

Ai-Xiang Sui, Gang Zhu and
Zong-Xun Tang*Department of Chemistry, Shaanxi Key
Laboratory of Physico-Inorganic Chemistry,
Northwest University, Xi'an, Shaanxi 710069,
People's Republic of China

Correspondence e-mail: tzxtq@163.com

Key indicators

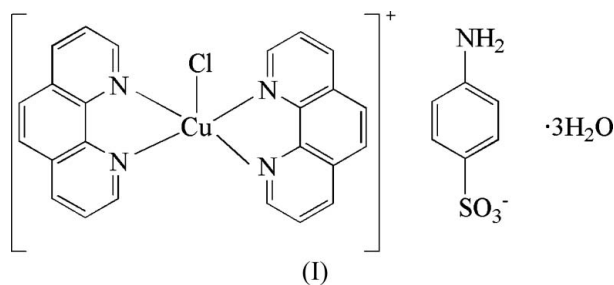
Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$
Disorder in main residue
 R factor = 0.037
 wR factor = 0.103
Data-to-parameter ratio = 12.7For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Chlorobis(1,10-phenanthroline- κ^2N,N')-
copper(II) 4-aminobenzenesulfonate
trihydrateThe crystal structure of the title compound, $[\text{CuCl}(\text{C}_{12}\text{H}_8\text{N}_2)_2](\text{C}_6\text{H}_6\text{NO}_3\text{S})\cdot 3\text{H}_2\text{O}$, contains Cu^{II} cations five-coordinated by one chloride anion and four N atoms of two 1,10-phenanthroline ligands. Between the the 4-aminobenzenesulfonate anions and the uncoordinated water molecules intermolecular hydrogen bonding is found.

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Comment

In comparison with other organic acid anions, such as carboxylates and phosphonates, organosulfonates have long been used in industry as dyes and surfactants, but their coordination chemistry has been less well investigated due to the perception that sulfonates are poor ligands. Recently, increasing attention has been paid to the coordination modes of organosulfonate ligands (Cote, 2003; Cai, 2004). Here, the synthesis and crystal structure of the title sulfonate complex, (I), are reported.



The molecular structure of (I) is shown in Fig. 1. The crystal structure of (I) is built up of $[\text{CuCl}(\text{phen})_2]^+$ cations (phen = 1,10-phenanthroline), 4-aminobenzenesulfonate anions and water molecules. Selected bond lengths are listed in Table 1. In the $[\text{CuCl}(\text{phen})_2]^+$ cation, the two phen molecules are almost perpendicular to each other. The coordination of the Cu atom can be described as distorted trigonal-bipyramidal, made up of one chloride anion and four N atoms of two phen molecules; this is similar to the coordination of the Cu atom in the complex $[\text{CuCl}(\text{C}_{12}\text{H}_8\text{N}_2)_2]_2(\text{C}_{10}\text{H}_4\text{O}_8)\cdot 2\text{H}_2\text{O}$ (Xiao *et al.*, 2004). The 4-aminobenzenesulfonate anion does not coordinate to the Cu atom, but is connected into chains by intermolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds (Table 2 and Fig. 2). These chains are connected into layers by two different types of hydrogen bonding. In the first type, the chains are linked, *via* only one water molecule, by $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds. These water molecules act as donors as well as acceptors (Fig. 2). In the second type of hydrogen bonding, two water molecules and two O atoms of the anion form eight-membered rings, built up of four intermolecular $\text{O}-\text{H}\cdots\text{O}$

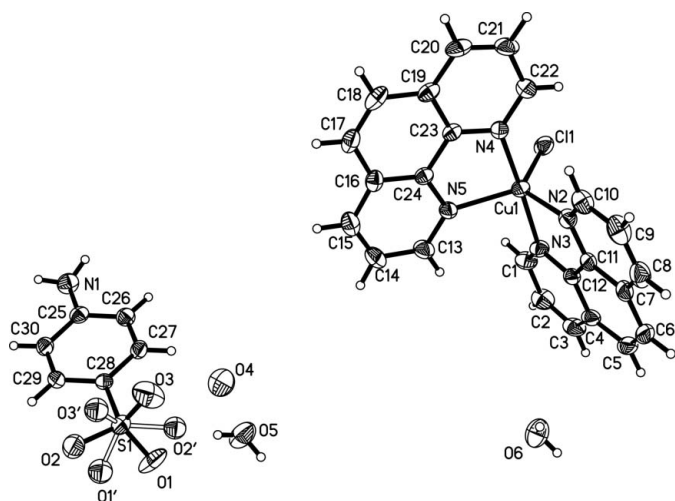


Figure 1

The asymmetric unit of (I), with the atom labelling. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as spheres of arbitrary radii. Both disorder components are shown.

