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CRYSTAL STRUCTURES OF COPPER(II) AND ZINC(II) COMPLEXES DERIVED FROM 3-(2-PYRIDYL)PYRAZOLE**X.B. Liu, D.H. Huan, G.H. Cui, L.H. Han**

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Two dinuclear complexes $[\text{Zn}(\mu\text{-L})(\text{NO}_3)(\text{H}_2\text{O})]_2$ (**1**) and $[\text{Cu}_2(\mu\text{-L})_2(\text{HL})_2](\text{NO}_3)_2(\text{C}_{12}\text{H}_8\text{Br}_2)_{0.5} \cdot \text{H}_2\text{O}$ (**2**), (HL = 3-(2-pyridyl)pyrazole, $\text{C}_{12}\text{H}_8\text{Br}_2$ = 4,4'-dibromobiphenyl) are synthesized under hydrothermal conditions and characterized by elemental analysis and X-ray single crystal diffraction. Crystal data for **1**: triclinic, $P\bar{1}$, $a = 8.8478(7) \text{ \AA}$, $b = 15.0550(11) \text{ \AA}$, $c = 16.4310(12) \text{ \AA}$, $\alpha = 107.588(4)^\circ$, $\beta = 112.498(3)^\circ$, $\gamma = 115.595(3)^\circ$, $V = 2099.8(9) \text{ \AA}^3$, $Z = 2$; for **2**: triclinic, $P\bar{1}$, $a = 7.2870(15) \text{ \AA}$, $b = 8.6840(17) \text{ \AA}$, $c = 9.3290(19) \text{ \AA}$, $\alpha = 107.588(4)^\circ$, $\beta = 112.498(3)^\circ$, $\gamma = 115.595(3)^\circ$, $V = 528.77(18) \text{ \AA}^3$, $Z = 1$. Complex **1** and **2** are both dinuclear structures which are further packed into a 1D supramolecular chain and a 3D supramolecular framework via weak C—H \cdots O hydrogen bond interactions respectively.

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The rational design and synthesis of metal-organic complexes have been attracting great interest in coordination and supramolecular chemistry because of their intricate structures and fascinating topologies as well as their potential applications as new functional materials [1–4]. Intermolecular interactions, especially hydrogen bonding, have proven to be an interesting tool in supramolecular syntheses and manipulation of the final architecture [5]. Nevertheless, it is still tremendously difficult and long-term challenge to construct target complexes with expected structures and properties due to the fact that many other factors, including organic ligands, temperatures, pH values, template, solvents, counter ions and crystallization methods, play significant roles in the self-assembly process [6–9]. The selection of appropriate organic ligands is very pivotal for obtaining target complexes with intriguing structures and properties [10, 11]. Among these ligands, the 3-(2-pyridyl)pyrazole ligand (HL) is a good choice to fabricate various metal-organic complexes due to the following characters. Firstly, it shows an excellent coordination ability with several coordination modes and has been extensively used as a bidentate ligand, quite similar to 2,2'-bipyridyl or 1,10-phenanthroline, and the complexes exhibit various applications in the areas of catalysis, photophysics, information processing, and host-guest chemistry [12]. Moreover, it acts as a tridentate chelate-bridging ligand after deprotonation of the pyrazolyl NH group and further coordination of the pyrazolyl N atom to another metal ion [13]. Secondly, this type of ligands contains both pyrazolyl ring and larger conjugated π system, capable of participating in the hydrogen bonding and π — π stacking interactions, especially in the aspect of packing multinuclear discrete subunits into a high-dimensional supramolecular framework [14]. In the last decades, the combination of HL and metal salts has attracted great interest of researchers [15–17]. In this work, we report the synthesis and crystal structures of Cu(II)

and Zn(II) complexes based on the 3-(2-pyridyl)pyrazole ligand: $[\text{Zn}(\mu\text{-L})\text{NO}_3(\text{H}_2\text{O})]_2$ (**1**) and $[\text{Cu}_2(\mu\text{-L})_2(\text{HL})_2](\text{NO}_3)_2(\text{C}_{12}\text{H}_8\text{Br}_2)_{0.5}\cdot\text{H}_2\text{O}$ (**2**).

