Triaqua(2,2′-bipyridine)copper(II) 7-oxa-dibenzofluorene-3,11-disulfonate dihydrate

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Key indicators

Single-crystal X-ray study

$T = 293$ K

Mean σ(C–C) = 0.005 Å

Disorder in main residue

R factor = 0.047

wR factor = 0.138

Data-to-parameter ratio = 12.7

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

The title compound, $[Cu(C_{10}H_8N_2)(H_2O)_3](C_{20}H_{10}O_7S_2)\cdot 2H_2O$, was obtained by a hydrothermal route. The asymmetric unit contains one copper complex cation including three coordinated water molecules, one organic anion, three coordinated water molecules and two uncoordinated water molecules. The Cu^{II} atom exists in a distorted square-pyramidal geometry. Face-to-face offset π–π stacking and intermolecular hydrogen-bond interactions generate a three-dimensional supramolecular array.
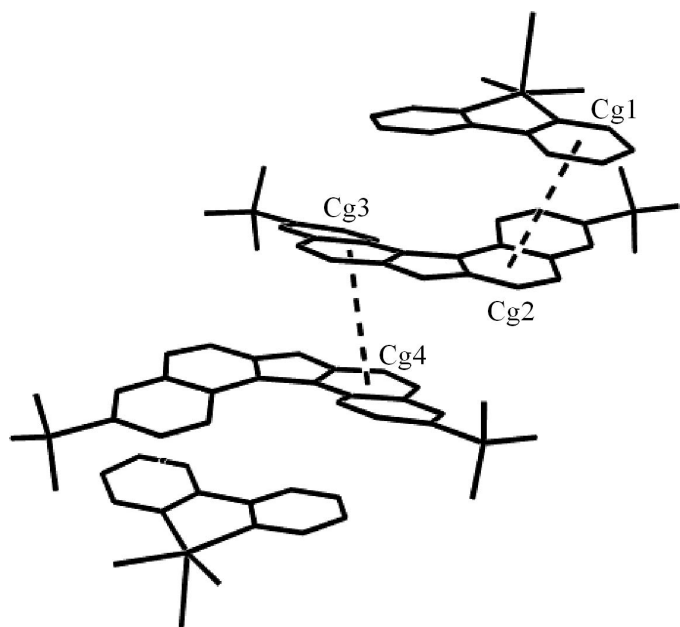
Comment

As a result of the weak coordination strength of sulfonate toward transition metal ions, most of the reported transition metal sulfonates prepared in aqueous solution consist of separate aquametal complex cations and sulfonate anions (Cai, Chen, Liao, Yao *et al.* 2001; Gunderman *et al.*, 1997; Kosnic *et al.*, 1992; Shubnell *et al.*, 1994). However, it has been found that sulfonate anions can compete with water molecules and coordinate with transition metals after introducing other organic ligands as auxiliaries to the metal centers (Cai, Chen, Liao, Feng *et al.* 2001; Cai, 2004). In this study, we used 2,2′-bipyridine as the nitrogen-containing auxiliary. However, there is still no direct coordination between the SO_3^- group and Cu^{2+} in the title compound, (I). This may be attributed to the rigidity and high steric effect of the 7-oxa-dibenzo-fluorene-3,11-disulfonate dianion, L^{2-}.

