Bis(benzylammonium) tetraaquabis(sulfato)-cuprate(II)

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The crystal structure of bis(benzylammonium) tetraaquabis-(sulfato)cuprate(II), $(C_7H_{10}N)_2[Cu(SO_4)_2(H_2O)_4]$, consists of alternating organic and inorganic layers. The organic layer contains the benzyl groups and the inorganic layer comprises the ammonium groups and centrosymmetric octahedral $[Cu(H_2O)_4(SO_4)_2]^{2-}$ anions. N—H···O and O—H···O hydrogen bonds form layers extending parallel to the ab plane.

Comment

The structure of bis(benzylammonium) tetraaquabis-(sulfato)cuprate(II), (I), was determined as part of an ongoing study on the structural characteristics of organic–inorganic hybrid materials. Only three related crystal structures containing *trans*-$[M(H_2O)_4(SO_4)_2]^{2-}$ anions, and all with ethylenediammonium cations, have been reported previously, *viz.* for M = Fe (Held, 2003), M = Mn (Chaabouni *et al.*, 1996) and M = Cu (Ben Ghozlen *et al.*, 1994). No crystal structure containing a monoammonium cation and an $[M(H_2O)_4(SO_4)_2]^{2-}$ anion, as observed in the title compound, could be located in the literature.

(I)
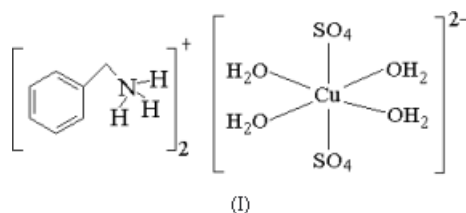
The asymmetric unit of (I) contains one benzylammonium cation, one tetrahedral SO_4^{2-} anion and one $Cu(H_2O)_2$ moiety, with the Cu atom located on a center of inversion at a special position (0,0,0). The molecular geometry and atom labeling are shown in Fig. 1. The crystal structure comprises alternating organic and inorganic layers, as shown in
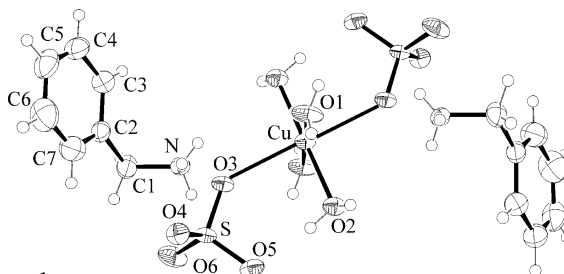

Figure 1

The molecular structure of (I), showing the atomic numbering scheme and displacement ellipsoids at the 50% probability level (*ORTEP*-3; Farrugia, 1997). Unlabeled atoms are related by the symmetry operator $(-x, -y, -z)$.
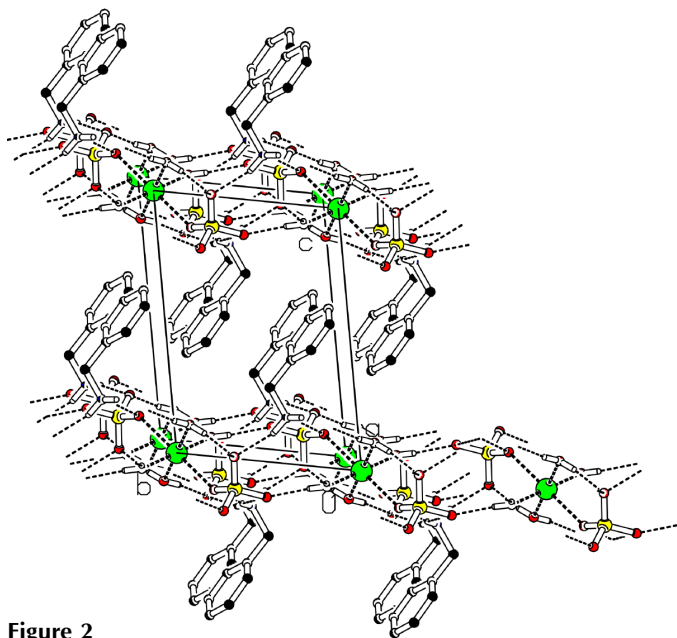
Figure 2
Packing diagram (Spek, 2000) showing layers parallel to the *ab* plane. Hydrogen bonds are shown as dashed lines. Color codes: green Cu, yellow S, red O and black C.

Fig. 2. The benzyl moieties form the organic layer, while the inorganic layer contains *trans*-[Cu(H$_2$O)$_4$(SO$_4$)$_2$]$^{2-}$ anions in which the Cu atom is coordinated in a distorted octahedral arrangement by four water molecules and two sulfate ligands.

In the organic layer, the benzyl moieties are interdigitated; however, no π–π stacking interactions are observed, the shortest aromatic centroid-to-centroid distance being 4.225 (6) Å. The atoms constituting the aromatic ring and C1 in the benzylammonium cation are essentially coplanar, with an r.m.s. deviation of 0.017 Å, and the aromatic groups are tilted by 55.56 (7)° relative to the layer plane.

The SO$_4$$^{2-}$ anions coordinated to the Cu atom, in the inorganic layer, display a slightly distorted tetrahedral geometry, with S—O bond lengths ranging from 1.4580 (18) to 1.4969 (17) Å, and O—S—O angles falling between 107.78 (9) and 110.52 (9)°.

