Crystal structure of diaqua-(5-sulfosalicylato)-(μ_2-hydroxyl)dicopper(II) hemihydrate, $Cu_2(H_2O)_2(C_7H_3O_6S)(OH) \cdot 0.5H_2O$

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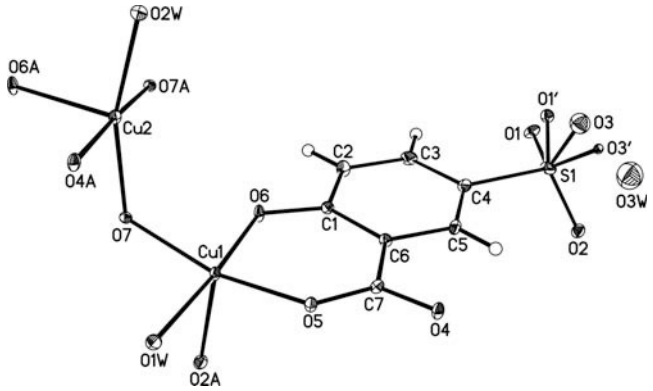
Received November 23, 2009, accepted and available on-line February 12, 2009; CCDC no. 1267/2841



Abstract

$C_{14}H_{18}Cu_4O_{19}S_2$, triclinic, $P\bar{1}$ (no. 2), a = 7.403(7) Å, b = 8.726(7) Å, c = 9.586(1) Å, α = 107.58(3)°, β = 96.66(4)°, γ = 102.51(1)°, V = 565.3 Å^3, Z = 1, $R_{gt}(F)$ = 0.036, $wR_{ref}(F^2)$ = 0.091, T = 173 K.

Source of material

A mixture of $CuCl_2 \cdot 2H_2O$ (0.5 mmol) and 5-sulfosalicylic acid (H_3L, 0.5 mmol) in 12 mL distilled water was heated at 450 K in a Teflon-lined stainless steel autoclave for seven days. The reaction system was then slowly cooled to room temperature. Green crystals of the title compound suitable for single crystal X-ray diffraction analysis were collected by filtration, washed several times with distilled water and dried in air at ambient temperature (yield 38 % based on Cu).

Experimental details

All H atoms were positioned geometrically with d(C—H) = 0.93 Å and U_{iso}(H) = 1.2 U_{eq}(carrier). The H atoms of the water molecules and hydroxy group were not located. The disordered sulfonate O atoms (O1, O1', O3 and O3') were refined using O atoms split over two sites, with a total occupancy of 1. The O3W was refined with the occupancy of 0.5 because of its large temperature factors.

Discussion

The carboxylate groups have a strong ability to bond various metal ions and afford abundant coordination modes, thus rigid carboxylate ligands have been widely used for the design and synthesis of a variety of structures [1]. Introduction of a sulfonate group into rigid carboxylate ligands may result in the formation of unexpected frameworks as the sulfonic group has a different shape and properties in terms of its coordination ability compared to the carboxylate group [2].

Cu1 atom is five-coordinated by five oxygen atoms from two different L ligands, one OH^- anion and one water molecule (O1W) in distorted square-pyramidal environment. The Cu2 atom is four-coordinated by four oxygen atoms from one L ligand, the same OH^- anion and one water molecule (O2W) in a strongly distorted tetrahedral coordination. The L trianions link neighboring Cu(II) atoms to form an one-dimensional chain.

Table 1. Data collection and handling.

Crystal:	green block, size 0.21 × 0.28 × 0.33 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	39.93 cm^{-1}
Diffractometer, scan mode:	Bruker APEX, φ/ω
$2\theta_{max}$:	52.18°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3158, 2211
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1851
$N(param)_{refined}$:	181
Programs:	SHELXS-97 [3], SHELXL-97 [4], SHELXTL-PLUS [5]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(2)	2*i*	0.3435	–0.1879	0.0613	0.024
H(3)	2*i*	0.1569	–0.3595	–0.1646	0.025
H(5)	2*i*	–0.2928	–0.2235	–0.0283	0.020

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	2*i*		0.1394(6)	–0.1026(5)	0.1581(5)	0.012(2)	0.013(2)	0.014(2)	0.004(2)	0.004(2)	0.004(2)
C(2)	2*i*		0.2150(6)	–0.1957(6)	0.0447(5)	0.015(2)	0.023(2)	0.018(2)	0.006(2)	0.005(2)	0.001(2)
C(3)	2*i*		0.1039(7)	–0.2987(6)	–0.0908(5)	0.030(3)	0.019(2)	0.015(2)	0.014(2)	0.008(2)	0.001(2)
C(4)	2*i*		–0.0879(7)	–0.3108(6)	–0.1160(5)	0.027(2)	0.017(2)	0.007(2)	0.008(2)	–0.002(2)	0.003(2)

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Table 3. Continued.

