Crystal structure of triaquasulfato-2,3-diaza-1,6-di(4-fluorobenzyl)-hexanecopper(II) dihydrate, $Cu(C_{16}H_{18}N_2F_2)(H_2O)_3(SO_4) \cdot 2H_2O$

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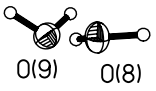

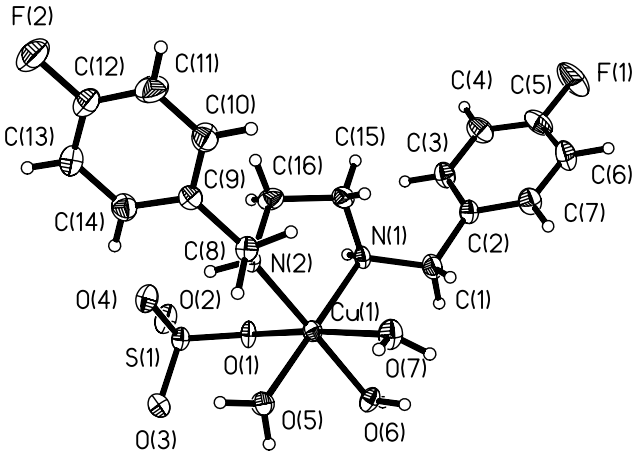

Abstract

$C_{16}H_{28}CuF_2N_2O_9S$, monoclinic, $P12_1/c1$ (No. 14), a = 15.169(8) Å, b = 12.614(6) Å, c = 11.387(6) Å, β = 94.651(7)°, V = 2171.6 Å^3, Z = 4, $R_{gt}(F)$ = 0.046, $wR_{ref}(F^2)$ = 0.138, T = 298 K.

Source of material

Ethylenediamine (abbreviated as en) and 4-fluorobenzaldehyde were condensed in anhydrous methanol and then reduced to obtain the colorless viscous free ligand L, 2,3-diaza-1,6-di-(4-fluorobenzyl)hexane. Copper(II) sulfate (1.0 mmol, 250 mg) and L (1.0 mmol, 317 mg) were suspended in water (20 ml) and stirred for ca. 1 hour to obtain a clear blue solution. After keeping the above solution in air for one week, large dark blue crystals were formed. The product was isolated, washed three times with water, and dried in a vacuum desiccator using $CaCl_2$ (yield 68%). All reagents and solvents were used as obtained without further purification.

Experimental details

The hydrogen atoms attached to C atoms were placed in geometrically idealised positions and constrained to ride on their parent atoms with C—H distance of 0.90 Å, and $U_{iso}(H) = 1.2\ U_{eq}(C)$. Due to the small size of the crystal used and the following weakness of intensity data at higher θ all reflections with $\theta \leq 23°$ and some significant reflections with $23° \leq \theta \leq 25°$ had been considered in the calculations. Nevertheless, all H atoms attached to O atoms could be localized from Fourier maps and were refined isotropically.

Discussion

Organic amine complexes with transition metal carboxylates represent an important branch in the field of coordination chemistry. The title compound is a monomeric Cu^{II} complex. Each unit of the complex consists of one coordination monomer and two lattice water molecules. In the monomer, the Cu(1) atom is in an octahedral geometry and is six-coordinated by two N atoms from one amine ligand, and four O atoms, one of which from a sulfate ligand and the other three from three coordination water molecules. N(1), N(2), O(5) and O(6) atoms constitute the basal plane (plane I) of the octahedron with the average deviation of 0.026 Å, and Cu(1) atom locates 0.01 Å above plane I toward the sulfate O(1) atom. The O(1) and O(7) atoms occupy the two axial positions. The average axial C—O distance is 2.428(3) Å, indicating an elongated octahedral geometry of Cu(1) atom. The two phenyl rings, C2-C3-C4-C5-C6-C7 (plane II) and C9-C10-C11-C12-C13-C14 (plane III), are at the angle of 74.1°. The dihedral angle between planes I and II (or III) is 66.9° (or 58.9°). All the oxygen and the nitrogen atoms in the complex contribute to the formation of hydrogen bonds. Strong inter- and one intramolecular (N2–H2···O4) hydrogen bonds link the complex to form a two-dimensional network in the *bc* plane.

Table 1. Data collection and handling.

