

## Hexaaquacopper(II) bis(4-hydroxybenzenesulfonate)

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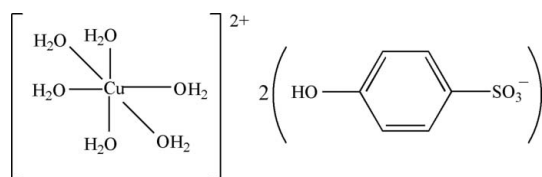
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 Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.027;  $wR$  factor = 0.079; data-to-parameter ratio = 11.5.

The title complex,  $[\text{Cu}(\text{H}_2\text{O})_6](\text{C}_6\text{H}_5\text{SO}_4)_2$ , was synthesized hydrothermally. The  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  cations lie on centres of symmetry and exhibit tetragonally elongated coordination geometry, typical of Jahn–Teller-distorted  $\text{Cu}^{\text{II}}$  complexes. An extensive network of  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds between the coordinated water molecules and the sulfonate groups of the anions links the molecules into layers. The hydroxy groups of the anions form  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds that link between layers.

### Related literature

For the structure of a related complex  $[\text{Ni}(\text{H}_2\text{O})_6](\text{C}_6\text{H}_5\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ , see: Kosnic *et al.* (1992).



### Experimental

#### Crystal data

$[\text{Cu}(\text{H}_2\text{O})_6](\text{C}_6\text{H}_5\text{SO}_4)_2$   
 $M_r = 517.99$   
 Monoclinic,  $P2_1/n$   
 $a = 6.9299$  (13) Å  
 $b = 6.1868$  (12) Å  
 $c = 23.531$  (4) Å  
 $\beta = 91.528$  (2)°

$V = 1008.5$  (3) Å<sup>3</sup>  
 $Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 1.36$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 $0.48 \times 0.48 \times 0.35$  mm

#### Data collection

Bruker SMART APEXII CCD diffractometer  
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)  
 $T_{\text{min}} = 0.530$ ,  $T_{\text{max}} = 0.620$

5886 measured reflections  
 1833 independent reflections  
 1734 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.052$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$   
 $wR(F^2) = 0.079$   
 $S = 1.09$   
 1833 reflections  
 159 parameters  
 9 restraints

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.35$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.29$  e Å<sup>-3</sup>

**Table 1**

Selected bond lengths (Å).

Cu1—O1	2.3842 (14)	Cu1—O3	1.9415 (13)
Cu1—O2	1.9645 (14)		

**Table 2**

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
O7—H7 <sup>i</sup> ···O1 <sup>i</sup>	0.82	1.99	2.763 (2)	158
O1—H1A <sup>i</sup> ···O4 <sup>ii</sup>	0.83 (1)	1.95 (2)	2.779 (2)	174 (3)
O1—H1B <sup>i</sup> ···O5 <sup>iii</sup>	0.83 (1)	1.93 (1)	2.752 (2)	171 (2)
O2—H2B <sup>i</sup> ···O4	0.83 (2)	1.87 (2)	2.698 (2)	174 (3)
O2—H2A <sup>i</sup> ···O6 <sup>iv</sup>	0.83 (1)	1.95 (1)	2.769 (2)	170 (2)
O3—H3B <sup>i</sup> ···O5 <sup>ii</sup>	0.83 (2)	1.94 (2)	2.744 (2)	164 (2)
O3—H3A <sup>i</sup> ···O6	0.83 (2)	1.93 (2)	2.740 (2)	165 (3)

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BI2224).

### References

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 Kosnic, E. J., McClymont, E. L., Hodder, R. A. & Squattrito, P. J. (1992). *Inorg. Chim. Acta*, **201**, 143–151.  
 Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.  
 Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

**supplementary materials**

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## Hexaaquacopper(II) bis(4-hydroxybenzenesulfonate)

Y.-Q. Liu and X.-R. Zeng

### Comment

In the title complex (Fig. 1), the  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  cations lies on centres of symmetry and exhibit tetragonally elongated coordination geometry, with atoms O2, O3, O2<sup>i</sup> and O3<sup>i</sup> forming the equatorial plane and atoms O1 and O1<sup>i</sup> lying in the axial positions [symmetry code (i):  $1 - x, 2 - y, -z$ ]. The Cu1—O1 bond length of 2.3842 (14) Å is significantly longer than the Cu1—O2 and Cu1—O3 bond lengths of 1.9645 (14) and 1.9615 (13) Å, respectively.

An extensive network of O—H $\cdots$ O hydrogen bonds between the coordinated water molecules and the sulfonate groups of the anions link the molecules into layers lying in the (002) planes (Fig. 2). The hydroxy groups of the anions form O—H $\cdots$ O hydrogen bonds between layers.

