Di-*μ*-hydroxo-bis[aqua(1,10-phen-anthroline-*κ*²*N,N′*)copper(II)] *trans*-bis(2-{[(*E*)-5-formyl-2-oxido-*κO*-benzylidene]amino-*κN*}ethane-sulfonato(2−))copper(II) hexahydrate

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The title compound, $[Cu_2(OH)_2(C_{12}H_8N_2)_2(H_2O)_2][Cu(C_{10}H_9NO_5S)_2]\cdot6H_2O$, is comprised of a copper-centred complex cation and a copper-centred complex anion; the cation lies about an inversion centre and in the anion the Cu atom lies on an inversion centre. In the doubly charged bridged dicopper cation, each Cu centre has distorted square-pyramidal geometry. In the square-planar dianion, two sulfonate ligands are *trans* coordinated to the Cu atom *via* a deprotonated hydroxyl O atom and an imine N atom, forming two six-membered chelate rings. The structure is stabilized by an extensive hydrogen-bond system and aromatic-ring stacking interactions.

Comment

Schiff base complexes containing sulfur, and complexes of amino acid Schiff bases (Casella & Gullotti, 1981, 1986; Wang *et al.*, 1994), have recently aroused increased interest because of their antiviral, anticancer and antibacterial activities. Taurine, an amino acid containing sulfur, is indispensable to human life and has important physiological functions. Recently, we have found that the Schiff base derived from taurine has manifold coordination modes (Zeng *et al.*, 2003; Jiang *et al.*, 2003). Aromatic-ring stacking interactions are an important characteristic of ternary complexes and have important functions, such as stabilizing the double-helix structure of DNA (Frieden, 1975) and the interactions between anticancer drugs and DNA (Hollis *et al.*, 1989). We report here the synthesis and crystal structure of the title novel copper(II) complex, (I), prepared by the reaction of $CuSO_4\cdot5H_2O$ with the potassium salt of the Schiff base ligand 2-({(*E*)-2-hydroxy-5-[(2-sulfoethyl)iminomethyl]benzylidene}-amino)ethanesulfonic acid, derived in turn by the reaction of taurine and 5-formyl-salicylaldehyde, and 1,10-phenanthroline (phen).
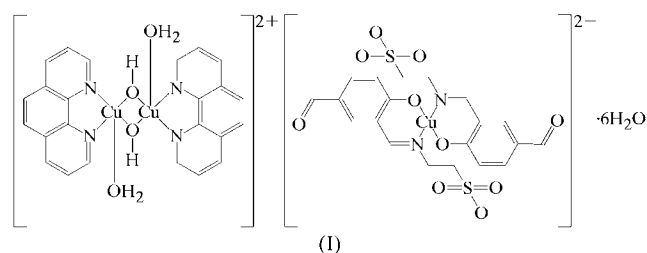
Compound (I) is comprised of a Cu-centred complex dication and dianion, both of which are centrosymmetric (Fig. 1 and Table 1). The doubly charged bridged dicopper cation, in which each Cu centre has distorted square-pyramidal geometry, occurs in five previously published crystal structures (Cambridge Structural Database, Version 5.0, July
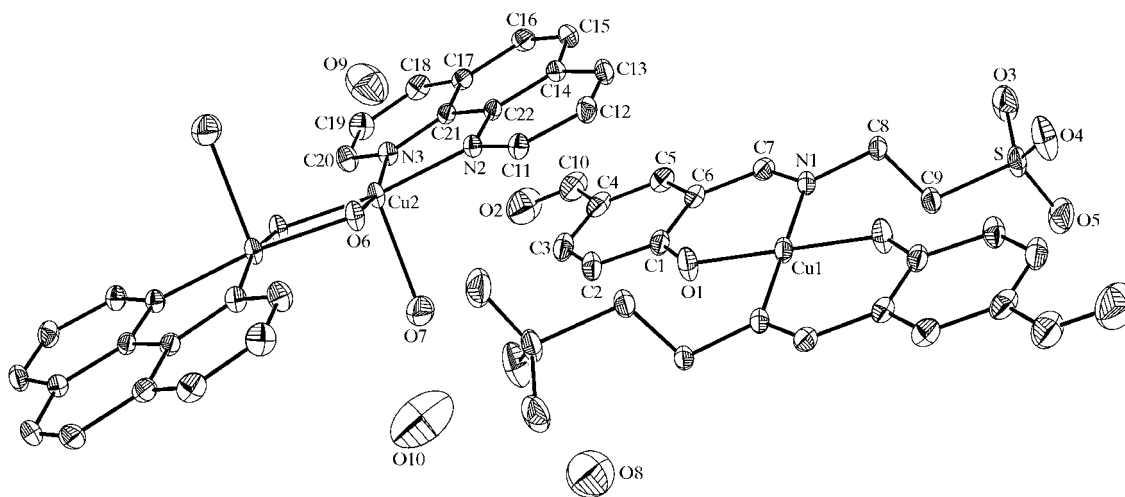

Figure 1
The components of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omittted for clarity.

