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Short communication

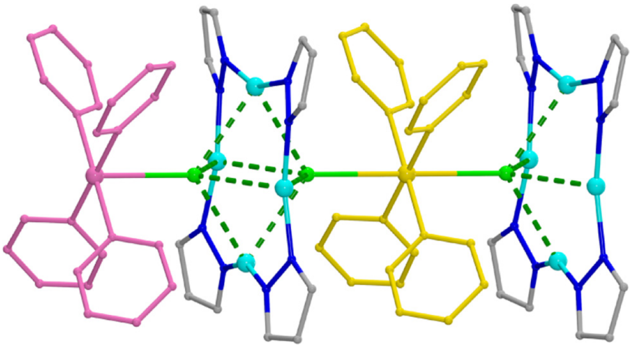
Two new coordination polymers based on a pyridine-pyrazole bifunctional linker: Synthesis, structure and luminescent properties

Wen-Juan Shi*, Chen-Yu Jiang, Li-Na Ma, Xiao-Qing Wang, Lei Hou

Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of the Ministry of Education, College of Chemistry and Materials Science, Northwest University, Xi'an 710069, PR China

GRAPHICAL ABSTRACT

Two new coordination polymers were constructed by a pyridine-pyrazole bifunctional ligand, revealing novel 3D supramolecular frameworks and strong luminescent properties.



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ABSTRACT

The solvothermal reaction of $CdCl_2$ or $CuCl_2$ with a pyridine-pyrazole bifunctional ligand 3,5-diethyl-4-(4-pyridyl)-pyrazole (Hdeppz) under different solvents afforded two coordination polymers $[Cd(Hdeppz)_2(Cl)_2]_n$ (**1**) and $[Cu_4^ICu^{II}(deppz)_4(Cl)_2]_n$ (**2**), respectively. Owing to different coordinated modes of Hdeppz and metal ions, **1** and **2** display different grid layer structures. In **1**, the neutral Hdeppz ligand behaves as a linear linker to connect two Cd^{2+} ions, while **2** contains not only the Y-shaped deppz linker but also the mixed valence of Cu^+ and Cu^{2+} ions. Meanwhile, an uncommon $Cu_4(pz)_4$ metallocyclic unit is formed in **2**, and which further produces an unprecedented $-(Cu^{II}Cl_2Cu^I_4)_n-$ supramolecular chain by Cu···Cl interactions. The strong solid-state blue-green luminescence was also observed in **1**.

Coordination polymers (CPs) due to ordered and designable architectures, versatile topologies and widespread application potentials in many fields have attracted considerable interests of researchers [1,2]. These CPs are assembled from inorganic metal ions/clusters and organic linkers. The various designs and durative constructions focused on these two components have built a wide variety of intriguing frameworks. However, several factors, such as the connectivity, type of coordinated sites, charge of inorganic and organic components as well as the geometry and length of linkers, play a key role in determining the final structures of CPs, therefore it is a rather challenging task to obtain a desired topological CP [3,4].

Profiting from advanced organic synthesis methods, a large number of linkers that contain various coordinated units with functionalized substituent groups have been designed and synthesized to assemble

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* Corresponding author.
E-mail address: swjuan2000@126.com (W.-J. Shi).

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versatile interesting CPs. These linkers mainly include the coordinated groups of carboxylic acid and N-containing pyridine, imidazole, pyrazole, triazole and tetrazole, in which all kinds of carboxylic acid linkers due to easy synthesis has been paid most attention in CP construction [5,6]. Although the abundant coordinated modes of carboxylates generate various frameworks for the same metal ions, but which also brings about a new dilemma to prepare a desired topological CPs, in contrast, pyrazole (Hpz) possesses simple coordination mode. It is most typical that the depronated pz binds two metal ions by two N atoms with a *syn* fashion. So the desired topology of CPs incorporating Hpz can be defined and facilely achieved [7].

In coordination chemistry, Hpz with various substituent groups in 3,5-positions, such as uncoordinated $-CH_3$, $-CF_3$ and $-C_6H_5$ [8–10] as well as coordinated $-COOH$ and $-C_6H_4N$ [11–13], have been widely adopted to prepare complexes. Meanwhile, in some metal-pz systems, two or three Hpz in 4-position are jointed together by phenyl spacers to serve as bridging linkers to construct CPs [14,15]. In contrast, the Hpz with the decorated pyridyl group in 4-position were rarely reported in known complexes though these ligands displayed strong coordination with varied metal ions [16–19]. We are interested in an uncommon pyridine-pyrazole ligand 3,5-diethyl-4-(4-pyridyl)-pyrazole (Hdeppz). As Hdeppz contains a 4-pyridyl group in 4-position of pyrazole, it possesses an unambiguous coordination habit of binding with metal ions through linear or Y-shaped fashion. Meanwhile, the two flexible ethyl groups in Hdeppz can adopt different configurations and thus influence the architectures and properties of CPs.

