

Poly[[bis(pyridine- κ N)copper(II)]- μ_3 -5-hydroxyisophthalato- κ^3 O:O':O'']

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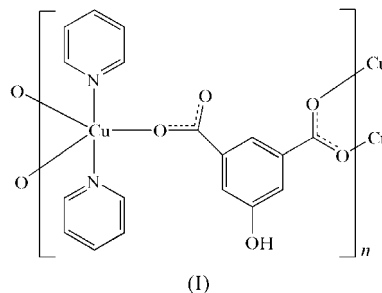
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In the title compound, $[\text{Cu}(\text{C}_8\text{H}_4\text{O}_5)(\text{C}_5\text{H}_5\text{N})_2]_n$ or $[\text{Cu}(\text{OH-BDC})(\text{py})_2]_n$ (where OH-H₂BDC is 5-hydroxyisophthalic acid and py is pyridine), the Cu atoms are coordinated by two N atoms from the pyridine ligands and by three O atoms from hydroxyisophthalate ligands in a highly distorted triangular bipyramidal environment, with Cu—O distances in the range 1.941 (4)–2.225 (5) Å and Cu—N distances of 2.014 (6) and 2.046 (6) Å. The $[\text{Cu}(\text{OH-BDC})]_n$ two-dimensional network is built up from interlocking 22-, 15- and eight-membered rings *via* sharing of Cu atoms and O—H...O hydrogen bonds. Consolidation of the packing structure is achieved by edge- or point-to-face C—H... π interactions and offset or slipped π – π stacking interactions.

Comment

The design and syntheses of supramolecular coordination polymer networks, especially those constructed *via* hydrogen bonding and π – π stacking interactions, has been a field of rapid growth because of the special physical properties of these compounds and their potential applications in functional materials (Atwood *et al.*, 1996; Barton *et al.*, 1999). Coordination polymers containing symmetric multidentate benzenecarboxylate molecules as bridging ligands have attracted increasing attention because of their interesting network structures and potential applications in many fields (Li *et al.*, 1999; Yaghi *et al.*, 1995; Chui *et al.*, 1999). Large numbers of coordination polymers have been prepared from metal ions and aromatic carboxylate ligands, such as benzenehexacarboxylate (Wu *et al.*, 1996), 1,3-benzenedicarboxylate (Reineke *et al.*, 1999) and 1,3,5-benzenetricarboxylate (Yaghi *et al.*, 1997; Daiguebonne *et al.*, 1999; Gutschke *et al.*, 1996). 5-Hydroxyisophthalic acid, OH-H₂BDC, like benzene-1,3,5-tricarboxylic acid, has two carboxylic acid groups arranged *meta* with respect to one another, but with a phenol hydroxy group *meta* to both (Plate *et al.*, 2001). This phenol hydroxy group was intended as a

mimic for the third carboxy group, which remains protonated in the reported layered and helical chain polymers (Foreman *et al.*, 1999; Cao *et al.*, 2004), as well as in the title compound. As part of our research interest in new poly(carboxylic acid)-bridged polymeric complexes, the title complex, (I), was obtained by the hydrothermal reaction of OH-H₂BDC with cupric acetate and pyridine (py).



As shown in Fig. 1, the Cu atoms in (I) are five-coordinate in a highly distorted triangular bipyramidal environment involving two N atoms from the pyridine ligands and three O atoms from hydroxyisophthalate ligands, with Cu—O distances in the range 1.941 (4)–2.225 (5) Å and Cu—N distances of 2.014 (6) and 2.046 (6) Å (Table 1). These bond distances are similar to those found in $[\{\text{Cu}_2(1,3\text{-bdc})(\text{py})_2\}_4]_n$ (1,3-bdc is 1,3-benzenedicarboxylate; Bourne, Lu *et al.*, 2001), $[\text{Cu}_3(\text{TMA})_2(\text{H}_2\text{O})_3]_n$ (TMA is benzene-1,3,5-tricarboxylate; Chui *et al.*, 1999), $[\text{Cu}_2(\text{bdc})_2(\text{Q})_2]_n$ (Q is quinoline; Moulton *et al.*, 2003) and the closest relative *catena*- $[\{\mu_3\text{-benzene-1,3-dicarboxylato}\}(\text{pyridine})_2\text{copper}]_n$, $[\text{Cu}(1,3\text{-bdc})(\text{py})_2]_n$ (Bourne, Mondal & Zaworotko, 2001). The dihedral angle between the two py rings that coordinate to the same Cu atom is 75.41°. The asymmetric unit thus consists of one Cu atom, two pyridine ligands and one hydroxyisophthalate ligand. The

