Crystal structure of diaquabis{4-[(2-pyridylmethylidene)-amino]benzenesulfonato-κ^2N,N']copper(II) dihydrate, $Cu(C_{12}H_9N_2O_3S)_2(H_2O)_2 \cdot 2H_2O$

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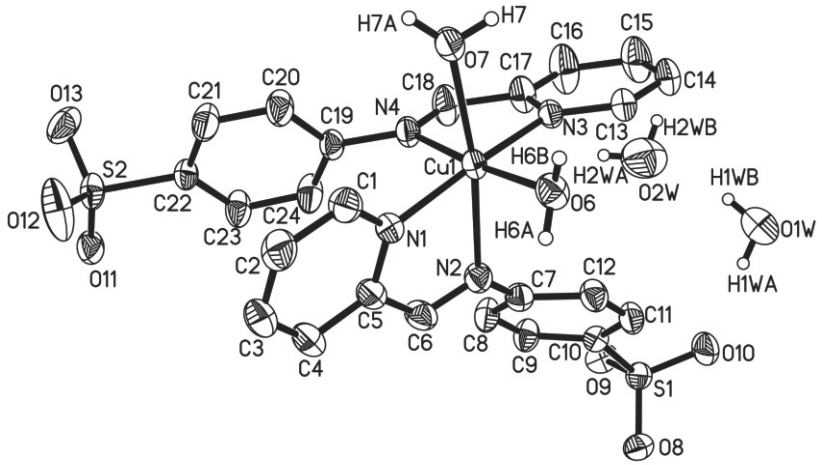

Abstract

$C_{24}H_{26}CuN_4O_{10}S_2$, triclinic, $P\bar{1}$ (no. 2), a = 9.538(2) Å, b = 11.257(2) Å, c = 14.446(2) Å, α = 98.669(2)°, β = 104.433(2)°, γ = 104.770(2)°, V = 1414.1 Å^3, Z = 2, $R_{gt}(F)$ = 0.034, $wR_{ref}(F^2)$ = 0.099, T = 296 K.

Source of material

All reagents and solvents were used as obtained commercially without further purification. *p*-Aminobenzenesulfonic acid (0.173 g, 1 mmol) and KOH (0.56 g, 1 mmol) were dissolved in a solution of water (10 ml) and methanol (10 ml), then 2-pyridinecarboxaldehyde (0.11 mL, 1 mmol) was added. The resulting pale yellow solution was stirred for 1 h at 333 K and was added to a solution of $CuCl_2 \cdot 2H_2O$ (0.086 g, 0.5 mmol) in water (5 ml) . The resulting mixture was stirred at 333 K for another 1 h. Then the mixture was filtred, and the filtrate was left to evaporate slowly at room temperature. After a week, blue block-shaped crystals of the title compound were isolated (yield 15 %).

Elemental analysis — found: C, 43.75 %; H, 4.03 %; N, 8.49 %; S, 9.70 %; calculated for $C_{24}H_{26}CuN_4O_{10}S_2$: C, 43.76 %; H, 3.95 %; N, 8.51 %; S, 9.72 %.

Experimental details

H atoms bonded to C atoms were positioned geometrically and refined using a riding model with d(C—H) = 0.93 Å and U_{iso}(H) = 1.2 U_{eq}(C). The water H atoms were located in difference Fourier maps and refined using a riding model with d(O—H) = 0.82-0.85 Å and U_{iso}(H) = 1.5 U_{eq}(O).

Discussion

During the past decades, Schiff-base compounds containing sulfonic group and amino acid functionality have aroused much interest owing to their versatile binding modes and their bioactivities [1-5]. Recently, we reported many complexes containing aminobenzenesulfonic acid Schiff base [6-10].

