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Crystal structure of poly[triaqua-(μ_4 -benzene-1,3,5-tricarboxylato- $\kappa^5 O^1, O^2:O^3:O^4:O^5$)-(μ_2 -5-(3-pyridyl)tetrazolato- $\kappa^2 N^1:N^3$)dizinc(II)], $C_{15}H_{13}N_5O_9Zn_2$

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.15 × 0.12 × 0.10 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	2.80 mm ⁻¹
Diffractometer, scan mode:	CCD, φ and ω
$\theta_{\max}$, completeness:	26.0°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	11135, 3451, 0.078
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2364
$N(\text{param})_{\text{refined}}$:	298
Programs:	Bruker [1], SHELX [2–5], Olex2 [6]

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Abstract

$C_{15}H_{13}N_5O_9Zn_2$, monoclinic, $P2_1/n$ (no. 14), $a = 6.7739(13)$ Å, $b = 14.160(3)$ Å, $c = 18.506(4)$ Å, $\beta = 97.908(4)^\circ$, $V = 1758.1(6)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0597$, $wR_{\text{ref}}(F^2) = 0.1125$, $T = 298(2)$ K.

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A part of the 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

The titled compound was synthesized by mixing 3-cyanopyridine (0.104 g, 1.0 mmol), sodium azide (0.066 g, 1.0 mmol), 1,3,5-benzenetricarboxylic acid ($H_3\text{bta}$, 0.210 g, 1.0 mmol) and $Zn(NO_3)_2 \cdot 6 H_2O$ (0.594 g, 2.0 mmol) in 15.0 mL distilled water solution in a 25.0 mL polytetrafluoroethylene reactor. The mixed solution was stirred at room

temperature for 30 minutes and then placed in an oven at 150 °C for three days. After slow cooling to room temperature at a rate of 5 K/min, the final product was collected manually, washed with water and air-dried to give colorless block-shaped crystals of the title compound (yield: 0.05 g).

Experimental details

Hydrogen atoms bonded to carbon were placed in their geometrically idealized positions and constrained to ride on their parent atoms and $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$. Water hydrogen atoms were located initially from the difference Fourier electron maps and refined with the constraints of $d_{O-H} = 0.82(1)$ Å, $d H \cdots H = 1.35(2)$ Å and $U_{\text{iso}}(H) = 1.5U_{\text{eq}}(O)$.

Comment

Metal organic framework and coordination polymers (CPs) have been intriguing researchers' more and more interests because of their potential application in materials chemistry, biochemistry, environmental science, etc [7–9]. As one building connector in the design of MOFs, and CPs nitrogen- and/or oxygen-containing ligand has often been deliberately screened in order to enrich their structural versatilities [10]. A good example of this is provided by a one-pot *in situ* reaction of nitrile/azide/metal, which can lead to some novel metal-tetrazole supramolecular assemblies [11]. Herein, we have chosen 3-cyanopyridine, sodium azide, 1,3,5-benzenetricarboxylic acid ($H_3\text{bta}$) and $Zn(NO_3)_2$ as the initial materials under the hydrothermal condition of 423 K.

The asymmetric unit consists of two zinc(II) cations, one ptz^- anion, one bta^{3-} anion and three coordinated water molecules. For both Zn(II) centers, they are five-coordinated