(I)
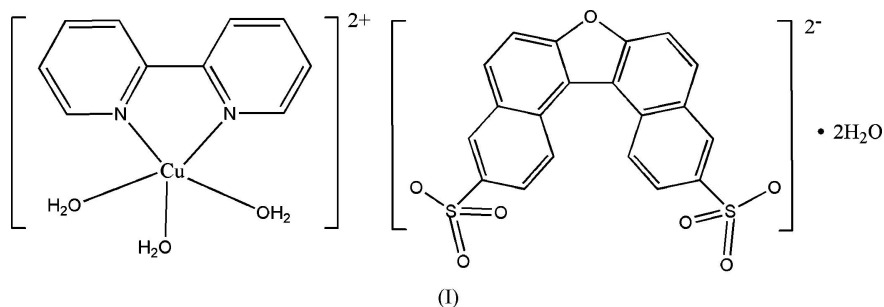
The asymmetric unit of (I) contains one copper complex cation including three coordinated water molecules, one organic anion, three coordinated water molecules and two uncoordinated water molecules. As illustrated in Fig. 1, the Cu^{2+} cation is coordinated by two N atoms from 2,2′-bipyridine, with Cu—N distances of 1.982 (3) and 2.000 (3) Å. The Cu—O distances of the three coordinated water molecules range from 1.959 (3) to 2.194 (3) Å (Table 1). A distorted square-pyramidal five-coordinate copper complex
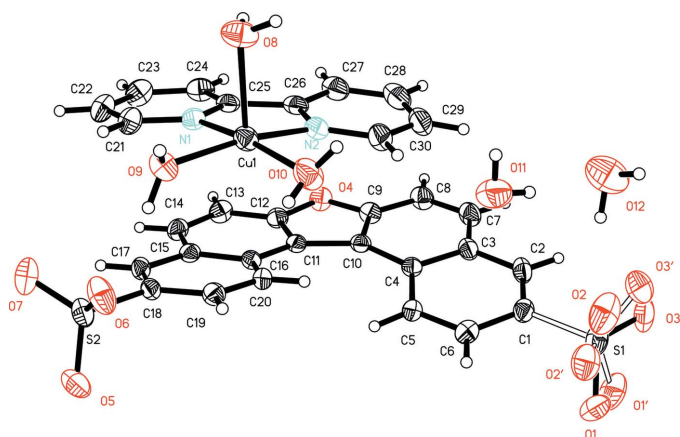
Figure 1
The asymmetric unit of (I), showing 30% probablity displacement ellipsoids and the atom-numbering scheme. One of the SO_3^- groups of the L^{2-} anion is disordered, and both components are shown.
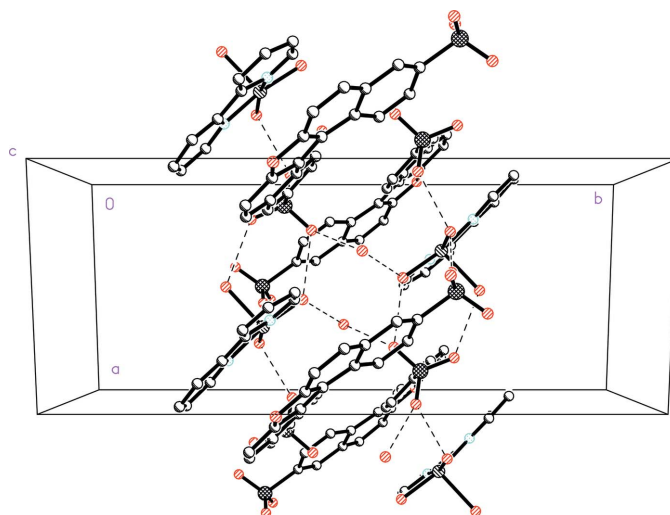

Figure 3
The hydrogen-bond (dashed lines) network in (I). H atoms have been omitted.

Figure 2
The π-stacking interactions.

Figure 4
A packing diagram for (I). H atoms have been omitted, and dashed lines indicate hydrogen bonds.
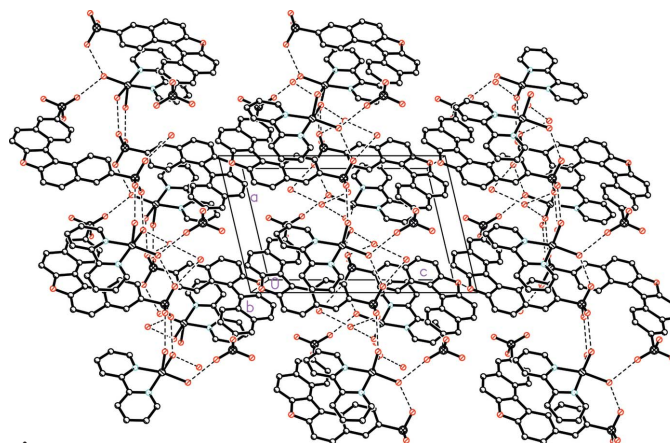
cation is thus formed. It should be noted that one of the SO_3^- groups of the L^{2-} anion is disordered.

Several forces govern the arrangement of the ions in the crystal structure of (I). Two types of π–π aromatic stacking interaction exist: one between the 2,2′-bipyridine molecule and naphthyl rings of the L^{2-} anion, and another between the naphthyl rings of adjacent L^{2-} anions, thus resulting in a cluster of two cations and two anions (Fig. 2).

The geometric parameters are within the acceptable range (Janiak, 2000). The $Cg1\cdots Cg2$ and $Cg3\cdots Cg4$ distances are 3.557 (2) and 3.715 (2) Å [$Cg1$ is the centroid of the ring containing N1, $Cg2$ is the centroid of the the ring containing C14, $Cg3$ is the centroid of the the ring containing C8 and $Cg4$ is the centroid of the the ring containing C8^i; symmetry code:

(i) $-x, -y + 1, -z$]. The perpendicular distances (from $Cg1$ to the plane of the ring containing $Cg2$ and from $Cg3$ to the plane of the ring containing $Cg4$) are 3.317 and 3.404 Å, respectively. The slippage angles (defined by the $Cg1\cdots Cg2$ and $Cg3\cdots Cg4$ vectors and the normals to the plane from $Cg1$ and $Cg3$, and calculated geometrically) are 72.2 and 66.3°, and the dihedral angles between the mean planes of the rings are 3.0 (2) and 0.0 (2)°. These parameters demonstrate that the rings are almost parallel and indicate that slipped π–π stacking generates a cluster of two cations and two anions.

