

Pseudo-isomeric zinc/copper coordination polymers based on 3-(2-pyridyl)pyrazole-5-carboxylic acid

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ABSTRACT

Reaction of 3-(2-pyridyl)pyrazole-5-carboxylic acid (H_2L) with Zn(II) or Cu(II) perchlorate yielded $[ZnL]_n$ (**1**) and $[CuL]_n$ (**2**) with similar composition. The ligand L^{2-} adopts the same $\mu_3\kappa^5$ coordination mode. The Zn(II) and Cu(II) atom takes square pyramid coordination polyhedron with some discrepancy. Bigger difference in the dimeric secondary building blocks leads to distinct two-dimensional metal-organic frameworks. The Zn(II) complex fluoresces stronger than the free ligand. The Cu(II) polymer displays strong antiferromagnetic intra-dimer exchange and ferromagnetic inter-dimer exchange.

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Transition-metal coordination polymers, especially the two- or three-dimensional metal-organic frameworks (MOFs) have attracted upsurging research interest owing to their diverse architectures and potential applications in such fields as nonlinear optics, catalysis, separation, gas storage, photoluminescence and magnetism [1]. Bridging ligands are essential for constructing an MOF. Semi-rigid chelating ligands containing N and O donor atoms simultaneously are suitable for biting various central metal atoms. The pyrazolecarboxylic acids have been utilized to prepare multinuclear complexes [2] and display variable coordination modes. One unique structural feature for this kind of complexes is the formation of monopyrazole or dipyrazole bridged $M(NN)M$ array or $M(NN)_2M$ ring. Introduction of an azaaryl group at the pyrazole parent ring would be expected to provide more binding sites and lead to structural diversity, but to date only one coordination chemistry study of the azaarylpyrazolecarboxylic acids has been reported [2f]. Here we present the first coordination compounds of 3-(2-pyridyl)pyrazole-5-carboxylic acid (H_2L), $[ZnL]_n$ (**1**) and $[CuL]_n$ (**2**) (see Supplementary material for synthesis and characterization details), which show interesting pseudo-isomeric structures (Scheme 1) and relevant photoluminescent or magnetic properties.

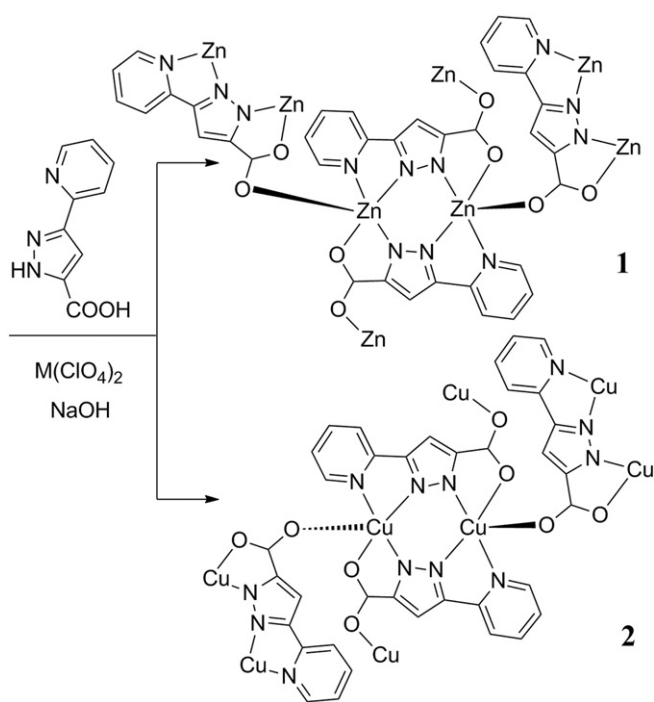
Both **1** and **2** crystallized in monoclinic $P2_1/c$ space group. The main structural features of complex **1** are illustrated in Fig. 1. The asymmetric unit of **1** is consisted of two crystallographically independent Zn(II) cations (Zn1 and Zn2) and two L^{2-} dianions (Fig. 1A). Both Zn1 and Zn2 are five-coordinated by three L^{2-} ligands and form distorted square

