Huan Zheng, Sisi Feng* and Liping Lu*

Crystal structure of poly[dipoly[aqua-di(μ_2 -pyrazin-2-olato- $\kappa^2N:N'$) zinc(II)], $C_8H_8N_4O_3Zn$

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.10 × 0.10 × 0.10 mm
Wavelength:	Synchrotron radiation (0.720 Å)
μ :	2.49 mm ⁻¹
Diffractometer, scan mode:	mar555,
$\theta_{\max}$, completeness:	29.3°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	4206, 1298, 0.065
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1194
$N(\text{param})_{\text{refined}}$:	76
Programs:	Processing method [1], Bruker [2], SHELX [3–5]

<https://doi.org/10.1515/ncrs-2021-0023>

Received January 14, 2021; accepted February 1, 2021;

published online February 24, 2021

Abstract

$C_8H_8N_4O_3Zn$, tetragonal, $P\bar{4}c2$ (no. 116), $a = 7.340(1)$ Å, $c = 18.285(4)$ Å, $V = 985.1(3)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0404$, $\omega R_{\text{ref}}(F^2) = 0.1214$, $T = 100$ K.

CCDC no.: 2046068

A part of the polymeric title crystal structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

All chemicals were of analytical grade and used without further purification. The 2(1*H*)-pyrazinone was generated by *in situ* hydrolysis of 2,2'-di(pyrazine2-yl)-[4,5'-biisindoline]-1,1',3,3'-tetraone during the hydrothermal reaction. A

mixture of $ZnSO_4 \cdot 7H_2O$ (0.3 mmol, 0.0861 g), 2,2'-di(pyrazine2-yl)-[4,5'-biisindoline]-1,1',3,3'-tetraone (0.1 mmol, 0.0448 g), distilled water (6 mL) and KOH (1.3 mL, 0.5 mol/L) was placed in a Teflon liner (17 mL) with constant stirring (pH = 8.0 after stirring for 30 min). Faint yellow filtrate and white powder was obtained after the solution was filtered. The filtrate was left at room temperature and brilliant yellow crystals of **1** were obtained after two weeks in 15% yield.

Experimental details

X-ray diffraction data was collected at 100(2) K in the Beijing Synchrotron Radiation Facility (BSRF) beamline 3W1A, which was mounted with a MARCCD-165 detector ($\lambda = 0.720$ Å) with the storage ring working at 2.5 GeV. Data were collected by the MARCCD diffractometer and processed using HKL 2000 [1]. Multi-scan program SADABS was used for absorption correction [2]. The structure was solved by direct methods and refined using the SHELX programs [3–5]. The topological analyses were performed on the TOPOS [6].

Comment

Pyrazine molecules have a high symmetry. The N electro-negativity and aromaticity of the molecules makes pyrazine

*Corresponding authors: Sisi Feng and Liping LU, Institute of Molecular Science, Key Laboratory of Chemical Biology and Molecular Engineering of the Education Ministry, Shanxi University, Taiyuan, Shanxi 030006, People's Republic of China, E-mail: ssfeng@sxu.edu.cn (S. Feng), luliping@sxu.edu.cn (L. Lu). <https://orcid.org/0000-0003-2357-2995> (S. Feng)

Huan Zheng, Institute of Molecular Science, Key Laboratory of Chemical Biology and Molecular Engineering of the Education Ministry, Shanxi University, Taiyuan, Shanxi 030006, People's Republic of China

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

Atom	x	y	z	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Zn1	1.0000	1.0000	0.0000	0.0095 (3)
Zn2	0.5000	0.5000	0.2500	0.0088 (3)
O1	0.2966 (3)	0.7034 (3)	0.2500	0.0175 (6)
H1A	0.2320	0.7455	0.2159	0.021*
O2	1.1083 (3)	0.7738 (3)	0.12711 (11)	0.0211 (6)
N1	0.6498 (3)	0.6443 (3)	0.16651 (12)	0.0130 (5)
N2	0.8517 (4)	0.8268 (3)	0.06075 (12)	0.0135 (5)
C1	0.8255 (4)	0.6630 (4)	0.17325 (14)	0.0144 (6)
H1	0.8827	0.6123	0.2152	0.017*
C2	0.5665 (4)	0.7166 (4)	0.10582 (16)	0.0180 (6)
H2	0.4385	0.7052	0.0996	0.022*
C3	0.6690 (4)	0.8054 (4)	0.05416 (17)	0.0173 (6)
H3	0.6097	0.8537	0.0122	0.021*
C4	0.9380 (4)	0.7568 (4)	0.12042 (15)	0.0141 (6)