These ion clusters are connected to one another by means of four types of intermolecular hydrogen bonds, water to water, coordinated water to water, coordinated water to SO_3^- groups of L^{2-} anions, and uncoordinated water to SO_3^- groups of L^{2-} anions. Thus, the title compound forms a hydrogen-bonded complex chain along the a axis (Fig. 3 and Table 2). By means of face-to-face offset π–π stacking interactions and intermolecular hydrogen bonds, complex (I) forms an intricate three-dimensional network (Fig. 4).

Experimental

Disodium 7-oxadibenzofluorene-3,11-disulfonate (Na_2L) was prepared according to a literature method (Guo *et al.*, 2005). Crystals of (I) were obtained by a hydrothermal route. A mixture of Na_2L (0.087 mmol, 50 mg), 2,2′-bipyridine (0.096 mmol, 15 mg), 4,4′-bipyridine (0.096 mmol, 15 mg), $Cu(CH_3COO)_2 \cdot 2H_2O$ (0.100 mmol, 20 mg) and H_2O (10 ml) was sealed in a Parr Teflon-lined stainless steel vessel (23 ml) after brief stirring, heated to 403 K and kept at that temperature for 60 h, then cooled to 373 K at a rate of 5 K h^{-1}, followed by further cooling to room temperature. Dark-green crystals of (I) were collected, washed with water and ethanol, and dried in air (yield 33.6%).

Crystal data

$[Cu(C_{10}H_8N_2)(H_2O)_3]$- $(C_{20}H_{10}O_7S_2) \cdot 2H_2O$	$D_x = 1.639$ Mg m^{-3}
$M_r = 736.20$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 943 reflections
$a = 9.1978$ (11) Å	$\theta = 2.9$–25.8°
$b = 22.423$ (3) Å	$\mu = 0.94$ mm^{-1}
$c = 14.8597$ (18) Å	$T = 293$ (2) K
$\beta = 103.287$ (2)°	Plate, green
$V = 2982.7$ (6) Å^3	$0.50 \times 0.39 \times 0.16$ mm
$Z = 4$	

Data collection

Bruker SMART 1000 CCD diffractometer	5731 independent reflections
φ and ω scans	3856 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$R_{int} = 0.024$
	$\theta_{max} = 26.0°$
$T_{min} = 0.650$, $T_{max} = 0.864$	$h = -10 \rightarrow 11$
10925 measured reflections	$k = -23 \rightarrow 27$
	$l = -8 \rightarrow 18$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0714P)^2 + 1.825P]$
$R[F^2 > 2\sigma(F^2)] = 0.047$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.138$	
$S = 1.02$	$(\Delta/\sigma)_{max} = 0.001$
5731 reflections	$\Delta\rho_{max} = 0.59$ e Å^{-3}
452 parameters	$\Delta\rho_{min} = -0.26$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	1.982 (3)	Cu1—O9	1.996 (3)
Cu1—N2	2.000 (3)	Cu1—O10	1.959 (3)
Cu1—O8	2.194 (3)		
O9—Cu1—N2	167.89 (12)	O10—Cu1—O9	90.49 (12)
O9—Cu1—O8	89.89 (11)	N1—Cu1—O8	95.10 (12)
O10—Cu1—N1	169.52 (13)	N1—Cu1—O9	92.97 (11)
O10—Cu1—N2	93.58 (13)	N1—Cu1—N2	81.13 (13)
O10—Cu1—O8	94.79 (12)	N2—Cu1—O8	101.11 (12)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O8—H8$A\cdots$O7^i	0.86	1.98	2.835 (4)	177
O8—H8$B\cdots$O3^{ii}	0.85	1.99	2.710 (9)	141
O9—H9$A\cdots$O2^{iii}	0.86	1.85	2.640 (7)	152
O9—H9$B\cdots$O6	0.86	1.94	2.787 (4)	172
O10—H10$A\cdots$O12	0.86	1.79	2.569 (4)	149
O10—H10$B\cdots$O5^i	0.86	1.91	2.758 (4)	167
O11—H11$A\cdots$O2^{iii}	0.87	1.96	2.745 (11)	149
O11—H11$B\cdots$O6	0.87	2.01	2.838 (5)	157
O12—H12$A\cdots$O5^{iv}	0.86	2.14	2.896 (5)	147
O12—H12$B\cdots$O11	0.86	1.87	2.702 (5)	163

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

H atoms attached to C atoms were placed in geometrically idealized positions, with C—H = 0.93 Å, and were constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$. H atoms attached to water O atoms were located in difference Fourier maps and constrained to ride on their parent atoms, with O—H = 0.85–0.87 Å and $U_{iso}(H) = 1.5U_{eq}(O)$. One of the SO_3^- groups of the L^{2-} anion is disordered. The major and minor disordered components have refined occupancies of 0.616 (13) and 0.384 (13), respectively. Additionally, although the S—O distances in the disordered sulfonate unit were restrained to be the same, we note that the spread of distances is quite large. The O atoms in the disordered sulfonate unit were restrained using a SIMU instruction to prevent the displacement parameters becoming too large.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus* (Bruker, 1999); program(s) used to solve structure: *SHELXTL* (Bruker, 1999); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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