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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	0.15344(10)	0.92395(5)	0.19101(4)	0.0231(2)
Zn2	0.30623(11)	0.42114(5)	−0.13972(4)	0.0233(2)
C1	0.1440(8)	0.8272(4)	−0.0115(3)	0.0166(13)
C2	0.1280(8)	0.8833(4)	−0.0733(3)	0.0179(13)
H2	0.1163	0.9484	−0.0686	0.021*
C3	0.1290(8)	0.8441(4)	−0.1424(3)	0.0156(13)
C4	0.1537(7)	0.7465(4)	−0.1471(3)	0.0157(12)
H4	0.1596	0.7193	−0.1925	0.019*
C5	0.1698(8)	0.6895(4)	−0.0862(3)	0.0162(12)
C6	0.1600(8)	0.7306(4)	−0.0190(3)	0.0156(13)
H6	0.1642	0.6924	0.0221	0.019*
C7	0.1502(9)	0.8720(4)	0.0617(3)	0.0212(14)
C8	0.1143(8)	0.9032(4)	−0.2097(3)	0.0187(13)
C9	0.2096(8)	0.5862(4)	−0.0934(3)	0.0212(14)
C10	0.1485(8)	0.7402(4)	0.4538(3)	0.0172(13)
C11	0.1602(8)	0.8154(4)	0.5020(3)	0.0210(14)
H11	0.1757	0.8759	0.4840	0.025*
C12	0.1369(8)	0.7179(4)	0.5997(3)	0.0227(14)
H12	0.1329	0.7100	0.6494	0.027*
C13	0.1288(9)	0.6387(4)	0.5554(3)	0.0266(15)
H13	0.1187	0.5787	0.5749	0.032*
C15	0.1525(8)	0.7589(4)	0.3759(3)	0.0188(13)
C14	0.1360(8)	0.6503(4)	0.4825(3)	0.0239(14)
H14	0.1325	0.5979	0.4521	0.029*
N1	0.1503(7)	0.8050(3)	0.5735(2)	0.0210(12)
N2	0.1631(7)	0.8453(3)	0.3482(2)	0.0219(12)
N3	0.1589(7)	0.8298(3)	0.2762(3)	0.0231(12)
N4	0.1450(8)	0.7386(3)	0.2620(3)	0.0299(13)
N5	0.1421(7)	0.6922(3)	0.3244(3)	0.0245(12)
O1	0.1748(7)	0.9583(3)	0.0693(2)	0.0318(11)
O2	0.1260(7)	0.8206(3)	0.1158(2)	0.0343(12)
O3	0.0568(6)	0.9879(3)	−0.2087(2)	0.0321(11)
O4	0.1699(6)	0.8652(3)	−0.2650(2)	0.0252(10)
O5	0.2050(6)	0.5529(3)	−0.1573(2)	0.0259(10)
O6	0.2536(6)	0.5358(3)	−0.0381(2)	0.0316(11)
O7	0.4104(8)	0.9944(3)	0.2133(3)	0.0414(13)
H7A	0.471(10)	0.986(4)	0.254(2)	0.062*
H7B	0.404(11)	1.0497(19)	0.202(3)	0.062*
O8	0.6173(7)	0.4646(3)	−0.1096(2)	0.0256(10)
H8A	0.634(9)	0.455(4)	−0.0659(12)	0.038*
H8B	0.637(9)	0.5194(19)	−0.120(3)	0.038*
O9	−0.0131(6)	0.3851(3)	−0.1477(3)	0.0384(12)
H9A	−0.105(7)	0.416(4)	−0.135(4)	0.058*
H9B	−0.056(9)	0.337(3)	−0.169(3)	0.058*

by {O₄N} donor sets, forming distorted square-pyramidal polyhedrons ($\tau = 0.43$ for Zn1 and 0.31 for Zn2) [12]. For Zn1, the {O₄N} donor set originates from two separated carboxylic groups (O1/O2 and O3 at $(-x, 2-y, -z)$), one tetrazole nitrogen N3 and one water O7 atom. Water O7 atom resides on the axial position and the other four atoms lies in the basal plane. The Zn1–O1 (2.328(4) Å) bond being significantly longer than the other four

Zn–O/N bonds ($d_{\text{Zn1–O2}} = 2.011(4)$ Å, $d_{\text{Zn1–O3}} = 1.955(4)$ Å, $d_{\text{Zn1–O7}} = 1.999(5)$ Å and $d_{\text{Zn1–N3}} = 2.061(5)$ Å) is largely due to its chelating effect which are comparable to some analogs in some literatures [13]. For Zn2, its coordination configuration is distinctly different from Zn1. For example, although a similar {O₄N} donor set is formed around Zn2, its coordination sphere is composed by two mono-dentated carboxylic oxygen atoms O4 and O5, two water O8 and O9 atoms and one pyridine nitrogen atom. Carboxylic O4 atom is on the axial position and the other four donor atoms (O5/O8/O9/N1) consist of the equatorial plane. The water involved Zn2–O8/Zn2–O9 (2.192(5)/2.207(4) Å) bonds are longer by ca. 0.2 Å than the mean bond distances of Zn2–O4/O5/N1 (2.002(4) Å).