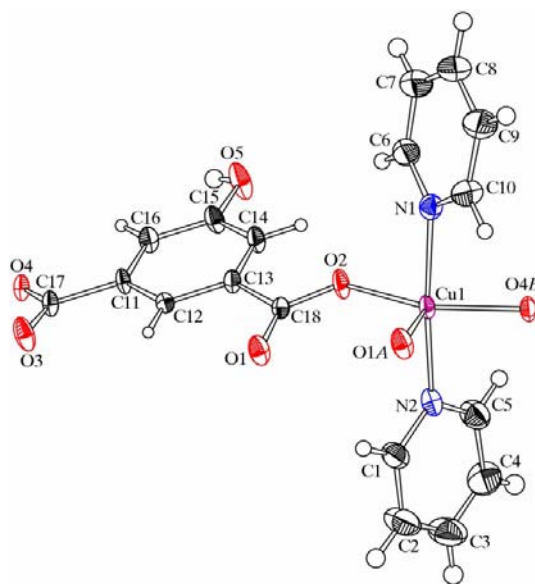


Figure 1

The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are plotted at the 30% probability level. Atoms labeled with the suffixes A and B are at the symmetry positions $(-x, 2-y, 1-z)$ and $(\frac{1}{2}+x, \frac{3}{2}-y, -\frac{1}{2}+z)$, respectively.

5-hydroxyisophthalate group acts as a tridentate ligand in this structure, with one carboxylate group bonding in a monodentate fashion to one Cu atom and the two remaining O atoms bonding in a monodentate fashion to two further Cu atoms. As illustrated in Fig. 2, the interesting feature of polymer (I) is that the OH-BDC ligands link copper centers in different ways to produce three different subrings, Cu \cdots Cu distances of 16.935 (5), 9.814 (2) and 4.523 (3) Å, respectively. The two-dimensional network of [Cu(OH-BDC)]_n moieties also contains an O—H \cdots O hydrogen bond [O5—H5A = 0.82 Å, H5A \cdots O3ⁱⁱⁱ = 1.94 Å, O5 \cdots O3ⁱⁱⁱ = 2.752 (8) Å and O5—H5A \cdots O3ⁱⁱⁱ = 174 Å; symmetry code: (iii) $-x - \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$] and can be envisaged as being built up from interlocking $R_1^1(15)$, $R_2^2(22)$ and eight-membered rings. The coordinated pyridine rings point to the layer regions alternately above and below the two-dimensional net as terminal ligands. Finally, as illustrated in Fig. 3, the two-dimensional [Cu(OH-BDC)(py)₂]_n layers are assembled into a three-dimensional framework *via* edge- or point-to-face C—H \cdots π interactions and offset or slipped π — π stacking interactions, in which the mean C—H \cdots π and π — π hydrogen-bonding distances are

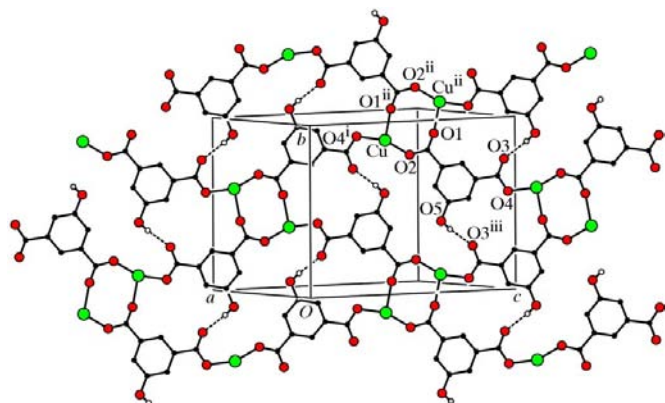


Figure 2
A view of (I), showing how the organization of the two different subrings contributes to the construction of the [Cu(OH-BDC)]_n two-dimensional network.