Ongoing our recent investigations on the coordination behaviors of Hdeppz ligand [20], the reaction of $CdCl_2$ or $CuCl_2$ with Hdeppz at 130 °C in different solvents have afforded the colorless and green crystals of $[Cd(Hdeppz)_2(Cl)_2]_n$ (**1**) and $[Cu_4^{I}Cu^{II}(deppz)_4(Cl)_2]_n$ (**2**) [21], respectively, showing novel three-dimensional (3D) supramolecular frameworks based on different grid layers.

Single-crystal X-ray structural analysis reveals the different layer structures of **1** and **2** [22]. **1** possesses a monoclinic *C*2/*c* space group, and contains half Cd^{2+} ion, one Hdeppz ligand and one Cl^- anionic ligand in the asymmetric unit. The Cd^{2+} ion is located at the *b* axis, and is coordinated by four N atoms (Cd-N = 2.3825(18) and 2.4797(18) Å, Table S1) of two pyridyl and two pyrazolyl groups from four Hdeppz in the equatorial plane as well as two axial positions of Cl^- anions (Cd-Cl = 2.6143(5) Å), giving rise to an octahedral geometry (Fig. 1). Hdeppz is non-deprotonated, in which the pyrazolyl $-NH$ group forms an intramolecular N$-$H$\cdots$Cl hydrogen bond (H$\cdots$Cl = 2.373 Å) with one Cl^- anion around Cd^{2+} centers. One Cd^{2+} ion is connected by four linear Hdeppz to afford a rhombic 4^4 grid layer (Cd$\cdots$Cd = 11.08 × 11.08 $Å^2$) parallel to the ī01 plane (Fig. 2a). The pyridyl and pyrazolyl rings in Hdeppz are nonplanar with a dihedral angle of 51.5°. Two ethyl groups with a *trans* configuration in Hdeppz fill the voids of grid, leading to a nonporous structure of **1**. The neighboring layers are stacked with a staggered fashion along the (101) direction by intermolecular C$-$H$\cdots$Cl hydrogen bonds (H$\cdots$Cl = 3.122 Å) between the pyridyl $-CH$ groups and Cl^- anions to produce a 3D supramolecular framework (Fig. 2b).

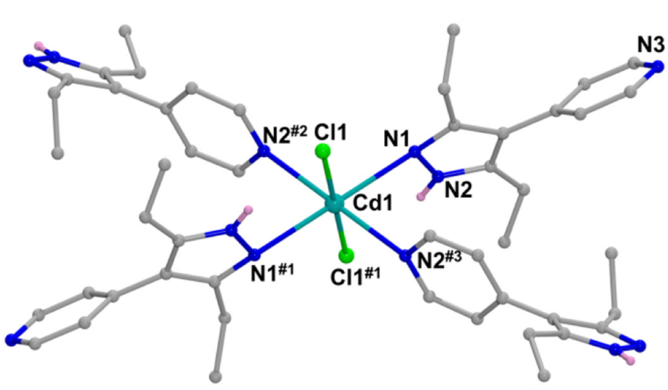

Fig. 1. Coordination environment of Cd^{2+} ions in **1**.

