Crystal structure of diaqua-bis(1,10-phenanthroline)-zinc(II) bis(thiophene-3-carboxy-4-carboxylate) heptahydrate, $[Zn(H_2O)_2(C_{12}H_8N_2)_2][(C_6H_3O_4S)_2]\cdot 7H_2O$, $C_{36}H_{40}N_4O_{17}S_2Zn$

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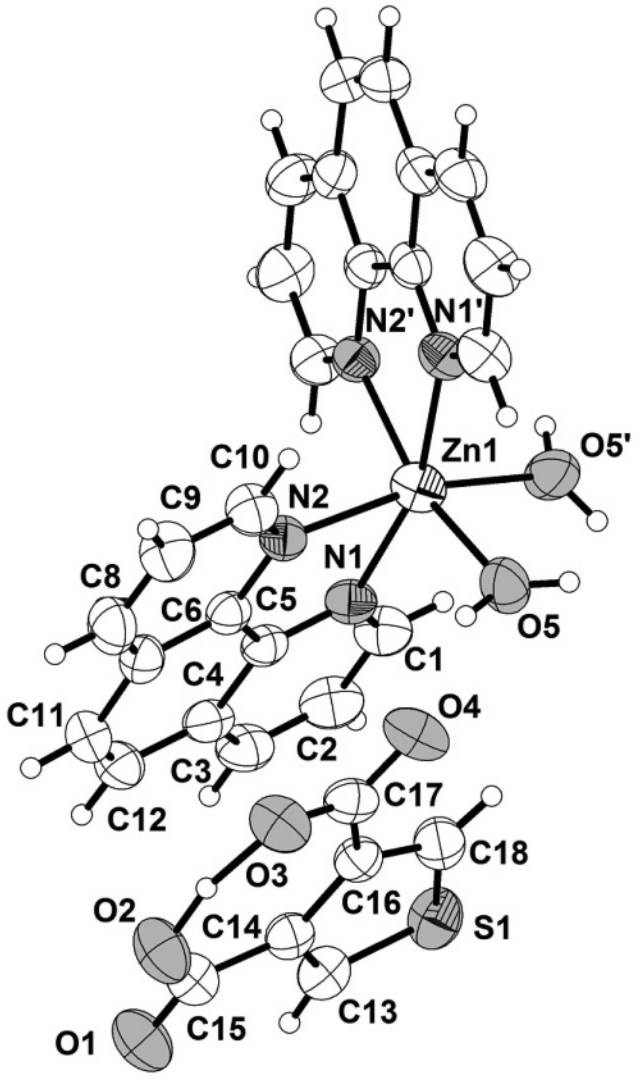

Abstract

$C_{36}H_{40}N_4O_{17}S_2Zn$, monoclinic, *C*2/*c* (no. 15), a = 16.690(3) Å, b = 22.905(2) Å, c = 12.940(2) Å, β = 124.849(6)°, V = 4059.6 Å^3, Z = 4, $R_{gt}(F)$ = 0.0473, $wR_{ref}(F^2)$ = 0.1327, T = 293 K.

Source of material

A mixture of $Zn(CH_3COO)_2\cdot 2H_2O$ (0.25 mmol, 0.055 g), 1,10-phenanthroline (*phen*, 0.25 mmol, 0.050 g), thiophene-3,4-dicarboxylic acid (0.25 mmol, 0.043 g) and H_2O (7 ml) were filled in a 23 ml Teflon-lined autoclave under autogenous pressure at 413 K for five days. After cooling to room temperature, yellow crystals were collected by filtration and washed with distilled water in 68% yield (based on Zn).

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Table 1. Data collection and handling.

Crystal:	yellow blocks, size 0.47×0.32×0.26 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	7.88 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω
$2\theta_{max}$:	50.0°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	13103, 3575
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3273
$N(param)_{refined}$:	276
Programs:	SHELX [7], DIAMOND [8]

