

Hexaaquacopper(II) 3-carboxy-4-hydroxybenzenesulfonate dihydrate

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Key indicators

Single-crystal X-ray study

T = 293 K

Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$

R factor = 0.032

wR factor = 0.093

Data-to-parameter ratio = 12.5

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

In the title compound, $[\text{Cu}(\text{H}_2\text{O})_6]L_2 \cdot 2\text{H}_2\text{O}$, where $HL =$ 3-carboxy-4-hydroxybenzenesulfonic acid ($\text{C}_7\text{H}_6\text{O}_6\text{S}$), each Cu^{II} cation lies on an inversion center and is octahedrally coordinated by six water molecules. The L^- anions do not coordinate to copper, but act as counter-anions. The crystal structure is composed of alternating layers of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ cations and sulfonate anions. The $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ cations, water molecules and L^- anions are connected through a complex pattern of hydrogen-bonding interactions.

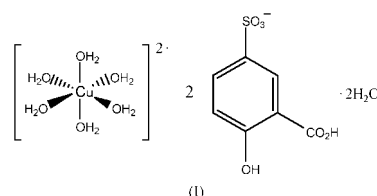
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Comment

The crystal structures of five transition metal (Mn, Co, Ni, Cu and Zn) 3-carboxy-4-hydroxybenzenesulfonates have been determined. The structures of the manganese (Ma *et al.*, 2003a), cobalt (Ma *et al.*, 2003b) and nickel compound (Ma *et al.*, 2003c) have been reported in the preceding papers. The crystal structure of the copper compound, (I), is presented here. The crystal structure of the related zinc compound is reported in the following paper.



The Cu^{II} atom is located on an inversion center, and all other atoms are in general positions. Selected bond lengths and angles are given in Table 1. Fig. 1 shows the asymmetric unit, together with the complete coordination environment of the Cu^{II} cation. Each Cu^{II} cation is coordinated by six water molecules, like the Mn(II) cation of the manganese compound (Ma *et al.*, 2003a). Due to the Jahn–Teller effect, the $\text{Cu1}-\text{OW1}$ distance, 2.4175 (18) Å , is much longer than those for $\text{Cu1}-\text{OW2}$, 1.9527 (18) Å , and $\text{Cu1}-\text{OW3}$, 1.9596 (18) Å .

The crystal structure of (I) is composed of alternating layers of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ cations and sulfonate anions, as shown in Fig. 2. Within the sulfonate layer, there are rows of anions with alternating orientations of the organic group. The aromatic ring is almost perpendicular to the layer of cations with a dihedral angle of 86.3 (3) $^\circ$, which is larger than the value for the manganese compound, 78.2 (2) $^\circ$ (Ma *et al.*, 2003a).

The $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ cations, water molecules and L^- anions are connected through a complex pattern of hydrogen-bonding interactions. Selected hydrogen-bond parameters are listed in Table 2.

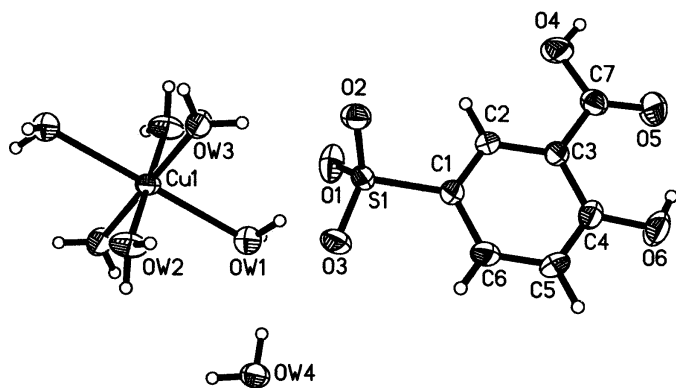


Figure 1
View of the asymmetric unit, expanded to show the complete coordination of Cu^{II}, with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

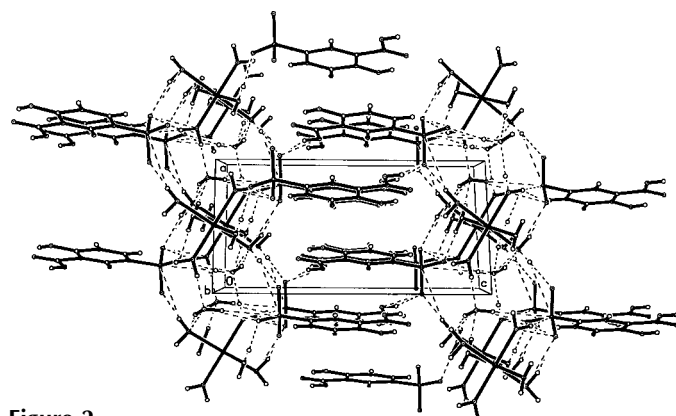


Figure 2
View of the alternating layers of cations and anions, along the *b* axis.

