Crystal structure of *tri*-aqua-(pyridine-4-carboxamide-*N*)copper(II)2,7-naphthalenedisulfonate trihydrate, $[Cu(H_2O)_3(C_6H_6N_2O)_2](C_{10}H_6O_6S_2)\cdot 3H_2O$, $C_{22}H_{30}CuN_4O_{14}S_2$

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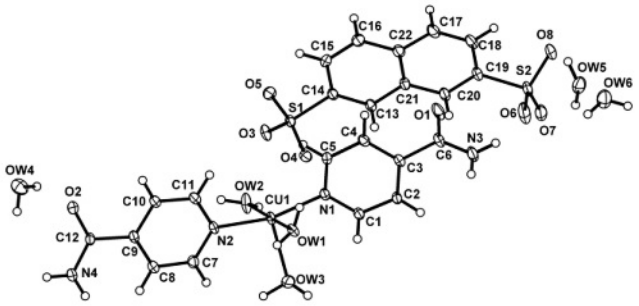

Abstract

$C_{22}H_{30}CuN_4O_{14}S_2$, monoclinic, *Cc* (no. 9), $a = 13.453(3)$ Å, $b = 15.082(3)$ Å, $c = 14.961(3)$ Å, $\beta = 99.41(3)°$, $V = 2994.7$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0444$, $wR_{ref}(F^2) = 0.1260$, $T = 298$ K.

Table 1. Data collection and handling.

Crystal:	blue blocks, size 0.20×0.40×0.50 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	9.42 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω scans
$2\theta_{max}$:	54.08°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	9381, 4772
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4453
$N(param)_{refined}$:	390
Programs:	SHELX [10]

Source of material

Isonicotinamide (INA, 0.048 g, 0.4 mmol) was added with constant stirring to an aqueous solution (20 ml) of $CuCl_2$ (0.036 g, 0.2 mmol). The solution was then treated with disodiumnaphthalene-2,7-disulfonate (0.66 g, 0.2mmol) (2,7-NDS). Blue crystals of the title complex were collected after a few days. (64% yield based on Cu.) Anal. Calcd for C 37.63%, H 4.31%, N 7.98%, Found: C 37.61%, H 4.27%, N 8.01%.

Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.93 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$. The O-bound H atoms were located in difference maps and refined as riding in their as-found relative positions with $U_{iso}(H) = 1.2U_{eq}(O)$.

Discussion

The properties of molecular materials in the crystalline state depend on the molecular arrangement via noncovalent interactions in the crystal structure. Thus, the strong and directional nature of hydrogen bonds is exploited in the organized self-assembly of molecules in the solid state [1-5]. The sulfonate group shows interesting functional properties owing to flexible coordination modes caused by weak interactions between the metal centers and the sulfonate groups [5]. Previous studies show that the SO_3 group can compete with water molecules and coordinate to metal ions in the presence of amino ligand [7]. On the other hand, the sulfonate group is a suitable hydrogen bond acceptor, and has been used in the crystal engineering to build extended framework. In our previous work, we obtained a few of supramolecular frameworks based on 1,5-NDS, and 2,6-ADS [8, 9]. However, 2,7-naphthalenedisulfonate (2,7-NDS) has been little explored. The asymmetric unit of the title compound consists of one Cu(II) ion, two INA molecules, one 2,7-NDS anion, three coordinated water molecules and three lattice water molecules. The metal center occupies a general position, and is placed in a square-based pyramidal environment defined by two nitrogen atoms from two trans-isonicotinamide ligands and two trans-coordinated water molecules in the basal plane, and the left aqua ligand occupying the apical position. The Cu–O distance are in the range of 1.977(3) to 2.242(4) Å, in which the $Cu–O_{apical}$ bond length is longer than that of $Cu–O_{basal}$. The Cu–N bond lengths are 2.009(3) and 2.013(3) Å, respectively. The angles subtended at the Cu center by *cis* pairs of ligating atoms cover the range from 85.98(14) to 96.32(19)°, and the coordination polyhedron of Cu^{2+} may be described as a distorted square-based pyramid. The 2,7-NDS anion does not participate in the coordination of the Cu atom. The distance between Cu and the closest O atom of the sulfonate group is 3.017 Å, which suggests a weak non-covalent interaction. The complex cations and 2,7-NDS anions align in a neat alternating mode. The copper cation are connected through N–H···O hydrogen bonds formed by amide groups and the coordinated water molecules, resulting in infinite chains. Adjacent chains are further linked by N–H···O hydrogen bonds between the amide groups to create two-dimensional cation sheets. The 2,7-NDS anions are located between the sheets, and interact with the framework via N–H···O and O–H···O hydrogen bonds formed by sulfonate groups and amide groups and coordinated water molecules, to generate a 3D network.

