Wu-Wu Li*, Min-Yan Zheng and Zun-Ting Zhang

The crystal structure of chlorido(2-(1*H*-pyrazol-3-yl)phenolato- $\kappa^2 N, O$)(2-(1*H*-pyrazol-3-yl)phenol- κN)copper(II), $C_{18}H_{15}ClCuN_4O_2$

Table 1: Data collection and handling.

Crystal:	Columnar, blue
Size:	0.37 × 0.28 × 0.18 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.44 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω -scans
$\theta_{\max}$, completeness:	25.1°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	4350, 3053, 0.031
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2287
$N(\text{param})_{\text{refined}}$:	236
Programs:	Bruker programs [1], SHELX [2]

<https://doi.org/10.1515/ncrs-2018-0086>

Received February 27, 2018; accepted May 8, 2018; available online May 22, 2018

Abstract

$C_{18}H_{15}ClCuN_4O_2$, triclinic, $P\bar{1}$ (no. 2), $a = 8.938(3)$ Å, $b = 9.228(3)$ Å, $c = 12.127(6)$ Å, $\alpha = 105.478(7)^\circ$, $\beta = 110.358(8)^\circ$, $\gamma = 99.727(6)^\circ$, $V = 865.0(6)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0504$, $wR_{\text{ref}}(F^2) = 0.1447$, $T = 296(2)$ K.

CCDC no.: 1842062

The molecular structure of the title crystal structure is shown in the figure. 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

Synthesis of the ligand: To a DMF solution (15 mL) of 2-hydroxy acetophenone (204 mg, 1.5 mmol) was added DMF-DMA (179 mg, 1.5 mmol). The solution was stirred under reflux at 353 K for 1 h. Hydrazine hydrate (80%, 125 mg,

2 mmol) was added to the reaction solution. After completion of the reaction, monitored by TLC, the mixture was quenched with saturated aqueous sodium chloride (20 mL). A yellow precipitate appeared, which was filtered and washed with water and hexane. The product was dried under vacuum and a yellow solid was obtained (yield 88.5%). **Synthesis of the copper(II) complex:** To a stirred solution of 2-(1*H*-pyrazol-3-yl)phenol (480 mg, 3.0 mmol) in ethanol (8 mL) was added $CuCl_2 \cdot 2H_2O$ (256 mg, 1.5 mmol) in ethanol (4 mL) at room temperature. The resultant blue solution was allowed to evaporate at room temperature in the dark for about 5 days. Blue columnar crystals were obtained.

Experimental details

Absorption corrections were applied using a multi-scan program. The hydrogen atoms were placed at calculated positions and refined as riding atoms with fixed isotropic displacement parameters.

Discussion

Many pyrazole derivatives are known to exhibit a wide range of biological properties such as inhibitor of CDK2 (cyclin dependent kinase 2), good activity against a range of human tumor cell lines [3], HIV-1 integrase inhibitors [4] and CB1 (cannabinoid type 1) receptor-ligand [5]. Meanwhile, pyrazole and its derivatives exhibits the ability to coordinate to metals and participate in hydrogen bonding [6–8]. Coordination compound of pyrazole-based ligands have potentially beneficial biological activities, viz. antimicrobial, anticancer,

*Corresponding author: Wu-Wu Li, College of Chemistry and Chemical Engineering, Xianyang Normal University, Xianyang 712000, P.R. China, e-mail: langyuan2012@126.com

Min-Yan Zheng: College of Chemistry and Chemical Engineering, Xianyang Normal University, Xianyang 712000, P.R. China