Experimental

A mixture of 3-carboxy-4-hydroxybenzenesulfonic acid (0.44 g, 2 mmol) and CuO (0.080 g, 1 mmol) in water (10 ml) was stirred at room temperature for 30 min. Blue crystals of compound (I) were obtained after leaving the solution to stand at room temperature for several days. Analysis calculated for C₁₄H₂₆CuO₂₀S₂: C 26.19, H 4.08%; found: C 26.25, H 4.03%.

Crystal data

[Cu(H₂O)₆](C₇H₅O₆S)₂·2H₂O
M_r = 642.01
 Triclinic, *P*1̄
a = 7.0298 (9) Å
b = 7.0749 (15) Å
c = 13.288 (4) Å
 α = 92.16 (2)°
 β = 90.259 (18)°
 γ = 112.236 (12)°
V = 611.2 (2) Å³

Z = 1
D_x = 1.744 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 20 reflections
 θ = 5.4–9.9°
 μ = 1.16 mm⁻¹
T = 293 (2) K
 Block, blue
 0.50 × 0.36 × 0.34 mm

Data collection

Siemens *P4* diffractometer
 ω scans
 Absorption correction: none
 3134 measured reflections
 2413 independent reflections
 2140 reflections with *I* > 2σ(*I*)
R_{int} = 0.017

θ_{\max} = 26.0°
 h = -1 → 8
 k = -8 → 8
 l = -16 → 16
 3 standard reflections every 97 reflections
 intensity decay: none

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.032
wR (*F*²) = 0.093
S = 1.10
 2413 reflections
 193 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0566P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.30 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.52 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

C4—O6	1.340 (3)	O3—S1	1.4608 (18)
C7—O5	1.221 (3)	OW1—Cu1	2.4175 (18)
C7—O4	1.310 (3)	OW2—Cu1	1.9527 (18)
O1—S1	1.462 (2)	OW3—Cu1	1.9596 (18)
O2—S1	1.4600 (17)		
O5—C7—O4	123.6 (2)	OW2—Cu1—OW3	90.67 (8)
O2—S1—O3	111.03 (11)	OW2—Cu1—OW1	92.19 (7)
O2—S1—O1	110.55 (11)	OW3—Cu1—OW1	89.13 (7)
O3—S1—O1	113.44 (13)		

Table 2

Hydrogen-bonding 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>
OW1—H1A...O2 ⁱ	0.888 (18)	1.890 (18)	2.774 (2)	173 (3)
OW1—H1B...O1	0.884 (18)	1.965 (18)	2.824 (3)	164 (3)
OW2—H2A...O3 ⁱⁱ	0.876 (18)	1.902 (18)	2.777 (3)	177 (3)
OW2—H2B...OW4 ⁱⁱ	0.873 (17)	1.880 (18)	2.752 (3)	177 (3)
OW3—H3A...OW4 ⁱⁱⁱ	0.879 (18)	1.790 (18)	2.668 (3)	177 (3)
OW3—H3B...O1	0.871 (17)	1.953 (18)	2.748 (3)	151 (3)
OW4—H4A...O3 ⁱⁱ	0.882 (17)	1.898 (18)	2.770 (3)	169 (3)
OW4—H4B...OW1	0.879 (18)	1.950 (19)	2.794 (3)	160 (3)
O4—H4...O2 ^{iv}	0.82	1.96	2.726 (2)	154
O6—H6A...O5	0.82	1.91	2.627 (3)	146

Symmetry codes: (i) 1 + *x*, *y*, *z*; (ii) 1 - *x*, 1 - *y*, 2 - *z*; (iii) *x* - 1, *y* - 1, *z*; (iv) -*x*, -*y*, 1 - *z*.

All H atoms on C atoms were positioned geometrically and refined as riding atoms, with C—H = 0.93 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C). The H atoms of the carboxyl group and hydroxyl group were also positioned geometrically and refined as riding atoms, with O—H = 0.82 Å and *U*_{iso}(H) = 1.5*U*_{eq}(O). The water H atoms were located in a difference Fourier map and refined with *U*_{iso}(H) = 1.5*U*_{eq}(O).

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

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