Yan-Ju Liu, An-Wen Li, Chen Xing and Xiao-Zhi Tian*

Crystal structure of tetrakis(1*H*-benzimidazol-2-amine)-κ*N*-bis(μ₂-sulfonato-κ²O:O')dizinc(II) - methanol (1/1), C₃₀H₃₆N₁₂O₁₀S₂Zn₂

Table 1: Data collection and handling.

Crystal:	Block, colorless
Size:	0.25 × 0.17 × 0.16 mm
Wavelength:	Mo Kα radiation (λ = 0.71073 Å)
μ:	1.374 mm ⁻¹
Diffractometer, scan mode:	Bruker D8 Venture, Φ and ω-scans
θ _{max} , completeness:	26.0°, >99%
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} , <i>R</i> _{int} :	10762, 3913, 0.0314
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2σ(<i>I</i> _{obs}), 2880
<i>N</i> (<i>param</i>) _{refined} :	291
Programs:	Bruker programs [1], SHELX [2, 3], DIAMOND [4]

<https://doi.org/10.1515/ncrs-2018-0165>

Received July 7, 2018; accepted August 21, 2018; available online September 5, 2018

Abstract

C₃₀H₃₆N₁₂O₁₀S₂Zn₂, monoclinic, *C*2/*c* (no. 15), *a* = 22.770(11) Å, *b* = 12.482(6) Å, *c* = 14.098(7) Å, β = 95.054(8)°, *V* = 3991(3) Å³, *Z* = 4, *R*_{gt}(*F*) = 0.0390, *wR*_{ref}(*F*²) = 0.1120, *T* = 293(2) K.

CCDC no.: 1863091

The crystal structure is shown in the figure. The solvent molecule methanol is omitted for clarity. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

All the reagents were used of chemical or analytical pure grade and obtained from commercial sources. A mixture of 1*H*-benzimidazol-2-amine (0.0058 g, 0.02 mmol) and ZnSO₄ · 7H₂O (0.0027 g, 0.02 mmol) was stirred in methanol (4 mL). The resultant solution was allowed to evaporate

slowly at room temperature for a week to give colorless crystals of the title complex.

Experimental details

The disordered sulfato ligand has been modelled by splitting it into two parts (S1, O1, O2, O3, O4 and S1', O1', O2', O3', O4'). The site occupation factors of which refined in a ratio of 0.840(7):0.160(7). Only one orientation of the sulfato ligand is shown in the figure. Hydrogen atoms were positioned geometrically and refined as riding atoms, with C–H = 0.93 Å (aromatic) or 0.96 Å (CH₃), N–H = 0.86 Å and O–H = 0.85 Å. *U*_{iso}(H) = 1.5*U*_{eq}(C,O) for methyl H atoms and hydroxy H atoms and 1.2*U*_{eq}(C,N) for others.

Discussion

Benzimidazoles as organic ligands have attracted interest in syntheses of metalorganic frameworks, not only because of their coordination abilities to metal ions but also significant potential applications in biological systems [5–11]. Each asymmetric unit contains one Zn(II), a SO₄²⁻ anion, two 1*H*-benzimidazol-2-amine ligands and a methanol molecule. As shown in the figure, Zn(II) is four-coordinated with irregular tetrahedral geometry surrounded by two nitrogen atoms (N1, N4) from two 1*H*-benzimidazol-2-amine ligands and two oxygen atoms from two sulfato ligands. The distances of Zn–N (1.973(3)–1.980(3) Å) and Zn–O (1.940(3)–2.008(3) Å) are close to those observed in

*Corresponding author: Xiao-Zhi Tian, Pharmacy College, Henan University of Traditional Chinese Medicine, Zhengzhou 450046, Henan Province, P.R. China, e-mail: 1564998828@qq.com

Yan-Ju Liu, An-Wen Li, and Chen Xing: Pharmacy College, Henan University of Traditional Chinese Medicine, Zhengzhou 450046, Henan Province, P.R. China

