Yu-Quan Feng*, Zhi-Guo Zhong and Zi-Long Yue

Crystal structure of hexakis(μ_2 -azido- $\kappa^2 N:N$)-diazido- $\kappa^1 N$ -tetrakis(phenanthroline- $\kappa^2 N, N'$) tetrazinc(II), $C_{48}H_{32}N_{32}Zn_4$

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.29 × 0.25 × 0.20 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.93 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	26.0°, 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	8227, 4969, 0.021
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3848
$N(\text{param})_{\text{refined}}$:	379
Programs:	Bruker [1], Olex2 [2], SHELX [3]

the yellow block crystals were isolated, washed with distilled water and dried at room temperature.

<https://doi.org/10.1515/ncrs-2019-0473>

Received July 6, 2019; accepted September 19, 2019; available online October 9, 2019

Abstract

$C_{48}H_{32}N_{32}Zn_4$, triclinic, $P\bar{1}$ (no. 2), $a = 9.9928(14)$ Å, $b = 10.1374(14)$ Å, $c = 14.2362(19)$ Å, $\alpha = 71.710(2)^\circ$, $\beta = 76.166(2)^\circ$, $\gamma = 71.086(2)^\circ$, $V = 1280.1(3)$ Å³, $Z = 1$, $R_{\text{gt}}(F) = 0.0314$, $wR_{\text{ref}}(F^2) = 0.0795$, $T = 296(2)$ K.

CCDC no.: 1951372

Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.20 g), 1,10-phenanthroline ($C_{12}H_8N_2$, 0.16 g), NaN_3 (0.10 g) and H_2O (3.0 mL) was transferred into 50 mL Teflon-lined stainless steel vessels and heated at 160 °C for 5 days. After cooling to room temperature,

Experimental details

H atoms were positioned geometrically and refined using a riding model, with C–H = 0.93 Å, with $U_{\text{iso}}(H) = 1.2$ times $U_{\text{eq}}(C)$.

Comment

A large number of metal coordination compounds containing various metal cations and organic ligands have been obtained with different dimensional structures. Currently, linking metal cations and organic ligands to build coordination compounds has become a popular synthetic strategy [4]. Polydentate ligands, such as N_3^- and NCS^- , can act as either bridging or chelating ligands to construct desired metal-organic coordination compounds [4–6]. As a part of an ongoing study [6, 7] we have synthesized a tetra-nuclear Zn^{2+} coordination compound formulated $[Zn_4(C_{12}H_8N_2)_4(N_3)_8]$ (**1**) containing two kinds of ligands.

Single crystal X-ray diffraction indicated that **1** belongs to the triclinic system with the space group $P\bar{1}$. The molecular structural unit of **1** contains four Zn^{2+} cations, four $C_{12}H_8N_2$ ligands and eight N_3^- anions as shown in the figure. Within the title complex Zn1 is six-coordinated by six N atoms from one $C_{12}H_8N_2$ ligand and four N atoms from four N_3^- ligands. Zn2 cation is five-coordinated by five N atoms from one $C_{12}H_8N_2$ ligand and three N atoms from three N_3^- ligands. The bond distances Zn–N, N–N and the bond angles of N–Zn–N are in the ranges of 1.966(3)–2.209(2) Å, 1.129(3)–1.196(3) Å

*Corresponding author: Yu-Quan Feng, College of Chemistry and Pharmacy Engineering, Nanyang Normal University, Nanyang 473061, China, e-mail: fengyuquan@nynu.edu.cn. <https://orcid.org/0000-0002-3232-1680>

Zhi-Guo Zhong and Zi-Long Yue: College of Chemistry and Pharmacy Engineering, Nanyang Normal University, Nanyang 473061, China

