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Key indicators

Single-crystal X-ray study
 T = 293 K
 Mean $\sigma(C-C) = 0.007 \text{ \AA}$
 R factor = 0.065
 wR factor = 0.145
 Data-to-parameter ratio = 14.2

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

catena-Poly[[aqua(piperazin-1-ium- κN^4)copper(II)]-
 μ -5-sulfonatoisophthalato- $\kappa O^1:\kappa O^3$]

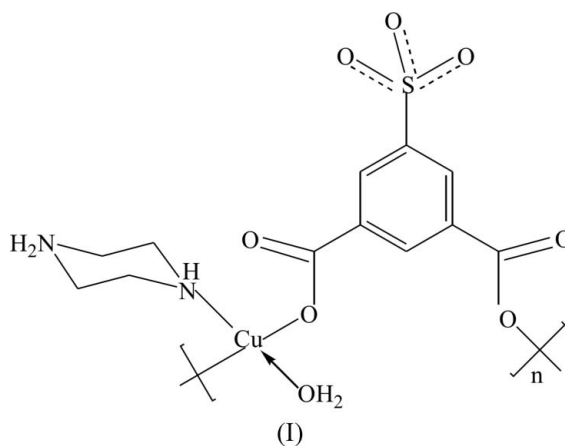
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Blue crystals of the title compound, $[\text{Cu}(\text{C}_8\text{H}_3\text{O}_7\text{S})(\text{C}_4\text{H}_{11}\text{N}_2)(\text{H}_2\text{O})]_n$, were obtained from the slow diffusion of a methanol solution of piperazine into an aqueous solution of sodium 5-sulfoisophthalate and copper nitrate. The Cu^{II} ion coordination is composed of two O atoms from two trianionic 5-sulfoisophthalic acid ligands, one N atom from the piperazinium cation and one water O atom in a distorted square-planar geometry. The Cu^{2+} ions are bridged by the sulfonate-carboxylate ligands to form a zigzag chain. Hydrogen bonds and π - π interactions among the chains produce a three-dimensional hydrogen-bonded architecture.

Comment

In the past few years, efforts have focused on the study of carboxylate-based (such as malonate, oxalate and benzene-1,3,5-tricarboxylate) coordination polymers because of their interesting network topologies (Moulton & Zaworotko, 2001; Virovets *et al.*, 1993; Yaghi *et al.*, 1996). In extending our own studies on benzene-1,3,5-tricarboxylates, we have also investigated the 5-sulfoisophthalate, and recently reported a series of lanthanide complexes of 5-sulfoisophthalic acid that demonstrates a lanthanide contraction effect (Liu & Xu, 2005b). Several Cd^{II} and Cu^{II} complexes of 5-sulfoisophthalic acid have also been reported (Sun, Cao, Sun, Li *et al.*, 2003; Liu & Xu, 2005a).

The self-assembly of the Cu^{2+} ion with the 5-sulfoisophthalate ion (sip) and piperazine (pip) yields the title complex, (I). The asymmetric unit of (I) consists of one copper(II) ion, one sip^{3-} anion, one piperazinium cation (Hpip^+) and one coordinated water molecule. As depicted in Fig. 1, the compound features a zigzag chain structure, which is



similar to the structure of the Cd compound (Liu & Xu, 2005c). The Cu atom is four-coordinated by two O atoms from

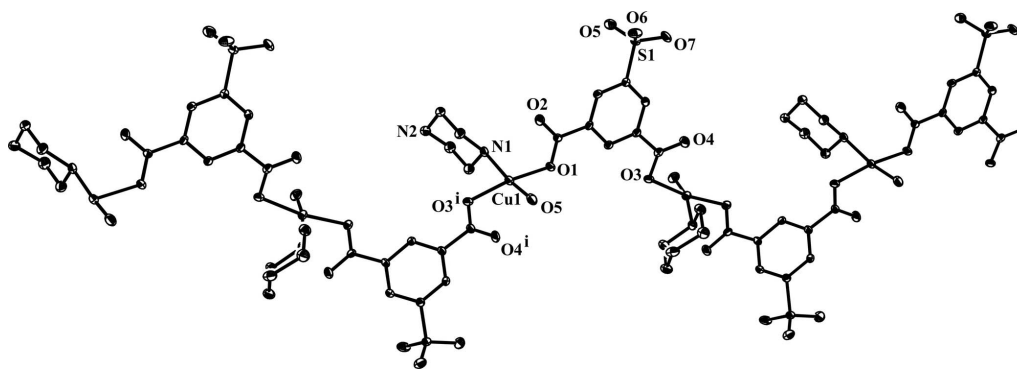


Figure 1
The title compound, with displacement ellipsoids drawn at the 35% probability level. H atoms have been omitted.

