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catena-Poly[[[bis(2-pyridinecarboxylato-κ^2N,O)-copper(II)]-μ-benzene-1,2,4,5-tetracarboxylic acid] dihydrate]

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In the title compound, $\{[\mathrm{Cu}(\mathrm{C_6H_4NO_2})_2(\mathrm{C_{10}H_6O_8})]\cdot 2\mathrm{H_2O}\}_n$, the $\mathrm{Cu^{II}}$ atom lies on an inversion centre in a distorted octahedral coordination environment. Two 2-carboxylatopyridine ligands chelate to each copper centre through their N and carboxylate O atoms. The axial coordination positions are occupied by carboxylate O atoms from different fully protonated 1,2,4,5-benzenetetracarboxylic acid molecules. These also bridge adjacent copper centres to form infinite one-dimensional chains. Hydrogen bonds formed by the ligand O atoms and water molecules link the individual chains.

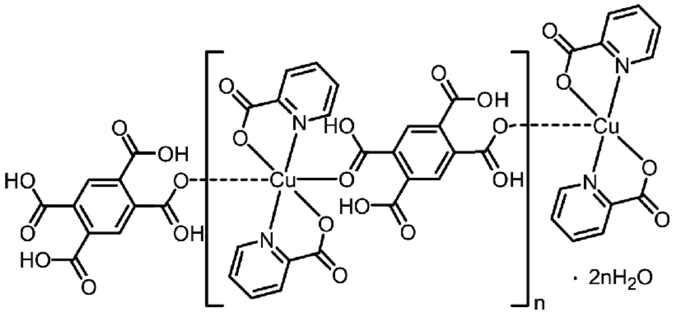
Key indicators

Single-crystal X-ray study
T = 153 K
Mean σ(C–C) = 0.002 Å
R factor = 0.027
wR factor = 0.072
Data-to-parameter ratio = 12.5

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

Comment

One-dimensional metal-organic coordination polymers have been attracting extensive interest owing to their interesting structural features and their potential applications (Gao *et al.*, 2003). One design strategy for constructing one-dimensional coordination polymers is to mediate the effect of multidentate aromatic polycarboxylate ligands, which have been widely used as bridging ligands for the synthesis of coordination polymers with multidimensional networks, by incorporating a chelate ligand into the system. This should have the effect of minimizing the expansion of the polymeric frameworks (Hagrman & Zubieta, 2000). We report here the application of this strategy to the synthesis of a new one-dimensional $\mathrm{Cu^{II}}$ complex with an infinite chain structure.



(I)

The title compound, (I), consists of one-dimensional infinite chains formed from octahedrally coordinated copper cations lying on inversion centres and linked by 1,2,4,5-benzenetetracarboxylic acid, $\mathrm{H_4bta}$, through the C=O O atoms of protonated carboxyl groups in mutually *para* positions on the benzene ring. Two chelating 2-carboxylatopyridine (picolinato) ligands also bind each Cu *via* their N and carboxylate O atoms in the equatorial plane of the octahedron (Fig. 1). The Cu1—O1 [1.9655 (11) Å] and Cu1—N1 [1.9654 (14) Å] bonds