Crystal:	dark blue block, size 0.18 × 0.25 × 0.33 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	11.84 cm^{-1}
Diffractometer, scan mode:	Siemens SMART CCD, φ/ω
$2\theta_{max}$:	46.0°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7395, 3329
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2407
$N(param)_{refined}$:	320
Programs:	SADABS [1], SHELXS-97 [2], SHELXL-97 [3], SHELXTL [4]

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

Atom	Site	x	y	z	U_{iso}
H(1)	4*e*	0.7994	0.5585	0.0554	0.036
H(2)	4*e*	0.8136	0.3223	0.2278	0.035
H(1A)	4*e*	0.8453	0.7169	0.1150	0.051
H(1B)	4*e*	0.7869	0.7107	0.2216	0.051
H(3)	4*e*	0.7033	0.6548	–0.0739	0.052
H(4)	4*e*	0.5960	0.7547	–0.1815	0.061
H(6)	4*e*	0.6010	0.9647	0.0801	0.065
H(7)	4*e*	0.7057	0.8635	0.1883	0.055
H(8A)	4*e*	0.7200	0.4276	0.3870	0.041
H(8B)	4*e*	0.8019	0.3560	0.4247	0.041
H(10)	4*e*	0.5858	0.3429	0.4256	0.062
H(11)	4*e*	0.4960	0.1942	0.4276	0.077
H(13)	4*e*	0.6863	0.0166	0.3078	0.059
H(14)	4*e*	0.7775	0.1640	0.3080	0.055
H(15A)	4*e*	0.6584	0.5449	0.0892	0.046
H(15B)	4*e*	0.6831	0.5513	0.2259	0.046
H(16A)	4*e*	0.7316	0.3836	0.0800	0.049
H(16B)	4*e*	0.6615	0.3743	0.1741	0.049
H(17)	4*e*	0.964(3)	0.356(1)	0.369(4)	0.05(2)
H(18)	4*e*	1.020(1)	0.443(4)	0.351(5)	0.10(2)
H(19)	4*e*	0.962(4)	0.660(3)	0.281(4)	0.12(3)
H(20)	4*e*	0.988(3)	0.640(3)	0.167(2)	0.07(2)
H(21)	4*e*	0.859(4)	0.667(2)	0.411(4)	0.09(2)
H(22)	4*e*	0.846(3)	0.577(4)	0.480(2)	0.08(2)
H(23)	4*e*	0.124(3)	0.576(1)	0.370(4)	0.06(2)
H(24)	4*e*	0.141(4)	0.485(3)	0.299(2)	0.09(2)
H(25)	4*e*	0.119(3)	0.395(2)	0.132(5)	0.09(2)
H(26)	4*e*	0.110(3)	0.495(3)	0.073(4)	0.09(2)