pyramids, as judged by the trigonality indexes for Zn1 and Zn2, which are $\tau = 0.176$ and 0.040 respectively ($\tau = (\beta - \alpha) / 60^\circ$, where β and α are the largest two angles in the coordination sphere; $\tau = 0$ for a perfect square pyramid and 1 for a perfect trigonal bipyramid) [3]. In the asymmetric unit Zn1 and Zn2 atoms are doubly bridged by N atoms from two pyrazolyl rings to form a $Zn_2(NN)_2$ six-membered ring, which takes a twist-boat form with the two Zn atoms at the bows. The Zn1–N1–N2–Zn2 and Zn1–N5–N4–Zn2 torsion angles are $5.4(3)$ and $3.4(3)^\circ$, respectively. The Zn1–O₂N₃ and Zn2–O₂N₃ square-pyramidal coordination polyhedra are roughly symmetric about a pseudo-two-fold axis. In the $Zn_2(NN)_2$ ring the Zn1 and Zn2 atoms are separated by $4.1539(7)$ Å, while the nearest inter-ring Zn–Zn separation is $5.6954(9)$ Å. Both Zn1 and Zn2 atoms are remarkably above the square bases as the distances to the base center for Zn1 and Zn2 are $0.6033(3)$ and $0.5890(3)$ Å, respectively. It is notable that the axial Zn1–O3 ($x, -y + 3/2, z - 1/2$) and Zn2–O2 ($-x + 2, y - 1/2, -z + 1/2$) are about 1.95 Å, among the shortest Zn–O lengths in ZnO_2N_3 square pyramids [4] and markedly shorter than the basal Zn–O or Zn–N bonds, which are all larger than 2.02 Å (Table S2). As can be seen in Scheme 1 and Fig. 1A, all the three N and two O atoms in an L^{2-} ligand are involved in ligation to connect three Zn(II) atoms.

The combination of Zn1 and Zn2 square-pyramids could be regarded as the secondary building block (SBU) for crystal packing. The covalent bonding of the SBUs is displayed in Fig. 1B. Every two neighboring SBUs are almost perpendicular and result in a 2D mesh-like layer approximately in the bc plane. The space-filling modeling reveals that there are two types of voids within the layer. The relatively big one has a roughly rectangular filter window sized by 3×2.5 Å, while the smaller

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Scheme 1. Synthesis and structural features of complexes **1** and **2**.

irregular one only allows a ball less than 1 Å through. The offset overlap of the adjacent layers caused by C–H⋯O and C–H⋯N hydrogen bonds (Table S3) prevents formation of open channels in the 3D supramolecular structure.

As regards complex **2**, the asymmetric unit is consisted of one Cu(II) cation and one L^{2-} dianion (Fig. 2A). This unit and its centrosymmetrically related part (symmetric code: $-x + 1, -y + 1, z$) constitute a $[Cu_2L_2]$ dimer. The small trigonality index (0.070) also implies the square pyramidal characteristic for the Cu(II) coordination polyhedron [3], like the Zn(II) ones in **1**. As can be seen in Fig. 2A and Scheme 1, the coordination modes for L^{2-} and the metal atom are very similar in **1** and **2**. The compositions of these two complexes are also analogous. So the two complexes could be viewed as pseudo-isomeric. However, there are some significant structural differences between **1** and **2**. In **2**, the Cu(II) atom is much closer to the square base, only 0.1656(3) Å from the base center. The axial Cu1–O1 ($-x + 1, y - 1/2, -z + 1/2$), 2.2956(16) Å, is much longer than the axial Zn–O distances in **1** despite the close radius of Zn(II) and Cu(II). In contrast, the equatorial coordination bonds in **2**, 1.9192(19) to 2.0229(18) Å, are shorter in general than the corresponding ones in **1**. So contrary to **1**, the axial Cu–O is greatly longer than the equatorial Cu–O or Cu–N bonds in **2**. Interestingly, the latter observation is common for the square pyramidal CuO_2N_3 polyhedra with an axial O atom [5].

While the $[Zn_2L_2]$ dimer in **1** is pseudo-two-fold-axis related, the $[Cu_2L_2]$ dimer in **2** is centro-symmetric and the two pyramidal apices (O1 atoms) are aligned to the opposite sides of the square bases. The centro-symmetric $Cu_2(NN)_2$ ring in **2** takes a chair conformation with a small Cu1–N2–N3–Cu1 ($-x + 1, -y + 1, -z$) torsion angle, $-11.8(3)^\circ$. The intra-ring distance between the two Cu(II) atoms is 3.9844(4) Å, shorter than the corresponding Zn⋯Zn distance in **1**, but the nearest inter-ring Cu⋯Cu separation, 5.9115(5) Å, is longer than the corresponding value in **1**. Analogous to **1**, the $[Cu_2L_2]$ dimers are the SBUs in the crystal packing of **2**. They covalently link together to form a rhombus 2D layer approximately in the bc plane, as shown in Fig. 2B. The resulting rhombic cavity is 2.8 Å wide in diameter. The C–H⋯O hydrogen bonds (Table S3) among the SBUs in adjacent layers also result in offset overlap of the adjacent layers, preventing the 3D supramolecular structure from forming open channels.

