Crystal structure of catena-((μ_2-4,4'-biphenyldisulfonato-*O*,*O'*)-diaqua-*bis*(isonicotinamide-*N*)-copper(II) tetrahydrate, $[Cu(H_2O)_2(C_6N_2H_6O)_2](C_{12}H_8S_2O_6)\cdot 4H_2O$, $C_{24}H_{32}CuN_4O_{14}S_2$

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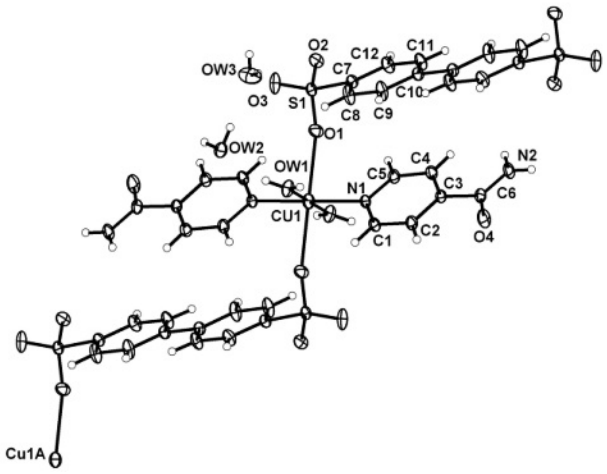

Abstract

$C_{24}H_{32}CuN_4O_{14}S_2$, triclinic, $P\bar{1}$ (no. 2), a = 6.796(5) Å, b = 10.414(2) Å, c = 11.55(1) Å, α = 75.33(5)°, β = 77.05(1)°, γ = 78.875(6)°, V = 762.8 Å^3, Z = 1, $R_{gt}(F)$ = 0.0651, $wR_{ref}(F^2)$ = 0.2086, T = 298 K.

Table 1. Data collection and handling.

Crystal:	blue blocks, size 0.30×0.32×0.36 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	9.27 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω
$2\theta_{max}$:	53.32°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8200, 3110
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2909
$N(param)_{refined}$:	206
Programs:	SHELX [7]

Source of material

Isonicotinamide (0.048 g, 0.4mmol) was added with constant stirring to an aqueous solution (20 ml) of $CuCl_2$ (0.036 g, 0.2mmol). The solution was then treated with disodium 4,4-biphenyldisulfonate (0.72 g, 0.2mmol). Blue crystals of the title complex were collected after 10 days (44% yield based on Cu input). Anal. Calcd for $C_{24}H_{32}CuN_4O_{14}S_2$: C 39.58%, H 4.43%, N 7.69%, Found: C 39.63%, H 4.48% N 7.58%.

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 construction of metal-organic supramolecular frameworks can be achieved via three kinds of interactions, i. e. covalent bonds, hydrogen bonds and aromatic interactions. Doubtless, hydrogen bond provides an ideal organizing force for supramolecular networks, because its moderately directional intermolecular interaction can effectively control short-range packing [1-2]. In construction of metal-containing hydrogen-bonded networks, the isonicotinamide (INA) is of special interest owing to the inherent coordination and hydrogen-bonding donor/acceptor functionalities. A few analogous compounds with INA ligands are observed in the literatures [1,3-6]. On the other hand, the sulfonate group is an excellent candidate for a hydrogen bond acceptor. The three O atoms from the sulfonate group can form up to six hydrogen bonds leading to extended networks [2]. The structure of the title compound is a unique three-dimensional supramolecular network in which the asymmetric unit contains one Cu(II) centre, one INA molecule, one coordinated water molecule, two lattice water molecules, and a half of a 4,4-biphenyldisulfonate (BPDS) anion. The Cu centre occupies an inversion centre, and is coordinated with two nitrogen atoms from two symmetry related INA molecules (Cu–N = 2.017(3) Å) and two aqua ligands with Cu–O = 1.976(3) Å. The distance between Cu and the closest oxygen atom of the sulfonate group is 2.4706(2) Å, which suggests a weak covalent interaction. From the above description, the coordination geometry of the Cu centre can be described as a Jahn-Teller-distorted octahedron with two sulfonate oxygen atoms occupying the apical position. The BPDS anion lies on crystallographic inversion centers, and is bidentate. The sulfonate groups of BPDS adopt an O-monodentate mode coordinated to the metal centers. The two isonicotinamide molecules are coordinated through the pyridine nitrogen atom with the amide groups pointing in opposite directions. The plane through the amide group and pyridine ring is coplanar. The interconnection of the Cu ions through bridging BPDS anions resulted in the formation of chains. The Cu–Cu separation within chains is 13.45 Å. The shortest through space inter-chain distance between Cu ions is 10.41 Å. Adjacent chains are linked by N–H···O hydrogen bonds between the amide groups and sulfonate groups, leading to two dimensional grid networks in the *bc*-plane.