In the *trans*-[Cu(H$_2$O)$_4$(SO$_4$)$_2$]$^{2-}$ anion, Jahn–Teller distortion occurs, and a long Cu—O bond of 2.4820 (19) Å to a sulfate ligand is observed. This Cu—O bond is significantly shorter than the corresponding bond length of 2.67 Å (no s.u. reported) observed in ethylenediammonium copper sulfate (Ben Ghozlen *et al.*, 1994). In addition, two shorter Cu—O bonds to the water molecules of 1.947 (2) and 1.9710 (19) Å are observed. Corresponding values for the ethylenediammonium copper sulfate structure are 1.940 and 1.943 Å (no s.u. values reported) (Ben Ghozlen *et al.*, 1994). In (I), the *cis*-O—Cu—O angles range from 84.56 (7) to 95.44 (7)°, indicating a slight distortion from ideal octahedral geometry. The *trans*-O—Cu—O angles are exactly 180° by virtue of the inversion symmetry.

In the crystal structure, hydrogen bonding results in the formation of layers extending parallel to the *ab* plane. In these layers, ammonium groups and water molecules interact with

sulfate ligands through N—H···O and O—H···O hydrogen bonds. Atom N is hydrogen bonded to four O atoms of three different sulfate groups through two normal and one bifurcated hydrogen bond. The water molecules containing atoms O1 and O2 are hydrogen bonded to two O atoms of two sulfate groups through two normal hydrogen bonds. Hydrogen-bonding parameters are listed in Table 2 and the hydrogen-bonding interactions in the inorganic layer are illustrated in Fig. 2.

Experimental

Benzylammonium sulfate was prepared by the dropwise addition of H$_2$SO$_4$ (98%, Associated Chemical Enterprises c.c) to a solution of benzylamine (99%, Saarchem) in chloroform. The resulting precipitate was filtered off. Bis(benzylammonium) tetraaquabis(sulfato)cuprate(II) was crystallized by dissolving stoichiometric amounts of benzylammonium sulfate and CuSO$_4$ (99%, Saarchem) (molar ratio 1:1) in water. Blue crystals formed on evaporation at room temperature.

Crystal data

(C$_7$H$_{10}$N)$_2$[Cu(SO$_4$)$_2$(H$_2$O)$_4$]	$Z = 1$
$M_r = 544.04$	$D_x = 1.609$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 6.549$ (5) Å	Cell parameters from 658
$b = 8.091$ (6) Å	reflections
$c = 11.354$ (8) Å	$\theta = 2$–31°
$\alpha = 78.79$ (6)°	$\mu = 1.22$ mm^{-1}
$\beta = 79.70$ (6)°	$T = 293$ (2) K
$\gamma = 73.76$ (6)°	Plate, blue
$V = 561.6$ (7) Å^3	$0.40 \times 0.30 \times 0.10$ mm

Data collection

Oxford Excalibur2 diffractometer	2860 reflections with $I > 2\sigma(I)$
ω–2θ scans	$R_{int} = 0.023$
Absorption correction: multi-scan	$\theta_{max} = 31.8°$
(Blessing, 1995)	$h = -9 \rightarrow 7$
$T_{min} = 0.641$, $T_{max} = 0.888$	$k = -11 \rightarrow 11$
5596 measured reflections	$l = -16 \rightarrow 16$
3424 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0529P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.033$	$+ 0.0951P]$
$wR(F^2) = 0.092$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} = 0.001$
3424 reflections	$\Delta\rho_{max} = 0.49$ e Å^{-3}
158 parameters	$\Delta\rho_{min} = -0.70$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

Cu—O1	1.947 (2)	S—O3	1.4665 (15)
Cu—O2	1.9710 (19)	S—O4	1.4744 (17)
Cu—O3	2.4820 (19)	S—O5	1.4969 (17)
S—O6	1.4580 (18)		
O1—Cu—O2	91.54 (9)	O3^i—Cu—O3	180
O1—Cu—O2^i	88.46 (9)	O6—S—O3	110.22 (10)
O2—Cu—O2^i	180	O6—S—O4	109.98 (10)
O1—Cu—O3^i	86.92 (8)	O3—S—O4	110.52 (9)
O2—Cu—O3^i	95.44 (7)	O6—S—O5	110.00 (10)
O1—Cu—O3	93.08 (8)	O3—S—O5	108.29 (9)
O2—Cu—O3	84.56 (7)	O4—S—O5	107.78 (9)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N—H1A···O5[ii]	0.89	1.97	2.825 (3)	160
N—H1B···O4	0.89	1.93	2.809 (3)	167
N—H1C···O3[iii]	0.89	1.97	2.829 (3)	163
N—H1C···O6[iii]	0.89	2.46	3.103 (3)	129
O2—H1D···O4[iv]	0.87 (3)	1.83 (3)	2.694 (3)	174 (2)
O2—H2E···O5	0.84 (2)	1.87 (3)	2.704 (2)	173 (2)
O1—H3F···O5[iv]	0.81 (3)	1.88 (3)	2.686 (3)	170 (3)
O1—H4G···O6[v]	0.80 (3)	1.91 (3)	2.698 (3)	167 (3)

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

H atoms of the coordinated water molecules were placed as observed in the Fourier map and refined. This resulted in the best placement of these atoms for the hydrogen-bonding motif, with O—H bond lengths ranging from 0.80 (3) to 0.87 (3) Å. All other H atoms were placed in calculated positions, with C—H distances of 0.93 Å and N—H distances of 0.89 Å, and were refined using a riding model, with $U_{iso}(H) = 1.2U_{eq}$ (1.5U_{eq} for methyl H atoms) of the parent atom.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2003); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997) and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *PLATON* (Spek, 2003) and *WinGX* (Farrugia, 1999).

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