Experimental. Materials and physical measurements. All the solvents and reagents for the synthesis were commercially available and used as received. HL was synthesized according to the literature method [18]. Elemental analyses were taken on a Perkin-Elmer 240C analyzer.

Synthesis of $[\text{Zn}(\mu\text{-L})\text{NO}_3(\text{H}_2\text{O})]_2$ (1**).** A mixture of HL (0.2 mmol, 29 mg), $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (0.2 mmol, 59 mg), ethanol (1 ml), and H_2O (10 ml) was stirred for 0.5 h in air, then the resulting mixture was transferred in a Teflon-lined stainless reactor and heated to 140 °C for 3 days under autogenous pressure and cooled to room temperature at a rate of 10 °C/h. Consequently, the colorless block-shaped crystals suitable for X-ray single crystal diffraction were obtained with a yield of 36.7 % (based on $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$). Anal. calcd. for $\text{C}_{16}\text{H}_{16}\text{Zn}_2\text{N}_8\text{O}_8$ ($M_r = 579.11$) (%): C 33.18, H 2.78, N 19.35. Found (%): C 32.97, H 2.62, N 19.11.

Synthesis of $[\text{Cu}_2(\mu\text{-L})_2(\text{HL})_2](\text{NO}_3)_2(\text{C}_{12}\text{H}_8\text{Br}_2)_{0.5}\cdot\text{H}_2\text{O}$ (2**).** HL (0.2 mmol, 29 mg), $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$ (0.2 mmol, 48 mg), 4,4'-dibromobiphenyl (0.01 mmol, 31 mg), ethanol (3 ml) were added to 12 ml H_2O , subsequently, the mixture was placed in a Teflon-lined stainless reactor and heated to 140 °C for 3 days under autogenous pressure. Finally, the blue block-shaped crystals suitable for X-ray single crystal diffraction were obtained with a yield of 32.7 % (based on $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$). Anal. calcd. for $\text{C}_{38}\text{H}_{30}\text{BrCu}_2\text{N}_{14}\text{O}_7$ ($M_r = 1001.75$) (%): C 45.56, H 3.02, N 19.58. Found (%): C 45.33, H 3.28, N 19.29.

Table 1

Crystal data and structure refinements for complexes **1** and **2**

Complex	1	2
Empirical formula	$\text{C}_{16}\text{H}_{16}\text{Zn}_2\text{N}_8\text{O}_8$	$\text{C}_{38}\text{H}_{30}\text{BrCu}_2\text{N}_{14}\text{O}_7$
Formula weight	579.11	1001.75
<i>T</i> , K	296(2)	296(2)
Wavelength, Å	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions:		
<i>a</i> , <i>b</i> , <i>c</i> , Å	7.28710(15), 8.6840(17), 9.3290(19)	13.381(3), 14.735(4), 15.440(4)
α, β, γ, deg.	112.73(3), 92.48(3), 101.52(3)	107.588(4), 112.498(3), 115.595(3)
<i>V</i> , Å ³	528.77(18)	2099.8(9)
<i>Z</i>	1	2
<i>D</i> _{calc} , g/cm ³	1.819	1.584
Absorption coefficient, mm ⁻¹	2.332	2.030
<i>F</i> (000)	292	1010
Crystal size, mm	0.24×0.23×0.19	0.20×0.16×0.15
θ range, deg.	3.41—25.02	1.72—25.68
<i>h</i> , <i>k</i> , <i>l</i> range	−8 ≤ <i>h</i> ≤ 8, −10 ≤ <i>k</i> ≤ 10, −11 ≤ <i>l</i> ≤ 11	−16 ≤ <i>h</i> ≤ 16, −17 ≤ <i>k</i> ≤ 16, −13 ≤ <i>l</i> ≤ 18
Reflections collected / unique	4453 / 1853	11047 / 7790
Max. and min. transmission	0.6892 and 0.6028	0.8068 and 0.6321
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	1853 / 3 / 154	7790 / 0 / 550
GOOF on <i>F</i> ²	1.033	1.010
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.1117, <i>wR</i> 2 = 0.2242	<i>R</i> 1 = 0.0733, <i>wR</i> 2 = 0.2069
<i>R</i> indices (all data)	<i>R</i> 1 = 0.2029, <i>wR</i> 2 = 0.2703	<i>R</i> 1 = 0.1295, <i>wR</i> 2 = 0.2323
Residual peak and hole., e/Å ³	0.853 and −0.717	0.690 and −0.530

