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Diaquatetrakis(pyridine-2,6-dicarboxylato-κ^2O^2,O^6)tetrakis(μ-pyridine-3,5-dicarboxylic acid-κ^2N:O)-tetracopper(II): a copper complex with tetrameric molecular units

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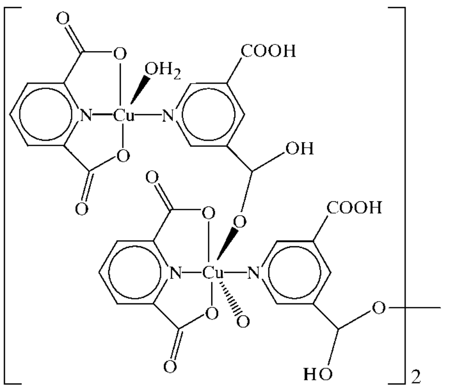
Crystals of the title tetramer, $[Cu_4(C_7H_3NO_4)_4(C_7H_5NO_4)_4(H_2O)_2]$, were synthesized hydrothermally at 433 K. The triclinic structure consists of tetrameric molecular species, which interact *via* strong hydrogen bonds. The Cu^{II} ions are distributed equally between one square-pyramidal site and one octahedral site distorted by the Jahn–Teller effect. This coordination complex exhibits the peculiarity of having Cu^{II} ions linked to both the 2,6- and the 3,5-isomers of pyridinedicarboxylic acid.

Comment

Hybrid microporous compounds exhibit structures built up from inorganic moieties connected by organic linkers. The anchorage of the organic molecules on the inorganic moieties is ensured by complexing functions such as carboxylates, phosphonates or heteroatoms involved in the coordination sphere of the metal ions (Férey, 2001, and references therein). Being able to act as ligands *via* both their carboxylate functions and the N atom of the aromatic ring, different isomers of pyridinedicarboxylic acid have been widely used in this field (Suga & Okabe, 1996; Sileo *et al.*, 1996, 1997; Min, Yoon, Jung *et al.*, 2001*a*). They principally give rise to coordination complexes with low-dimensional structures. The chelation of the metal ion by one N atom and one O atom is often observed for isomers in which one carboxylate function is located at the 2- or 6-position of the pyridine ring. In order to modulate the connectivity of the metal ion with the pyridinedicarboxylic acids, we have tried to incorporate two different isomers into the same structure: pyridine-2,6-dicarboxylic acid (or dipicolinic acid) gives rise to chelation, whereas pyridine-3,5-dicarboxylic acid (or dinicotinic acid) favours polymerization processes (Min, Yoon, Lee *et al.*, 2001*b*).



(I)

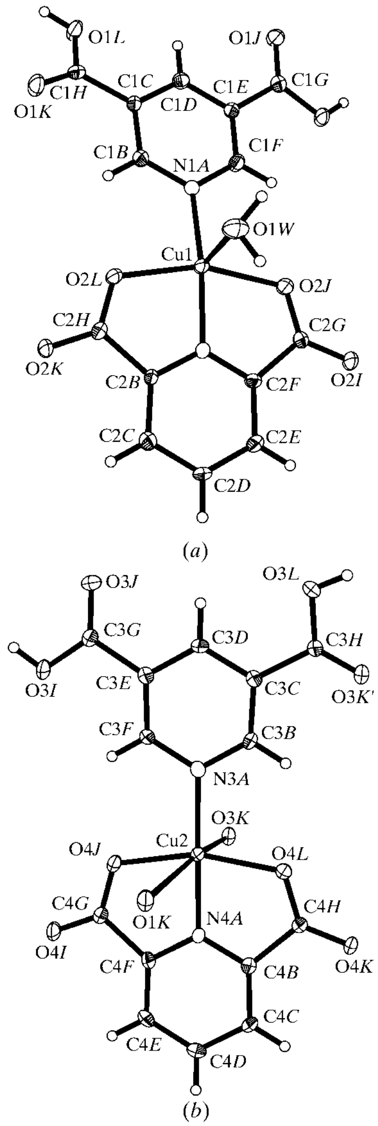


Figure 1
The two elementary complexes, showing the different neighbourhoods of (*a*) atom Cu1 and (*b*) atom Cu2. H atoms are shown as circles of arbitrary radii.

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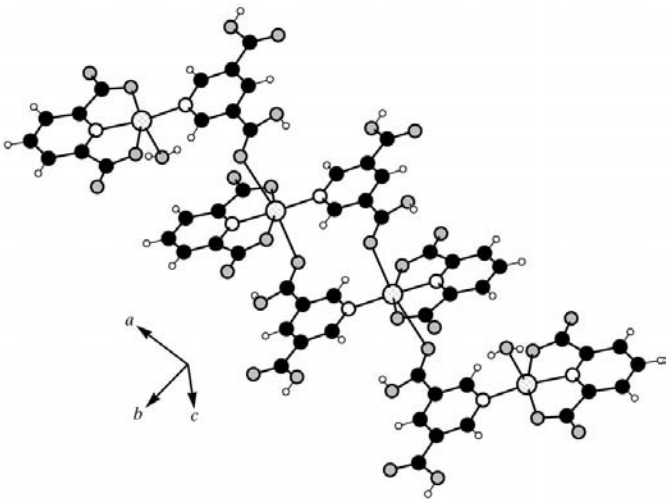

Figure 2
A view of the tetrameric moiety of (I).