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U _{iso} [*] /U _{eq}
Zn1	0.06371(2)	0.10601(3)	0.05902(2)	0.04346(15)
S1	−0.06455(3)	0.14146(6)	−0.05756(5)	0.04085(19)
O1	−0.02076(12)	0.1161(3)	0.02427(19)	0.0573(11)
O2	−0.07496(19)	0.0427(2)	−0.1157(2)	0.0492(9)
O3	−0.04229(17)	0.2241(2)	−0.1173(2)	0.0632(11)
O4	−0.11881(14)	0.1752(4)	−0.0176(3)	0.0677(12)
S1′	−0.06455(3)	0.14146(6)	−0.05756(5)	0.04085(19)
O1′	−0.0572(9)	0.0305(9)	−0.0949(15)	0.089(11)
O2′	−0.0069(4)	0.1786(14)	−0.0183(14)	0.085(7)
O3′	−0.0857(10)	0.2088(14)	−0.1395(10)	0.103(8)
O4′	−0.1076(8)	0.1403(19)	0.0124(12)	0.095(9)
N1	0.12458(12)	0.1301(2)	−0.02995(18)	0.0499(7)
N2	0.17854(13)	0.1666(3)	−0.1506(2)	0.0651(8)
H2A	0.1870	0.1853	−0.2065	0.078
N3	0.07619(14)	0.1992(3)	−0.1727(2)	0.0738(9)
H3B	0.0422	0.1970	−0.1504	0.089
H3C	0.0793	0.2221	−0.2296	0.089
N4	0.07341(10)	0.1977(2)	0.17376(16)	0.0429(6)
N5	0.09209(13)	0.2587(2)	0.32134(18)	0.0553(7)
H5B	0.1005	0.2586	0.3820	0.066
N6	0.09335(18)	0.0710(3)	0.2982(2)	0.0840(11)
H6B	0.0901	0.0177	0.2594	0.101
H6C	0.1013	0.0600	0.3581	0.101
C1	0.12411(15)	0.1670(3)	−0.1190(2)	0.0522(8)
C2	0.21832(17)	0.1307(3)	−0.0770(3)	0.0647(10)
C3	0.27857(19)	0.1163(4)	−0.0706(3)	0.0895(15)
H3A	0.3007	0.1314	−0.1213	0.107
C4	0.3042(2)	0.0781(5)	0.0154(4)	0.1116(19)
H4A	0.3449	0.0685	0.0228	0.134
C5	0.2716(2)	0.0535(5)	0.0909(4)	0.1116(19)
H5A	0.2905	0.0269	0.1473	0.134
C6	0.21044(17)	0.0684(4)	0.0830(3)	0.0797(12)
H6A	0.1881	0.0533	0.1335	0.096
C7	0.18473(15)	0.1061(3)	−0.0017(3)	0.0584(9)
C8	0.08593(15)	0.1710(3)	0.2653(2)	0.0494(8)
C9	0.07066(12)	0.3100(2)	0.1720(2)	0.0418(7)
C10	0.05842(16)	0.3796(3)	0.0962(3)	0.0592(9)
H10A	0.0498	0.3544	0.0345	0.071
C11	0.0596(2)	0.4883(3)	0.1163(4)	0.0819(13)
H11A	0.0518	0.5372	0.0671	0.098
C12	0.0722(2)	0.5253(3)	0.2083(4)	0.0881(14)
H12A	0.0731	0.5989	0.2189	0.106
C13	0.08329(18)	0.4579(3)	0.2845(3)	0.0712(11)
H13A	0.0909	0.4837	0.3463	0.085
C14	0.08251(14)	0.3490(3)	0.2647(2)	0.0475(7)
O5	0.20411(14)	0.2354(3)	0.6688(2)	0.1151(13)
H5	0.1821	0.2116	0.6217	0.173
C15	0.2414(4)	0.3098(8)	0.6428(5)	0.217(5)
H15A	0.2201	0.3747	0.6268	0.326
H15B	0.2600	0.2850	0.5883	0.326
H15C	0.2708	0.3233	0.6943	0.326

other Zn(II) complexes [12, 13]. The title complex is a binuclear complex and the two Zn(II) ions are connected through SO₄^{2−}. The distance of Zn1···Zn1′ (′ = −x, −y, −z) is 4.1634(14) Å. There are two kinds of intramolecular N(3)—H···O(3) and N6—H···O2′ hydrogen bonds. Four kinds of N—H···O hydrogen bonds and one kind of O—H···O hydrogen bonds form the 1-D chain.

