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catena-Poly[[[aqua[3-(2-pyridylsulfanyl)propionato *N*-oxide-κO^1]-copper(II)]-μ-[3-(2-pyridylsulfanyl)propionato *N*-oxide-$\kappa^3 O^3$:O^1,$O^{1'}$] dihydrate]

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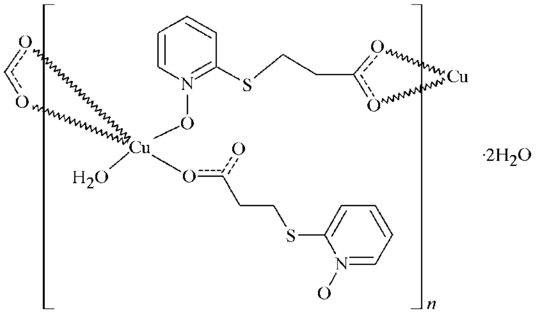
In the title complex, $\{[Cu(C_8H_8NO_3S)_2(H_2O)]\cdot 2H_2O\}_n$, the Cu^{II} cation has a distorted square-pyramidal coordination environment consisting of five O atoms, one from a water molecule, one from an N—O group and the other three from the carboxylate groups of two 3-(2-pyridylsulfanyl)propionate *N*-oxide anions. The aqua[3-(2-pyridylsulfanyl)propionato *N*-oxide]copper(II) moieties are bridged by 3-(2-pyridylsulfanyl)propionate *N*-oxide anions to form an infinite three-dimensional coordination polymer with a zigzag chain structure. The crystal structure is stabilized by hydrogen bonds.

Comment

In recent years, intense research activity has been directed towards the design and construction of novel coordination polymers based on covalent interactions (Fujita *et al.*, 1994) or supramolecular contacts, such as hydrogen bonds and π–π stacking interactions (Desiraju, 1995). These polymers are of interest not only due to their fascinating structures, but also because of their unexpected properties for potential application in areas such as gas adsorption, catalysis and optoelectronic devices (Matsumoto *et al.*, 1999; Chui *et al.*, 1999). The key step in the design of coordination polymers is to select suitable multidentate bridging ligands and spacers. Many pyridine-based carboxylate ligands (Kumaresan *et al.*, 2006; Hussain, 1996; Fariati *et al.*, 1998) have been used to obtain coordination polymers but, to the best of our knowledge, very little is known about the coordination chemistry of 1-oxopyridinium-2-thiopropionic acid, HOPTP (Ramasubramanian *et al.*, 2007). The HOPTP ligand possesses several features. It is a polydentate ligand with up to four donor atoms. The *N*-oxide group has proved to be more versatile in its coordination mode than pyridine, because the lone pairs of the O atom of the *N*-oxide provide more coordination flexibility than the pyridine N atom, which affords only a straight coordination geometry. Steric hindrance is much smaller for *N*-oxide and, in addition, it has the capability of forming hydrogen bonds. Finally, some *N*-oxides possess important antimicrobial activity (Danish & Rajendraprasad, 2003) and they are also recognized as potential DNA-cleaving agents (Ganley *et al.*, 2001). In view of the above facts and our interest in the synthesis and characterization of coordination complexes, we report here the synthesis and single-crystal characterization of the title complex, (I).



(I)

Complex (I) is a one-dimensional polymer, the units $[Cu(OPTP)(H_2O)]^+$ and $OPTP^-$ being the elemental links that define the chain structure. The Cu^{II} metal centre is strongly bonded to four O atoms and weakly bonded to a fifth O atom, displaying a distorted square-pyramidal geometry, as evidenced by the bond angles around atom Cu1 (Fig. 1 and Table 1): the dihedral angle between the O1/Cu1/O2($-x + 2$, $y + \frac{1}{2}$, $-z + \frac{1}{2}$) and O5/Cu1/O7 planes is 49.66 (8)°. The O atoms involved in the coordination of the Cu^{II} ion belong to the $OPTP^-$ anions (O2, O3 and O5), the pyridine *N*-oxide (O1) and the water molcule (O7) (Fig. 1). Two water molecules (O8 and O9) are left uncoordinated in the crystal structure.

An infinite three-dimensional coordination polymer with a zigzag chain structure is formed by the Cu^{II} cations, μ_3-bridging and terminal $OPTP^-$ anions, and one terminal water molecule (Fig. 2). The Cu—O(carboxylate) bond lengths are in the range 1.914 (2)–2.755 (1) Å (Table 1), within which the semi-coordinating Cu1—O3 distance [2.755 (1) Å] is considerably longer than the Cu—O distance reported earlier (2.010 Å; Zou *et al.*, 1998), while the Cu1—O5 distance of 1.914 (2) Å is shorter than the normal literature value (1.927 Å; Hu *et al.*, 2003). The pyridine *N*-oxide rings are nonplanar. The puckering parameters (φ_2, θ_2 and Q; Cremer & Pople, 1975) for the N1/C1–C5 and N2/C9–C13 rings indicate that these rings are in envelope (^5E) and half-chair ($^5H_4$) conformations, respectively.