The structure of the title compound, (I), contains two cationic sites occupied by Cu^{2+} ions. Atom Cu1 (Fig. 1 and Table 1) is fivefold coordinated in a distorted square pyramid. It is doubly chelated by one dipicolinate anion, sharing one N atom and two O atoms provided by the two α-located carboxylate functions; the two remaining apices are filled by an N ligand from the dinicotinic acid molecule, completing the basal plane of the pyramid, and one terminal water molecule, perpendicularly disposed. Atom Cu2 is sixfold coordinated, creating an elongated octahedron. In the equatorial plane, atom Cu2 is doubly chelated by the dipicolinate anion and the N atom of the dinicotinic acid molecule. Axially, atom Cu2 forms two long bonds with O atoms of the carboxylate functions of two pyridine-3,5-dicarboxylic acid complexes. As a consequence, the complex moieties built around atom Cu2 give rise to a polycondensation process, whereas the complex around atom Cu1 terminates a similar mechanism. Indeed, each Cu2 complex is linked to a similar entity, forming a dimeric central core onto which two Cu1 complexes are grafted (Fig. 2).

Inside this tetrameric unit, all the pyridine-3,5-dicarboxylic acid molecules are fully protonated and all the dipicolinate moieties are fully deprotonated. The stability of the structure is ensured *via* a network of intermolecular hydrogen bonds involving both the OH groups of the carboxyl functions and the water molecules (Table 2). Although the nuclearity and the resulting complexity of the tetrameric unit is high, no intramolecular hydrogen bonding is observed. The title compound shows that the connection of the multidentate dipicolinate ligand to the metal ion is strongly anisotropic. The double chelation requires that all the donor–acceptor bonds are on the same side of the coordination sphere of the cation, meaning that the opposite side remains open. This structural observation allows us to project the synthesis of new dipicolinate compounds, incorporating other kinds of ligands utilizing the available part of the coordination sphere.

Experimental

Compound (I) was prepared from a mixture of copper dichloride dihydrate, pyridine-2,6-dicarboxylic acid, pyridine-3,5-dicarboxylic acid and deionized water in a 1:0.25:0.25:250 molar ratio. This mixture was sealed in a Teflon-lined Parr autoclave and was then heated for 48 h at 433 K under autogeneous pressure. The pH measured before and after heating remained at 1 throughout the synthesis. After cooling to room temperature, the solid was separated from the liquid phase by filtration, washed with water and dried in air. The pure compound was obtained in the form of small blue platelets. Thermogravimetric experiments performed under an O_2 flow show a small initial weight loss at 523 K, corresponding to dehydration (measured 2.3%, calculated 2.22%), followed by combustion of the organic linkers at 593 K (measured 78.8%, calculated 79.9% for the CuO residue). The calcined residue is amorphous.

Crystal data

$[Cu_4(C_7H_3NO_4)_4(C_7H_5NO_4)_4(H_2O)_2]$
$M_r = 1619.09$
Triclinic, $P\bar{1}$
$a = 7.1350\ (2)$ Å
$b = 11.8614\ (1)$ Å
$c = 17.0675\ (3)$ Å
$\alpha = 96.480\ (1)^\circ$
$\beta = 94.971\ (1)^\circ$
$\gamma = 95.229\ (1)^\circ$
$V = 1422.36\ (5)$ Å^3

$Z = 1$
$D_x = 1.890$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3414 reflections
$\theta = 1.2–27.0^\circ$
$\mu = 1.59$ mm^{-1}
$T = 296\ (2)$ K
Parallelepiped, blue
$0.16 \times 0.10 \times 0.06$ mm

Data collection

Bruker SMART 1K CCD
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
$T_{min} = 0.785$, $T_{max} = 0.911$
8996 measured reflections
6126 independent reflections

3728 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$
$\theta_{max} = 27.0^\circ$
$h = -9 \rightarrow 9$
$k = -15 \rightarrow 11$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.138$
$S = 0.99$
6126 reflections
471 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0645P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.53$ e Å^{-3}
$\Delta\rho_{min} = -1.00$ e Å^{-3}

Table 1
Selected interatomic distances (Å).

Cu1—N1*A*	1.973 (3)	Cu2—N4*A*	1.889 (3)
Cu1—N2*A*	1.899 (3)	Cu2—O1*K*	2.724 (4)
Cu1—O2*J*	2.032 (3)	Cu2—O3*K*	2.541 (4)
Cu1—O2*L*	2.010 (3)	Cu2—O4*J*	2.001 (3)
Cu1—O1*W*	2.249 (4)	Cu2—O4*L*	1.999 (3)
Cu2—N3*A*	1.946 (4)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*I*—H1*I*···O4*I*^{i}	0.82	1.76	2.569 (4)	171
O1*L*—H1*L*···O4*K*^{ii}	0.82	1.81	2.583 (4)	157
O1*W*—H1*W*···O1*J*^{i}	0.89 (5)	2.17 (5)	3.051 (5)	172 (6)
O1*W*—H2*W*···O2*I*^{iii}	0.87 (5)	2.32 (5)	3.180 (5)	170 (6)
O3*I*—H3*I*···O2*I*^{i}	0.82	1.76	2.574 (4)	172
O3*L*—H3*L*···O2*K*^{ii}	0.82	1.76	2.536 (4)	157

Symmetry codes: (i) $-x, -y, -z$; (ii) $-x, -y, 1 - z$; (iii) $1 - x, 1 - y, -z$.

The H atoms of the pyridine rings and the carboxylic acid functions were positioned geometrically, whereas those of the water molecules were found from difference Fourier syntheses and then restrained to give two similar O—H bond lengths close to 0.85 Å.

Data collection: *SMART* (Bruker, 1996); cell refinement: *SAINT* (Bruker, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1996); software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR1072). Services for accessing these data are described at the back of the journal.

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