The asymmetric unit of the title crystal structure consists of one Cu(II) ion, two deprotonated L^- ligands, two coordinating water molecules and two crystallized water molecules. Cu(II) ion is six-coordinated by four N atoms from two deprotonated L^- ligands (d(Cu1—N1) = 2.012 Å, d(Cu1—N2) = 2.340 Å, d(Cu1—N3) = 1.999 Å, d(Cu1—N4) = 2.074 Å), and two O atoms from water molecules (d(Cu1—O6) = 1.9778 Å, d(Cu1—O7) = 2.3306 Å) in a slightly distorted octahedral manner. In the octahedron, N1, N2, N3 and O7 constitute the basal plane, and O6, N4 occupy the apexes with ∠N4–Cu1–O6 = 173.78(8)°. The sum of the bond angles ∠N1–Cu1–N2 = 76.70(8)°, ∠N2–Cu1–N3 = 95.41(8)°, ∠N3–Cu1–O7 = 89.69(8)°, and ∠O7–Cu1–N1 = 97.65(8)° is 359.45°, which indicates that N1, N2, N3 and O7 are nearly coplanar. The Cu(II) ion deviates from the least-squares plane of the basal plane N1–N2–N3–O7 by 0.1080 Å. In the complex, the sulfonic oxygen atoms do not coordinate the metal ions but participate in the formation of hydrogen bonding, which is similar to the reported sulfonic complexes [4,5]. There are intramolecular as well as intermolecular hydrogen-bonding interactions. The guest water O atom forms hydrogen bonds O1W–H1WB···O2W and O1W–H1WA···O10 with coordinated-water atom O2W and sulfonic O10 from the same mononuclear unit. O–H···O hydrogen bonds are also formed between adjacent mononuclear units (O6–H6A···O9^{i}, O6–H6B···O2W^{i}, O7–H7A···O12^{ii}, O7–H7···O11^{iii}, O2W–H2WB···O12^{iiii}, symmetry code i: x+1,y,z; ii: –x+2,–y+2,–z+1; iii: x,y–1,z; iiii: x–1,y–1,z) . The molecules are assembled into a 3D supramolecular network through the strong hydrogen bonds mentioned above.

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Table 1. Data collection and handling.

Crystal:	blue block, size 0.28 × 0.33 × 0.36 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	9.82 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	50.02°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8552, 4857
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3736
$N(param)_{refined}$:	370
Programs:	SHELXS-97, SHELXL-97, SHELXTL [11]

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

Atom	Site	x	y	z	U_{iso}
H(1)	2*i*	1.1278	0.8257	0.6984	0.069
H(2)	2*i*	1.3022	1.0220	0.7344	0.087
H(3)	2*i*	1.2698	1.1895	0.8287	0.093
H(4)	2*i*	1.0667	1.1559	0.8936	0.087
H(6)	2*i*	0.8326	1.0059	0.9102	0.069
H(8)	2*i*	0.5610	0.9423	0.8583	0.071
H(9)	2*i*	0.3669	0.9022	0.9296	0.069
H(11)	2*i*	0.4851	0.6091	1.0112	0.066
H(12)	2*i*	0.6748	0.6447	0.9358	0.067
H(13)	2*i*	0.7202	0.4407	0.7769	0.059
H(14)	2*i*	0.4906	0.2892	0.7438	0.074
H(15)	2*i*	0.2740	0.3187	0.6514	0.103
H(16)	2*i*	0.2924	0.5032	0.5943	0.110
H(18)	2*i*	0.4611	0.7093	0.5781	0.081
H(20)	2*i*	0.8376	0.8422	0.5297	0.083
H(21)	2*i*	0.8882	1.0308	0.4820	0.083
H(23)	2*i*	0.6527	1.1568	0.6439	0.077
H(24)	2*i*	0.5869	0.9624	0.6832	0.079
H(6A)	2*i*	1.0132	0.6853	0.8737	0.088
H(6B)	2*i*	1.0086	0.5894	0.7985	0.088
H(7A)	2*i*	0.9297	0.6345	0.5598	0.105
H(7)	2*i*	0.8702	0.5345	0.5998	0.105
H(1WB)	2*i*	0.0672	0.3982	0.8691	0.154
H(1WA)	2*i*	0.1436	0.4544	0.9666	0.154
H(2WA)	2*i*	0.1369	0.5303	0.7344	0.203
H(2WB)	2*i*	0.0422	0.4088	0.7176	0.203