Discussion

The design and synthesis of new materials based on organic ligands have received much attention in the field of crystal engineering and supramolecular chemistry due to their potential applications in the fields of luminescence, gas storage, adsorption, nonlinear optics, magnetism, catalysis, ion exchange, and so on [1-2]. On the other hand, studying of hydrogen-bonded water aggregations in materials are important as they provide clues to better understand how aggregations stabilize the overall structure. At present, a number of different water clusters $(H_2O)_n$ have been structurally characterized in a variety of organic and metal-organic frameworks [3-6]. Hydrogen bonds are well suited for the design of polymeric arrangements because of their important directional interactions, and because they can interlink 1-D, or 2-D structures into higher-dimensionality systems. Herein, we report hydrothermal synthesis and crystal structure of a new hybrid material. In the title crystal structure, the asymmetric unit contains one half of a Zn(II) ion, one *phen* ligand, one coordinated water molecule, one uncoordinated mono-anionic thiophene-3-carboxy-4-carboxylate (*tdc*) ligand and four lattice water molecules. Each Zn(II) ion exhibits a distorted octahedral $[N_4O_2]$ coordination geometry with four nitrogen atoms from two 1,10-*phen* ligands, two oxygen atoms from two coordinated water molecules. One oxygen atom and three nitrogen atoms occupy four equatorial coordination sites, and the two remaining axial positions are taken by another oxygen atom and nitrogen atom. The Zn–O bond lengths are 2.074(2) Å, and the bond lengths of Zn–N are 2.167(3) and 2.184(2) Å, respectively. The mono-deprotonated *tdc* anions are, not only compensating for the charge of the $[Zn(phen)_2(H_2O)_2]^{2+}$ complex but also providing potential hydrogen-bond acceptors. The lattice water molecules O6, O7, O8 and O9, serves not only as hydrogen bonding donor but also as hydrogen bonding acceptor, while the coordinated water molecule act only as hydrogen bonding donors. Extensive intermolecular O–H···O hydrogen bonding interactions between

water molecules, cations and anions connect them into an intricate 3D supramolecular network. A striking feature of the title complex is identification of a discrete acyclic water enneamer that was present in the crystal structure. For the enneamer, values of O···O distances (range 2.677(4)-2.880(5) Å) and O···H···O angles (range 130.57°-179.42°) suggest strong H-bonding interactions among the water molecules.