### Experimental

A mixture of 4-hydroxybenzenesulfonic acid (0.348 g, 0.002 mol) and CuO (0.079, 0.001 mol) was added to 20 ml water and the mixture was sealed in a teflon-lined steel autoclave and heated at 418 K for 4 days. Single crystals of the title compound formed on cooling in air.

### Refinement

H atoms bound to C atoms and of the OH group were placed geometrically and refined as riding with C—H = 0.93 Å and O—H = 0.82 Å, and with  $U_{\text{eq}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$  or  $1.5 U_{\text{eq}}(\text{O})$ . The H atoms of the water molecules were located in difference Fourier maps and refined with the O—H bond lengths restrained to 0.83 (2) Å and with  $U_{\text{iso}}(\text{H})$  refined freely.

### Figures

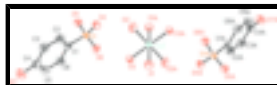


Fig. 1. The molecular structure of the title compound showing 30% probability displacement ellipsoids. H atoms are omitted. The suffix A denotes symmetry code  $1 - x, 2 - y, -z$ .

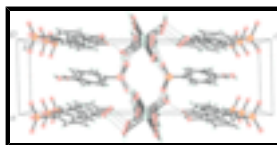


Fig. 2. Packing diagram viewed along the  $a$  axis showing a layer in the (002) plane. Hydrogen bonds are shown as dashed lines.

## Hexaaquacopper(II) bis(4-hydroxybenzenesulfonate)

### Crystal data

$[\text{Cu}(\text{H}_2\text{O})_6](\text{C}_6\text{H}_5\text{SO}_4)_2$

$F_{000} = 534.0$

# supplementary materials

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$M_r = 517.99$

Monoclinic,  $P2_1/n$

Hall symbol: -P 2yn

$a = 6.9299$  (13) Å

$b = 6.1868$  (12) Å

$c = 23.531$  (4) Å

$\beta = 91.528$  (2)°

$V = 1008.5$  (3) Å<sup>3</sup>

$Z = 2$

$D_x = 1.706$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

$\lambda = 0.71073$  Å

Cell parameters from 6039 reflections

$\theta = 2.6$ – $28.3$ °

$\mu = 1.36$  mm<sup>-1</sup>

$T = 293$  (2) K

Block, blue

$0.48 \times 0.48 \times 0.35$  mm

## Data collection

Bruker SMART APEX II CCD  
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293$ (2) K

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(SADABS; Sheldrick, 1996)

$T_{\min} = 0.530$ ,  $T_{\max} = 0.620$

5886 measured reflections

1833 independent reflections

1734 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.052$

$\theta_{\text{max}} = 25.5$ °

$\theta_{\text{min}} = 3.1$ °

$h = -8$ → $8$

$k = -7$ → $7$

$l = -27$ → $28$

## Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.027$

$wR(F^2) = 0.079$

$S = 1.09$

1833 reflections

159 parameters

9 restraints

Primary atom site location: structure-invariant direct  
methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring  
sites

H atoms treated by a mixture of  
independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.05P)^2 + 0.2229P]$$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.002$

$\Delta\rho_{\text{max}} = 0.35$  e Å<sup>-3</sup>

$\Delta\rho_{\text{min}} = -0.29$  e Å<sup>-3</sup>

Extinction correction: SHELXL97 (Sheldrick, 1997),

$$F_c^* = kF_c[1 + 0.001 \times F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$$

Extinction coefficient: 0.073 (4)

