Crystal structure of (4-carboxy-2-sulfonato-κ*O*-benzoato-κ*O*)-bis(2,2'-bipyrindine-κ^2*N*,*N'*)zinc(II) dihydrate, $C_{28}H_{24}N_4O_9SZn$

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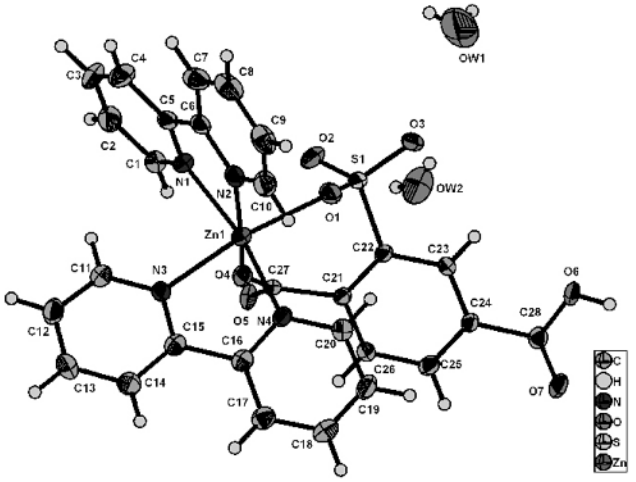
Received July 04, 2013, accepted September 24, 2013, available online October 02, 2013, CCDC no. 1267/4035



Abstract

$C_{28}H_{24}N_4O_9SZn$, triclinic, $P\bar{1}$ (No. 2), a = 8.972(1) Å, b = 9.735 (1) Å, c = 16.162(2) Å, α = 100.767(2)°, β = 98.720(2)°, γ = 91 .693(2)°, V = 1368.4 Å^3, Z = 2, $R(F)$ = 0.0481, $wR_{ref}(F^2)$ = 0.12 32, T = 173 K.

Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.29×0.30×0.34 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	10.38 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω
$2\theta_{max}$:	54.26°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11721, 5926
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4157
$N(param)_{refined}$:	389
Programs:	SAINT [12], DIAMOND [13], SHELX [14]

Source of material

A mixture of *STP* (potassium 2,5-dicarboxybenzenesulfonate, 0.018g, 0.1 mmol), $Zn(CH_3COO)_2$ (0.020 g, 0.1 mmol), 2, 2'-bipyridine (*bipy*, 0.016 g, 0.1 mmol), NaOH (0.2 M, 1.5 mL) and H_2O (10 mL) was stirred for about 30 min. The resulting solution was sealed in a Teflon-lined stainless autoclave and heated to 393 K for 3 days. The bottle was cooled to ambient temperature spontaneously. Colourless single crystals (about 56%, based on Zn input) were recovered by vacuum filtration, and drying in air. **Elemental analysis** calcd for (1): C 51.11, H 3.68, N 8.51%; found: C 51.13, H 3.66, N 8.53%.

Experimental details

The C–bound H atoms were geometrically placed (C–H = 0.95 Å) and refined as riding with U_{iso}(H) = 1.2U_{eq}(C). The O-bound H atoms were geometrically placed (O–H = 0.84 Å) and refined as riding with U_{iso}(H) = 1.5U_{eq}(O). The hydrogen atoms of water molecules were located from the difference Fourier map at the final state of refinement, and refined as riding atoms with U_{iso}(H) = 1.2U_{eq}(O).