2004 release; Allen, 2002). In all of these examples, the ions are also centrosymmetric. The geometry of the cation in (I) is similar to that in the other examples. In the square-planar dianion, two sulfonate ligands are each *trans* coordinated to Cu *via* a deprotonated hydroxyl O atom and an imine N atom, forming two six-membered chelate rings (Table 2). There may be a weak interaction between atoms Cu1 and O2 [3.194 (4) Å] of adjacent anions in the fifth and sixth quasi-octahedral positions (Fig. 2). The sulfonate group itself is not coordinated to Cu, but is packed in the crystal structure to form hydrogen bonds by which the group is stabilized.

There are a number of hydrogen bonds in (I) (Fig. 2). The anion and cation, which are attracted to each other by electrostatic forces, are also linked by hydrogen bonds between atoms O6 and O5^i, and O7 and O4^i [symmetry code: (i) $-x$, $1-y, 1-z$]. Other hydrogen bonds are listed in Table 2. The O8$\cdots$O4^i distance of 2.862 (5) Å, the O8$\cdots$O10^{ii} distance of 2.702 (8) Å and the O8$\cdots$O8^{ii} distance of 2.569 (7) Å indicate that there may be possible hydrogen-bond interactions involving these water molecules and the sulfonate group [symmetry code: (ii) $1-x, 2-y, 2-z$]. These bonds form a hydrogen-bond network, which extends along the *ac* plane of the cell and links the cations and anions to form a two-dimensional network. Also, two sulfonate groups of the anion stretch to two adjacent *ac* planes to form hydrogen bonds. Thus, the network is extended to a three-dimensional structure.

The anions and cations are arranged in alternate layers parallel to the *ab* plane (Fig. 2). Both the anion and cation have two independent aromatic rings. The anion uses one of its
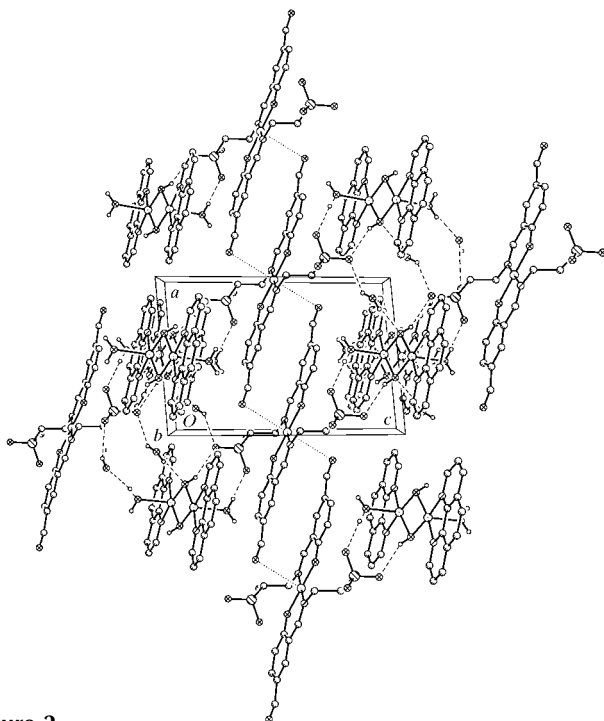

Figure 3
A perspective view of the aromatic ring interactions in (I). Only the aromatic rings and the Cu atoms are included.

benzene (*B*) rings and the cation uses one of its phen (*P*) rings to take part in π–π stacking interactions, forming infinite columns along the *c* axis (Fig. 3). In each cell, the aromatic rings stack in the column in the sequence *P*–*B*–*B*–*P*. The other aromatic rings of each anion and cation take part in the stacking of four adjacent columns, thus forming a three-dimensional structure. The dihedral angle and average distance between *P* and *B* rings are 3.52 (11)° and 3.348 Å, respectively. The two *B* rings are parallel, with an average distance of 3.362 Å, while the two *P* rings in two adjacent cells are also parallel, with an average distance of 3.429 Å. The structure of (I) is thus stabilized by the hydrogen-bond system and aromatic-ring stacking interactions.

Experimental

The potassium salt of the Schiff base ligand 2-({(*E*)-2-hydroxy-5-[(2-sulfoethyl)iminomethyl]benzylidene}amino)ethanesulfonic acid, *L*, was synthesized according to the method of Zeng *et al.* (2003). The salt (1.0 mmol) was dissolved in aqueous methanol (25 ml). To this solution, CuSO$_4$·5H$_2$O (1.0 mmol) was added, and the mixture was stirred and refluxed at 323 K for 6 h. 1,10-Phenanthroline (1.0 mmol) was then added and the reaction continued for another 6 h. After cooling to room temperature and subsequent filtration, the filtrate was left to stand at room temperature. Dark-green crystals of (I) suitable for X-ray diffraction were obtained in a yield of 40%. Analysis found: C 42.87, H 4.21, N 6.56%; C$_{44}$H$_{52}$Cu$_3$N$_6$O$_{20}$S$_2$ requires: C 42.59, H 4.19, N 6.78%. IR (KBr, ν, cm^{-1}): 1032.0, 1037.0, 1160.2, 1185.0 (SO$_3$), 1618.5 (C=N), 1601.7, 1522.3 (C=N + C=C), 3419.7 (O—H).

