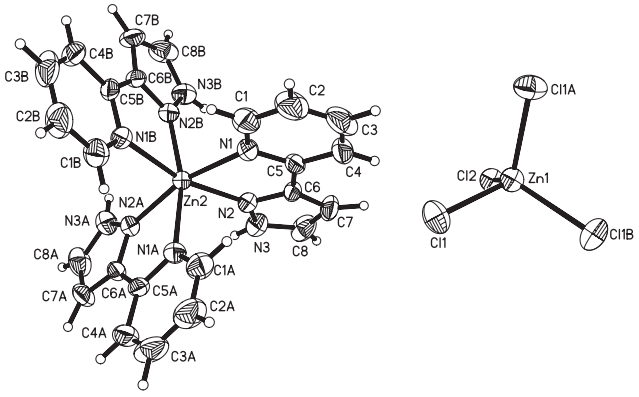
Open Access

Guang-Zhou Zhu, Chun-Ling Li, Ao-Lan Wang, Shi-Yu Wang, Dan-Ling Zou, Xiao-Jing Zhang and Feng-Lei Yang*

Crystal structure of tris(3-(2-pyridyl)pyrazole) zinc(II)tetrachlorido zincate(II), $C_{24}H_{21}Cl_4N_9Zn_2$



DOI 10.1515/ncrs-2015-0104
Received May 25, 2015; accepted December 16, 2015; available online February 11, 2016

Abstract

$C_{24}H_{21}Cl_4N_9Zn_2$, trigonal, $R\bar{3}c$ (no. 161), $a = 13.3310(13)$ Å, $b = 13.3310(13)$ Å, $c = 58.070(9)$ Å, $V = 8937.3(19)$ Å$_3$, $Z = 12$, $R_{gt}(F) = 0.0409$, $wR_{ref}(F^2) = 0.1491$, $S = 1.006$, $T = 296(2)$ K.

CCDC no.: 1442796

The crystal structure is shown in the figure, Tables 1–3 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

First, 3-(2-pyridyl)pyrazole was prepared by using 2-acetyl pyridine, dimethylformamide dimethyl acetal and hydrazine under conditions according to the previousely discribed method [1]. Then, the 1 mL aqueous solution of $ZnCl_2$ (0.1 mol/L) was slowly droped into the 10 mL nitromethane solution of 3-(2-pyridyl)pyrazole (14.5 mg, 0.1 mmol). The mixture solution was stirred at room temperature for 30 minutes. After filtration, it was stood to evaporate for one week to form colorless block-shaped crystals of the title compound suitable for X-ray diffraction.

Table 1: Data collection and handling.

Crystal:	Colorless, block, size 0.10×0.10×0.10 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	20.00 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD area-detector, φ and ω scans
$2\theta_{max}$:	53.24°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	36116, 2032
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1307
$N(param)_{refined}$:	118
Programs:	SHELX [8] Diamond [9]

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

Atom	Site	x	y	z	U_{iso}
H(3A)	36*f*	0.1250	0.1765	0.1324	0.079
H(1A)	36*f*	0.0632	−0.0949	0.0390	0.096
H(2A)	36*f*	0.2177	−0.0573	0.0174	0.125
H(3B)	36*f*	0.3995	0.0763	0.0302	0.124
H(4A)	36*f*	0.4202	0.1736	0.0645	0.101
H(7A)	36*f*	0.4214	0.2612	0.1045	0.100
H(8A)	36*f*	0.3260	0.2904	0.1390	0.104

Experimental details

The H atoms were calculated geometrically and refined as riding, with C—H = 0.93–0.98°.

