Crystal structure of aqua-((*E*)-*N*-(2-(2-hydroxybenzylideneamino)ethyl)-4-methylbenzenesulfonamide)-copper(II), Cu(H₂O)(C₁₆H₁₇N₂O₃S)

Shu-Ni Li^{*,II}, Xiao-Yun Wei^{II}, Man-Cheng Hu^{II}, Jun Li^I and Feng-Xing Zhang^I

^I Northwest University, Department of Chemistry, Xi'an 710069, P. R. China

^{II} Shaanxi Normal University, School of Chemistry and Materials Science, Xi'an 710062, P. R. China

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Abstract

C₁₆H₁₈CuN₂O₄S, triclinic, *P* $\bar{1}$ (no. 2), *a* = 7.4366(5) Å, *b* = 7.5339(4) Å, *c* = 16.617(1) Å, α = 84.597(1)°, β = 79.284(1)°, γ = 62.564(3)°, *V* = 811.8 Å³, *Z* = 2, *R*_{gt}(*F*) = 0.034, *wR*_{ref}(*F*²) = 0.095, *T* = 296 K.

* Correspondence author (e-mail: lishuni@snnu.edu.cn)

Source of material

The sulfonamide Schiff base ligand (*E*)-*N*-(2-(2-hydroxybenzylideneamino)ethyl)-4-methylbenzenesulfonamide (*L*) was synthesized by reacting tosyl-ethylenediamine with one equivalent of salicylaldehyde in ethanol. It is formed as yellow crystals (m.p. 126–127 °C). To 20 mL hot ethanol solution containing 0.214 g (1 mmol) *L*, 0.199 g Cu(CH₃COO)₂ · H₂O (1 mmol) in 10 mL ethanol was added under stirring for 1 h. A dark green solution was formed and filtrated. The filtrate was left for slow evaporation. Dark green block-shaped crystals of the title compound were obtained after 2 weeks.

Experimental details

The H atoms were located in difference maps. While the water H atom positions were refined, the other H atoms were fixed in idealized positions and refined as riding with *U*_{iso}(H) = 1.2*U*_{eq} or 1.5*U*_{eq}.

Discussion

In the title crystal structure copper(II) atom is chelated by one unsymmetrical Schiff base ligand providing their amide, amine N atoms and phenolate O atom and one water molecule (figure, top). A distorted square planar CuN₂O₂ environment arises with the N1...N2 and O1...O4 distances (2.605 Å and 2.662 Å, respectively) shorter than the N1...O1 and N2...O4 distances (2.801 Å and 2.902 Å, respectively). The Cu1—N1 distance (1.923 Å) is shorter than Cu1—N2 (1.969 Å) suggesting that the imine nitrogen atom is a slightly better donor than amide nitrogen atom because the electron density is delocalized into the sulfonyl group. The Cu1—O4(water) distance is longer than Cu1—O1(phenolate). The four coordinated atoms (N₂O₂) are arranged in a *cis*-conformation. In the molecule, the chelated five-membered ring (Cu1–N1–C8–C9–N2) and six-membered ring (Cu1–O1–C2–C1–C7–N1) also contribute to the stability of the complex. The bond-valence sum for the Cu center is calculated to be 2.2, which is close to the expected value of 2 [1].

A strong intramolecular O—H...O hydrogen bond helps to stabilize the molecular conformation (O4—H4B...O2 with 0.66(7) Å, 2.02(7) Å, 2.603(3) Å, 149(8)°). The resulting six-membered chelate ring (Cu1–N2–S1–O2...H4B–O4) is planar with a mean deviation of 0.0830 Å. The crystal packing may be further stabilized by C—H...O, C—H...π and π...π interactions (figure, middle). The resulting C12—H12...O3 hydrogen bonds among different symmetric motifs link the structure in layers running parallel to the *a* axis and shows a centrosymmetric arrangement mode. In the structure, there are the two π...π interactions formed between two rings of one molecule and its symmetry equivalent by inversion (−*x*, −*y*, −*z*). The Cg...Cgⁱ distance is 3.515 Å, where Cg and Cgⁱ are the centroids of ring 1 (Cu1–O1–C2–C1–C7–N1) and ring 2 (C10

to C15) (figure, middle). Two molecules are arranged in a head-to-tail mode and thus formed a subunit. The subunits are linked by hydrogen bonding and form two-dimensional layers parallel to the *b* axis (figure, bottom).

Table 1. Data collection and handling.

Crystal:	dark green plate, size 0.11 × 0.27 × 0.38 mm
Wavelength:	Mo <i>K</i> _α radiation (0.71073 Å)
μ :	14.97 cm ⁻¹
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{\max}$:	50.18°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	4093, 2820
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2385
$N(\text{param})_{\text{refined}}$:	195
Programs:	SHELXS-97 [2], SHELXL-97 [3], SHELXTL [4]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(11)	2i	0.3834	0.2480	0.3027	0.069
H(12)	2i	0.3617	0.4434	0.4075	0.077
H(14)	2i	0.1752	0.1121	0.5723	0.063
H(15)	2i	0.1969	-0.0834	0.4676	0.053
H(3)	2i	0.1725	0.0948	-0.1500	0.076
H(4)	2i	-0.0726	0.3202	-0.2260	0.086
H(5)	2i	-0.3580	0.5904	-0.1642	0.088
H(6)	2i	-0.4151	0.6325	-0.0259	0.069
H(7)	2i	-0.3328	0.5249	0.1052	0.051
H(8A)	2i	-0.3192	0.4028	0.2393	0.051
H(8B)	2i	-0.1374	0.4528	0.2432	0.051
H(9A)	2i	-0.0815	0.1841	0.3309	0.051
H(9B)	2i	-0.1256	0.0700	0.2683	0.051
H(16A)	2i	0.3772	0.3704	0.5892	0.123
H(16B)	2i	0.1423	0.4306	0.6124	0.123
H(16C)	2i	0.2170	0.5592	0.5484	0.123
H(4A)	2i	0.513(8)	0.037(8)	0.106(3)	0.123
H(4B)	2i	0.520(9)	-0.108(9)	0.126(4)	0.123