the small, convenient and flexible molecule or group for the construction of metal complexes. Studies have shown that pyrazine can form coordination polymers with multi-dimensional network structure [7]. Compared with pyridine heterocycles, pyrazine has more active sites to form hydrogen bonds and coordination bond. When substituents are introduced into pyrazine heterocycles, it is speculated that new hydrogen bond active sites may be formed according to the charge distribution of organic molecules [8]. We recently investigated the formation of a zinc complex containing pyrazine groups by hydrothermal *in situ* reaction with transition metal self-assembly using 2,2'-di(pyrazine-2-yl)-[4,5'-biisindoline]-1,1',3,3'-tetraone as a precursor. Here we report the three-dimensional structure of [Zn(2-pyz)₂(H₂O)]_n (**1**) (2(1H)-pyz = 2(1H)-pyrazinone).

Single crystal X-ray diffraction reveals that the title coordination polymer (see the Figure) crystallizes in the tetragonal space group *P* $\bar{4}$ c2 exhibiting an interesting 3D to 3D 2-fold interpenetrated framework. The asymmetric unit contains half a Zn(II) cation (Zn1 and Zn2 with 0.25 occupancy respectively), one 2-pyz[−] anion and half a water molecule. 2(1H)-pyz was generated by *in situ* hydrolysis of 2,2'-di(pyrazine-2-yl)-[4,5'-biisindoline]-1,1',3,3'-tetraone. There are two different coordination environments for the two crystallographically independent Zn(II) atoms. Zn1 atom locates in a tetrahedral coordination sphere and is connected to with four N atoms from four different 2-pyz[−] anions with the same Zn-N bond length (Zn1-N = 2.009(1) Å). While Zn2 atom is located in an octahedral coordination geometry defined by four equatorial N atoms with identical

Zn-N bond length (Zn2-N = 2.159(1) Å) and two axial water molecules (Zn2-O = 2.111(2) Å). The Zn2 atom lies on a 222 Wyckoff site. Meanwhile, the Zn1 atom lies on a $\bar{4}$ site. The ligand is similar to the Cd compounds [CdX₂(2-pyz)₂]_n (X = halide ions) [9], however, it adopts different coordination modes. It provides one N atom coordinated with cadmium in [CdX₂(2-pyz)₂]_n, but each 2-pyz[−] provides two N atoms coordinated with two different zinc ions in **1**. Every 2-pyz[−] building block connects with two Zn atoms in a bidentate fashion and acts as a linker, just like 4,4'-bipyridine, due to its terminal N atoms. The four-coordinated Zn atoms connect with the six-coordinated Zn atoms through 2-pyz[−] building blocks in different directions to expand to 3D network with large cavities. Eight four-coordinated Zn atoms lie in the vertex of the cage and six hexa-coordinated Zn atoms situate in the center of faces or edges of the cage, leaving two types of windows. The presence of large cavities induces self-catenation in the framework to stabilize the whole structure. As a result of 2-fold self-interpenetration, the pore volume reduces significantly. From the topological view, we can simply assign the Zn atoms as 4-connected nodes, and the 2-pyz[−] anions as linkers. The whole structure contains two identical networks, which are of the same topological structure. Each of the interpenetrated networks can be defined as an intriguing (4,4)-connected framework with the net symbol of (4².8⁴).

Acknowledgments: We acknowledge Zengqiang Gao (BSRF) for the help of single-crystal X-ray diffraction data collection (line 3 W1A).

Author contribution: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: Natural Science Foundation of China (Grant No 21671124) and the Scientific Instrument Center of Shanxi University of China.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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