Discussion

The 3-(2-pyridyl)pyrazoles have been widely studied as important complex ligands [2] and as precursors of the preparation for pharmaceutical active compounds [3, 4]. Herein, we report the crystal structure of the title compound. In the title compound, all the bond lengths are within normal ranges [5], similar to its two analogues [6, 7]. One Zn(II) is

***Corresponding author: Feng-Lei Yang,** School of Chemistry & Chemical Engineering, Jiangsu Key Laboratory, of Green Synthetic Chemistry for Functional Materials, Jiangsu Normal University, Xuzhou Jiangsu 221116, P. R. China, e-mail: yangfl@jsnu.edu.cn
Guang-Zhou Zhu, Chun-Ling Li, Ao-Lan Wang, Shi-Yu Wang, Dan-Ling Zou and Xiao-Jing Zhang: School of Chemistry & Chemical Engineering, Jiangsu Key Laboratory, of Green Synthetic Chemistry for Functional Materials, Jiangsu Normal University, Xuzhou Jiangsu 221116, P. R. China

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)	12*c*	0.6667	0.3333	0.01427(1)	0.0540(3)	0.0540(3)	0.0483(4)	0.0270(2)	0	0
Cl(1)	36*f*	0.49952(8)	0.31332(9)	−0.00031(1)	0.0647(6)	0.1080(8)	0.0687(6)	0.0508(5)	−0.0085(4)	−0.0059(5)
Cl(2)	12*c*	0.6667	0.3333	0.05277(2)	0.0583(5)	0.0583(5)	0.0477(7)	0.0291(3)	0	0
Zn(2)	12*c*	0	0	0.08514(1)	0.0400(3)	0.0400(3)	0.0603(4)	0.0200(2)	0	0
N(1)	36*f*	0.1432(2)	0.0145(2)	0.06411(5)	0.050(2)	0.055(2)	0.071(2)	0.027(1)	0.010(1)	−0.002(1)
N(2)	36*f*	0.1506(2)	0.1195(2)	0.10328(4)	0.046(2)	0.044(1)	0.061(2)	0.020(1)	−0.002(1)	−0.002(1)
N(3)	36*f*	0.1761(2)	0.1794(2)	0.12302(5)	0.064(2)	0.061(2)	0.062(2)	0.023(2)	−0.004(1)	−0.000(1)
C(1)	36*f*	0.1363(4)	−0.0394(3)	0.04417(7)	0.083(3)	0.076(3)	0.087(3)	0.044(2)	0.014(2)	−0.007(2)
C(2)	36*f*	0.2273(5)	−0.0185(4)	0.03121(9)	0.119(4)	0.107(3)	0.109(3)	0.074(3)	0.035(3)	0.000(3)
C(3)	36*f*	0.3344(5)	0.0610(5)	0.03884(9)	0.117(4)	0.123(4)	0.111(3)	0.090(4)	0.057(3)	0.038(3)
C(4)	36*f*	0.3472(3)	0.1187(3)	0.05920(8)	0.056(2)	0.077(3)	0.124(4)	0.037(2)	0.029(2)	0.034(3)
C(5)	36*f*	0.2488(3)	0.0933(3)	0.07164(6)	0.048(2)	0.053(2)	0.079(2)	0.031(2)	0.016(2)	0.021(2)
C(6)	36*f*	0.2512(3)	0.1476(3)	0.09353(6)	0.037(2)	0.043(2)	0.079(2)	0.016(1)	−0.000(2)	0.014(2)
C(7)	36*f*	0.3424(3)	0.2270(3)	0.10740(8)	0.039(2)	0.063(2)	0.127(4)	0.011(2)	−0.014(2)	0.015(2)
C(8)	36*f*	0.2893(4)	0.2435(3)	0.12637(8)	0.079(3)	0.067(2)	0.086(3)	0.015(2)	−0.034(2)	−0.004(2)

coordinated by three organic ligands to form a cation, the other Zn(II) is coordinated by four chlorido ligands to form an anion. These anions (see the figure; 30% probability of the displacement ellipsoids; symmetry codes: A: $-y$, $x-y$, z; B: $-x+y$, $-x$, z) are interlinked to form 3D supramolecular networks by one classic intermolecular H-bondings N3—H3A$\cdots$Cl1 ($-y+1/3$, $-x+2/3$, $z+1/6$) (length 2.383(2) Å, angle 163.65(4)°) and two non-classical type of intermolecular H-bond C2—H2A$\cdots$Cl1 (y, $-x+y$, $-z$) and C8—H8A$\cdots$Cl1 ($1/3+x-y$, $2/3-y$, $1/6-z$) (length 2.761(3) Å and 2.782(3) Å, angle 132.3(19)° and 139.9(1)°, respectively).