Overall, the structure of (I) does not depart from what might be expected, but its most interesting feature is its self-assembly into a three-dimensional structure. This process is achieved through a dense network of C—H···O hydrogen

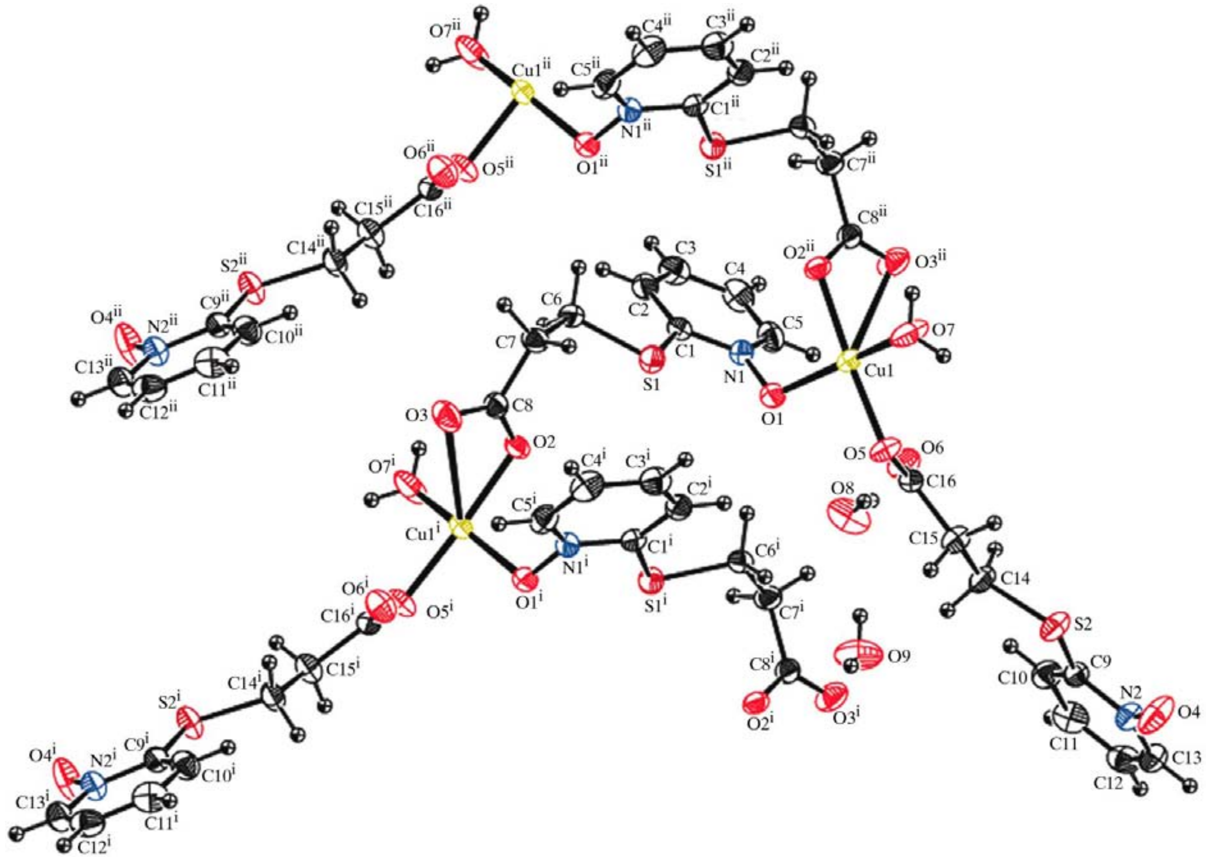


Figure 1

A view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $-x + 2, y - \frac{1}{2}, -z - \frac{1}{2}$; (ii) $-x + 2, y + \frac{1}{2}, -z + \frac{1}{2}$.]

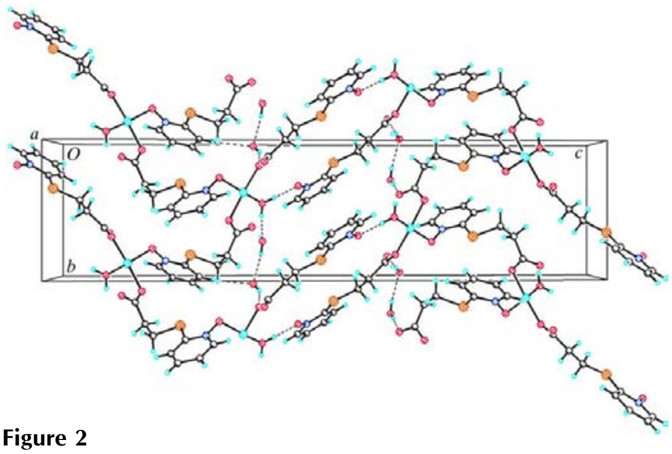


Figure 2

A perspective view of the hydrogen bonding in (I). Dashed lines indicate O—H···O and C—H···O interactions.