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
C(10)	2i	0.2923(2)	0.0629(2)	0.37477(6)	0.036(1)	0.038(2)	0.029(1)	-0.012(1)	-0.006(1)	0.005(1)
C(11)	2i	0.3417(2)	0.2207(2)	0.35676(6)	0.074(2)	0.061(2)	0.044(2)	-0.037(2)	-0.013(2)	0.016(2)
C(12)	2i	0.3287(3)	0.3378(2)	0.41951(8)	0.085(3)	0.050(2)	0.072(3)	-0.038(2)	-0.033(2)	0.014(2)
C(13)	2i	0.2663(3)	0.2971(2)	0.50027(7)	0.046(2)	0.045(2)	0.060(2)	-0.007(1)	-0.024(2)	-0.008(2)
C(14)	2i	0.2170(2)	0.1393(2)	0.51828(6)	0.050(2)	0.068(2)	0.031(2)	-0.022(2)	-0.001(1)	-0.005(1)
C(15)	2i	0.2300(2)	0.0222(2)	0.45553(6)	0.048(2)	0.052(2)	0.033(2)	-0.025(1)	-0.004(1)	0.003(1)
C(1)	2i	-0.1533(2)	0.3889(2)	-0.00043(7)	0.053(2)	0.059(2)	0.039(2)	-0.040(2)	-0.017(1)	0.015(1)
C(2)	2i	0.0290(2)	0.2335(2)	-0.03873(6)	0.071(2)	0.053(2)	0.032(2)	-0.043(2)	-0.013(1)	0.004(1)
C(3)	2i	0.0572(3)	0.2032(3)	-0.12464(6)	0.107(3)	0.073(2)	0.035(2)	-0.062(2)	-0.014(2)	0.002(2)
C(4)	2i	-0.0906(3)	0.3383(3)	-0.16992(7)	0.117(3)	0.110(3)	0.038(2)	-0.090(3)	-0.029(2)	0.017(2)
C(5)	2i	-0.2636(3)	0.4991(3)	-0.13266(8)	0.087(3)	0.122(4)	0.052(2)	-0.079(3)	-0.039(2)	0.040(2)
C(6)	2i	-0.2970(3)	0.5248(3)	-0.05015(8)	0.055(2)	0.087(3)	0.052(2)	-0.048(2)	-0.023(2)	0.026(2)
Cu(1)	2i	0.17992(5)	0.10221(5)	0.11628(2)	0.0501(2)	0.0365(2)	0.0250(2)	-0.0057(2)	-0.0030(2)	-0.0019(1)
S(1)	2i	0.3030(1)	-0.0811(1)	0.29415(4)	0.0559(5)	0.0359(4)	0.0276(4)	-0.0059(3)	-0.0075(3)	0.0008(3)
O(1)	2i	0.1808(4)	0.1086(3)	0.0012(1)	0.075(2)	0.045(1)	0.028(1)	-0.020(1)	-0.006(1)	-0.0025(9)
O(2)	2i	0.5102(4)	-0.1570(4)	0.2480(1)	0.055(1)	0.070(2)	0.034(1)	0.013(1)	-0.005(1)	0.001(1)
O(3)	2i	0.2434(4)	-0.2299(3)	0.3324(1)	0.114(2)	0.042(1)	0.049(1)	-0.035(1)	-0.028(1)	0.010(1)
O(4)	2i	0.4714(5)	-0.0780(5)	0.0944(2)	0.069(2)	0.098(2)	0.039(2)	0.026(2)	0.001(1)	0.011(2)
N(1)	2i	-0.0978(3)	0.3098(3)	0.1392(1)	0.040(1)	0.040(1)	0.031(1)	-0.018(1)	-0.007(1)	0.003(1)
N(2)	2i	0.1510(4)	0.0682(4)	0.2362(1)	0.046(1)	0.042(1)	0.026(1)	-0.008(1)	-0.004(1)	0.001(1)
C(7)	2i	-0.2074(4)	0.4181(5)	0.0860(2)	0.037(2)	0.048(2)	0.044(2)	-0.022(1)	-0.010(1)	0.008(1)
C(8)	2i	-0.1714(4)	0.3527(4)	0.2272(2)	0.038(2)	0.048(2)	0.033(2)	-0.014(1)	-0.003(1)	-0.003(1)
C(9)	2i	-0.0663(4)	0.1585(4)	0.2733(2)	0.049(2)	0.046(2)	0.030(2)	-0.021(1)	-0.003(1)	-0.001(1)
C(16)	2i	0.2491(6)	0.4262(6)	0.5689(3)	0.075(3)	0.066(2)	0.092(3)	-0.007(2)	-0.036(2)	-0.029(2)

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