# ORIGINAL PAPER

# Synthesis, Crystal Structures and Properties of Two Copper (II) Complexes with Pyridazine Derivative Ligand

Xiu-rong Li $\cdot$ Zhi-hui Zhang  $\cdot$ Xiu-feng Liu $\cdot$ Hong Gao $\cdot$ Xiang-nan Zhang  $\cdot$ Zhi-jin Fan

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Abstract Two new complexes,  $[Cu(L)_2(CH_3OH)] \cdot (ClO_4)_2$ (1) and  $[Cu(L)_2(H_2O)] \cdot (NO_3)_2$  (2), have been synthesized and their crystal structures have been determined by X-ray analysis, where L = 3-(3,5-bimethylpyrazole-yl)-6-chloropyridazine]. The complex 1 crystallizes in the monoclinic, space group C2/c, and the coordination configuration of copper (II) is better described as trigonal pyramidal geometry with four N atoms from L and one Oimethanol The coordination configuration of 2 is quite similar to that of 1except Owater instead of Omethanol The intermolecular hydrogen bonds link the repeat units and extend the molecules to multinuclear structures in both compounds. The spectral properties of the title compounds have been studied and discussed. Furthermore, the antibacterial activities of the title compounds have been detected, the results indicate that the ligands and two copper(II) complexes exhibit certain fungicidal activities again several bacteria.

**Keywords** 3,5-Dimethylpyrazole · Pyridazine · Copper(II) complex · Crystal structure · Fungicidal activity

## Introduction

The effect of the property of the counter ion on the molecular structures of the metal complexes have been paid attention in construction of crystal engineering [1]. The reasons are: First, the coordination ability of the counter ion can change the configurations of the complexes; second, the non-coordinated bond provided by the counter ion can develop the repeat units to higher-dimension structures; third, the

interaction of the counter ion with the solvent affects on the coordinated configuration of the metal complexes. Pyridazine and its derivatives are the important compounds in synthesis of agricultural chemicals and medicines owing to the biological activities of these compounds [2, 3]. However, pyridazine derivatives are more difficult to prepare because of the poor electron on the pyridazine ring, the substituted group on 3 or 6 sites on pyridazine rings influents on the reactivity of pyridazines [4–7]. Pyrazole derivatives bridging link more than two metal atoms in various coordination models to form multi-nuclear coordination polymers. Diversion pyrazole derivatives have been used in the coordination chemistry and metal organic chemistry areas [8-10]. In order to study the effect of the counter ion on the molecular structure of the copper (II) complexes and to find the new compounds with higher drug activity and simple molecular structure, in this paper, a new ligand contained pyridazine with substituted pyrazole groups and their two copper (II) complexes with various counter ions have been synthesized, and the properties of the title compounds have been studied.

# Experimental

Materials and General Methods

All of the starting materials and solvents were commercially purchased and purified by standard methods prior to use. 3,5-bimethyl-pyrazole is synthesized by the literature method [11]. IR spectra were recorded on a Bruker Vector 22 FT-IR spectrometer with KBr discs. Elemental analysis (C, H, N) were carried out with a Perkin-Elmer 240 analyzer. Electronic spectra were recorded on Shimadzu Uv-265 FW instrument.

X. Li · Z. Zhang (⊠) · X. Liu · H. Gao · X. Zhang · Z. Fan The College of Chemistry, Nankai University, Tianjin 300071, China e-mail: zhangzh67@nankai.edu.cn

Synthesis of the Ligands

The ligand (L) was synthesized referenced the literature method [12]: Metal Na pieces (0.598 g, 0.026 mol) were added carefully to the solution of 3,5-bimethyl-pyrazole (2.5 g, 0.026 mol) in dry THF (75 mL) under N<sub>2</sub> protecting. The reaction mixture was stirring for 30 min, 3,6-bichloropyridazine (3.87 g, 0.026 mol) was added to the reaction mixture mentioned above. The reaction mixture was refluxing for 4 h, it was filtered. The filtrate was recrystallized in methanol to isolate the L, yield: 68.6%. Anal. Calcd for C<sub>9</sub>H<sub>9</sub>N<sub>4</sub>Cl (mol. Wt. 208.5): C, 51.81; H, 4.35; N, 26.85. Found: C, 51.76; H, 4.39; N, 26.80. IR. (KBr pellets, cm<sup>-1</sup>): 3201 m, 3143(s), 3093(m), 3052(m), 2982(m), 2929(m), 1574(m), 1539(m), 1427(s), 1361(m), 1137(m), 1084(s), 972(m), 855(m), 790(m), 742(w), 507(w).