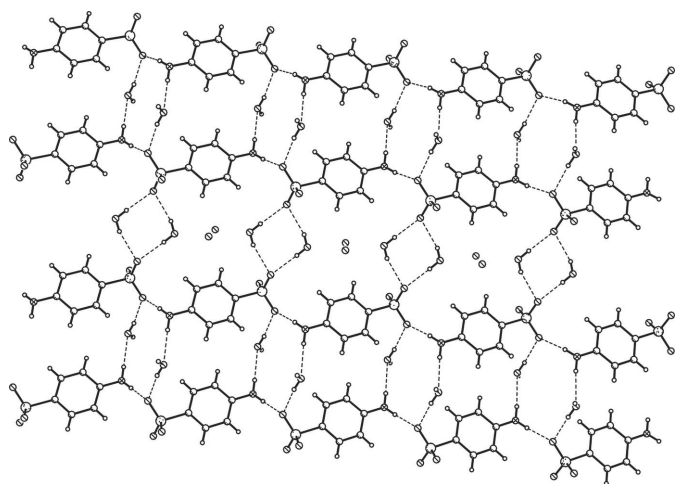


Figure 2

The packing of the anions and the water molecules (I), viewed along the *b* axis. The cations are not shown for clarity. Dashed lines indicate hydrogen bonds.

hydrogen bonds. The rings may be further connected by water molecule O4, but the H atoms attached to it could not be detected in a difference map. Layers are formed which are perpendicular to the *b* axis.

Experimental

All reagents were of analytical grade from commercial sources and were used without further purification. A solution of ethanol (10 ml) containing $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.5 mmol, 0.852 g) and 1,10-phenanthroline (0.5 mmol, 0.991 g) was added slowly to a solution of sodium 4-aminobenzenesulfonate (1 mmol, 0.195 g) dissolved in water (10 ml). After stirring for 3 h, the mixture was left to stand at room temperature for about 2 d, affording green crystals suitable for X-ray diffraction. Elemental analysis found: C 52.75, H 3.55, N 10.07%; calculated for $\text{C}_{30}\text{H}_{20}\text{ClCuN}_5\text{O}_6\text{S}$: C 52.55, H, 4.12, N 10.21%.

Crystal data

$[\text{CuCl}(\text{C}_{12}\text{H}_8\text{N}_2)_2](\text{C}_6\text{H}_6\text{NO}_3\text{S}) \cdot 3\text{H}_2\text{O}$
 $M_r = 683.61$
 Triclinic, $P\bar{1}$
 $a = 8.1734$ (5) Å
 $b = 13.3367$ (8) Å
 $c = 14.9091$ (10) Å
 $\alpha = 67.682$ (1)°
 $\beta = 84.243$ (1)°

$\gamma = 79.368$ (1)°
 $V = 1476.81$ (16) Å³
 $Z = 2$
 $D_x = 1.537$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 0.95$ mm⁻¹
 $T = 293$ (2) K
 Block, green
 $0.35 \times 0.33 \times 0.29$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2002)
 $T_{\min} = 0.650$, $T_{\max} = 0.696$
 (expected range = 0.708–0.758)

7595 measured reflections
 5178 independent reflections
 3770 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.016$
 $\theta_{\max} = 25.1^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.103$
 $S = 1.09$
 5178 reflections
 409 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.056P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.34$ e Å⁻³
 $\Delta\rho_{\min} = -0.32$ e Å⁻³

Table 1

Selected bond lengths (Å).

Cu1–N4	1.984 (2)	Cu1–N5	2.122 (2)
Cu1–N3	1.989 (2)	Cu1–Cl1	2.2804 (9)
Cu1–N2	2.119 (2)		

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N1–H1N1...O6 ⁱ	0.86	2.15	3.000 (4)	168
N1–H2N1...O2 ⁱⁱ	0.86	2.23	3.040 (4)	157
O5–H1O5...O1 ⁱⁱⁱ	0.82	2.00	2.822 (3)	174
O5–H2O5...O1	0.82	2.12	2.900 (4)	160
O6–H1O6...O2 ^{iv}	0.82	2.11	2.905 (4)	163
N1–H1N1...O6 ⁱ	0.86	2.15	3.000 (4)	168

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

The N–H and water H atoms on O5 and O6 were located in a difference Fourier map; their bond lengths were set to ideal values and they were refined with fixed isotropic displacement parameters using a riding model, with O–H = 0.82 Å, N–H = 0.86 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O}, \text{N})$. The water H atoms on O4 were not located. The C–H H atoms were placed in calculated positions and were refined isotropically using a riding model, with C–H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The sulfonate group is disordered over two orientations and was refined using a split model [occupancies 0.83 (1) and 0.17 (1)].

Data collection: SMART (Bruker, 1999); cell refinement: SAINT (Bruker, 1999); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Siemens, 1995); software used to prepare material for publication: SHELXTL.

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