Zun-Ting Zhang: School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an 710062, P.R. 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}
Cu1	0.10737(6)	0.63634(6)	0.46792(5)	0.0392(2)
Cl1	0.17004(15)	0.90584(13)	0.54930(12)	0.0528(3)
N1	0.3223(4)	0.6418(4)	0.5929(3)	0.0425(9)
N2	0.3697(4)	0.5088(4)	0.5869(3)	0.0396(9)
H2B	0.311282	0.418704	0.529577	0.048*
N3	−0.0830(4)	0.6232(4)	0.3207(3)	0.0409(9)
N4	−0.1404(5)	0.7453(4)	0.3053(4)	0.0524(10)
H4	−0.101634	0.838429	0.360796	0.063*
O1	0.3649(4)	0.2070(3)	0.5347(3)	0.0531(9)
H1	0.318964	0.113934	0.516838	0.080*
O2	0.0568(4)	0.4110(3)	0.4046(3)	0.0444(7)
C1	0.4448(6)	0.7518(5)	0.6943(5)	0.0576(14)
H1A	0.446702	0.856347	0.724076	0.069*
C2	0.5688(6)	0.6901(5)	0.7494(5)	0.0562(14)
H2	0.668022	0.744885	0.820022	0.067*
C3	0.5188(5)	0.5336(5)	0.6808(4)	0.0419(11)
C4	0.5973(5)	0.4099(5)	0.7002(4)	0.0413(11)
C5	0.7562(6)	0.4533(6)	0.7970(5)	0.0522(12)
H5	0.811845	0.559175	0.842812	0.063*
C6	0.8310(6)	0.3433(7)	0.8254(5)	0.0620(15)
H6	0.936969	0.374558	0.889974	0.074*
C7	0.7501(6)	0.1853(6)	0.7586(5)	0.0601(14)
H7	0.800750	0.110328	0.779286	0.072*
C8	0.5944(6)	0.1391(6)	0.6614(5)	0.0538(13)
H8	0.540134	0.032984	0.615313	0.065*
C9	0.5194(5)	0.2514(5)	0.6330(4)	0.0419(11)
C10	−0.2658(7)	0.7026(6)	0.1923(5)	0.0685(16)
H10	−0.325834	0.766657	0.161122	0.082*
C11	−0.2894(6)	0.5497(6)	0.1317(5)	0.0649(15)
H11	−0.367498	0.488777	0.050589	0.078*
C12	−0.1743(5)	0.5001(5)	0.2137(4)	0.0426(11)
C13	−0.1416(5)	0.3491(5)	0.1922(4)	0.0417(11)
C14	−0.2283(7)	0.2321(6)	0.0715(5)	0.0648(15)
H14	−0.308218	0.253062	0.009389	0.078*
C15	−0.1993(8)	0.0908(6)	0.0431(5)	0.0787(19)
H15	−0.258843	0.016411	−0.037400	0.094*
C16	−0.0811(7)	0.0565(6)	0.1338(5)	0.0658(16)
H16	−0.060458	−0.040535	0.113984	0.079*
C17	0.0064(6)	0.1665(5)	0.2539(5)	0.0492(12)
H17	0.086365	0.143266	0.314379	0.059*
C18	−0.0247(5)	0.3134(5)	0.2854(4)	0.0418(11)

ACE (angiotensin-converting-enzyme) inhibition, and anti-inflammatory agents [9–11].

The crystal structure of the title compound comprises of a neutral 2-(1*H*-pyrazol-3-yl)phenol ligand, a chloride and a 2-(1*H*-pyrazol-3-yl)phenolate ligand, and Cu(II). As shown in the figure, each Cu(II) is coordinated by two N atoms and one oxygen atom (O2) from two ligands and one chlorine atom, displaying a distorted square planar coordination geometry. Bond angle sum of coordination bonds around Cu(II) (O2–Cu1–N3 = 89.53°, Cl1–Cu1–N3 = 91.73°,

Cl1–Cu1–N1 = 91.19° and O2–Cu1–N1 = 87.75°) is 360.2°. In title compound, π – π stacking links adjacent molecules. There are some hydrogen bonds: O1–H1...Cl1ⁱ and N4–H4...Cl1ⁱⁱ. symmetry code: (i) $x, -1 + y, z$; (ii) $-x, 2 - y, 1 - z$.

Acknowledgements: This research was supported by Youth Backbone Teachers Project funded by Xianyang Normal University (XSYGG201606), Scientific Research Program funded by Shaanxi Provincial Education Department (16JK1822), Natural Science Basic Research Plan funded by Shaanxi Province of China (2016JM5024), Science and Technology Projects of Xianyang City (2017k02–19), University Students Research and Innovation Training Program of Xianyang Normal University (2017060 and 201710722003) and University Students Research and Innovation Training Program of Shaanxi Province (2490).