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

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	2*i*	0.83030(3)	0.70648(3)	0.73631(2)	0.0421(2)	0.0342(2)	0.0482(2)	0.0098(1)	0.0124(1)	0.0136(1)
S(1)	2*i*	0.28270(8)	0.74376(7)	1.05136(5)	0.0528(4)	0.0520(4)	0.0515(4)	0.0102(3)	0.0199(3)	0.0129(3)
S(2)	2*i*	0.83275(9)	1.25964(7)	0.52664(6)	0.0639(5)	0.0486(4)	0.0768(5)	0.0265(4)	0.0369(4)	0.0338(4)
C(1)	2*i*	1.1153(3)	0.8929(3)	0.7381(2)	0.053(2)	0.058(2)	0.062(2)	0.009(1)	0.027(2)	0.012(2)
C(2)	2*i*	1.2196(4)	1.0104(3)	0.7590(2)	0.056(2)	0.080(2)	0.074(2)	–0.002(2)	0.028(2)	0.022(2)
C(3)	2*i*	1.2015(4)	1.1091(3)	0.8156(3)	0.077(2)	0.055(2)	0.080(2)	–0.015(2)	0.025(2)	0.009(2)
C(4)	2*i*	1.0803(4)	1.0895(3)	0.8538(2)	0.086(2)	0.043(2)	0.073(2)	0.000(2)	0.026(2)	0.003(2)
C(5)	2*i*	0.9802(3)	0.9694(2)	0.8316(2)	0.055(2)	0.043(2)	0.054(2)	0.009(1)	0.018(1)	0.007(1)
C(6)	2*i*	0.8527(3)	0.9409(3)	0.8730(2)	0.065(2)	0.045(2)	0.062(2)	0.017(1)	0.028(2)	0.002(1)
C(7)	2*i*	0.6433(3)	0.8029(2)	0.8959(2)	0.055(2)	0.047(2)	0.050(2)	0.015(1)	0.020(1)	0.010(1)
C(8)	2*i*	0.5477(3)	0.8766(3)	0.8905(2)	0.073(2)	0.059(2)	0.067(2)	0.031(2)	0.036(2)	0.033(2)
C(9)	2*i*	0.4316(3)	0.8526(3)	0.9333(2)	0.065(2)	0.060(2)	0.065(2)	0.031(2)	0.028(2)	0.029(2)
C(10)	2*i*	0.4115(3)	0.7563(2)	0.9811(2)	0.051(2)	0.046(2)	0.044(2)	0.013(1)	0.014(1)	0.012(1)
C(11)	2*i*	0.5016(3)	0.6770(3)	0.9814(2)	0.066(2)	0.043(2)	0.065(2)	0.020(1)	0.027(2)	0.021(1)
C(12)	2*i*	0.6162(3)	0.6991(3)	0.9375(2)	0.064(2)	0.046(2)	0.067(2)	0.023(1)	0.027(2)	0.017(2)
C(13)	2*i*	0.6328(3)	0.4529(2)	0.7391(2)	0.051(2)	0.042(1)	0.057(2)	0.015(1)	0.019(1)	0.020(1)
C(14)	2*i*	0.4956(3)	0.3618(3)	0.7198(2)	0.064(2)	0.044(2)	0.079(2)	0.008(1)	0.024(2)	0.026(2)
C(15)	2*i*	0.3679(4)	0.3792(3)	0.6654(3)	0.050(2)	0.068(2)	0.120(3)	–0.008(2)	0.008(2)	0.040(2)
C(16)	2*i*	0.3790(4)	0.4887(3)	0.6308(3)	0.047(2)	0.081(2)	0.130(3)	0.000(2)	–0.006(2)	0.057(2)
C(17)	2*i*	0.5181(3)	0.5743(3)	0.6508(2)	0.047(2)	0.050(2)	0.074(2)	0.008(1)	0.006(2)	0.027(2)