The molecular structure of the ligand L is shown as Chart 1.

Synthesis of  $[Cu(L)_2(CH_3OH)] \cdot (ClO_4)_2$  (1)

A solution of Cu(ClO<sub>4</sub>)<sub>2</sub> · 6H<sub>2</sub>O (0.37 g, 0.1 mmol) in methanol (5 mL) was added dropwise to the methanol solution (5 mL) of L (0.1 mmol), which was continuously stirring for 30 min. The reaction mixture was filtered, and the filtrate was kept to stand for over 3 weeks. The green single crystals of **1** suitable for X-ray analysis were obtained, yield: 60%. IR (KBr pellets, cm<sup>-1</sup>): 3453(br), 3118(w), 1584(m), 1482(m), 1425(s), 1276(w), 1075(s), 835(m), 799(m), 627(m), 523(w). Anal. Calcd for C<sub>19</sub>H<sub>22</sub>Cl<sub>4</sub>CuN<sub>8</sub>O<sub>9</sub>: C, 32.06; H, 3.12; N, 15.74%. Found: C, 32.01; H, 3.16; N, 15.70%.

Synthesis of  $[Cu(L)_2(H_2O)] \cdot (NO_3)_2$  (2)

Running the same procedure as that of **1**, except  $Cu(NO_3)_2 \cdot 3H_2O$  instead of  $Cu(CIO_4)_2 \cdot 6H_2O$ . The blue green single crystals of **2** suitable for X-ray analysis were isolated, yield: 42%. IR. (KBr pellets, cm<sup>-1</sup>): 3460(br), 3096(w), 1626(w), 1583(m), 1478(m), 1425(s), 1382(s), 1209(w), 1161(m), 1122(m), 1074(w), 997(m), 840(m),



Chart 1 The molecular structure of L

799(w). Anal. Calcd for C<sub>18</sub>H<sub>20</sub>Cl<sub>2</sub>CuN<sub>10</sub>O<sub>7</sub>: C, 34.71; H, 3.24; N, 22.49 %. Found: C, 34.67; H, 3.29; N, 22.46%.

# X-ray Crystallography

The crystals of two copper(II) complexes were mounted on a glass fiber, respectively. Determination of the unit cell and data collection were performed using MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å) on a Bruker SMART 1000 diffractometer equipped with a CCD camera. The  $\omega - 2\theta$  scan technique was employed. The structures were solved primarily by direct methods and secondly by Fourier difference techniques and refined using the full-matrix least-squares method. The computations were performed with the SHELXS-97 and the SHELXL-97 programs [13]. All nonhydrogen atoms were refined anisotropically. All the hydrogen atoms were located on the calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. Crystal parameters and structure refinements for the compounds are summarized in Table 1.

#### **Results and Discussion**

Description of the Structures

 $[Cu(L)_2(CH_3OH)] \cdot (ClO_4)_2$  (1). The perspective view of **1** is given in Fig. 1. The selected bond lengths and angles are summarized in Table 2.

From the Fig. 1, it can be seen that the coordination configuration of the Cu(II) atom is best described a trigonal bipyramidal configuration with the bond angles being N(1)- $Cu(1)-O(1) = 100.63^{\circ}$  and  $N(3A)-Cu(1)-O(1) = 130.86^{\circ}$ , which has be tested by Addision  $\tau$  rule [14] ( $\tau = 0.9387$ indicates the configuration is closed the idea trigonal bipyramid). The mean plane is defined by O(1), N(3) and N(3A), N(1) and N(1A) occupy the apical sites with the bond angle N(1)–Cu(1)– $N(1A) = 176.9^{\circ}$ . The total bond angles of  $N(3)-Cu(1)-N(3A) = 128.51^{\circ}$ , N(3)-Cu(1)-O(1) = $100.63^{\circ}$  and N(3A)–Cu(1)–O(1) =  $130.86^{\circ}$  is  $360^{\circ}$ , which is shown that Cu(1) atom is in the mean plane. Two molecules of 1 are linked by the weaker intermolecular action through perchlorate ion in  $\mu$ -O,O model to present a binuclear structure (Fig. 2). The data of the inter-molecular action is summarized in Table 3.