References

1. Bruker. APEX2 and SAINT. Bruker AXS Inc., Madison, WI, USA (2012).
2. Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr.* **C71** (2015) 3–8.
3. Wyatt, P. G.; Woodhead, A. J.; Berdini, V.; Boulstridge, J. A.; Carr, M. G.; Cross, D. M.; Davis, D. J.; Devine, L. A.; Early, T. R.; Feltell, R. E.; Lewis, E. J.; Mcmenamin, R. L.; Navarro, E. F.; O'Brien, M. A.; O'Reilly, M.; Reule, M.; Saxty, G.; Seavers, L. C.; Smith, D. M.; Squires, M. S.; Trewartha, G.; Walker, M. T.; Woolford, A. J.: Identification of *N*-(4-piperidiny)-4-(2,6-dichlorobenzoylamino)-1*H*-pyrazole-3-carboxamide (AT7519); a novel cyclin dependent kinase inhibitor using fragment-based X-ray crystallography and structure based drug design. *J. Med. Chem.* **51** (2008) 4986–4999.
4. Langford, H. M.; Williams, P. D.; Homnick, C. F.; Acca, J. P.; Felock, P. J.; Stillmock, K. A.; Witmer, M. V.; Hazuda, D. J.; Gabryelski, L. J.; Schleif, W. A.: Design and synthesis of substituted 4-oxo-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyrazine-2-carboxamides, novel HIV-1 integrase inhibitors. *Bioorg. Med. Chem. Lett.* **18** (2008) 721–725.
5. Donohue, S. R.; Dannals, R. F.; Halldin, C.; Pike, V. W.: *N*-(4-cyanotetrahydro-2*H*-pyran-4-yl) and *N*-(1-cyanocyclohexyl) derivatives of 1,5-diarylpyrazole-3-carboxamides showing high affinity for 18 kDa translocator protein and/or cannabinoid receptors. *J. Med. Chem.* **54** (2011) 2961–2970.
6. Foces-Foces, C.; Echevarria, A.; Jagerovic, N.; Alkorta, I.; Elguero, J.; Langer, U.; Klein, O.; Minguet-Bonvehí, M.; Limbach, H. H.: A solid-state NMR, X-ray diffraction, and ab initio computational study of hydrogen-bond structure and dynamics of pyrazole-4-carboxylic acid chains. *J. Am. Chem. Soc.* **123** (2001) 7898–7906.
7. García-Pacios, V.; Arroyo, M.; Antón, N.; Miguel, D.; Villafañe, F.: Non-covalent interactions at bis(pyrazole) silver(i) or -gold(i) cations. *Dalton Trans.* **38** (2009) 2135–2141.
8. Han, W.; Cheng, M. L.; Liu, Q.; Wang, L. D.; Wu, Y. J.: Syntheses, crystal structures and electrochemical properties of

- cobalt and nickel complexes based on 5-methyl-1*H*-pyrazole-3-carboxylic acid ligand. *Chin. J. Inorg. Chem.* **28** (2012) 1997–2004.
9. Saha, N. C.; Biswas, C.; Ghorai, A.; Ghosh, U.; Seth, S. K.; Kar, T.: Synthesis, structural characterisation and cytotoxicity of new iron(III) complexes with pyrazolyl thiosemicabazones. *Polyhedron* **34** (2012) 1–12.
10. Sobiesiak, M.; Lorenz, I. P.; Mayer, P.; Woźniczka, M.; Kufelnicki, A.; Krajewska, U.; Rozalski, M.; Budzisz, E.: Synthesis, X-ray structure and cytotoxic effect of nickel(II) complexes with pyrazole ligands. *Eur. J. Med. Chem.* **46** (2011) 5917–5926.
11. Mandal, S.; Sadhukhan, R.; Ghosh, U.; Mandal, S.; Saha, M.; Butcher, R. J.; Saha, N. C.: Synthesis and characterization of two Cu(II) complexes with a new pyrazole-based schiff base ligand: crystallography, DNA interaction and antimicrobial activity of Ni(II) and Cu(II) complexes. *J. Coord. Chem.* **69** (2016) 1618–1634.