C(18)	2*i*	0.5426(3)	0.6905(3)	0.6169(2)	0.052(2)	0.062(2)	0.085(2)	0.016(2)	0.002(2)	0.040(2)
C(19)	2*i*	0.7046(3)	0.8834(2)	0.6105(2)	0.052(2)	0.041(1)	0.049(2)	0.017(1)	0.013(1)	0.020(1)
C(20)	2*i*	0.7976(4)	0.9045(3)	0.5514(2)	0.108(3)	0.050(2)	0.083(2)	0.043(2)	0.058(2)	0.032(2)
C(21)	2*i*	0.8304(4)	1.0183(3)	0.5249(2)	0.099(3)	0.061(2)	0.082(2)	0.040(2)	0.060(2)	0.037(2)
C(22)	2*i*	0.7794(3)	1.1138(2)	0.5606(2)	0.048(2)	0.042(1)	0.052(2)	0.018(1)	0.019(1)	0.021(1)
C(23)	2*i*	0.6888(4)	1.0931(3)	0.6197(2)	0.087(2)	0.052(2)	0.088(2)	0.042(2)	0.055(2)	0.036(2)
C(24)	2*i*	0.6503(4)	0.9767(3)	0.6439(2)	0.078(2)	0.063(2)	0.091(2)	0.036(2)	0.053(2)	0.042(2)
N(1)	2*i*	0.9962(2)	0.8723(2)	0.7731(2)	0.046(1)	0.040(1)	0.047(1)	0.009(1)	0.014(1)	0.010(1)
N(2)	2*i*	0.7702(3)	0.8281(2)	0.8581(2)	0.057(1)	0.046(1)	0.055(1)	0.016(1)	0.027(1)	0.014(1)
N(3)	2*i*	0.6454(2)	0.5577(2)	0.7059(1)	0.045(1)	0.035(1)	0.044(1)	0.0108(9)	0.011(1)	0.0125(9)
N(4)	2*i*	0.6761(2)	0.7665(2)	0.6407(2)	0.052(1)	0.039(1)	0.052(1)	0.013(1)	0.014(1)	0.018(1)
O(6)	2*i*	0.9598(2)	0.6316(2)	0.8239(1)	0.055(1)	0.051(1)	0.066(1)	0.0194(9)	0.007(1)	0.015(1)
O(7)	2*i*	0.8936(3)	0.6110(2)	0.6045(2)	0.105(2)	0.043(1)	0.075(1)	0.020(1)	0.052(1)	0.016(1)
O(8)	2*i*	0.3675(2)	0.8276(2)	1.1460(1)	0.072(1)	0.065(1)	0.048(1)	0.015(1)	0.019(1)	0.008(1)
O(9)	2*i*	0.1577(2)	0.7848(2)	0.9993(1)	0.051(1)	0.082(1)	0.064(1)	0.025(1)	0.018(1)	0.014(1)
O(10)	2*i*	0.2353(3)	0.6127(2)	1.0568(2)	0.085(2)	0.054(1)	0.080(2)	0.006(1)	0.039(1)	0.022(1)
O(11)	2*i*	0.7713(3)	1.3441(2)	0.5781(2)	0.112(2)	0.044(1)	0.080(2)	0.029(1)	0.053(1)	0.022(1)
O(12)	2*i*	0.9948(3)	1.2985(2)	0.5517(3)	0.059(2)	0.089(2)	0.211(3)	0.020(1)	0.044(2)	0.087(2)
O(13)	2*i*	0.7626(3)	1.2329(2)	0.4218(2)	0.153(2)	0.086(2)	0.067(2)	0.068(2)	0.056(2)	0.044(1)
O(1W)	2*i*	0.0914(3)	0.3845(2)	0.9264(2)	0.107(2)	0.074(2)	0.120(2)	0.023(2)	0.033(2)	0.011(2)
O(2W)	2*i*	0.0982(4)	0.4741(3)	0.7618(2)	0.157(3)	0.136(3)	0.124(3)	0.085(2)	0.028(2)	0.017(2)

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