Table 2

Selected bond lengths (Å) and angles (deg.) for complexes **1** and **2**

Parameter	Value	Parameter	Value	Parameter	Value
[Zn(μ-L)(NO ₃)(H ₂ O)] ₂ (1)		[Cu ₂ (μ-L) ₂ (HL) ₂](NO ₃) ₂ (C ₁₂ H ₈ Br ₂) _{0.5} ·H ₂ O (2)			
Zn1—N1	2.029(10)	Cu1—N2	1.962(5)	Cu2—N8	1.969(6)
Zn1—O1W	2.128(9)	Cu1—N9	1.966(6)	Cu2—N3	1.970(6)
Zn1—O1	2.263(9)	Cu1—N5	2.036(5)	Cu2—N11	2.001(6)
N1—Zn1—N2A	101.3(4)	Cu1—N1	2.045(6)	Cu2—N7	2.060(6)
N1—Zn1—O1W	96(4)	Cu1—N4	2.310(6)	Cu2—N10	2.315(7)
N2A—Zn1—O1W	108.1(4)	N2—Cu1—N9	95.2(2)	N8—Cu2—N3	96.5(2)
N1—Zn1—N3A	174.5(4)	N9—Cu1—N5	163.8(2)	N8—Cu2—N11	172.9(2)
N2A—Zn1—N3A	79.2(4)	N9—Cu1—N5	95.4(2)	N3—Cu2—N11	90.6(2)
Zn1—N2A	2.057(10)	N2—Cu1—N1	81.1(2)	N8—Cu2—N7	80.6(2)
Zn1—N3A	2.145(10)	N9—Cu1—N1	155.3(2)	N3—Cu2—N7	168.1(2)
O1W—Zn1—O1	92.2(3)	N5—Cu1—N1	94.1(2)	N11—Cu2—N10	92.4(2)
N3A—Zn1—O1	89.8(4)	N2—Cu1—N4	89.7(2)	N8—Cu2—N10	104.1(2)
O1W—Zn1—N3A	89.0(4)	N9—Cu1—N4	110.5(2)	N3—Cu2—N10	97.6(2)
N1—Zn1—O1	87.7(4)	N5—Cu1—N4	75.1(2)	N11—Cu2—N10	75.1(2)
N2A—Zn1—O1	156.5(4)	N1—Cu1—N4	94.0(2)	N7—Cu2—N10	94.2(2)

Symmetry code for **1**: A: $-x, -y+1, -z+1$.

Syntheses and general methods. Complexes **1** and **2** were prepared by the reaction of copper(II)/zinc(II) salt, HL ligand in the 1:1 molar ratio in the water/alcohol system. The results of elemental analyses for the two complexes were in good agreement with the theoretical requirements of their compositions (X-ray analysis results). 4,4'-dibromobiphenyl was added into the reaction system due to a mistake operation; it was involved in complex **2**. However, without it, the reaction of HL and Cu(NO₃)₂·3H₂O in the same situation did not afford suitable crystals of **2**; 4,4'-dibromobiphenyl is likely to further stabilize the complex **2** crystal packing via a supramolecular interaction.