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(5)	2*i*		–0.1648(6)	–0.2168(6)	–0.0084(5)	0.015(2)	0.019(2)	0.015(2)	0.004(2)	–0.002(2)	0.005(2)
C(6)	2*i*		–0.0560(6)	–0.1118(5)	0.1297(5)	0.013(2)	0.014(2)	0.012(2)	0.004(2)	0.004(2)	0.003(2)
C(7)	2*i*		–0.1530(6)	–0.0241(5)	0.2418(5)	0.013(2)	0.017(2)	0.011(2)	0.006(2)	0.004(2)	0.006(2)
O(1)	2*i*	0.50	–0.088(1)	–0.517(1)	–0.3814(8)	0.039(5)	0.025(4)	0.010(4)	0.023(4)	–0.006(3)	–0.005(3)
O(1')	2*i*	0.50	–0.151(1)	–0.566(1)	–0.3566(9)	0.017(2)	0.017(2)	0.017(2)	0.0044(8)	0.0034(8)	0.0053(9)
O(2)	2*i*		–0.3147(4)	–0.3572(4)	–0.3636(3)	0.019(2)	0.021(2)	0.015(2)	0.008(1)	0.001(1)	0.005(1)
O(3)	2*i*	0.50	–0.337(1)	–0.577(1)	–0.2513(9)	0.037(2)	0.036(2)	0.036(2)	0.008(1)	0.007(1)	0.012(1)
O(3')	2*i*	0.50	–0.4177(8)	–0.5436(7)	–0.2366(6)	0.007(1)	0.009(1)	0.009(1)	0.003(1)	0.002(1)	0.002(1)
O(7)	2*i*		0.4483(4)	0.1385(4)	0.5493(3)	0.013(1)	0.011(1)	0.013(2)	0.005(1)	0.002(1)	0.001(1)
O(1W)	2*i*		0.1650(4)	0.3035(4)	0.6362(3)	0.023(2)	0.022(2)	0.012(2)	0.013(1)	0.003(1)	0.000(1)
O(6)	2*i*		0.2538(4)	–0.0130(4)	0.2873(3)	0.009(1)	0.022(2)	0.015(2)	0.006(1)	–0.001(1)	–0.005(1)
O(5)	2*i*		–0.0667(4)	0.0767(4)	0.3721(3)	0.011(1)	0.018(2)	0.012(2)	0.007(1)	0.002(1)	–0.002(1)
O(4)	2*i*		–0.3296(4)	–0.0527(4)	0.2085(3)	0.009(1)	0.021(2)	0.014(2)	0.004(1)	0.001(1)	0.003(1)
O(2W)	2*i*		0.3583(4)	–0.2750(4)	0.6477(3)	0.019(2)	0.016(2)	0.018(2)	0.005(1)	0.005(1)	0.006(1)
O(3W)	2*i*	0.50	–0.607(1)	–0.514(1)	–0.106(1)	0.052(6)	0.055(6)	0.053(6)	0.016(5)	0.008(5)	0.013(5)
Cu(1)	2*i*		0.19695(7)	0.13645(6)	0.45376(6)	0.0089(3)	0.0141(3)	0.0105(3)	0.0043(2)	0.0000(2)	–0.0006(2)
Cu(2)	2*i*		0.43567(7)	–0.05249(7)	0.62456(6)	0.0096(3)	0.0149(3)	0.0129(3)	0.0046(2)	0.0026(2)	0.0023(2)
S(1)	2*i*		–0.2354(2)	–0.4513(1)	–0.2830(1)	0.0442(8)	0.0126(6)	0.0115(6)	0.0085(5)	–0.0083(5)	–0.0012(4)

Acknowledgment. The authors thank Jilin Normal University for supporting this work.

References

1. Song, J.-L.; Lei, C.; Mao, J.-G.: Syntheses, Crystal Structures, and Luminescent Properties of Novel Layered Lanthanide Sulfonate-Phosphonates. Inorg. Chem. **43** (2004) 5630-5634.
2. Sun, Z.-M.; Mao, J.-G.; Sun, Y.-Q.; Zeng, H.-Y.; Clearfield, A.: Synthesis, Characterization, and Crystal Structures of Three New Divalent Metal Carboxylate-Sulfonates with a Layered and One-Dimensional Structure. Inorg. Chem. **43** (2004) 336-341.
3. Sheldrick, G. M.: SHELXS-97. Program for the Solution of Crystal Structures. University of Göttingen, Germany 1997.
4. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.
5. Sheldrick, G. M., SHELXTL-PLUS, Structure Determination Program, Siemens Analytical X-Ray Instrument Inc., Madison, Wisconsin, USA 1990.