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(3C)	4*a*	0.6868	0.5071	0.3861	0.064
H(3D)	4*a*	0.6230	0.4259	0.3754	0.064
H(4C)	4*a*	–0.4380	0.1797	0.2871	0.052
H(4D)	4*a*	–0.3491	0.1654	0.2410	0.052
H(1A)	4*a*	0.2003	0.2751	0.4338	0.044
H(1B)	4*a*	0.1380	0.2076	0.3834	0.044

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Table 2. continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(2A)	4*a*	0.0838	0.4712	0.1851	0.070
H(2B)	4*a*	–0.0050	0.4555	0.2275	0.070
H(3A)	4*a*	0.1948	0.2246	0.1866	0.064
H(3B)	4*a*	0.0835	0.2472	0.1527	0.064
H(4A)	4*a*	–0.4890	0.1749	0.5225	0.080
H(4B)	4*a*	–0.4395	0.2681	0.4953	0.080
H(5A)	4*a*	0.9018	0.3903	0.8267	0.074
H(5B)	4*a*	0.9103	0.3340	0.7447	0.074
H(6A)	4*a*	0.9220	0.5272	0.4699	0.088
H(6B)	4*a*	1.0221	0.5405	0.4855	0.088
H(1)	4*a*	0.3308	0.2998	0.2962	0.047
H(2)	4*a*	0.4896	0.3617	0.3169	0.047

Table 2. continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(4)	4*a*	0.3665	0.5948	0.3639	0.044
H(5)	4*a*	0.2100	0.5265	0.3402	0.039
H(7)	4*a*	–0.0528	0.2495	0.1931	0.046
H(8)	4*a*	–0.2168	0.2155	0.2019	0.046
H(10)	4*a*	–0.1818	0.3317	0.4457	0.048
H(11)	4*a*	–0.0178	0.3620	0.4319	0.055
H(13)	4*a*	0.4032	0.3896	0.5804	0.041
H(15)	4*a*	0.2259	0.6063	0.5624	0.050
H(16)	4*a*	0.3644	0.6963	0.5775	0.054
H(17)	4*a*	0.5529	0.7134	0.5921	0.058
H(18)	4*a*	0.7093	0.6522	0.6097	0.059
H(20)	4*a*	0.5888	0.4075	0.6058	0.048