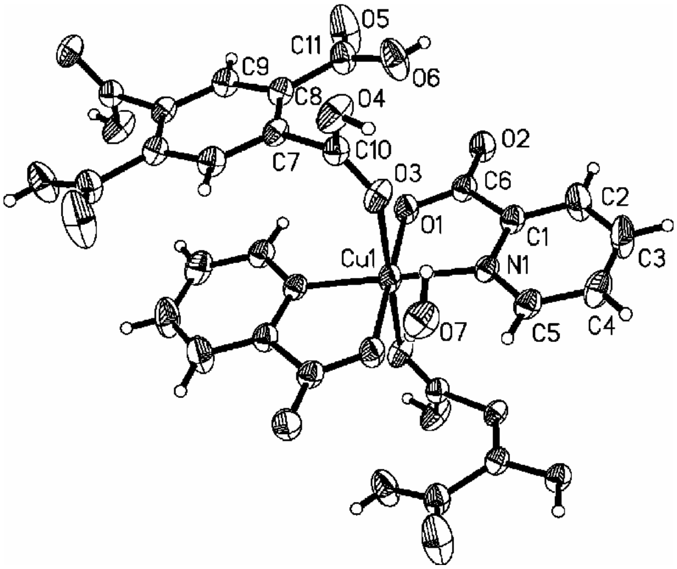


Figure 1
Part of the polymeric structure, showing the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level. One water molecule and half of the atoms from one of the H_4bta molecules have been omitted. Unlabelled atoms are related to labelled atoms by ($\frac{1}{2} - x$, $\frac{1}{2} - y$, $1 - z$) for the second picolinate and incomplete H_4bta ligands, and by ($-x$, $-y$, $1 - z$) for the complete H_4bta ligand.

of the picolinato ligands are unremarkable (Table 1), while the longer Cu1—O3 bonds [2.5113 (12) Å] reflect the presence of a strong Jahn–Teller distortion in the complex (Castineiras *et al.*, 2002; Schveigkardt *et al.*, 2002). The crystal structure is stabilized by an extensive network of hydrogen bonds. Atom O7 acts as a triple H-atom donor. It also acts as an H-atom acceptor. Atom O2 acts as a double H-atom acceptor. These hydrogen bonds are listed in Table 2 and shown in Fig. 2. In the crystal structure, adjacent chains are arranged in the form of a cross as a result of hydrogen bonding between them (Fig. 3). The angle between the pairs of chains is 82.40 (16)°.

Experimental

A mixture of $CuCl_2$ (0.1 mmol), H_4bta (0.1 mmol), pyridine-2-carboxylic acid ethyl ester (0.2 mmol) and water (10 ml) was heated in a sealed Teflon-lined autoclave at 423 K for 4 d. After the mixture has been cooled to room temperature, blue crystals of (I) were isolated by filtration and air-dried (yield *ca* 65%). Analysis found: C 44.0, H 3.1, Cu 10.9, N 4.4%; calculated for $C_{22}H_{14}N_2O_{14}Cu$: C 44.2, H 3.0, Cu 10.6, N 4.7%. IR (cm^{-1}, KBr): 3434 (*m*), 3028 (*m*, *b*), 1727 (*s*), 1692 (*s*), 1633 (*s*), 1599 (*s*), 1571 (*m*), 1503 (*m*), 1478 (*m*), 1443 (*m*), 1368 (*s*), 1296 (*s*), 1249 (*s*), 1156 (*w*), 1111 (*m*), 1051 (*m*), 853 (*m*), 819 (*m*), 766 (*m*), 714 (*m*), 695 (*m*).

Crystal data

$[Cu(C_6H_4NO_2)_2(C_{10}H_6O_8)]\cdot 2H_2O$
$M_r = 597.92$
Monoclinic, $C2/c$
$a = 14.5546 (6)$ Å
$b = 11.5095 (4)$ Å
$c = 13.9115 (6)$ Å
$\beta = 90.487 (2)°$
$V = 2330.32 (16)$ Å^3
$Z = 4$
$D_x = 1.704$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2670 reflections
$\theta = 2.3–27.5°$
$\mu = 1.02$ mm^{-1}
$T = 153 (2)$ K
Block, blue
0.45 × 0.26 × 0.16 mm