Acknowledgements: We are grateful to a Project Funded by the Main Research Project of the Natural Science Foundation of the Jiangsu Higher Education Institutions (14KJB150008) and the Major Basic Research Project (11KJA430009), the Major Research Project of the Natural Science Foundation of the Jiangsu Normal University (13XLA04), National Natural Science Foundation of China (NSFC) 21271091, and PAPD of Jiangsu Higher Education Institutions for financial support.

References

1. Fleming, J. S.; Psillakis, E.; Couchman, S. M.; Jeffery, J. C.; McCleverty, J. A.; Ward, M. D.: Complexes of the potentially hexadentate ligand bis{3-[6-(2,2′-bipyridyl)]pyrazol-1-yl} hydroborate with representative s-, p-, d- and f-block metal ions: factors promoting formation of mononuclear or double-helical dinuclear complexes. J. Chem. Soc. Dalton Trans. **27** (1998) 537–543.
2. Zhu, G. Z.; Xing, B. B.; Yang, F. L.; Li, X. L.: Five new mononuclear complexes of 2-(5-methyl-1*H*-pyrazol-3-yl)pyridine: Synthesis, crystalline architectures through supramolecular interactions and spectroscopy. Polyhedron. **81** (2014) 705–714.
3. David, S.; Perkins, R. S.; Fronczek, F. R.; Kasiri, S.; Mandal, S.S.; Srivastava, R.S.: Synthesis, characterization, and anticancer activity of ruthenium-pyrazole complexes. J. Inorg. Biochem. **111** (2012) 33–39.
4. Bonesi, M.; Loizzo, M. R.; Statti, G. A.; Michel, S.; Tillequin, F.; Menichini, F.: The synthesis and Angiotensin Converting Enzyme (ACE) inhibitory activity of chalcones and their pyrazole derivatives. Bioorg. Med. Chem. Lett. **20** (2010) 1990–1993.
5. Rice, C. R.; Onions, S.; Vidal, N.; Wallis, J. D.; Senna, M.-C.; Pilkington, M.; Stoeckli-Evans, H.: The Coordination Chemistry of 3,3′-Diamino-2,2′-bipyridine and Its dication: Exploring the role of the amino groups by X-ray crystallography. Eur. J. Inorg. Chem. **2002** (2002) 1985–1997.
6. Younes, A. H.; Clark, R. J.; Zhu, L.: Zn^{II} and Pb^{II} coordination chemistry of 2,6-bis(1,2,3-triazol-4-yl)pyridine (clickate) and the metal ion-dependent emission of 'clickate'-appended anthracene. Supra. Chem. **24** (2012) 696–706.
7. Xu R.-B.; Xu, X.-Y.; Shi, P.-F.; Wang, D.-Q.; Gao, J.; Yang, X.-J.; Lu, L.-D.; Wang, X.; Xu G.-X.: Synthesis and crystal structure of a new complex [bis(dien)zinc(II)] zinc(II) tetrachloride (dien = Diethylenetriamine). Chinese J. Struct. Chem. **26** (2007) 1441–1444.
8. Sheldrick, G.M.: A short history of SHELX. Acta Cryst. **A64** (2008) 112–122.
9. Brandenburg, K.: DIAMOND. Visual Crystal Structure Information System. Version 2.0 f. Crystal Impact, Bonn, Germany 1998.