bonds involving most of the available H atoms of the $[Cu(OPTP)(H_2O)]^+$ units and only one H atom of the $OPTP^-$ units (Table 2). The two solvent water molecules interlink neighbouring $[Cu(OPTP)(H_2O)]^+$ units through O—H···O hydrogen-bond interactions (Table 2). The O atom of the coordinated water molecule (O7) is involved in intermolecular hydrogen-bond interactions with the N—O group of the $OPTP^-$ ion and with solvent water molecule (O9). These interactions stabilize the crystal packing (Fig. 2). On the whole, the network of C—H···O and O—H···O hydrogen bonds can be described by Etter's hydrogen-bond notation (Etter, 1990) as $R^2_2(22)$, $R^8_6(30)$, $R^3_3(28)$, $R^3_2(11)$, $R^2_2(19)$ and $R^2_2(18)$. Among these, the two adjacent hydrogen-bonded rings $R^2_2(22)$ and $R^8_6(30)$ form an infinite ladder in the crystal structure *via* O—H···O interactions.

Experimental

A mixture of $CuSO_4·5H_2O$ (0.0624 g, 0.25 mmol), HOPTP (0.0995 g, 0.50 mmol) and NaOH (0.040 g, 0.50 mmol) in ethanol (20 ml) was stirred for 10 h at room temperature. The stirred solution was filtered and kept for slow evaporation. After a week, peacock-blue coloured crystalline blocks of (I) appeared. The crystals were collected by filtration, washed with deionized water followed by diethyl ether, and then dried (yield 0.090 g, 70%).

Crystal data

$[Cu(C_8H_8NO_3S)_2(H_2O)]·2H_2O$
$M_r = 514.02$
Monoclinic, $P2_1/c$
$a = 6.9091$ (5) Å
$b = 8.6855$ (7) Å
$c = 34.899$ (3) Å
$\beta = 92.9740$ (10)°

$V = 2091.4$ (3) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 1.30$ mm^{-1}
$T = 298$ (2) K
0.36 × 0.22 × 0.14 mm

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Data collection

Bruker APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)
$T_{\rm min}$ = 0.653, $T_{\rm max}$ = 0.839
10850 measured reflections
3769 independent reflections
3567 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.021

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.117
S = 1.19
3769 reflections
289 parameters
9 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\rm max}$ = 0.77 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.27 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O5	1.914 (2)	O1—N1	1.342 (4)
Cu1—O7	1.926 (3)	O2—C8	1.273 (4)
Cu1—O2$^{\rm i}$	1.933 (2)	O3—C8	1.235 (4)
Cu1—O3$^{\rm i}$	2.755 (1)	O4—N2	1.321 (4)
Cu1—O1	1.950 (2)		
O5—Cu1—O7	86.80 (11)	O1—Cu1—O2$^{\rm i}$	93.12 (10)
O5—Cu1—O2$^{\rm i}$	175.57 (11)	O7—Cu1—O3$^{\rm i}$	94.38 (1)
O7—Cu1—O2$^{\rm i}$	88.78 (11)	O1—Cu1—O3$^{\rm i}$	99.40 (1)
O5—Cu1—O1	91.22 (10)	C8—O2—Cu1$^{\rm ii}$	110.9 (2)
O7—Cu1—O1	164.02 (14)	C16—O5—Cu1	119.8 (2)

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O7—H7*C*···O9$^{\rm i}$	0.822 (17)	1.86 (2)	2.664 (4)	164 (4)
O7—H7*D*···O4$^{\rm iii}$	0.839 (17)	1.750 (18)	2.589 (4)	178 (4)
O9—H9*C*···O3$^{\rm iv}$	0.811 (17)	1.961 (18)	2.772 (4)	177 (4)
O9—H9*D*···O8$^{\rm v}$	0.798 (17)	1.98 (2)	2.754 (5)	162 (3)
O8—H8*C*···O6$^{\rm vi}$	0.837 (17)	1.919 (19)	2.754 (4)	176 (3)
O8—H8*D*···O5$^{\rm ii}$	0.847 (18)	1.99 (2)	2.770 (4)	154 (3)

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

Water H atoms were located and refined subject to O—H distance restraints of 0.82 (1) Å. The remaining H atoms were refined using a riding model, with C—H = 0.97 Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C) for idealized secondary CH$_2$, and C—H = 0.93 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) for aromatic CH groups.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2004); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR3018). Services for accessing these data are described at the back of the journal.

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