 $[Cu(L)_2(H_2O)] \cdot (NO_3)_2$  (2). The molecular configuration of **2** is quite similar to that of **1** except a H<sub>2</sub>O coordinated instead of CH<sub>3</sub>OH coordinated (Fig. 3), and the selected bond distances and angles are summarized in Table 4. There is weaker interaction between **2** and NO<sub>3</sub><sup>-</sup> ion in the unit cell of **2** (Fig. 4). The Cu(L)<sub>2</sub>(H<sub>2</sub>O)<sup>2+</sup> ions are linked by the intermolecular hydrogen bond to form a

Table 1 Crystallographic data and structures refinements for Complexes 1 and 2  $\,$ 

Complex	1	2
Empirical formula	C19H22Cl4CuN8O9	C <sub>18</sub> H <sub>20</sub> Cl <sub>2</sub> CuN <sub>10</sub> O <sub>7</sub>
Formula weight	711.79	626.88
Temperature (K)	294(2)	294(2)
System, space group	Monoclinic, C2/c	Orthorhombic, Ccc2
a (Á)	2.4082(14)	1.8041(3)
<i>b</i> (Á)	7.672(4)	2.1397(3)
<i>c</i> (Á)	1.8261(10)	6.7417(11)
α (°)	90	90
β (°)	121.592(8)	90
γ (°)	90	90
$V (nm^3)$	2874 (3)	2602.4(7)
Z	4	4
Crystal size (mm <sup>3</sup> )	$0.26 \times 0.24 \times 0.16$	$0.22 \times 0.18 \times 0.14$
$D_{\text{calcd}} \text{ (g cm}^{-3})$	1.645	1.590
$\mu$ (MoK $\alpha$ ) mm <sup>-1</sup>	1.193	1.103
F (000)	1444	1268
$2\theta$ range (°)	2.62-26.55	1.48–26.41
Limiting indices	$\begin{array}{l} -12 \leq h \leq 30, \\ -9 \leq k \leq 9 \leq, \\ -22 \leq l \leq 15 \end{array}$	$\begin{array}{l} -22 \leq h \leq 22, \\ -19 \leq k \leq 26, \\ -7 \leq l \leq 8 \end{array}$
Reflec. collect/uniqu	7863/2965 [R(int) = 0.0339]	7202/2463 [R(int) = 0.0320]
GOF on F <sup>2</sup>	1.030	1.012
Data/restrs./params	2965/110/234	2463/7/175
$R_1$ and $wR_2 [I > 2\sigma(I)]$	$\begin{array}{l} R_1 = 0.0425, \\ wR_2 = 0.1105 \end{array}$	$R_1 = 0.0346,$ $wR_2 = 0.0827$
R indices (all data)	$\begin{array}{l} R_1 = 0.0670, \\ wR_2 = 0.1256 \end{array}$	$\begin{array}{l} R_1 = 0.0500, \\ wR_2 = 0.0900 \end{array}$
Largest diff. Peak hole (e $\acute{A}^{-3}$ )	0.483 and -0.441	0.279 and -0.410