X-ray crystallography. X-ray single crystal diffraction data for the title complexes were collected on a Bruker Smart 1000 CCD diffractometer with graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å) and ω -2 θ scan mode at 296 K. A semi-empirical absorption correction was applied using the SADABS program [19]. The structures were solved by direct methods using the SHELXS-97 program [20] and refined using SHELXL-97 by the full-matrix least-squares fitting on F^2 [21]. All non-hydrogen atoms were refined anisotropically. In **2**, one water molecule is disordered and the structure was refined by the SQUEEZE routine of the PLATON program [22]. Crystallographic data and experimental details for structural analyses of complexes **1** and **2** are summarized in Table 1. Selected bond lengths and angles are listed in Table 2. All H bonding geometries are given in Table 3. CCDC 1044332-1044333 contains the supplementary crystallographic data. These data can be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk.

Results and discussion. Crystal structure of [Zn(μ-L)(NO₃)(H₂O)]₂ (1**).** The X-ray single crystal diffraction analysis reveals that complex **1** crystallizes in the triclinic, $P\bar{1}$ space group. This zinc compound is isostructural to the copper counterpart [Cu(μ-L)(NO₃)(H₂O)]₂ [23]. As shown in Fig. 1, *a*, the asymmetric unit of complex **1** consists of one independent Zn(II) ion, one deprotonated L ligand, one nitrate anion, and one coordinated water molecule. The Zn(II) ion is five-coordinated by three nitrogen atoms from two L ligands, one oxygen atom from the nitrate anion, and one oxygen atom from the coordinated water molecule to form a distorted square-pyramidal geometry with the

Table 3

Hydrogen bonding geometry (Å, deg.) for complexes **1** and **2**

D—H···A	D—H	H···A	D—A	D—H···A
[Zn(μ -L)(NO ₃)(H ₂ O)] ₂ (1)				
C33—H33···O2B	0.93	2.53	3.326	144
[Cu ₂ (μ -L) ₂ (HL) ₂](NO ₃) ₂ (C ₁₂ H ₈ Br ₂) _{0.5} ·H ₂ O (2)				
C4—H4A···O1A	0.93	2.41	3.253	151
C7—H7···O2A	0.93	2.56	3.473	167
C16—H16···O2B	0.93	2.33	3.237	165
C34—H34···O2C	0.93	2.60	3.510	166

Symmetry code: for **1**: B: $-x, -y+2, -z+1$.Symmetry codes: for **2**: A: $-x+1, -y+1, -z+1$, B: $-x, -y+1, -z+1$, C: $x, y, z-1$.

value $\tau_5 = 0.3$ ($\tau_5 = (\beta - \alpha)/60$; α, β are the two largest of the basic angles, $\tau_5 = 1$ for an ideal trigonal bipyramid, and $\tau_5 = 0$ for an ideal square pyramid) [24]. The three nitrogen atoms of two different L ligands (one pyridine N and two pyrazole N) and one oxygen atom of the nitrate anion contribute to the basal plane at Zn. The apical position is occupied by one oxygen atom the coordinated water molecule. Each Zn atom is displaced by 0.2831 Å from the mean basal plane toward O1W. The Zn—N bond lengths vary from 2.029(10) Å to 2.145(10) Å, and the Zn—O bond distances are 2.263(8) Å (Zn1—O1) and 2.128(9) Å (Zn1—O1W), which are both within acceptable ranges [25, 26]. In complex **1**, L acts as a terdentate chelating/bridging ligand via the deprotonation of the pyrazole NH group.