two symmetry-related sip^{3-} ligands, one N atom from Hpip^+ and one water O atom. The bond dimensions involving Cu are normal (Table 1), and are comparable to the values in related copper complexes (Sun, Cao, Sun, Bi *et al.*, 2003). The $[\text{CuNO}_3]$ group assumes a square planar configuration, with a mean deviation of 0.1922 Å; the maximum deviation of 0.2439 (3) Å is for atoms O5, which is involved in hydrogen bonding. Piperazine should be protonated to achieve charge balance, which is borne out by the existence of the two hydrogen bonds to atom N2. The Hpip^+ ion coordinates to the metal center, and is different from the unit found in the copper complex $[\text{Cu}(\text{Hsip})(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O} \cdot 0.5\text{pip}$, which has a free pip molecule (Sun, Cao, Sun, Li *et al.*, 2003).

Each sip^{3-} anion bridges two neighboring Cu^{2+} ions through its two monodentate carboxylate groups (Fig. 1). The

sulfonate group is uncoordinated and engages in hydrogen bonding to the coordinated water and Hpip^+ ion. The three identical S—O bond distances imply extensive electron delocalization. The linking of the Cu^{2+} ions through the carboxylate groups of sip^{3-} anions leads to the formation of a zigzag chain propagating along *b*. The benzene rings in the chain are twisted with respect to each other with a dihedral angle of *ca* 11.6 (6)°.

The extensive hydrogen bonds and π – π stacking interactions among the chains are responsible for the three-dimensional supramolecular framework structure (Figs. 2 and 3.) Four types of hydrogen bond are observed: hydrogen bonds between (i) the coordinated water molecules and carboxylate O atoms; (ii) the coordinated water molecules and sulfonate O atoms; (iii) the coordinated N atom of Hpip^+ and carboxylate O atoms; (iv) the non-coordinated N atom of Hpip^+ and sulfonate O atoms. The Hpip^+ cations appear to fill up the voids of the framework. Additionally, π – π stacking interactions between the parallel aromatic rings of adjacent sip^{3-} anions in an offset fashion with a face-to-face distance of *ca* 3.614 Å are observed. Similar hydrogen bonds and π – π interactions are also observed in the related Cd^{II} and Cu^{II} complexes (Liu & Xu, 2005c; Sun, Cao, Sun, Li *et al.*, 2003).

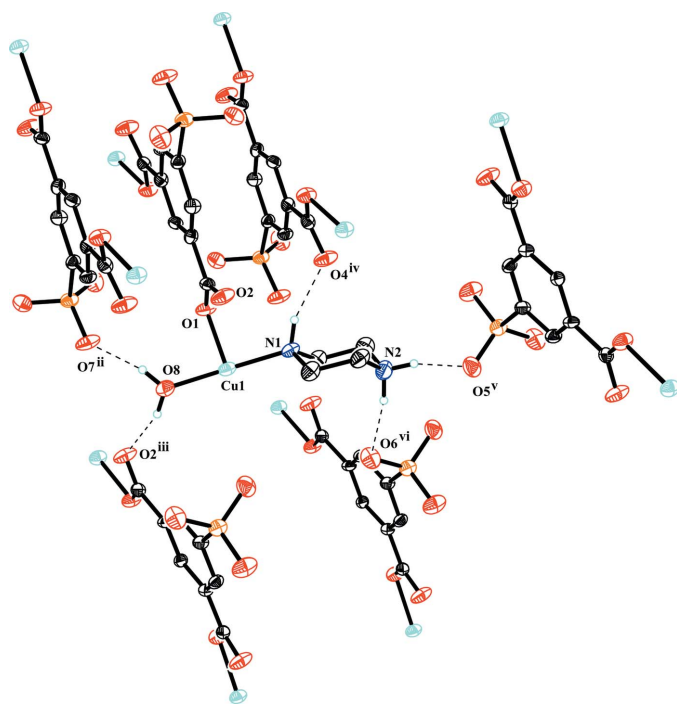


Figure 2
View of the hydrogen bonds (dashed lines) in the title compound. H atoms not involved in hydrogen bonding have been omitted. Symmetry codes are given in Table 2.

Experimental

An aqueous solution (15 ml) of 5-sulfoisophthalic acid sodium salt (0.134 g, 0.5 mmol) and copper(II) nitrate hemipentahydrate (0.116 g, 0.5 mmol) was layered on top of a methanol solution (10 ml) of piperazine (0.047 g, 0.5 mmol). Blue prismatic crystals were obtained after several days (yield 59%). Analysis calculated for $\text{C}_{12}\text{H}_{16}\text{N}_2\text{O}_8\text{SCu}$: C 34.96, H 3.88, N 6.80%; found: C 34.93, H 3.79, N 6.79%.