## Special details

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.5000	1.0000	0.0000	0.03006 (16)
S1	0.00308 (6)	0.60798 (7)	0.098056 (18)	0.03163 (17)
C3	-0.0610 (3)	0.6358 (4)	0.26714 (9)	0.0446 (5)
H3	-0.1090	0.7334	0.2933	0.053*
C6	0.0787 (3)	0.3434 (3)	0.18887 (8)	0.0391 (4)
H6	0.1254	0.2455	0.1626	0.047*
C2	-0.0607 (3)	0.6884 (3)	0.21002 (9)	0.0415 (5)
H2	-0.1075	0.8219	0.1978	0.050*
C1	0.0092 (3)	0.5428 (3)	0.17107 (8)	0.0330 (4)
C5	0.0783 (3)	0.2909 (4)	0.24607 (9)	0.0430 (5)
H5	0.1238	0.1566	0.2582	0.052*
C4	0.0103 (3)	0.4375 (4)	0.28548 (9)	0.0427 (5)
O3	0.4870 (2)	0.7127 (2)	0.03289 (6)	0.0377 (3)
O6	0.1696 (2)	0.5037 (2)	0.07292 (7)	0.0407 (4)
O1	0.6894 (2)	1.1065 (2)	0.08131 (6)	0.0424 (4)
O2	0.2623 (2)	1.0915 (2)	0.03679 (7)	0.0476 (4)
O5	-0.1792 (2)	0.5252 (2)	0.07440 (7)	0.0431 (4)
O4	0.0127 (2)	0.8432 (2)	0.09386 (6)	0.0416 (4)
O7	0.0198 (3)	0.3770 (3)	0.34066 (6)	0.0596 (5)
H7	-0.0249	0.4731	0.3604	0.089*
H1A	0.7892 (16)	1.032 (3)	0.0829 (13)	0.053 (8)*
H2A	0.234 (3)	1.2081 (16)	0.0517 (9)	0.062 (8)*
H3A	0.395 (2)	0.662 (4)	0.0504 (9)	0.052 (7)*
H1B	0.741 (3)	1.2271 (14)	0.0803 (14)	0.069 (9)*
H2B	0.193 (3)	1.012 (2)	0.0558 (10)	0.052 (8)*
H3B	0.575 (2)	0.653 (4)	0.0513 (10)	0.079 (10)*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cu1	0.0321 (2)	0.0257 (2)	0.0325 (2)	0.00063 (11)	0.00330 (13)	0.00130 (11)
S1	0.0316 (3)	0.0290 (3)	0.0342 (3)	-0.00129 (17)	-0.00018 (17)	0.00307 (17)
C3	0.0422 (11)	0.0510 (12)	0.0407 (11)	0.0057 (9)	0.0051 (8)	-0.0053 (9)
C6	0.0415 (11)	0.0383 (10)	0.0374 (10)	0.0047 (8)	-0.0003 (7)	-0.0003 (8)
C2	0.0396 (11)	0.0403 (11)	0.0447 (11)	0.0068 (8)	0.0012 (8)	0.0002 (9)
C1	0.0291 (9)	0.0353 (9)	0.0344 (9)	-0.0009 (7)	-0.0011 (7)	0.0019 (8)
C5	0.0438 (11)	0.0420 (11)	0.0431 (11)	0.0061 (9)	-0.0025 (8)	0.0074 (9)
C4	0.0365 (11)	0.0554 (12)	0.0359 (10)	-0.0004 (10)	-0.0005 (7)	0.0036 (9)
O3	0.0354 (7)	0.0305 (7)	0.0474 (8)	-0.0011 (6)	0.0016 (6)	0.0074 (6)

## supplementary materials

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O6	0.0424 (9)	0.0372 (8)	0.0430 (8)	0.0019 (5)	0.0085 (6)	0.0007 (5)
O1	0.0402 (8)	0.0347 (8)	0.0519 (8)	-0.0026 (6)	-0.0046 (6)	-0.0013 (6)
O2	0.0479 (9)	0.0306 (8)	0.0654 (10)	0.0017 (7)	0.0241 (7)	0.0018 (7)
O5	0.0400 (8)	0.0415 (8)	0.0469 (9)	-0.0062 (6)	-0.0113 (6)	0.0066 (6)
O4	0.0435 (8)	0.0305 (7)	0.0511 (8)	-0.0011 (5)	0.0032 (6)	0.0058 (6)
O7	0.0698 (11)	0.0737 (12)	0.0353 (8)	0.0148 (9)	0.0028 (7)	0.0072 (8)