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*a*	0.12054(3)	0.34846(3)	0.30124(4)	0.0201(2)	0.0339(2)	0.0425(3)	–0.0043(2)	–0.0000(2)	0.0048(2)
S(1)	4*a*	0.19478(7)	0.42018(7)	0.55644(8)	0.0249(4)	0.0404(5)	0.0319(6)	–0.0031(4)	0.0011(4)	–0.0005(4)
S(2)	4*a*	0.78615(8)	0.47576(9)	0.6195(1)	0.0230(5)	0.0565(7)	0.0638(9)	–0.0067(4)	–0.0042(5)	–0.0048(6)
N(1)	4*a*	0.2565(2)	0.4069(2)	0.3165(3)	0.024(2)	0.030(2)	0.038(2)	–0.003(1)	0.000(1)	0.003(1)
N(2)	4*a*	–0.0207(2)	0.3106(2)	0.3112(3)	0.022(2)	0.034(2)	0.039(2)	–0.007(1)	–0.000(1)	0.005(2)
N(3)	4*a*	0.6282(3)	0.4827(3)	0.3756(4)	0.029(2)	0.049(2)	0.079(4)	–0.010(2)	–0.003(2)	–0.001(2)
N(4)	4*a*	–0.3766(3)	0.1914(3)	0.2821(3)	0.027(2)	0.052(2)	0.053(3)	–0.010(2)	0.009(2)	–0.011(2)
O(1)	4*a*	0.5480(3)	0.6139(2)	0.3592(3)	0.040(2)	0.038(2)	0.104(4)	–0.017(2)	–0.007(2)	0.007(2)
O(2)	4*a*	–0.3592(2)	0.2885(2)	0.3974(3)	0.031(2)	0.053(2)	0.069(3)	–0.009(1)	0.014(2)	–0.016(2)
O(3)	4*a*	0.1286(2)	0.4505(2)	0.4758(2)	0.027(2)	0.062(2)	0.043(2)	–0.005(1)	–0.008(1)	0.011(2)
O(4)	4*a*	0.2282(2)	0.3295(2)	0.5481(2)	0.038(2)	0.040(2)	0.040(2)	–0.003(1)	0.001(1)	–0.004(1)
O(5)	4*a*	0.1520(3)	0.4322(2)	0.6384(3)	0.044(2)	0.052(2)	0.044(2)	–0.004(1)	0.015(2)	–0.007(2)
O(6)	4*a*	0.7777(3)	0.3849(3)	0.6482(5)	0.035(2)	0.061(2)	0.151(6)	–0.002(2)	–0.007(3)	0.023(3)
O(7)	4*a*	0.8108(3)	0.4817(4)	0.5290(3)	0.034(2)	0.110(4)	0.062(3)	–0.003(2)	0.005(2)	–0.024(3)
O(8)	4*a*	0.8517(3)	0.5299(3)	0.6844(3)	0.028(2)	0.089(3)	0.074(3)	–0.005(2)	–0.010(2)	–0.021(2)
OW(1)	4*a*	0.1784(2)	0.2506(2)	0.3833(2)	0.033(2)	0.035(1)	0.039(2)	–0.009(1)	–0.005(1)	0.003(1)
OW(2)	4*a*	0.0570(2)	0.4480(3)	0.2270(3)	0.023(2)	0.063(2)	0.087(3)	0.001(1)	0.001(2)	0.039(2)
OW(3)	4*a*	0.1485(3)	0.2634(3)	0.1850(3)	0.046(2)	0.061(2)	0.050(2)	0.008(2)	–0.001(2)	–0.016(2)
OW(4)	4*a*	–0.4794(4)	0.2404(3)	0.5279(3)	0.073(3)	0.073(3)	0.052(3)	–0.015(2)	0.008(2)	0.001(2)
OW(5)	4*a*	0.9250(3)	0.3424(3)	0.8048(4)	0.047(2)	0.061(2)	0.078(3)	0.013(2)	0.012(2)	0.008(2)
OW(6)	4*a*	0.9639(4)	0.5702(3)	0.4710(4)	0.056(3)	0.065(3)	0.102(4)	0.001(2)	0.018(3)	0.010(3)