Crystal data

$[\text{Cu}(\text{C}_8\text{H}_3\text{O}_7\text{S})(\text{C}_4\text{H}_{11}\text{N}_2)(\text{H}_2\text{O})]$
 $M_r = 411.87$
 Monoclinic, $P2_1/c$
 $a = 7.4257$ (12) Å
 $b = 17.214$ (2) Å
 $c = 12.028$ (2) Å
 $\beta = 106.863$ (7)°
 $V = 1471.4$ (4) Å³
 $Z = 4$

$D_x = 1.859$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 2385 reflections
 $\theta = 3.1$ – 27.5 °
 $\mu = 1.67$ mm⁻¹
 $T = 293.2$ K
 Prism, blue
 $0.18 \times 0.12 \times 0.10$ mm

Data collection

Rigaku Mercury70 CCD diffractometer
 ω scans
 Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2000)
 $T_{\min} = 0.788$, $T_{\max} = 0.848$
 11319 measured reflections

3374 independent reflections
 2493 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.069$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -9 \rightarrow 8$
 $k = -22 \rightarrow 14$
 $l = -15 \rightarrow 15$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.065$
 $wR(F^2) = 0.145$
 $S = 1.00$
 3374 reflections
 237 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0382P)^2 + 8.9617P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.51 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.67 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

Cu1—O1	1.949 (4)	O5—S1	1.449 (4)
Cu1—O8	1.974 (4)	O6—S1	1.450 (4)
Cu1—O3 ⁱ	1.986 (4)	O7—S1	1.453 (4)
Cu1—N1	2.007 (5)		
O1—Cu1—O8	89.63 (17)	O8—Cu1—N1	163.55 (18)
O8—Cu1—O3 ⁱ	91.04 (17)	O3 ⁱ —Cu1—N1	88.65 (17)
O1—Cu1—N1	93.61 (17)		

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

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O8—H8A ⁱⁱ ···O7 ⁱⁱⁱ	0.90 (4)	1.82 (5)	2.700 (6)	165 (6)
O8—H8B···O2 ⁱⁱⁱ	0.90 (5)	1.82 (3)	2.687 (6)	162 (8)
N1—H1A···O4 ^{iv}	0.93 (4)	2.07 (5)	2.958 (6)	159 (5)
N2—H2B···O5 ^v	0.93 (5)	1.88 (3)	2.735 (6)	153 (6)
N2—H2C···O6 ^{vi}	0.93 (6)	1.94 (7)	2.842 (7)	165 (8)

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

H atoms attached to C atoms were placed in calculated positions and treated using a riding-model approximation [$C-H = 0.93 \text{ \AA}$ for aromatic H atoms, $C-H = 0.97 \text{ \AA}$ for methylene H and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$]. The H atoms bonded to O atoms and N atoms were visible in the difference map and were included in the refinement with an O—H distance restraint of $0.90 (1) \text{ \AA}$ and an N—H distance restraint of $0.93 (1) \text{ \AA}$.

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve

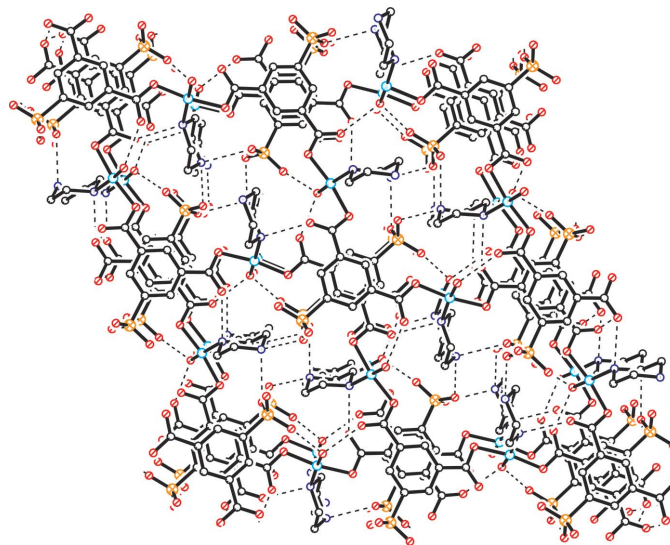


Figure 3

View, along a , of the three-dimensional hydrogen-bonded supramolecular architecture. H atoms have been omitted and hydrogen bonds are shown as dashed lines.

structure: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *SHELXTL* (Sheldrick, 1997b); software used to prepare material for publication: *SHELXTL*.

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