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Zn1	0.96883(3)	0.48546(3)	0.39409(2)	0.03393(10)
Zn2	0.88633(3)	0.73656(3)	0.19268(2)	0.03761(11)
N1	1.1150(2)	0.5437(2)	0.45028(17)	0.0394(5)
N2	1.2159(3)	0.5871(2)	0.40522(19)	0.0414(6)
N3	1.3122(3)	0.6298(3)	0.3629(3)	0.0736(9)
N4	0.8220(2)	0.6963(2)	0.34560(17)	0.0373(5)
N5	0.7053(3)	0.7486(2)	0.38436(18)	0.0402(6)
N6	0.5956(3)	0.7995(3)	0.4215(2)	0.0673(8)
N7	1.1003(2)	0.2713(2)	0.39573(16)	0.0330(5)
N8	0.8249(2)	0.3800(2)	0.37051(17)	0.0347(5)
N9	1.0572(2)	0.5552(2)	0.23774(18)	0.0398(6)
N10	1.1254(3)	0.4710(3)	0.18963(19)	0.0458(6)
N11	1.1915(4)	0.3893(3)	0.1455(2)	0.0845(11)
N12	0.8074(3)	0.6455(3)	0.1233(2)	0.0552(7)
N13	0.6897(3)	0.6693(3)	0.1126(2)	0.0553(7)
N14	0.5763(4)	0.6887(5)	0.0986(3)	0.1084(14)
N15	0.7298(2)	0.9507(2)	0.16269(17)	0.0398(6)
N16	1.0149(2)	0.8784(2)	0.14230(16)	0.0355(5)
C1	1.2365(3)	0.2204(3)	0.4061(2)	0.0421(7)
H1	1.2821(3)	0.2812(3)	0.4151(2)	0.0505(8)*
C2	1.3152(3)	0.0802(3)	0.4041(2)	0.0489(8)
H2	1.4111(3)	0.0483(3)	0.4121(2)	0.0587(9)*
C3	1.2506(3)	−0.0093(3)	0.3904(2)	0.0464(7)
H3	1.3021(3)	−0.1033(3)	0.3886(2)	0.0557(9)*
C4	1.1062(3)	0.0401(3)	0.37888(19)	0.0368(6)
C5	1.0357(3)	0.1840(3)	0.38149(18)	0.0310(6)
C6	0.8880(3)	0.2409(3)	0.36952(19)	0.0316(6)
C7	0.8151(3)	0.1526(3)	0.3572(2)	0.0391(6)
C8	0.8895(3)	0.0064(3)	0.3575(2)	0.0452(7)
H8	0.8406(3)	−0.0535(3)	0.3511(2)	0.0543(9)*
C9	1.0275(3)	−0.0461(3)	0.3669(2)	0.0450(7)
H9	1.0735(3)	−0.1414(3)	0.3654(2)	0.0539(9)*
C10	0.6716(3)	0.2133(3)	0.3461(2)	0.0512(8)
H10	0.6186(3)	0.1577(3)	0.3388(2)	0.0615(9)*
C11	0.6094(3)	0.3530(4)	0.3460(3)	0.0557(8)
H11	0.5140(3)	0.3948(4)	0.3373(3)	0.0668(10)*
C12	0.6888(3)	0.4329(3)	0.3588(2)	0.0470(7)
H12	0.6445(3)	0.5288(3)	0.3593(2)	0.0564(9)*
C13	0.5884(3)	0.9844(3)	0.1731(2)	0.0498(8)
H13	0.5437(3)	0.9103(3)	0.1969(2)	0.0597(9)*
C14	0.5045(3)	1.1257(4)	0.1500(3)	0.0586(9)
H14	0.4055(3)	1.1450(4)	0.1576(3)	0.0703(11)*
C15	0.5667(4)	1.2352(4)	0.1163(2)	0.0561(9)
H15	0.5111(4)	1.3303(4)	0.1003(2)	0.0674(10)*
C16	0.7156(3)	1.2047(3)	0.1058(2)	0.0459(7)
C17	0.7924(3)	1.0595(3)	0.1297(2)	0.0375(6)
C18	0.9458(3)	1.0205(3)	0.12060(19)	0.0359(6)
C19	1.0153(3)	1.1295(3)	0.0917(2)	0.0429(7)
C20	0.9337(4)	1.2765(3)	0.0690(2)	0.0540(8)
H20	0.9801(4)	1.3491(3)	0.0497(2)	0.0648(10)*
C21	0.7913(4)	1.3119(3)	0.0750(2)	0.0579(9)
H21	0.7407(4)	1.4088(3)	0.0588(2)	0.0695(11)*

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C22	1.1637(3)	1.0852(3)	0.0869(2)	0.0512(8)
H22	1.2150(3)	1.1536(3)	0.0687(2)	0.0614(9)*
C23	1.2336(3)	0.9424(4)	0.1088(2)	0.0511(8)
H23	1.3326(3)	0.9124(4)	0.1049(2)	0.0614(9)*
C24	1.1549(3)	0.8419(3)	0.1369(2)	0.0420(7)
H24	1.2034(3)	0.7443(3)	0.1527(2)	0.0504(8)*

and 76.53(8)–168.68(9)°, respectively. These above mentioned bond distances and angles are all in their normal ranges. They can be compared with those previously reported compounds [8]. By means of such connected modes, a tetra-nuclear coordination compound was generated. The distances of Zn···Zn are 3.251 Å and 3.338 Å. It is worth noting that the eight N₃[−] ligands exhibited two types of coordination fashions: six N₃[−] ligands as bridged ligands linked to two Zn²⁺ cations (Zn1 and Zn2) and two N₃[−] ligands as terminal ligands connected to Zn2. In addition, C—H···N hydrogen bonds are found in the packing structure of **1**.

Acknowledgements: This work was financially supported by the National Natural Science Foundation of China (no. 21601095).

References

1. Bruker. APEX2, SAINT v7.60A and SAINT v7.60A. Bruker AXS Inc., Madison, WI, USA (2008).
2. 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.
3. Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr.* **C71** (2015) 3–8.
4. Gao, E.-Q.; Bai, S.-Q.; Wang, C.-F.; Yue, Y.-F.; Yan, C.-H.: Structural and magnetic properties of three one-dimensional azido-bridged copper(II) and manganese(II) coordination polymers. *Inorg. Chem.* **42** (2003) 8456–8464.
5. Yue, Y.-F.; Gao, E.-Q.; Bai, S.-Q.; He, Z.; Yan, C.-H.: High-dimensional azido-bridged cadmium(II) polymeric complexes with bis(bidentate) diazine ligands. *CrystEngComm* **6** (2004) 549–555.
6. Zhang, W.; Feng, Y.-Q.: A novel dinuclear bismuth(III) coordination compound: bis(μ-pyridine-2,6-dicarboxylato)-κ⁴O²,N,O⁶:O⁶;κ⁴O²:O²,N,O⁶-bis[(azido-κN)(1,10-phenanthroline-κ²N,N′)bismuth(III)]tetrahydrate. *Acta Crystallogr.* **C70** (2014) 562–565.
7. Feng, X.; Feng, Y.-Q.; Liu, L.; Wang, L.-Y.; Song, H.-L.; Ng, S.-W.: A series of Zn-4f heterometallic coordination polymers and a zinc complex containing a flexible mixed donor dicarboxylate ligand. *Dalton Trans.* **42** (2013) 7741–7754.
8. Sun, J.-Y.; Wang, X.-X.: Di-μ-1,1-azido-bis[azido(5,5′-dimethyl-2,2′-bipyridine-κ²N,N′)zinc(II)]. *Acta Crystallogr.* **E63** (2007) m1138–m1139.