Two such asymmetric units are connected to construct a six-membered ring containing two Zn(II) ions and two L ligands (Zn1···Zn1A = 3.919 Å, symmetry code for A: $-x, -y+1, -z+1$). The molecules of **1** are linked by intermolecular C33—H33···O2B hydrogen bonds between L ligands and nitrate oxygen atoms (H33···O2B = 2.53 Å, C33—H33···O2B = 144°, symmetry code for B: $-x, -y+2, -z+1$) to construct a 1D supramolecular chain (Fig. 1, *b*). The π — π stacking interactions between the pyridine ring and the neighboring pyrazole ring from different L ligands (Cg1···Cg2B = 3.739 Å, Cg1: N1—N2—C24—C20—C21, Cg2B: N3—C18—C17—C33—C30—C25) further stabilize the crystal packing.

Crystal structure of [Cu₂(μ -L)₂(HL)₂](NO₃)₂(C₁₂H₈Br₂)_{0.5}·H₂O (2**).** Complex **2** also crystallizes in the triclinic, $P\bar{1}$ space group. The asymmetric unit is made of two independent Cu atoms, two HL, and two deprotonated L ligands, two coordinated nitrate anions, and a half of lattice 4,4'-dibromobiphenyl molecule. As illustrated in Fig. 2, each of Cu atoms is coordinated by one oxygen atom from nitrate anions (Cu1—O1 = 2.7784 Å, Cu2—O4 = 2.7544 Å), two nitrogen atoms from two distinct L ligands, and two nitrogen atoms from one HL ligand. The Cu—N bond lengths range from 1.962(5) Å to 2.310(6) Å (for Cu1) and 1.969(6) Å to 2.315(7) Å (for Cu2). Thus, the environment of Cu atoms is best described as a highly distorted octahedral geometry.

In **2** there also exists a binuclear six-membered ring furnished by two L ligands and two HL ligands, and the Cu1···Cu2 distance is 3.8909 Å. Each L1 ligand acts two types of roles, chelating one Cu(II) center and simultaneously bridging another one, showing a terdentate chelating-bridging mode. The distinction from **1** is that L and HL coexist in complex **2**, and a neutral HL ligand coordinated to each Cu(II) center is in a chelating coordination mode. The 3D supramolecular framework is further constructed by weak C—H···O hydrogen bonds (Table 3, H···A: 2.33—2.60 Å; D—H···A: 151—167°).