2 crystallizes in a tetragonal *P*4/*nnc* space group, and is composed of two independent copper metal ions with 12.5% and 50% site occupancies, half depronated deppz ligand and one quarter of Cl^- anion in the asymmetric unit. Notably, Cu1 and Cu2 centers reveal +1 and +2 valences, respectively, in which Cu1 is ligated by two pyrazolyl N atoms from two deppz, while Cu2 that resides on a fourfold axis is six-coordinated by four pyridyl N atoms from four deppz and two Cl^- anions (Fig. 3a). The typical linear and octahedral coordination geometries for Cu1 and Cu2 match well with their monovalent and divalent cationic features, respectively. For the divalent Cu2 ion, the axial Cu$-$Cl bond (2.864 Å) is long due to Jahn-Teller Effect. Resembling with **1**, deppz is also nonplanar with a dihedral of 45.2° for two aromatic rings, as well as a *trans* configuration for two ethyl groups. However, distinguishing from **1**, deppz in **2** is depronated, and adopts a Y-shaped coordinated mode to link three metal centers by pyridyl and pyrazolyl groups. In particular, four Cu^+ ions and four pyrazolyl groups connect each other to form an interesting $Cu_4(pz)_4$ metallocyclic unit. Each unit is extended by four pyridyls to produce a layer paralleling to the *ab* plane (Fig. 3b). In the layer, besides the formation of 12-membered $Cu_4(pz)_4$ rings, there also exists a bigger 32-membered ring interconnected by four deppz, two Cu^+ and two Cu^{2+} ions.

It is well known that the assembly of Cu^+ ions and pyrazolates can form various $Cu_n(pz)_n$ metallomacrocycles, but a majority of them were based on the triangular $Cu_3(pz)_3$ cycles [9,17,24–26]. In contrast, $Cu_4(pz)_4$ systems were rarely reported [27–30]. Moreover, in spite of that sporadic $Cu_4(pz)_4$ cyclic complexes were created by Cu^+ ions and pyrazolates with various substituent groups, wherein the $Cu_4(pz)_4$ units form saddle-shaped rings [27–29]. Differently, the $Cu_4(pz)_4$ unit in **2** is unusually coplanar, this unique shape significantly influences the final skeleton of framework. Firstly, four Cu^+ ions with Lewis acidity in $Cu_4(pz)_4$ unit form strong interactions with two Lewis basic Cl atoms coordinated to Cu^{2+} ions in neighboring layers, reflected by the short Cu$\cdots$Cl separations of 2.877 Å, correspondingly, which cause a significant deviation from 180° for the N-Cu-N angle (154.47(15)°, Table S1) around Cu1 atoms. Secondly, the Cu$\cdots$Cl interactions lead to the superposed arrangement of the grids in neighboring layers along the *c* axis, giving rise to a 3D supramolecular framework with 1D channels occupied by ethyl groups (Fig. 3c). Thirdly, an interesting supramolecular $-(Cu^{II}Cl_2Cu^{I}_4)_n-$ chain was also generated between copper metal ions and Cl atoms (Fig. 3d), which was previously unreported and also significantly differed from the known Cu$\cdots$Cl/Br/I triple-decker trimers in which two halide atoms were sandwiched by three $Cu_4(pz)_4$ units in $\{(MX)_2[Cu_4(NO_2\text{-}pz)_4]_3\}$ (M = Na/K, X = Cl/Br/I) [30]. Topologically, regarding the $Cu_4(pz)_4$ unit in **2** as a 6-connected node, **2** forms a typical uninodal 6-connected pcu net with the point symbol of $4^{12}\cdot6^3$.

The mixed valences of Cu^+ and Cu^{2+} in **2** were further confirmed by X-ray photoelectron spectroscopy (XPS). In the Cu 2p3/2 XPS spectrum of **2**, the higher binding energy (BE) of 933.5 eV is assigned to Cu^{2+} ions, accompanied by the characteristic Cu^{2+} satellite peak with a BE of 943.4 eV (Fig. S1a) [31]. The lower BE of 931.6 eV indicates the existence of Cu^+ ions, meanwhile, Auger Cu LMM spectrum with a BE of 570.5 eV further demonstrated the presence of Cu^+ ions (Fig. S1b) [32].

Although employing the same chloride anionic salts and similar reaction conditions, **1** and **2** reveal completely different structures due to the different properties of Cd^{2+} and Cu^{2+} ions. As is known, under the solvothermal conditions the Cu^{2+} ions are not stable and can be easily reduced to Cu^+ ions by N-containing ligands. The rich-N atoms of Hdeppz and CH_3CN solvents provide a necessary condition to form Cu^+ ions from Cu^{2+} ions during the formation of **2**. Furthermore, the strong coordination ability of pyrazolate with Cu^+ ions contributes to the formation of $Cu_4(pz)_4$ rings in **2**, in which the Cu^+ ion is two-coordinated. These low coordinated numbers of Cu^+ ions also lead to the formation of uncommon $-(Cu^{II}Cl_2Cu^{I}_4)_n-$ supramolecular chains by Cu$\cdots$Cl interactions in **2**. However, the Cd^{2+} ion not only has very