Discussion

During the last decade, intense activity has been focused on the formation of metal organic frameworks, owing to their potential applications in the fields of material chemistry [1]. Some carboxylate ligands, especially benzene multi-carboxylates, such as 1,3,5-benzenetricaboxylate, 1,2,4-benzenetricaboxylate and 1,2,4,5-benzenetetracarboxylate, have been widely used to prepare such hybrid complexes [2-5]. The ligand, 2-sulfoterephthalic acid (*STP*), containing two different kinds of coordination groups, has received considerable attention. Some compounds based on *STP* ligands have been reported [6-9]. In these compounds, the *STP* ligand can adopt diverse coordination mode according to the different chemical environments. We consider that the simultaneous use of 2,2'-bipyridine (*bipy*) and *STP* ligand will contribute to the formation of various architectures and help chemists understand the process of self-assembly. In this contribution, our research efforts afforded a novel coordination compound. The asymmetric unit is comprised of one zinc(II) ion, two *bipy* molecules, one STP^{2-} ion, and two lattice water molecules. The metal centre is in an octahedral coordination sphere, which is defined by four N atoms from two *bipy* ligands, one carboxylic oxygen atoms and one sulfonate oxygen atom from *STP* ligand. N1, N2, N4, and O4 atoms are located at the equatorial positions, and O2 and N3 atoms occupy the axial positions. The bond lengths of Zn–O and Zn–N are in the range of 2.037(2)-2.154(2) Å and 2.131(3)-2.185(3) Å, respectively. These distances fall in the normal range found in other zinc complexes [10]. The *STP* ligand is bidentate coordinated via its one carboxylate group and one oxygen atom of the sulfonate group. The whole *STP* adopts μ_2-η^1:η^1:η^0 mode coordinated to one zinc(II) ions, which is similar to those found in $[Cu_2(OH)(SIP)(2,2'\text{-}bipy)(H_2O)]_n$ [11]. While in a comparable structure [9], the *STP* ligands adopt a μ_2 mode and bridge a pair of Cu(II) ions to result in a 14-membered ring. In the title compound, the zinc(II) complexes are linked by hydrogen bonds formed between carboxylate oxygen atoms and protonated carboxyl groups, to result in an infinite chain structure, along *b* axis. The lattice water molecules are located between the chains, and form cyclic tetramer via hydrogen bonds.

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(6)	2*i*	0.3203	1.1749	0.0852	0.042
H(1)	2*i*	0.3809	0.2572	0.2543	0.030
H(2)	2*i*	0.2976	0.0981	0.3309	0.038
H(3)	2*i*	0.4097	0.1118	0.4724	0.045
H(4)	2*i*	0.5979	0.2856	0.5354	0.042
H(7)	2*i*	0.7435	0.4746	0.5892	0.039
H(8)	2*i*	0.9338	0.6532	0.6326	0.043
H(9)	2*i*	1.0214	0.7638	0.5314	0.040
H(10)	2*i*	0.9154	0.6913	0.3883	0.035
H(11)	2*i*	0.7258	0.1708	0.2939	0.028
H(12)	2*i*	0.9039	0.0129	0.2599	0.036
H(13)	2*i*	1.0878	0.0716	0.1828	0.037
H(14)	2*i*	1.0906	0.2937	0.1446	0.032
H(17)	2*i*	1.0610	0.4837	0.0995	0.030
H(18)	2*i*	1.0230	0.6991	0.0590	0.034
H(19)	2*i*	0.8355	0.8378	0.1105	0.032
H(20)	2*i*	0.6997	0.7600	0.2064	0.030
H(23)	2*i*	0.3521	0.9189	0.1900	0.024
H(25)	2*i*	0.3427	0.7493	–0.0595	0.024
H(26)	2*i*	0.3545	0.5270	–0.0257	0.022
H(1A)	2*i*	0.1625	0.8857	0.4552	0.159
H(1B)	2*i*	0.0183	0.9359	0.4129	0.159
H(2A)	2*i*	0.7138	0.8885	0.3759	0.173
H(2B)	2*i*	0.8269	1.0154	0.4482	0.173