Figure 2
A perspective drawing of (I). H atoms have been omitted for clarity, except for those involved in hydrogen-bond interactions. Hydrogen bonds are indicated by dashed lines and the quasi-octahedral interactions (see text) are indicated by dotted lines.
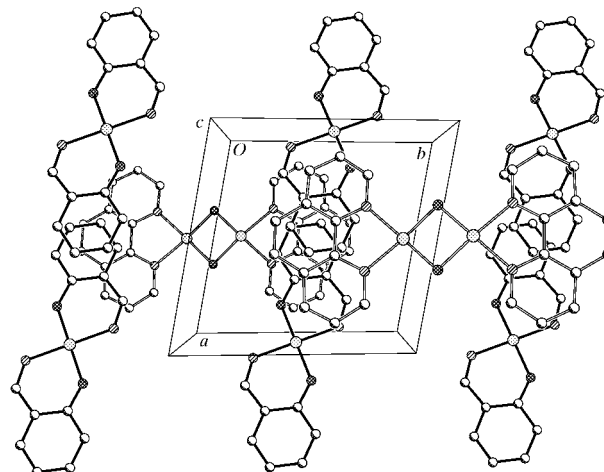
Crystal data

[Cu$_2$(OH)$_2$(C$_{12}$H$_8$N$_2$)$_2$(H$_2$O)$_2$]-[Cu(C$_{10}$H$_9$NO$_5$S)$_2$]·6H$_2$O	$Z = 1$
$M_r = 1239.66$	$D_x = 1.664$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 9.370$ (2) Å	Cell parameters from 35
$b = 9.793$ (2) Å	reflections
$c = 13.860$ (4) Å	$\theta = 2.6$–18.7°
$\alpha = 98.02$ (2)°	$\mu = 1.45$ mm^{-1}
$\beta = 93.61$ (3)°	$T = 296$ (2) K
$\gamma = 99.63$ (2)°	Block, green
$V = 1236.8$ (5) Å^3	$0.48 \times 0.38 \times 0.34$ mm

Data collection

Siemens *P*4 diffractometer	$R_{int} = 0.011$
ω scans	$\theta_{max} = 25.3°$
Absorption correction: empirical	$h = 0 \rightarrow 11$
($SADABS$; Sheldrick, 1996)	$k = -11 \rightarrow 11$
$T_{min} = 0.531$, $T_{max} = 0.611$	$l = -16 \rightarrow 16$
4950 measured reflections	3 standard reflections
4476 independent reflections	every 97 reflections
3411 reflections with $I > 2\sigma(I)$	intensity decay: 2.1%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0517P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.034$	$+ 0.112P]$
$wR(F^2) = 0.092$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} = 0.001$
4476 reflections	$\Delta\rho_{max} = 0.61$ e Å^{-3}
364 parameters	$\Delta\rho_{min} = -0.44$ e Å^{-3}
H atoms treated by a mixture of	
independent and constrained	
refinement	

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.894 (2)	Cu2—N3	2.014 (2)
Cu1—N1	2.001 (3)	Cu2—N2	2.016 (2)
Cu2—O6^i	1.939 (2)	Cu2—O7	2.326 (3)
Cu2—O6	1.950 (2)	Cu2···Cu2^i	2.9070 (10)
O1—Cu1—N1	91.46 (10)	O6—Cu2—N3	166.94 (10)
O6^i—Cu2—O6	83.25 (9)	O6^i—Cu2—N2	172.26 (10)
O6^i—Cu2—N3	96.57 (9)		

Symmetry code: (i) $1 - x, 2 - y, 2 - z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O6—H6O···O5^i	0.82 (3)	2.26 (2)	3.005 (4)	152 (4)
O7—H7OA···O4^i	0.82 (3)	2.04 (4)	2.844 (5)	169 (5)
O7—H7OB···O10	0.82 (3)	2.04 (4)	2.841 (7)	167 (4)
O9—H9OA···O6	0.82 (3)	2.05 (5)	2.868 (5)	172 (6)
O9—H9OB···O5^{ii}	0.82 (3)	2.54 (4)	3.265 (6)	148 (7)
O10—H10A···O3^{iii}	0.83 (4)	2.36 (5)	2.903 (7)	123 (5)

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

The H atoms on atoms O6, O7 and O9, and one H atom on O10 were located in a difference Fourier map and their positions and isotropic displacement parameters were refined, with O—H restraints which led to O—H values in the range 0.82 (3)–0.83 (3) Å. All other H atoms were positioned geometrically, treated as riding atoms and refined isotropically, with C—H distances of 0.93–0.97 Å and with U_{iso}(H) $= 1.2U_{eq}$(C).

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Siemens, 1994); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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