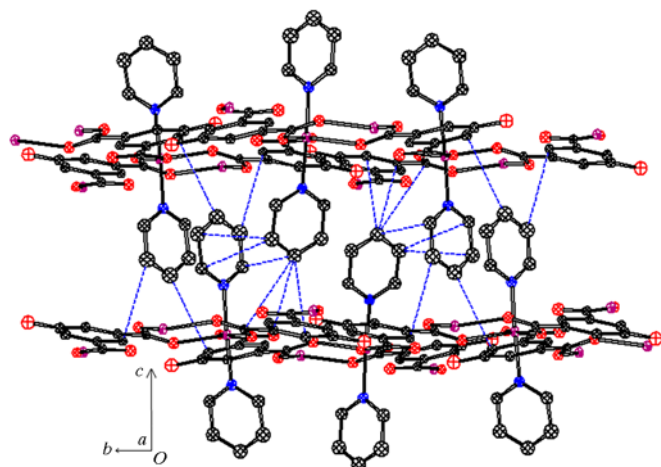


Figure 3
A packing diagram of the title compound, showing the complex C—H \cdots π and π — π interactions, with hydrogen bonds shown as dashed lines.

3.627 (8) and 3.653 (3) Å, respectively (Janiak, 2000). The dihedral angle between two π — π interacting py rings is 22.83° and the distance between the centroids of the two py rings is 4.131 (1) Å.

Experimental

For the preparation of the title compound, a mixture of Cu-(CH₃CO₂)₂·H₂O (0.4 mmol), OH-H₂BDC (0.3 mmol), pyridine (0.6 mmol), NaOH (0.5 mmol) and water (15 ml) was sealed in a 25 ml stainless steel reactor with a Teflon liner. The reaction system was heated at 433 K for 60 h, and then cooled slowly to room temperature. A large number of green crystals of the title complex were obtained and collected by filtration, washed with water and dried in air (56.2% yield based on H₃OABDC).

Crystal data

[Cu(C₈H₄O₅)(C₅H₅N)₂]
 M_r = 401.85
 Monoclinic, $P2_1/n$
 a = 10.1055 (9) Å
 b = 11.6854 (11) Å
 c = 15.7236 (14) Å
 β = 102.415 (2)°
 V = 1813.3 (3) Å³
 Z = 4

D_x = 1.472 Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 2698 reflections
 θ = 2.7–25.1°
 μ = 1.24 mm⁻¹
 T = 293 (2) K
 Prism, green
 0.40 × 0.30 × 0.20 mm

Data collection

Siemens SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: empirical (SADABS; Sheldrick, 1996)
 T_{\min} = 0.802, T_{\max} = 1.000
 5825 measured reflections

3159 independent reflections
 2455 reflections with $I > 2\sigma(I)$
 R_{int} = 0.048
 θ_{max} = 25.1°
 h = -12 → 7
 k = -13 → 12
 l = -18 → 16

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)]$ = 0.071
 $wR(F^2)$ = 0.192
 S = 1.07
 3159 reflections
 235 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0665P)^2 + 13.3127P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.72 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.45 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Cu—O2	1.941 (4)	Cu—N1	2.046 (6)
Cu—O4 ⁱ	1.955 (4)	Cu—O1 ⁱⁱ	2.225 (5)
Cu—N2	2.014 (6)		
O2—Cu—O4 ⁱ	157.2 (2)	N2—Cu—N1	175.0 (2)
O2—Cu—N2	94.0 (2)	O2—Cu—O1 ⁱⁱ	108.26 (19)
O4 ⁱ —Cu—N2	89.6 (2)	O4 ⁱ —Cu—O1 ⁱⁱ	93.81 (18)
O2—Cu—N1	88.9 (2)	N2—Cu—O1 ⁱⁱ	95.1 (2)
O4 ⁱ —Cu—N1	86.2 (2)	N1—Cu—O1 ⁱⁱ	88.0 (2)

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

All H atoms were placed at calculated positions and refined with isotropic displacement parameters, using a riding model [C—H = 0.93 Å, O—H = 0.82 Å, and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and $1.5U_{\text{eq}}(\text{O})$].

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: AV1213). Services for accessing these data are described at the back of the journal.

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