1A...O4 ^v	0.91 (8)	2.44 (8)	3.294 (6)	157 (7)
O2—H2B...O4 ^{vi}	0.82 (6)	1.74 (6)	2.554 (5)	174 (6)

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

Hydroxy and water H atoms were located from difference maps and refined freely. H atoms bonded to C or N atoms were placed in calculated positions and refined with isotropic displacement parameters using a riding model, with C—H = 0.93 Å and N—H = 0.86 Å, and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$.

Data collection: SMART (Siemens, 1996); cell refinement: SMART and SAINT (Siemens, 1994); data reduction: XPREP in SHELXTL (Siemens, 1994); program(s) used to solve structure: SHELXTL; program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ1020). Services for accessing these data are described at the back of the journal.

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