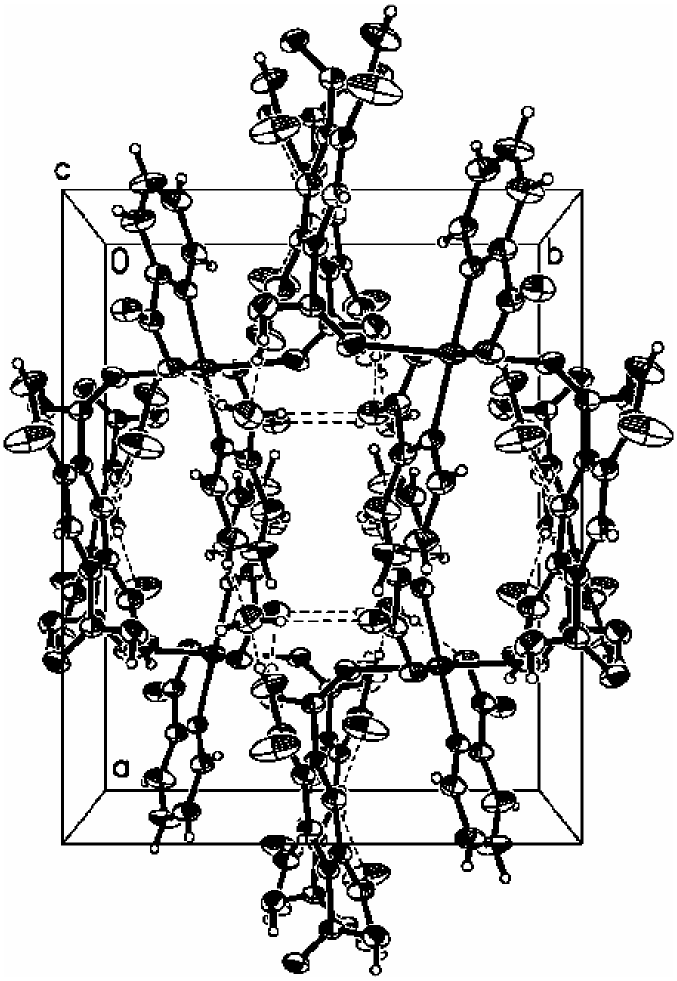


Figure 2
A packing diagram for (I), viewed down the *c* axis. Hydrogen bonds are shown as dashed lines.

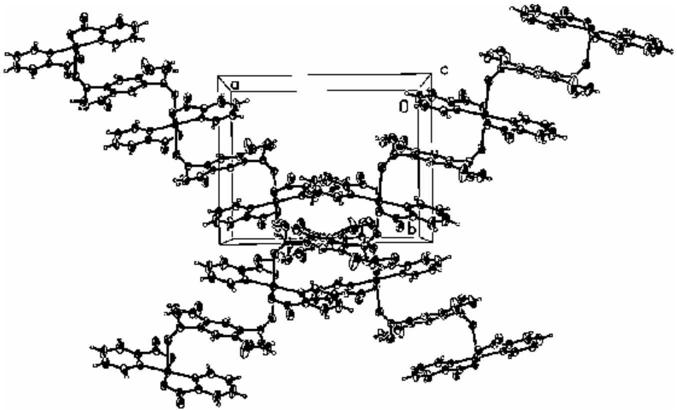


Figure 3
Two adjacent chains in (I) forming a cross.

Data collection

Rigaku R-AXIS RAPID IP diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.749$, $T_{max} = 0.846$
2670 measured reflections
2670 independent reflections
2083 reflections with $I > 2\sigma(I)$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 18$
$k = 0 \rightarrow 14$
$l = -18 \rightarrow 17$

Acta Cryst. (2005). E61, m958–m960 Wang et al. • $[Cu(C_6H_4NO_2)_2(C_{10}H_6O_8)]\cdot 2H_2O$ m959

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.072$
$S = 0.95$
2670 reflections
214 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0434P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	1.9654 (14)	Cu1—O3	2.5113 (12)
Cu1—O1	1.9655 (11)		
N1—Cu1—O1	83.14 (5)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O7—H7*A*···O1^{i}	0.85 (3)	2.06 (3)	2.8973 (19)	168 (3)
O7—H7*B*···O2^{ii}	0.86 (3)	2.19 (3)	2.922 (2)	144 (2)
O7—H7*B*···O3	0.86 (3)	2.60 (3)	3.1498 (18)	123 (2)
O4—H4*A*···O2^{ii}	0.85 (2)	1.79 (2)	2.6397 (17)	173 (2)
O6—H6*A*···O7^{iii}	0.79 (3)	1.90 (3)	2.677 (2)	171 (3)

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

All the H atoms were found in difference Fourier maps and were refined freely [C—H = 0.874 (19)–0.931 (18) Å].

Data collection: *RAPID-AUTO* (Rigaku, 2001); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Bruker, 1998); software used to prepare material for publication: *SHELXL97*.

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m960 Wang *et al.* • $[Cu(C_6H_4NO_2)_2(C_{10}H_6O_8)]\cdot 2H_2O$ *Acta Cryst.* (2005). E**61**, m958–m960