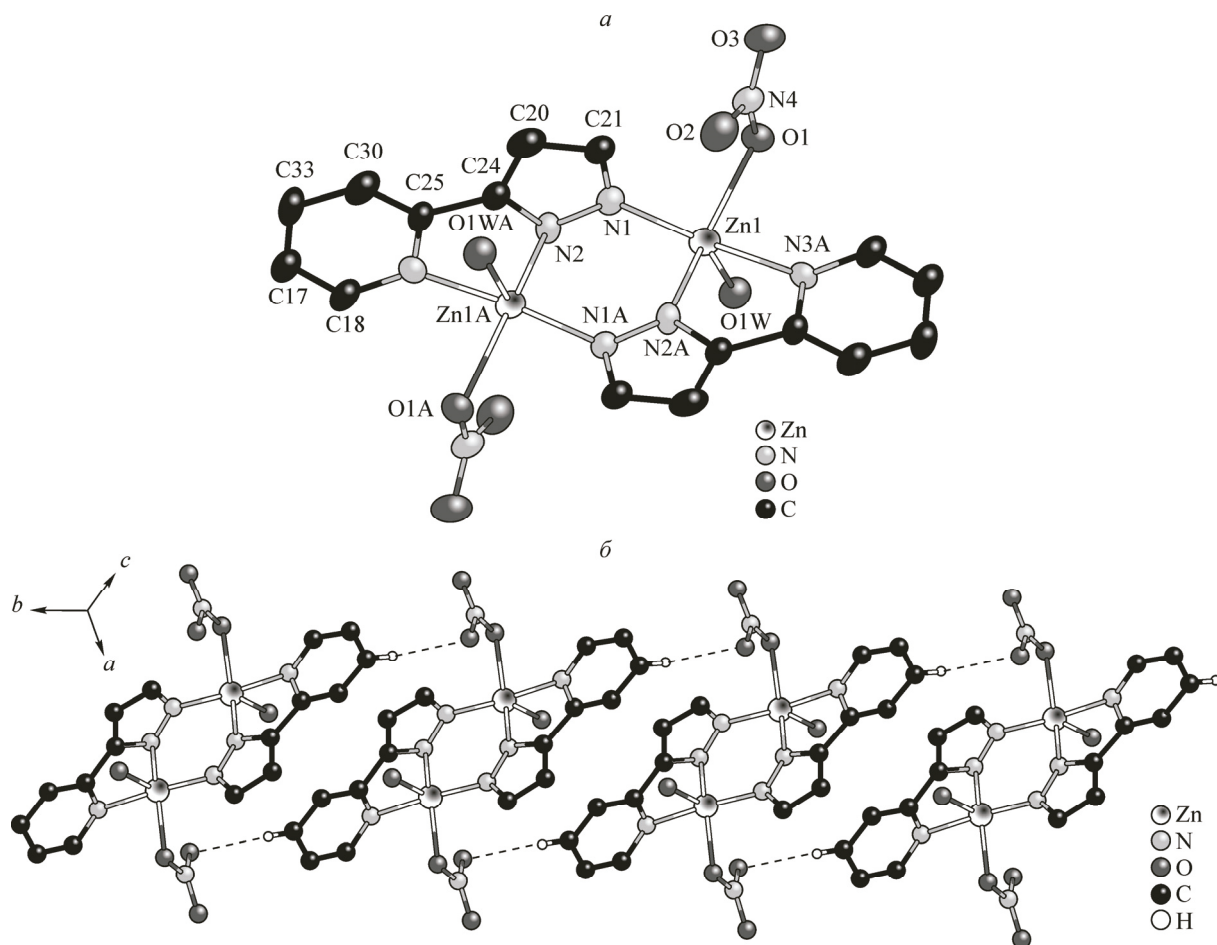


Fig. 1. Coordination environment of the Zn(II) ion in complex 1 (a). All the hydrogen atoms are omitted for clarity (symmetry code 1: A = $-x, -y+1, -z+1$). 1D supramolecular chain constructed from C—H...O hydrogen bond interactions in 1 (b)

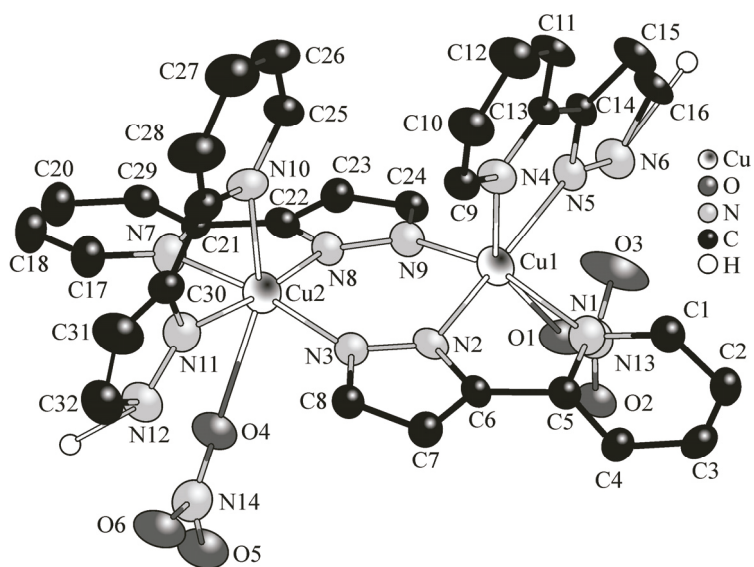


Fig. 2. Coordination environment of the Cu(II) ion in complex 2. All the hydrogen atoms are omitted for clarity (except for the H atom of the pyrazole NH group)

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