C(1)	4*a*	0.3380(3)	0.3599(3)	0.3098(4)	0.027(2)	0.034(2)	0.055(3)	–0.003(2)	0.000(2)	–0.007(2)
C(2)	4*a*	0.4340(3)	0.3967(3)	0.3224(4)	0.022(2)	0.035(2)	0.058(3)	–0.001(2)	0.001(2)	–0.007(2)
C(3)	4*a*	0.4459(3)	0.4856(3)	0.3431(3)	0.029(2)	0.034(2)	0.034(2)	–0.006(2)	–0.003(2)	0.005(2)
C(4)	4*a*	0.3612(3)	0.5347(3)	0.3500(3)	0.036(2)	0.029(2)	0.043(3)	–0.005(2)	–0.001(2)	0.000(2)
C(5)	4*a*	0.2671(3)	0.4930(3)	0.3359(3)	0.025(2)	0.034(2)	0.037(2)	–0.000(2)	0.004(2)	0.004(2)
C(6)	4*a*	0.5467(3)	0.5323(3)	0.3600(4)	0.029(2)	0.043(2)	0.047(3)	–0.011(2)	–0.004(2)	0.004(2)
C(7)	4*a*	–0.0795(3)	0.2662(3)	0.2442(3)	0.031(2)	0.048(2)	0.038(2)	–0.005(2)	0.008(2)	–0.002(2)
C(8)	4*a*	–0.1773(3)	0.2453(3)	0.2494(3)	0.031(2)	0.042(2)	0.038(3)	–0.005(2)	–0.001(2)	–0.003(2)
C(9)	4*a*	–0.2169(3)	0.2684(3)	0.3252(3)	0.024(2)	0.031(2)	0.041(3)	–0.003(1)	0.000(2)	0.004(2)
C(10)	4*a*	–0.1566(3)	0.3141(3)	0.3942(3)	0.030(2)	0.049(2)	0.041(3)	–0.007(2)	0.003(2)	–0.011(2)
C(11)	4*a*	–0.0589(4)	0.3328(4)	0.3850(4)	0.034(2)	0.056(3)	0.045(3)	–0.009(2)	0.001(2)	–0.017(2)
C(12)	4*a*	–0.3242(3)	0.2493(3)	0.3375(3)	0.022(2)	0.036(2)	0.043(3)	0.001(2)	0.004(2)	–0.001(2)
C(13)	4*a*	0.3966(3)	0.4510(3)	0.5800(3)	0.029(2)	0.035(2)	0.036(2)	–0.001(2)	–0.002(2)	0.004(2)
C(14)	4*a*	0.3034(3)	0.4886(3)	0.5697(3)	0.028(2)	0.039(2)	0.034(2)	–0.003(2)	0.001(2)	–0.002(2)
C(15)	4*a*	0.2902(4)	0.5819(3)	0.5690(4)	0.033(2)	0.044(2)	0.048(3)	0.007(2)	0.008(2)	–0.006(2)
C(16)	4*a*	0.3727(4)	0.6351(3)	0.5780(4)	0.042(3)	0.036(2)	0.056(3)	0.004(2)	0.003(2)	–0.003(2)
C(17)	4*a*	0.5596(4)	0.6520(3)	0.5950(4)	0.043(3)	0.038(2)	0.060(4)	–0.009(2)	–0.002(2)	0.000(2)
C(18)	4*a*	0.6529(4)	0.6159(3)	0.6055(4)	0.039(2)	0.047(2)	0.058(3)	–0.016(2)	–0.002(2)	–0.004(2)
C(19)	4*a*	0.6642(3)	0.5226(3)	0.6101(4)	0.026(2)	0.049(2)	0.044(3)	–0.005(2)	–0.004(2)	–0.002(2)
C(20)	4*a*	0.5808(3)	0.4688(3)	0.6027(4)	0.027(2)	0.039(2)	0.051(3)	–0.005(2)	–0.001(2)	0.001(2)
C(21)	4*a*	0.4833(3)	0.5057(3)	0.5903(3)	0.027(2)	0.041(2)	0.035(2)	–0.002(2)	–0.001(2)	0.000(2)
C(22)	4*a*	0.4719(3)	0.5989(3)	0.5881(4)	0.037(2)	0.040(2)	0.043(3)	–0.001(2)	–0.001(2)	–0.002(2)

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