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}
Zn(1)	2*i*	0.64738(5)	0.48662(4)	0.27681(2)	0.0244(2)	0.0215(2)	0.0165(2)	0.0043(2)	0.0049(2)	0.0067(2)
S(1)	2*i*	0.3730(1)	0.6938(1)	0.27531(5)	0.0399(6)	0.0245(5)	0.0181(4)	0.0159(4)	0.0145(4)	0.0107(4)
O(1)	2*i*	0.5331(3)	0.6768(3)	0.3067(2)	0.042(2)	0.030(2)	0.018(1)	0.015(1)	0.007(1)	0.007(1)
O(2)	2*i*	0.2774(3)	0.5737(3)	0.2763(2)	0.043(2)	0.037(2)	0.032(2)	0.010(1)	0.017(1)	0.021(1)
O(3)	2*i*	0.3265(3)	0.8253(3)	0.3186(2)	0.058(2)	0.034(2)	0.023(1)	0.026(1)	0.021(1)	0.012(1)
O(4)	2*i*	0.4937(3)	0.4153(2)	0.1697(1)	0.027(1)	0.021(1)	0.018(1)	0.007(1)	0.000(1)	0.007(1)
O(5)	2*i*	0.2891(3)	0.3498(2)	0.0733(2)	0.026(1)	0.015(1)	0.027(1)	0.001(1)	0.001(1)	0.008(1)
O(6)	2*i*	0.3289(3)	1.0987(2)	0.1023(2)	0.049(2)	0.014(1)	0.025(1)	0.006(1)	0.010(1)	0.009(1)
O(7)	2*i*	0.3183(3)	1.0104(3)	–0.0363(2)	0.057(2)	0.022(1)	0.021(1)	0.010(1)	0.006(1)	0.012(1)
N(1)	2*i*	0.5358(3)	0.3615(3)	0.3466(2)	0.025(2)	0.022(2)	0.019(1)	0.003(1)	0.006(1)	0.008(1)
N(2)	2*i*	0.7700(3)	0.5470(3)	0.4042(2)	0.027(2)	0.022(2)	0.021(2)	0.010(1)	0.004(1)	0.004(1)
N(3)	2*i*	0.7998(3)	0.3222(3)	0.2421(2)	0.023(2)	0.016(2)	0.016(1)	0.002(1)	0.003(1)	0.002(1)
N(4)	2*i*	0.7934(3)	0.5801(3)	0.2075(2)	0.026(2)	0.018(2)	0.017(1)	0.001(1)	0.003(1)	0.005(1)
C(1)	2*i*	0.4260(4)	0.2625(4)	0.3120(2)	0.029(2)	0.023(2)	0.025(2)	0.006(2)	0.007(2)	0.007(2)
C(2)	2*i*	0.3756(5)	0.1677(4)	0.3570(3)	0.035(2)	0.025(2)	0.038(2)	0.003(2)	0.011(2)	0.007(2)
C(3)	2*i*	0.4414(5)	0.1766(4)	0.4403(3)	0.050(3)	0.030(2)	0.041(2)	0.006(2)	0.018(2)	0.022(2)
C(4)	2*i*	0.5528(5)	0.2785(4)	0.4776(3)	0.044(2)	0.043(3)	0.025(2)	0.011(2)	0.009(2)	0.017(2)
C(5)	2*i*	0.5987(4)	0.3716(4)	0.4290(2)	0.028(2)	0.026(2)	0.021(2)	0.014(2)	0.010(2)	0.008(2)
C(6)	2*i*	0.7195(4)	0.4831(4)	0.4629(2)	0.027(2)	0.025(2)	0.018(2)	0.013(2)	0.005(2)	0.005(2)
C(7)	2*i*	0.7795(5)	0.5207(4)	0.5485(2)	0.036(2)	0.044(3)	0.020(2)	0.018(2)	0.005(2)	0.008(2)
C(8)	2*i*	0.8919(5)	0.6257(4)	0.5739(2)	0.038(2)	0.042(3)	0.021(2)	0.015(2)	–0.006(2)	–0.004(2)
C(9)	2*i*	0.9438(5)	0.6909(4)	0.5148(3)	0.035(2)	0.028(2)	0.030(2)	0.006(2)	–0.005(2)	–0.004(2)
