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Tetraaquabis[2-(4-pyridyl)ethanesulfonato-*κN*]-copper(II)

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Key indicators

Single-crystal X-ray study
T = 130 K
Mean σ(C–C) = 0.007 Å
R factor = 0.055
wR factor = 0.141
Data-to-parameter ratio = 12.8

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

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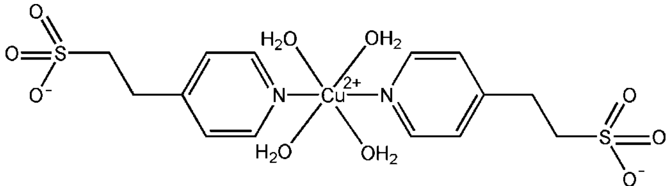
The centrosymmetric title compound, $[Cu(C_7H_8O_3S)_2(H_2O)_4]$, forms a pillared hydrogen-bonded layered network. The coordination geometry of the Cu^{II} ion is distorted octahedral, involving four aqua ligands and two N-atom donors of two 2-(4-pyridyl)ethanesulfonate (PES) ligands. The sulfonate group of PES is not involved in coordination to the metal, but participates in hydrogen bonds with the aqua ligands.

Comment

As robust and reliable intermolecular interactions, hydrogen bonds often play a dominant role in crystal engineering. Their selectivity and directionality often control the design of various molecular assemblies (Desiraju & Steiner, 1999; Steiner, 2002). In principle, by placing functional groups properly, supramolecular motifs, for example, tapes, two- and three-dimensional (*n*D) networks, can be formed *via* hydrogen bonds (Desiraju, 2002; Moulton & Zaworotko, 2001). In this context, 2-(4-pyridyl)ethanesulfonic acid (HPES) was chosen as a building unit due to its predictable and interesting supramolecular properties and complementary hydrogen-bonding capabilities (Zhang *et al.*, 2004). We report here a new pillared hydrogen-bonded layered network, $Cu(PES)_2(H_2O)_4$, (I).



(I)

Fig. 1 shows the coordination of the Cu^{II} ion of (I). Each Cu^{II} ion is located on a center of symmetry, coodinated, in distorted octahedral fashion, by four aqua ligands in the equatorial plane, and two N atoms of PES ligands in the axial sites (Table 1). The sulfonate group of PES is not involved in coordination to the metal, but participation in hydrogen bonds with aqua ligands. As shown in Fig. 2, three O atoms of a sulfonate group form four hydrogen bonds with four different

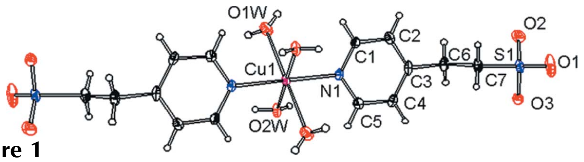


Figure 1
A view of (I), with 30% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii. Unlabeled atoms are related to labeled atoms by $(1-x, 1-y, -z)$

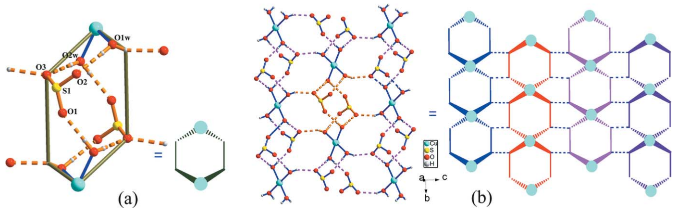


Figure 2
(*a*) Schematic representation of the hexagonal ring with a chair conformation. (*b*) Schematic representation of the two-dimensional hydrogen-bonded (dashed lines) layered structure in (I).

aqua ligands (Table 2). Two sulfonate groups and two $Cu(H_2O)_2$ units are linked by hydrogen bonds, creating a hexagonal ring with a chair conformation (Fig. 2*a*). These rings are connected with Cu atoms as the hinges, resulting in a one-dimensional zigzag chain. Each chain links two adjacent antiparallel chains through hydrogen bonds (O1*W*—H···O3), forming a two-dimensional layer (Fig. 2*b*). The two-dimensional layers are further pillared by (4-pyridyl)ethane units to complete the final three-dimensional network.