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1A)	2*i*	0.3201	0.4900	–0.1591	0.058
H(1B)	2*i*	0.4252	0.3797	–0.1467	0.058
H(2C)	2*i*	0.6546	0.2006	–0.2221	0.060
H(2D)	2*i*	0.5655	0.2979	–0.3210	0.060
H(3A)	2*i*	0.8005	0.4144	–0.4195	0.115
H(3B)	2*i*	0.7408	0.4042	–0.5360	0.115
H(2A)	2*i*	0.0673	1.2580	–0.2591	0.063
H(2B)	2*i*	0.2627	1.1741	–0.2327	0.063
H(1)	2*i*	0.0829	0.6380	–0.0158	0.047
H(2)	2*i*	–0.0858	0.8459	–0.0873	0.051
H(4)	2*i*	0.4445	0.9917	–0.1662	0.052
H(5)	2*i*	0.5971	0.7807	–0.0893	0.050
H(8)	2*i*	0.5728	0.6180	–0.3635	0.069
H(9)	2*i*	0.3853	0.8052	–0.4640	0.067
H(11)	2*i*	0.7776	1.0347	–0.4436	0.061
H(12)	2*i*	0.9701	0.8474	–0.3466	0.060

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)	1*e*	½	½	0	0.0513(5)	0.0361(4)	0.0521(5)	0.0025(3)	–0.0218(3)	–0.0059(3)
S(1)	2*i*	0.9256(1)	0.57119(8)	–0.26089(7)	0.0362(5)	0.0271(5)	0.0402(5)	0.0008(3)	–0.0164(3)	0.0000(3)
O(1)	2*i*	0.8209(4)	0.5611(3)	–0.1351(2)	0.046(2)	0.050(2)	0.045(2)	0.000(1)	–0.008(1)	0.008(1)
O(2)	2*i*	1.1325(4)	0.5993(3)	–0.2766(3)	0.036(1)	0.048(2)	0.052(2)	–0.002(1)	–0.018(1)	0.003(1)
O(3)	2*i*	0.9160(6)	0.4581(3)	–0.3094(3)	0.085(2)	0.030(1)	0.089(2)	0.012(1)	–0.054(2)	–0.017(1)
O(4)	2*i*	–0.1454(5)	1.0785(3)	–0.1791(4)	0.044(2)	0.040(2)	0.109(3)	0.004(1)	–0.031(2)	0.002(2)
OW(1)	2*i*	0.3891(4)	0.4464(3)	–0.1220(3)	0.055(2)	0.042(1)	0.056(2)	0.012(1)	–0.032(1)	–0.016(1)
OW(2)	2*i*	0.5341(4)	0.2521(3)	–0.2441(3)	0.045(2)	0.044(2)	0.059(2)	0.005(1)	–0.015(1)	–0.012(1)
OW(3)	2*i*	0.7046(8)	0.3924(5)	–0.4630(3)	0.120(4)	0.134(4)	0.057(2)	–0.072(3)	–0.002(2)	–0.032(2)
N(1)	2*i*	0.3562(4)	0.6886(3)	–0.0478(3)	0.039(1)	0.026(1)	0.038(1)	0.000(1)	–0.014(1)	–0.002(1)
N(2)	2*i*	0.1339(5)	1.1816(3)	–0.2309(4)	0.049(2)	0.028(2)	0.072(2)	0.001(1)	–0.019(2)	0.005(1)
C(1)	2*i*	0.1562(5)	0.7099(3)	–0.0467(3)	0.040(2)	0.031(2)	0.047(2)	–0.004(1)	–0.016(1)	0.001(1)
C(2)	2*i*	0.0541(6)	0.8346(4)	–0.0899(4)	0.036(2)	0.033(2)	0.057(2)	–0.001(1)	–0.015(2)	–0.005(2)
C(3)	2*i*	0.1601(5)	0.9433(3)	–0.1371(3)	0.037(2)	0.029(2)	0.043(2)	0.002(1)	–0.013(1)	–0.005(1)