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

Atom	Site	x	y	z	U_{iso}
H(5A)	8*f*	0.0792	0.0477	0.1630	0.108
H(5B)	8*f*	0.0185	0.0003	0.1603	0.108
H(6)	8*f*	0.0086	0.2805	0.7225	0.262
H(7A)	8*f*	0.7327	0.1284	0.4885	0.192
H(7B)	8*f*	0.6872	0.1442	0.5426	0.192
H(8A)	8*f*	0.8591	0.1554	0.7150	0.180
H(8B)	8*f*	0.9230	0.1977	0.7949	0.180
H(9A)	8*f*	0.8984	0.9355	0.0209	0.157
H(9B)	8*f*	0.9895	0.9046	0.1303	0.157
H(1)	8*f*	0.1217	0.0663	0.5457	0.072
H(2)	8*f*	0.2678	0.0889	0.7290	0.081
H(3)	8*f*	0.3758	0.1500	0.7268	0.074
H(8)	8*f*	0.2422	0.2565	0.1738	0.080
H(9)	8*f*	0.0898	0.2322	0.0027	0.083
H(10)	8*f*	–0.0090	0.1732	0.0270	0.069
H(11)	8*f*	0.3711	0.2472	0.4102	0.077
H(12)	8*f*	0.4158	0.2121	0.5983	0.072
H(13)	8*f*	0.5249	0.0592	0.6467	0.071
H(18)	8*f*	0.2417	–0.0021	0.3608	0.073
H(2A)	8*f*	0.395(4)	0.128(2)	0.262(5)	0.12(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}
Zn(1)	4*e*	0	0.10070(2)	$\frac{1}{4}$	0.0423(3)	0.0565(3)	0.0465(3)	0	0.0239(2)	0
S(1)	8*f*	0.38381(8)	0.00372(4)	0.56605(9)	0.0915(7)	0.0641(6)	0.0688(6)	0.0016(4)	0.0540(5)	0.0078(4)
N(1)	8*f*	0.1368(2)	0.1138(1)	0.4314(2)	0.047(1)	0.060(2)	0.045(1)	0.005(1)	0.026(1)	0.004(1)
N(2)	8*f*	0.0795(2)	0.1612(1)	0.2088(2)	0.045(1)	0.051(1)	0.042(1)	0.000(1)	0.021(1)	0.001(1)
O(1)	8*f*	0.5740(2)	0.1323(1)	0.5500(2)	0.066(2)	0.100(2)	0.060(2)	–0.023(1)	0.030(1)	–0.016(1)
O(2)	8*f*	0.4701(2)	0.1390(1)	0.3463(2)	0.077(2)	0.094(2)	0.060(2)	–0.024(1)	0.038(1)	0.002(1)
O(3)	8*f*	0.3095(2)	0.1019(1)	0.1820(2)	0.064(1)	0.092(2)	0.048(1)	–0.005(1)	0.029(1)	0.005(1)
O(4)	8*f*	0.1902(2)	0.0489(1)	0.1573(2)	0.051(1)	0.109(2)	0.059(1)	–0.008(1)	0.029(1)	–0.011(1)
O(5)	8*f*	0.0448(2)	0.0337(1)	0.1863(3)	0.071(2)	0.064(2)	0.103(2)	–0.013(1)	0.063(2)	–0.018(1)
O(6)	4*e*	0	0.2491(3)	$\frac{1}{4}$	0.268(9)	0.090(4)	0.201(7)	0	0.154(7)	0
O(7)	8*f*	0.7435(2)	0.1410(2)	0.5573(3)	0.079(2)	0.225(4)	0.083(2)	–0.041(2)	0.048(2)	–0.063(2)
O(8)	8*f*	0.9121(2)	0.1612(2)	0.7867(3)	0.097(2)	0.140(3)	0.095(2)	–0.008(2)	0.038(2)	0.005(2)
O(9)	8*f*	0.9485(2)	0.9325(1)	0.0962(3)	0.116(2)	0.088(2)	0.067(2)	–0.014(2)	0.027(2)	–0.011(2)
C(1)	8*f*	0.1640(2)	0.0916(2)	0.5429(3)	0.059(2)	0.074(2)	0.051(2)	0.008(2)	0.032(2)	0.010(2)
C(2)	8*f*	0.2521(3)	0.1048(2)	0.6533(3)	0.067(2)	0.086(3)	0.044(2)	0.015(2)	0.028(2)	0.010(2)
C(3)	8*f*	0.3163(2)	0.1411(2)	0.6522(3)	0.051(2)	0.072(2)	0.045(2)	0.009(2)	0.017(1)	–0.003(1)
C(4)	8*f*	0.2921(2)	0.1648(1)	0.5386(3)	0.045(2)	0.054(2)	0.044(2)	0.009(1)	0.019(1)	–0.006(1)
C(5)	8*f*	0.1998(2)	0.1502(1)	0.4292(3)	0.044(1)	0.045(2)	0.045(2)	0.006(1)	0.025(1)	–0.002(1)
C(6)	8*f*	0.1701(2)	0.1750(1)	0.3103(2)	0.045(1)	0.042(2)	0.043(1)	0.004(1)	0.023(1)	–0.004(1)
C(7)	8*f*	0.2341(2)	0.2108(1)	0.3025(3)	0.055(2)	0.044(2)	0.055(2)	–0.001(1)	0.030(1)	–0.003(1)
C(8)	8*f*	0.2020(3)	0.2325(2)	0.1834(3)	0.070(2)	0.060(2)	0.072(2)	–0.009(2)	0.042(2)	0.006(2)
C(9)	8*f*	0.1117(3)	0.2181(2)	0.0821(3)	0.079(2)	0.071(2)	0.052(2)	–0.003(2)	0.035(2)	0.012(2)
C(10)	8*f*	0.0526(2)	0.1827(1)	0.0975(3)	0.057(2)	0.064(2)	0.044(2)	–0.001(1)	0.024(1)	0.003(1)
C(11)	8*f*	0.3280(2)	0.2236(1)	0.4150(3)	0.054(2)	0.054(2)	0.078(2)	–0.009(1)	0.034(2)	–0.005(2)
C(12)	8*f*	0.3549(2)	0.2023(2)	0.5268(3)	0.046(2)	0.059(2)	0.058(2)	–0.004(1)	0.020(1)	–0.009(2)
C(13)	8*f*	0.4644(2)	0.0509(1)	0.5730(3)	0.068(2)	0.060(2)	0.051(2)	0.004(2)	0.034(2)	–0.001(1)
C(14)	8*f*	0.4315(2)	0.0758(1)	0.4596(3)	0.054(2)	0.050(2)	0.048(2)	0.004(1)	0.032(1)	–0.004(1)
C(15)	8*f*	0.4967(2)	0.1179(2)	0.4544(3)	0.058(2)	0.066(2)	0.052(2)	–0.005(2)	0.034(2)	–0.007(1)
C(16)	8*f*	0.3353(2)	0.0548(1)	0.3624(3)	0.051(2)	0.049(2)	0.052(2)	0.004(1)	0.033(1)	–0.003(1)
C(17)	8*f*	0.2736(2)	0.0697(1)	0.2243(3)	0.051(2)	0.065(2)	0.051(2)	0.007(1)	0.031(2)	–0.007(1)
C(18)	8*f*	0.3024(2)	0.0159(1)	0.4093(3)	0.064(2)	0.060(2)	0.067(2)	–0.002(2)	0.042(2)	–0.005(2)

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