Pillar-layered architectures, which have been proven to be an effective and controllable route to design three-dimensional frameworks with large channels, have received much research attention. Among these architectures, the layers are often constructed by coordination bonds. However, there are fewer reports of architectures with hydrogen-bonding layers sustained by pillars, although an isostructural complex, $Zn(PES)_2(H_2O)_4$, has been reported (Zeng *et al.*, 2000). In this paper, we have illustrated an unusual pillared hydrogen-bonded layered architecture.

Experimental

A mixture of 2-(4-pyridyl)ethanesulfonic acid (0.093 g, 0.5 mmol) and $Cu(NO_3)_2\cdot 3H_2O$ (0.12 g, 0.5 mmol) in CH_3OH–H_2O (3:1 *v*/*v*, 20 ml) was heated to 313 K for 1 h with vigorous stirring. After cooling, the reaction mixture was filtered and well shaped crystals of $Cu(PES)_2(H_2O)_4$ were obtained from the mother liquor by slow evaporation at room temperature over several days (yield 85%).

Crystal data

$[Cu(C_7H_8O_3S)_2(H_2O)_4]$
$M_r = 508.04$
Monoclinic, $P2_1/c$
$a = 9.0089$ (11) Å
$b = 8.7859$ (11) Å
$c = 12.7866$ (16) Å
$\beta = 93.402$ (2)°
$V = 1010.3$ (2) Å^3
$Z = 2$

$D_x = 1.670$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2454 reflections
$\theta = 2.3$–25.0°
$\mu = 1.34$ mm^{-1}
$T = 130.0$ K
Prism, blue
0.30 × 0.20 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.732$, $T_{max} = 0.874$
2781 measured reflections

1713 independent reflections
1683 reflections with $I > 2\sigma(I)$
$R_{int} = 0.031$
$\theta_{max} = 25.0°$
$h = -10 \rightarrow 10$
$k = -7 \rightarrow 10$
$l = -7 \rightarrow 15$

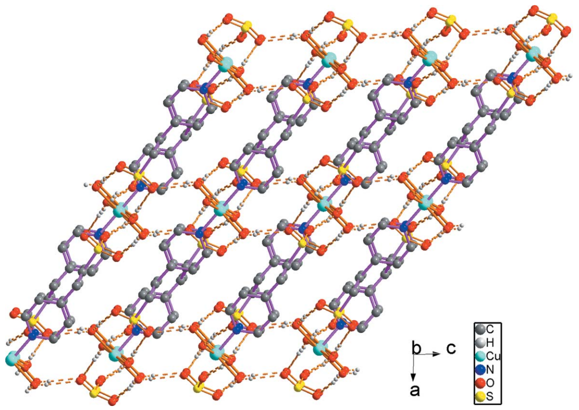


Figure 3
The three-dimensional packing structure of (I), showing the pillared hydrogen-bonded (dashed lines) layered architecture.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.141$
$S = 1.06$
1713 reflections
134 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0629P)^2 + 4.7962P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.61$ e Å^{-3}
$\Delta\rho_{min} = -0.69$ e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.054 (4)

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	1.999 (4)	Cu1—O1*W*	2.419 (3)
Cu1—O2*W*	2.004 (3)		
N1—Cu1—O2*W*	88.96 (14)	O2*W*—Cu1—O1*W*	88.74 (13)
N1—Cu1—O1*W*	92.33 (14)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*WA*···O2^{i}	0.82	2.01	2.827 (5)	179
O1*W*—H1*WB*···O3^{ii}	0.82	2.11	2.875 (5)	157
O2*W*—H2*WA*···O1^{iii}	0.81	1.94	2.742 (5)	176
O2*W*—H2*WB*···O3^{i}	0.81	1.90	2.713 (4)	175

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

The H atoms were positioned geometrically and refined using a riding model [C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$; O—H = 0.82 Å and $U_{iso}(H) = 1.2U_{eq}(O)$].

Data collection: *SMART* (Siemens, 1996); cell refinement: *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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