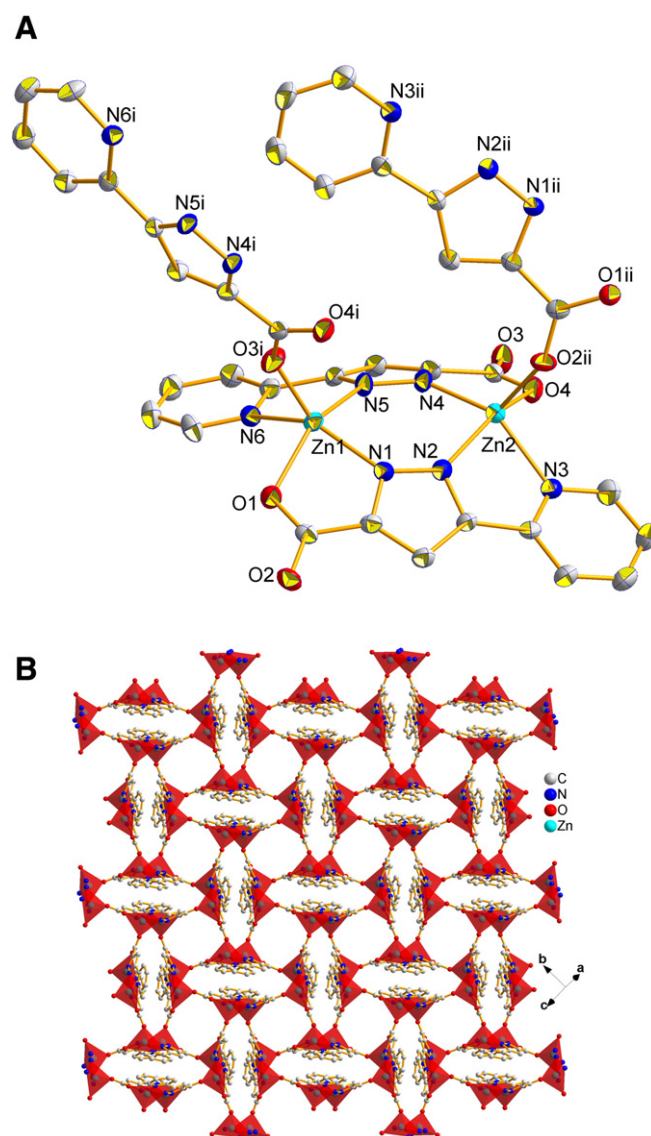


Fig. 1. (A) ORTEP plot (50% thermal ellipsoids) showing coordination environment in **1** with H atoms omitted for clarity. Symmetry codes: (i) $x, -y + 3/2, z - 1/2$; (ii) $-x + 2, y - 1/2, -z + 1/2$. (B) Covalent 2D layer in the crystal of **1** with the coordination polyhedra of Zn(II) shown in red.

In previously reported complexes $[CdI(HL1)]_n$ and $[CdI(HL2)(H_2O)]_n \cdot nH_2O$ [2f], where H_2L1 [5-(3-pyridyl)pyrazole-3-carboxylic acid] and H_2L2 [5-(2-pyrazinyl)pyrazole-3-carboxylic acid] are similar to H_2L but differ at the aryl substituents in the pyrazole moiety, the two ligands are both mono-deprotonated and ligate the Cd(II) atoms by $\mu_3\kappa^4$ and $\mu_2\kappa^3$ coordination modes, respectively. Herein H_2L is di-deprotonated and binds Zn(II) or Cu(II) atoms both by $\mu_3\kappa^5$ mode, contributing to different coordination frameworks from the former two.

Both **1** and **2** are air-stable and insoluble in common solvents. Their powder X-ray diffraction patterns for the as-synthesized crystalline products are in good agreement with the corresponding simulated diffractograms based on the single crystal data (Fig. S3), suggesting good phase purity and allowing bulky physical property studies of these complexes.

The zinc(II) complex (**1**) shows increased photoluminescence compared to the free ligand, as can be seen in Fig. 3. Upon excitation at 290 nm, H_2L emits at 365 nm. For **1** this emission band remains and increases as a shoulder to the main strong peak at 380 nm. The reason is that within the framework of **1** the ligand rigidity is enhanced, thermal

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