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)	4*e*	0.87987(3)	0.49829(4)	0.24039(4)	0.0327(3)	0.0267(5)	0.0303(3)	–0.0001(2)	–0.0000(2)	0.0044(2)
F(1)	4*e*	0.5301(2)	0.9279(3)	–0.1235(3)	0.090(2)	0.098(3)	0.081(2)	0.055(2)	–0.015(2)	0.013(2)
F(2)	4*e*	0.5311(2)	0.0077(3)	0.3687(3)	0.075(2)	0.061(3)	0.090(2)	–0.031(2)	0.002(2)	0.004(2)
N(1)	4*e*	0.7881(2)	0.5752(3)	0.1304(3)	0.038(2)	0.020(3)	0.031(2)	0.005(2)	0.001(1)	0.002(2)
N(2)	4*e*	0.7883(2)	0.3841(3)	0.2491(2)	0.038(2)	0.022(2)	0.027(2)	0.002(1)	0.001(1)	0.001(2)
O(1)	4*e*	0.9296(2)	0.4100(2)	0.0684(2)	0.055(2)	0.018(2)	0.037(2)	0.004(1)	0.007(1)	–0.000(1)
O(2)	4*e*	0.9486(2)	0.2743(3)	–0.0734(2)	0.071(2)	0.038(3)	0.029(2)	–0.007(2)	0.016(1)	–0.005(1)
O(3)	4*e*	1.0390(2)	0.2732(3)	0.1095(3)	0.045(2)	0.039(2)	0.065(2)	0.008(2)	–0.006(2)	0.001(2)
O(4)	4*e*	0.8848(2)	0.2312(3)	0.1075(2)	0.058(2)	0.037(2)	0.035(2)	–0.006(2)	0.013(1)	0.004(1)
O(5)	4*e*	0.9641(2)	0.4240(3)	0.3527(3)	0.043(2)	0.033(3)	0.056(2)	–0.004(2)	–0.009(1)	0.020(2)
O(6)	4*e*	0.9715(2)	0.6093(2)	0.2300(2)	0.048(2)	0.027(2)	0.031(2)	–0.008(1)	0.003(1)	0.002(2)
O(7)	4*e*	0.8389(2)	0.6011(3)	0.4083(3)	0.063(2)	0.040(3)	0.036(2)	0.002(2)	0.004(1)	–0.001(2)
O(8)	4*e*	0.1352(2)	0.5080(3)	0.3709(3)	0.058(2)	0.035(3)	0.044(2)	0.004(2)	0.000(2)	0.004(2)
O(9)	4*e*	0.1423(2)	0.4575(3)	0.1236(3)	0.047(2)	0.046(3)	0.050(2)	–0.003(2)	0.000(2)	0.001(2)
S(1)	4*e*	0.94956(7)	0.2978(1)	0.05399(8)	0.0426(6)	0.0248(9)	0.0272(5)	0.0001(5)	0.0050(4)	0.0006(5)
C(1)	4*e*	0.7892(3)	0.6918(4)	0.1394(4)	0.050(3)	0.032(4)	0.045(3)	0.009(2)	–0.006(2)	–0.001(2)
C(2)	4*e*	0.7162(3)	0.7505(4)	0.0688(4)	0.042(2)	0.027(3)	0.035(2)	0.002(2)	0.004(2)	0.002(2)
C(3)	4*e*	0.6828(3)	0.7174(4)	–0.0426(4)	0.052(3)	0.038(4)	0.039(2)	0.009(2)	0.004(2)	–0.004(2)
C(4)	4*e*	0.6193(3)	0.7768(5)	–0.1074(4)	0.053(3)	0.061(4)	0.039(2)	0.013(3)	–0.001(2)	0.007(3)
C(5)	4*e*	0.5924(3)	0.8677(5)	–0.0593(4)	0.047(3)	0.063(5)	0.056(3)	0.021(3)	0.001(2)	0.020(3)
C(6)	4*e*	0.6221(3)	0.9021(5)	0.0494(4)	0.066(3)	0.040(4)	0.056(3)	0.018(3)	0.006(2)	–0.005(3)
C(7)	4*e*	0.6847(3)	0.8415(4)	0.1132(4)	0.054(3)	0.042(4)	0.042(2)	0.006(2)	0.002(2)	0.000(2)
C(8)	4*e*	0.7528(3)	0.3654(4)	0.3656(3)	0.041(2)	0.032(3)	0.030(2)	0.000(2)	0.005(2)	0.001(2)
C(9)	4*e*	0.6926(3)	0.2689(4)	0.3665(3)	0.037(2)	0.037(4)	0.030(2)	0.001(2)	0.003(2)	0.002(2)
C(10)	4*e*	0.6067(3)	0.2775(5)	0.4023(4)	0.046(3)	0.045(4)	0.067(3)	0.001(2)	0.020(2)	–0.007(3)
C(11)	4*e*	0.5528(3)	0.1890(5)	0.4031(5)	0.042(3)	0.068(5)	0.084(4)	–0.012(3)	0.018(3)	–0.007(3)
C(12)	4*e*	0.5840(3)	0.0950(4)	0.3678(4)	0.056(3)	0.042(4)	0.045(3)	–0.014(3)	–0.001(2)	0.002(2)
C(13)	4*e*	0.6667(3)	0.0824(4)	0.3318(4)	0.059(3)	0.034(4)	0.053(3)	–0.002(2)	0.007(2)	0.001(2)
C(14)	4*e*	0.7207(3)	0.1709(4)	0.3319(4)	0.046(3)	0.042(4)	0.051(3)	0.002(2)	0.009(2)	0.004(2)
C(15)	4*e*	0.7028(3)	0.5263(4)	0.1518(4)	0.034(2)	0.036(4)	0.044(2)	0.001(2)	–0.002(2)	0.007(2)
C(16)	4*e*	0.7158(3)	0.4090(4)	0.1559(4)	0.040(2)	0.047(4)	0.035(2)	–0.008(2)	–0.007(2)	0.004(2)

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