C(4)	2*i*	0.3678(6)	0.9214(4)	–0.1363(4)	0.039(2)	0.033(2)	0.055(2)	–0.003(1)	–0.010(2)	–0.003(2)
C(5)	2*i*	0.4583(5)	0.7943(4)	–0.0906(4)	0.035(2)	0.032(2)	0.057(2)	–0.001(1)	–0.012(2)	–0.006(2)
C(6)	2*i*	0.0383(6)	1.0758(4)	–0.1849(4)	0.048(2)	0.031(2)	0.051(2)	0.005(1)	–0.015(2)	–0.005(1)
C(7)	2*i*	0.7921(5)	0.7136(3)	–0.3462(3)	0.038(2)	0.032(2)	0.038(2)	–0.003(1)	–0.015(1)	–0.001(1)
C(8)	2*i*	0.6160(7)	0.7014(4)	–0.3806(5)	0.064(3)	0.031(2)	0.088(3)	–0.008(2)	–0.048(2)	0.000(2)
C(9)	2*i*	0.5035(7)	0.8146(4)	–0.4411(5)	0.058(2)	0.031(2)	0.088(3)	–0.005(2)	–0.050(2)	–0.001(2)
C(10)	2*i*	0.5611(5)	0.9399(3)	–0.4681(3)	0.041(2)	0.033(2)	0.036(2)	–0.001(1)	–0.015(1)	–0.002(1)
C(11)	2*i*	0.7371(6)	0.9509(4)	–0.4294(4)	0.044(2)	0.032(2)	0.077(3)	–0.008(2)	–0.030(2)	0.009(2)
C(12)	2*i*	0.8522(6)	0.8385(4)	–0.3702(4)	0.042(2)	0.039(2)	0.068(3)	–0.009(2)	–0.027(2)	0.007(2)

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References

1. Beatty, A.M.: Open-framework coordination complexes from hydrogen bonded networks: toward host/guest complexes. Coord. Chem. Rev. **246** (2003) 131-143.
2. Holman, K, T.; Pivovar, A. M.; Swift, J. A; Ward, M. D.: Metric Enggineering of soft molecular host frameworks. Acc. Chem. Res. **34** (2001) 107-118.
3. Aakeröy, C. B.; Beatty,A, M.: Crystal Engineering of hydrogen bonded assemblies- A progress report. Aust. J. Chem. **54** (2001) 409-421.
4. Lian, Z. X.; Zhao, N.; Liu, P.: Crystal structure of trans-tetraaquabis(nicotinamide)Zinc(II) 4,4'-biphenyldisulfonate, $[Zn(H_2O)_4(C_6H_6N_2O)_2][C_{12}H_8S_2O_6]$. Z. Kristallogr. NCS. **225** (2010) 379-380.
5. Beatty, A.M.: Hydrogen bonded networks of coordination complexes. CrystEngComm. **3** (2001) 1-13.
6. Lian, Z. X.; Zhao, N.; Liu,P.: Crystal structure of pentaaqua(pyridine-3-carboxamide-N) cobalt(II) 1,5-naphthalenedisulfonate monohydrate, $[Co(H_2O)_5(C_6H_6N_2O)](C_{10}H_6S_2O_6)\cdot H_2O$. Z. Kristallogr. NCS. **225** (2010) 371-373.
7. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.