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

Cu1—O1	2.3842 (14)	C6—C1	1.385 (3)
Cu1—O2	1.9645 (14)	C6—H6	0.930
Cu1—O3	1.9415 (13)	C2—C1	1.382 (3)
Cu1—O1 <sup>i</sup>	2.3842 (14)	C2—H2	0.930
Cu1—O2 <sup>i</sup>	1.9645 (14)	C5—C4	1.389 (3)
Cu1—O3 <sup>i</sup>	1.9415 (13)	C5—H5	0.930
S1—O4	1.4605 (15)	C4—O7	1.351 (3)
S1—O5	1.4595 (15)	O3—H3A	0.83 (2)
S1—O6	1.4608 (16)	O3—H3B	0.83 (2)
S1—C1	1.7641 (19)	O1—H1A	0.83 (1)
C3—C2	1.383 (3)	O1—H1B	0.83 (1)
C3—C4	1.387 (3)	O2—H2A	0.83 (1)
C3—H3	0.930	O2—H2B	0.83 (2)
C6—C5	1.385 (3)	O7—H7	0.820
O3 <sup>i</sup> —Cu1—O3	180.00 (8)	C5—C6—H6	120.2
O3 <sup>i</sup> —Cu1—O2 <sup>i</sup>	92.28 (6)	C1—C6—H6	120.2
O3—Cu1—O2 <sup>i</sup>	87.72 (6)	C1—C2—C3	120.05 (19)
O3 <sup>i</sup> —Cu1—O2	87.72 (6)	C1—C2—H2	120.0
O3—Cu1—O2	92.28 (6)	C3—C2—H2	120.0
O2 <sup>i</sup> —Cu1—O2	180.00 (12)	C2—C1—C6	120.34 (18)
O3 <sup>i</sup> —Cu1—O1	92.10 (6)	C2—C1—S1	119.81 (15)
O3—Cu1—O1	87.90 (6)	C6—C1—S1	119.82 (15)
O2 <sup>i</sup> —Cu1—O1	89.03 (6)	C4—C5—C6	120.3 (2)
O2—Cu1—O1	90.97 (6)	C4—C5—H5	119.8
O3 <sup>i</sup> —Cu1—O1 <sup>i</sup>	87.90 (6)	C6—C5—H5	119.8
O3—Cu1—O1 <sup>i</sup>	92.10 (6)	O7—C4—C5	116.9 (2)
O2 <sup>i</sup> —Cu1—O1 <sup>i</sup>	90.97 (6)	O7—C4—C3	123.5 (2)
O2—Cu1—O1 <sup>i</sup>	89.03 (6)	C5—C4—C3	119.64 (19)
O1—Cu1—O1 <sup>i</sup>	180.0	Cu1—O3—H3A	126.0 (16)
O4—S1—O5	111.39 (8)	Cu1—O3—H3B	125.3 (17)
O4—S1—O6	112.00 (8)	H3A—O3—H3B	97.9 (19)
O5—S1—O6	112.05 (9)	Cu1—O1—H1A	108.8 (19)
O4—S1—C1	107.08 (9)	Cu1—O1—H1B	117 (2)
O5—S1—C1	106.82 (9)	H1A—O1—H1B	98.1 (18)
O6—S1—C1	107.14 (9)	Cu1—O2—H2A	130.5 (15)
C2—C3—C4	120.05 (19)	Cu1—O2—H2B	125.1 (15)
C2—C3—H3	120.0	H2A—O2—H2B	98.1 (18)

C4—C3—H3	120.0	C4—O7—H7	109.5
C5—C6—C1	119.58 (19)		

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

*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O7—H7 $\cdots$ O1 <sup>ii</sup>	0.82	1.99	2.763 (2)	158
O1—H1A $\cdots$ O4 <sup>iii</sup>	0.83 (1)	1.95 (2)	2.779 (2)	174 (3)
O1—H1B $\cdots$ O5 <sup>iv</sup>	0.83 (1)	1.93 (1)	2.752 (2)	171 (2)
O2—H2B $\cdots$ O4	0.83 (2)	1.87 (2)	2.698 (2)	174 (3)
O2—H2A $\cdots$ O6 <sup>v</sup>	0.83 (1)	1.95 (1)	2.769 (2)	170 (2)
O3—H3B $\cdots$ O5 <sup>iii</sup>	0.83 (2)	1.94 (2)	2.744 (2)	164 (2)
O3—H3A $\cdots$ O6	0.83 (2)	1.93 (2)	2.740 (2)	165 (3)

Symmetry codes: (ii)  $-x+1/2, y-1/2, -z+1/2$ ; (iii)  $x+1, y, z$ ; (iv)  $x+1, y+1, z$ ; (v)  $x, y+1, z$ .

Fig. 1

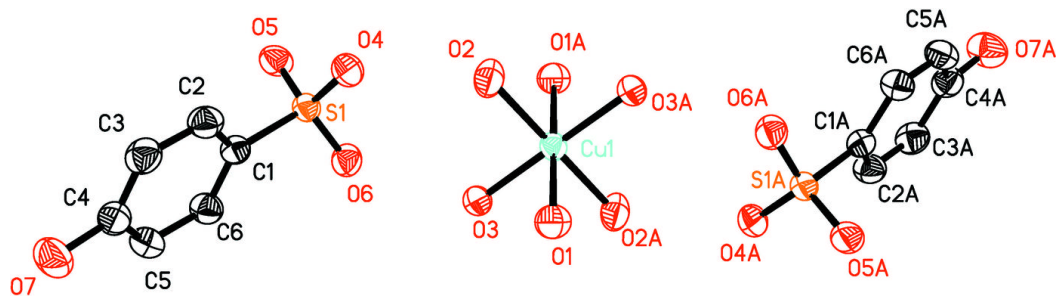




Fig. 2