The crystal packing of the three-dimensional coordination polymer was constructed by bta^{3-} and ptz^- and Zn^{2+} ions. Despite of its abundant potential coordinated sites and numerous coordination styles for ptz^- , each ptz^- ligand only acts as a bidentated ligand linking two metal ions ($\text{Zn1} \cdots \text{Zn2} = 8.271$ Å) in a μ_2 -bridging mode, which has been observed in some analogs [14, 15]. The bta^{3-} anions adopt μ_4 -bridging modes connecting four Zn(II) cations with the $\text{Zn1} \cdots \text{Zn2}$ distance linked by O3/O4 group is 4.710(2) Å (see the figure). In more details, the ptz^- anions link the adjacent Zn(II) cations along the [001] axis and the O3/O4 carboxylic acid group link the adjacent Zn(II) along the [100] axis. The btc^{3-} anions singly link these Zn(II) centers into a 2D layer structure parallel to the {101} plane. Thus, a final 3D coordination polymer is formed. Furthermore the coordinated water ligands are extensively hydrogen-bonded with symmetry-related water and carboxylate O atoms and tetrazole nitrogen atom of the ptz^- anion. A *platon* analysis indicates that $\pi \cdots \pi$ stacking interactions exist with the centroid-to-centroid distances of 3.669(2) Å and 3.718(2) Å between adjacent phenyl rings of btc^{3-} and tetrazole ring/pyridine ring of ptz^- , respectively [16].

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References

1. Bruker. SMART and SAINT. Bruker AXS Inc., Madison, WI, USA (2003).
2. Sheldrick, G. M.: SHELXS97. Crystal Structure Solution. University of Göttingen, Göttingen (1990).
3. Sheldrick, G. M.: SHELXTL – integrated space-group and crystal-structure determination. *Acta Crystallogr. A* **71** (2015) 3–8.
4. Sheldrick, G. M.: Crystal structure refinement with SHELX. *Acta Crystallogr. C* **71** (2015) 3–8.

5. Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr. A* **64** (2008) 112–122.
6. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H.: OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **42** (2009) 339–341.
7. Zhao, H.; Qu, Z. R.; Ye, H. Y.; Xiong, R. G.: *In situ* hydrothermal synthesis of tetrazole coordination polymers with interesting physical properties. *Chem. Soc. Rev.* **37** (2008) 84–100.
8. Chen, X. M.; Tong, M. L.: Solvothermal *in-situ* metal/ligand reactions: a new bridge between coordination chemistry and organic synthetic chemistry. *Acc. Chem. Res.* **40** (2006) 162–170.
9. Zhang, W.; Xiong, R. G.: Ferroelectric metal–organic frameworks. *Chem. Rev.* **112** (2011) 1163–1195.
10. Almeida Paz, F. A.; Klinowski, J.; Vilela, S. M. F.; Tomé, J. P. C.; Cavaleiro, J. A. S.; Rocha, J.: Ligand design for functional metal–organic frameworks. *Chem. Soc. Rev.* **41** (2012) 1088–1110.
11. Lin, Z. J.; Lü, J.; Hong, M.; Cao, R.: Metal–organic frameworks based on flexible ligands (FL-MOFs): structures and applications. *Chem. Soc. Rev.* **43** (2014) 5867–5895.
12. Wang, X. S.; Tang, Y.-Z.; Huang, X. F.; Qu, Z. R.; Che, C. M.; Chan, P. W. H.; Xiong, R.-G.: Syntheses, crystal structures, and luminescent properties of three novel zinc coordination polymers with tetrazolyl ligands. *Inorg. Chem.* **44** (2005) 5278–5285.
13. Wang, X. L.; Zhao, J.; Lin, H. Y.; Le, M.; Liu, G. C.; Wang, X.: Flexible bis(pyridyl-tetrazole) ligand-induced ring-containing metal–organic coordination polymers: synthesis, structures and properties. *J. Coord. Chem.* **71** (2018) 1114–1126.
14. Lu, W. G.; Wang, X. B.; Liu, H. W.; Hong, X. L.: Two coordination polymers constructed by Cd(II) and Zn(II) with *in situ* generated 5-(3-pyridyl)tetrazolate ligand: syntheses, crystal structures and luminescence properties. *Chin. J. Struct. Chem.* **35** (2016) 383–391.
15. Sun, L.; Li, X. J.; Yu, N. Q.; Chen, S. S.; Yao, S. Q.; Deng, H.: Hydrothermal syntheses, crystal structures and properties of three new zinc(II) coordination polymers with *in situ* formed 5-(3-pyridyl) tetrazolate. *Inorg. Chem. Commun.* **24** (2012) 241–246.
16. Spek, A. L.: Structure validation in chemical crystallography. *Acta Crystallogr. D* **65** (2009) 148–155.