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

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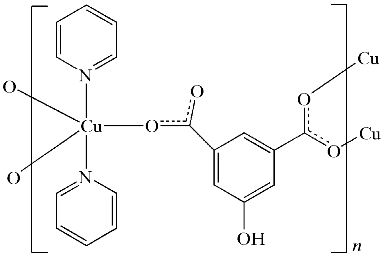
In the title compound, $[Cu(C_8H_4O_5)(C_5H_5N)_2]_n$ or $[Cu(OH\text{-}BDC)(py)_2]_n$ (where OH-H_2BDC is 5-hydroxyisophthalic acid and py is pyridine), the Cu atoms are coordinated by two N atoms from the pyridine ligands and by three O atoms from hydroxyisophthalate ligands in a highly distorted triangular 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 $[Cu(OH\text{-}BDC)]_n$ 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-H_2BDC, 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-H_2BDC with cupric acetate and pyridine (py).



(I)

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 $\{[Cu_2(1,3\text{-bdc})_2(py)_2]_4\}_n$ (1,3-bdc is 1,3-benzenedicarboxylate; Bourne, Lu *et al.*, 2001), $[Cu_3(TMA)_2(H_2O)_3]_n$ (TMA is benzene-1,3,5-tricarboxylate; Chui *et al.*, 1999), $[Cu_2(bdc)_2(Q)_2]_n$ (Q is quinoline; Moulton *et al.*, 2003) and the closest relative *catena*-[(μ_3-benzene-1,3-dicarboxylato)bis(pyridine)copper], $[Cu(1,3\text{-bdc})(py)_2]_n$ (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

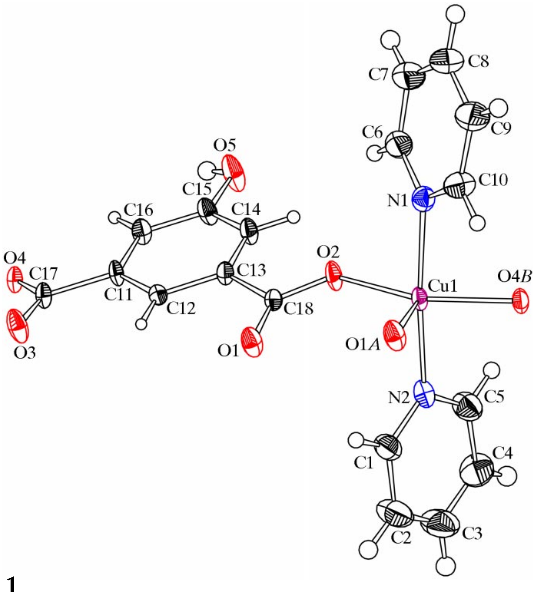


Figure 1
The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are plotted at the 30% probability level. Atoms labeled with the suffixes *A* and *B* are at the symmetry positions ($-x$, $2-y$, $1-z$) and ($\frac{1}{2}+x$, $\frac{3}{2}-y$, $-\frac{1}{2}+z$), respectively.

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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 $[\mathrm{Cu(OH\text{-}BDC)}]_n$ moieties also contains an O—H$\cdots$O hydrogen bond [O5—H5*A* = 0.82 Å, H5*A*$\cdots$O3$^{\rm iii}$ = 1.94 Å, O5$\cdots$O3$^{\rm iii}$ = 2.752 (8) Å and O5—H5*A*$\cdots$O3$^{\rm iii}$ = 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 $[\mathrm{Cu(OH\text{-}BDC)(py)_2}]_n$ layers are assembled into a three-dimensional framework *via* edge- or point-to-face C—H$\cdots\pi$ interactions and offset or slipped π–π stacking interactions, in which the mean C—H$\cdots\pi$ and π–π hydrogen-bonding distances are 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.

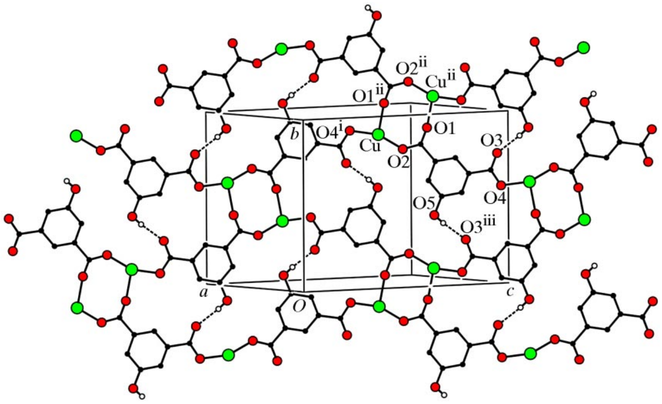

Figure 2
A view of (I), showing how the organization of the two different subrings contributes to the construction of the $[\mathrm{Cu(OH\text{-}BDC)}]_n$ two-dimensional network.

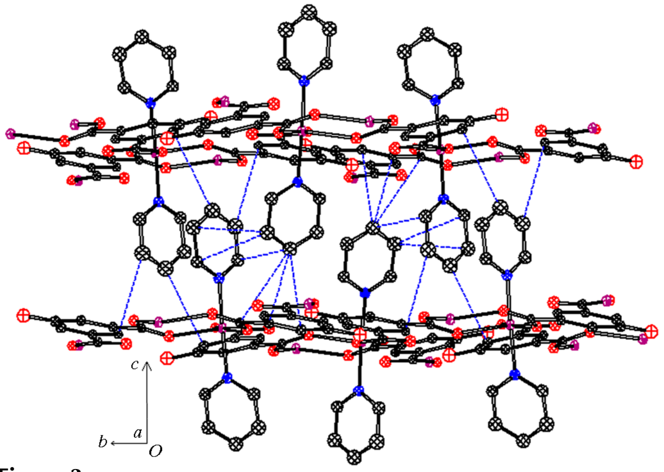

Figure 3
A packing diagram of the title compound, showing the complex C—H$\cdots\pi$ and π–π interactions, with hydrogen bonds shown as dashed lines.

Experimental

For the preparation of the title compound, a mixture of Cu(CH$_3$CO$_2$)$_2$·H$_2$O (0.4 mmol), OH-H$_2$BDC (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 H$_3$OABDC).

Crystal data

$[\mathrm{Cu(C_8H_4O_5)(C_5H_5N)_2}]$
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) Å^3
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)
$T_{\rm min}$ = 0.802, $T_{\rm max}$ = 1.000
5825 measured reflections

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

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 $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.72 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.45 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu—O2	1.941 (4)	Cu—N1	2.046 (6)
Cu—O4$^{\rm i}$	1.955 (4)	Cu—O1$^{\rm ii}$	2.225 (5)
Cu—N2	2.014 (6)		
O2—Cu—O4$^{\rm i}$	157.2 (2)	N2—Cu—N1	175.0 (2)
O2—Cu—N2	94.0 (2)	O2—Cu—O1$^{\rm ii}$	108.26 (19)
O4$^{\rm i}$—Cu—N2	89.6 (2)	O4$^{\rm i}$—Cu—O1$^{\rm ii}$	93.81 (18)
O2—Cu—N1	88.9 (2)	N2—Cu—O1$^{\rm ii}$	95.1 (2)
O4$^{\rm i}$—Cu—N1	86.2 (2)	N1—Cu—O1$^{\rm ii}$	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 $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) and 1.5$U_{\rm eq}$(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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