Acknowledgements: This work was supported by the Key Scientific Research Project of Colleges and Universities in Henan Province (Grant No. 16A350002) and Henan Province Basic and Frontier Technology Research Projects (Grant No. 152300410214).

References

1. Bruker. APEX3, SADABS and SAINT. Bruker AXS Inc., Madison, WI, USA (2016).
2. Sheldrick, G. M.: SHELXT – Integrated space-group and crystal-structure determination. *Acta Crystallogr.* **A71** (2015) 3–8.
3. Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr.* **C71** (2015) 3–8.
4. Brandenburg, K.: DIAMOND 4.0. Visual crystal structure information system. Crystal Impact, Bonn, Germany (2012).
5. Gu, W.; Miao, T.-T.; Hua, D.-W.; Jin, X.-Y.; Tao, X.-B.; Huang, C.-B.; Wang, S.-F.: Synthesis and *in vitro* cytotoxic evaluation of new 1*H*-benzo[d]imidazole derivatives of dehydroabietic acid. *Bioorg. Med. Chem. Lett.* **27** (2017) 1296–1300.
6. Kim, M. K.; Shin, H.; Park, K. S.; Kim, H.; Park, J.; Kim, K.; Nam, J.; Choo, H.; Chong, Y.: Benzimidazole derivatives as potent JAK1-selective inhibitors. *J. Med. Chem.* **58** (2015) 7596–7602.
7. Sharma, P.; Reddy, T. S.; Thummuri, D.; Senwar, K. R.; Kumar, N. P.; Naidu, V. G. M.; Bhargava, S. K.; Shankaraiah, N.: Synthesis and biological evaluation of new benzimidazole-thiazolidinedione hybrids as potential cytotoxic and apoptosis inducing agents. *Eur. J. Med. Chem.* **124** (2016) 608–621.
8. Hu, J.-Z.; Deibert, B. J.; Li, J.: Luminescent metal-organic frameworks for chemical sensing and explosive detection, *Chem. Soc. Rev.* **43** (2014) 5815–5840.
9. Liu, J.; Chen, L.; Cui, H.; Zhang, J.; Zhang, L.; Su, C.-Y.: Applications of metal-organic frameworks in heterogeneous supramolecular catalysis, *Chem. Soc. Rev.* **43** (2014) 6011–6061.
10. Lin, Z.-J.; Lv, J.; Hong, M.; Cao, R.: Metal-organic frameworks based on flexible ligands (FL-MOFs): structures and applications, *Chem. Soc. Rev.* **43** (2014) 5867–5895.
11. Jian, S.-J.; Liang, Z.; Yang, Y.-Q.; Yang, H.-X.: Crystal structure of catena-poly[diaqua-bis(benzene-1,2,4,5-tetracarboxylato-κN)(m₂-2-(1*H*-1,2,4-triazol-1-ylmethyl)-1*H*-3,1-benzimidazol-3-ium-κ²O:O′)zinc(II)] dihydrate, C₃₀H₃₀N₁₀O₁₂Zn, *Z. Kristallogr. NCS.* **231** (2016) 431–433.
12. Luo, Y.; Fu, L.-L.; Xiang, J.: Three new Zn(II) coordination compounds based on the *in-situ* formed tetrazolate

- ligand: syntheses, crystal structures and luminescence properties. *Chinese J. Struct. Chem.* **34** (2015) 95–102.
13. Liang, Y.-H.; Zhang, J.-G.; Cui, Y.; Zhang, T.-L.; Zhou, Z.-N.; Yang, L.: Two novel nitrogen-rich energetic coordination compounds $M_2(DAT)_5(H_2O)_3(TNR)_2$ ($M = Zn$ and Co): synthesis, characterization, thermal properties and sensitivity. *Chin. J. Struct. Chem.* **31** (2012) 327–338.