C(10)	2*i*	0.8795(4)	0.6474(4)	0.4299(2)	0.034(2)	0.024(2)	0.029(2)	0.003(2)	0.003(2)	0.004(2)
C(11)	2*i*	0.8013(4)	0.1961(4)	0.2633(2)	0.026(2)	0.022(2)	0.024(2)	0.001(2)	0.006(2)	0.007(2)
C(12)	2*i*	0.9063(5)	0.1013(4)	0.2431(2)	0.041(2)	0.019(2)	0.030(2)	0.002(2)	0.005(2)	0.007(2)
C(13)	2*i*	1.0146(5)	0.1360(4)	0.1982(2)	0.035(2)	0.024(2)	0.034(2)	0.009(2)	0.009(2)	0.003(2)
C(14)	2*i*	1.0161(4)	0.2670(4)	0.1754(2)	0.025(2)	0.028(2)	0.030(2)	0.005(2)	0.009(2)	0.007(2)
C(15)	2*i*	0.9063(4)	0.3582(4)	0.1988(2)	0.021(2)	0.022(2)	0.018(2)	–0.002(1)	–0.000(1)	0.005(1)
C(16)	2*i*	0.8968(4)	0.4983(4)	0.1751(2)	0.019(2)	0.023(2)	0.017(2)	0.000(1)	–0.002(1)	0.005(1)
C(17)	2*i*	0.9858(4)	0.5413(4)	0.1203(2)	0.023(2)	0.030(2)	0.025(2)	0.004(2)	0.004(2)	0.010(2)
C(18)	2*i*	0.9634(4)	0.6683(4)	0.0966(2)	0.030(2)	0.032(2)	0.027(2)	–0.002(2)	0.007(2)	0.012(2)
C(19)	2*i*	0.8545(4)	0.7507(4)	0.1273(2)	0.037(2)	0.022(2)	0.024(2)	0.001(2)	0.002(2)	0.010(2)
C(20)	2*i*	0.7733(4)	0.7026(4)	0.1837(2)	0.029(2)	0.022(2)	0.024(2)	0.004(2)	0.006(2)	0.006(2)
C(21)	2*i*	0.3678(4)	0.5896(3)	0.1025(2)	0.016(2)	0.017(2)	0.017(2)	0.004(1)	0.005(1)	0.007(1)
C(22)	2*i*	0.3659(4)	0.7074(4)	0.1664(2)	0.020(2)	0.020(2)	0.018(2)	0.007(1)	0.006(1)	0.009(1)
C(23)	2*i*	0.3539(4)	0.8393(4)	0.1461(2)	0.027(2)	0.016(2)	0.018(2)	0.007(1)	0.008(1)	0.004(1)
C(24)	2*i*	0.3446(4)	0.8558(3)	0.0616(2)	0.019(2)	0.018(2)	0.020(2)	0.005(1)	0.006(1)	0.008(1)
C(25)	2*i*	0.3472(4)	0.7390(4)	–0.0019(2)	0.022(2)	0.023(2)	0.017(2)	0.002(1)	0.003(1)	0.007(1)
C(26)	2*i*	0.3562(4)	0.6069(3)	0.0185(2)	0.021(2)	0.016(2)	0.018(2)	0.002(1)	0.004(1)	0.003(1)
C(27)	2*i*	0.3840(4)	0.4405(4)	0.1182(2)	0.023(2)	0.018(2)	0.018(2)	0.005(1)	0.012(1)	0.006(1)
C(28)	2*i*	0.3300(4)	0.9963(4)	0.0369(2)	0.018(2)	0.021(2)	0.023(2)	0.005(1)	0.003(1)	0.008(2)
OW(1)	2*i*	0.1134(7)	0.9291(5)	0.4191(4)	0.163(5)	0.070(3)	0.215(6)	0.038(3)	0.161(5)	0.049(4)
OW(2)	2*i*	0.7746(8)	0.9586(5)	0.3988(4)	0.255(8)	0.086(4)	0.151(5)	0.087(4)	0.139(5)	0.080(4)

Acknowledgments. The work was financially supported by the Natural Science Foundation of Henan Insititute of Science and Technology (Grant Nos.7031).

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