Table 2 The bond length (Å) and bond angle (°) of the complex 1

Bond lengths			
Cu(1)–N(1)	1.957(3)	$Cu(1)-N(1)^a$	1.957(3)
Cu(1)–N(3)	2.053(3)	Cu(1)-N(3) <sup>a</sup>	2.053(3)
Cu(1)–O(1)	2.155(5)	$Cu(1)-O(1)^{a}$	2.155(5)
Bond angles			
N(1)-Cu(1)-N(1) <sup>a</sup>	179.24(16)	N(1)-Cu(1)-N(3)	78.93(10)
N(1) <sup>a</sup> -Cu(1)-N(3)	100.73(10)	N(1)-Cu(1)-N(3) <sup>a</sup>	100.73(10)
$N(1)^{a}$ -Cu(1)-N(3) <sup>a</sup>	78.93(10)	N(3)-Cu(1)-N(3) <sup>a</sup>	128.51(15)
N(1)-Cu(1)-O(1) <sup>a</sup>	93.28(18)	$N(1)^{a}$ -Cu(1)-O(1) <sup>a</sup>	87.45(18)
N(3)-Cu(1)-O(1) <sup>a</sup>	130.86(18)	$N(3)^{a}$ -Cu(1)-O(1) <sup>a</sup>	100.63(17)
N(1)-Cu(1)-O(1)	87.45(18)	N(1) <sup>a</sup> -Cu(1)-O(1)	93.28(18)
N(3)-Cu(1)-O(1)	100.63(17)	N(3) <sup>a</sup> -Cu(1)-O(1)	130.86(17)
O(1) <sup>a</sup> -Cu(1)-O(1)	30.2(3)		

Symmetry transformations used to generate equivalent atoms: <sup>a</sup> -x, y, -z + 1/2

tetra-nuclear structure unit, and the tetra-nuclear structures are extended further to 1D chain supermolecular structure by the intermolecular action as shown in Fig. 5.

In contrast **1** with **2**, it is found that there is competition coordination between  $H_2O$  and  $CH_3OH$  in the same system, the coordinated ability of  $H_2O$  and  $CH_3OH$  might be arise from the various affinity of the counter ions,  $CIO_4^-$  and  $NO_3^-$ , to  $H_2O$  and  $CH_3OH$ . In **1**, methanol molecule coordinates with the Cu (II) atom might be due to the larger affinity of  $CIO_4^-$  to  $H_2O$  than that of  $CIO_4^-$  to  $CH_3OH$ ; while the larger affinity of NO<sub>3</sub> to  $CH_3OH$  than that of  $NO_3^-$  to  $H_2O$  might lead to a  $H_2O$  molecule coordinates with Cu (II) in **2**. It reminds that the affinity of counter ions is one of the factors of the controlling configuration of the complex.



Fig. 1 ORTEP view of the complex 1





Table 3 The data of hydrogen bonds and the inter-molecular action in the complex  $\mathbf{1}$ 

D–H····A	H…A (Å)	D…A (Å)	∠D–H…A (°)
C3AB–H3AB…O2A <sup>a</sup>	2.545	3.354	145.7
C3AA–H3AA…O2B <sup>a</sup>	2.545	3.354	145.7
O5A…O1C <sup>b</sup>		2.563	
O5B…O1C <sup>b</sup>		2.563	

Symmetry codes: <sup>a</sup> 0.5 + x, 1.5 - y, 0.5 + z; <sup>b</sup> 0.5 - x, 0.5 + y, 0.5 - z

Table 4 Selected bond distance (A) and bond angle (°) for 2

Bond lengths				
Cu(1)–N(1)	1.951(3)	Cu(1)-N(1A)	1.951(3)	
Cu(1)–O(1)	1.993(6)	Cu(1)–N(3A)	2.086(3)	
Cu(1)–N(3)	2.086(3)			
Bond angles				
N(1)-Cu(1)-N(1A) <sup>a</sup>	177.2(2)	N(1)-Cu(1)-O(1)	91.42(11)	
N(1A)-Cu(1)-O(1)	91.42(11)	N(1)-Cu(1)-N(3A)	99.93(12)	
N(1A)-Cu(1)-N(3A)	<sup>a</sup> 78.63(11)	O(1)-Cu(1)-N(3A)	119.56(8)	
N(1)-Cu(1)-N(3)	78.64(11)	N(1A)-Cu(1)-N(3)	99.93(12)	
O(1)-Cu(1)-N(3)	119.56(8)	N(3A)-Cu(1)-N(3)	120.88(17)	

Symmetry transformations used to generate equivalent atoms: <sup>a</sup> -x + 2, y, -z + 1/2

## The Spectra Properties of the Complexes

In IR spectra of **1**, the vibration bands of the pyridazine and pyrazole rings are at  $1,574-1,360 \text{ cm}^{-1}$ , a stronger broad peak for O–H bond of methanol at  $3,453 \text{ cm}^{-1}$ . A broad strong peak at 1075 cm<sup>-1</sup> is the contribution of ClO<sub>4</sub>. In the IR spectra of **2**, there is doublet character peaks at 1,425 and  $1,382 \text{ cm}^{-1}$  assigned to that of NO<sub>3</sub> ion [15]. IR spectra are consistent with the results of X-ray analysis.

The electronic spectra and assignments of the title complexes are summarized in Table 5. The strong transferring bands in the ligand have been observed, while the d-d bands of the metal complexes 1 and 2 have not



Fig. 3 ORTEP view of the complex 2



Fig. 4 The weaker hydrogen bond action of adjacent molecules in 2



Fig. 5 The 1D chain linked by the intermolecular hydrogen bond in 2

Table 5 The electronic spectra of the title complexes

Compound	$\lambda_{\rm max} \ (\epsilon/{\rm mol}^{-1} \ {\rm dm}^3 \ {\rm cm}^{-1})$	Assignment [16]
Complex 1	261 (18170)	LMCT
	211 (9200)	$\Pi \rightarrow \Pi$
Complex 2	268 (14600)	LMCT

found, which might be due to it is covered by that of ligands.

## **Biological Activity**

The fungicidal activity of the ligand and the metal complexes has been tested in vitro against *Alternaria solani*, *Gibberella zeae*, *Physalospora piricola*, *Phomaasparagi*, *Cercospora arachidicola* and their relative inhibitory ratio (%) has been determined by using the mycelium growth rate method [17]. After the mycelia grew completely, the diameters of the mycelia have been measured and the inhibition rate is calculated according to the formula:

$$\mathbf{I} = \frac{\overline{\mathbf{D}}\mathbf{1} - \overline{\mathbf{D}}\mathbf{0}}{\overline{\mathbf{D}}\mathbf{1}} \times 100\%$$

In the formula, I is the inhibition rate,  $\overline{D}1$  is the average diameter of mycelia in the blank test, and  $\overline{D}0$  is the average diameter of mycelia in the presence of the compounds.

The inhibition ratio of the compounds at 50  $\mu$ g/cm<sup>3</sup> has been determined, and the experimental results are summarized in Table 6. The screening data indicate that L exhibits certain activity against only *Physalospora piricola*. Both complexes exhibit higher antibacterial activities than that of the ligand, which might be owing to the biological activity of the copper(II) ion [18]. The activity of **2** is better than that of **1**, the relationship of the activity with the molecular structure is being studied.

In summary, two copper(II) complexes,  $[Cu(L)_2 (CH_3OH)] \cdot (ClO_4)_2 \mathbf{1}$  and  $[Cu(L)_2(H_2O)](NO_3)_2 \mathbf{2}$ , have been prepared and characterized. There are hydrogen bond and weaker inter-molecular action to extend further the discrete subunits to a pseudo dimmer in  $\mathbf{1}$  and a tetranuclear structure in  $\mathbf{2}$ , respectively. The spectra properties of the copper(II) complexes have been studied. Moreover, the antibacterial function of the title compounds has been tested and the results indicate that copper complexes exhibit higher activity than that of the ligand due to the biological activity of the copper ion.

#### **Supplementary Material**

The structures data have been deposited with the Cambridge Crystallographic Data-base Center. **CCDC**677872 for **1** and **CCDC** 619411 for **2**.

<b>Table 6</b> Fungicidal activity of the ligand and the title complexes	Compound	Relative Gibberellaz zeae	Inhibitory Alternaria solani	Ratio (%) <sup>a</sup> Cercospora arachidicola	Physalospora piricola	Phoma asparagi
	L	0	0	0	39.7	0
<sup>a</sup> The data is the average of three tested results	1	0	0	12.5	47.1	0
	2	0	23.5	25.0	47.1	0

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