

Short communication

Temperature/anion-dependent self-assembly of Co(II) coordination polymers based on a heterotopic imidazole-tetrazole-bifunctional ligand: Structures and magnetic properties



Song-Liang Cai, Yu Huang, Yong Gao, Jun Fan, Sheng-Run Zheng*, Wei-Guang Zhang

School of Chemistry and Environment, South China Normal University, Guangzhou 510006, PR China

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ABSTRACT

Reactions of Co(II) with 5-(3-(1H-imidazol-1-yl)phenyl)-1H-tetrazolate (HIPT) resulted in three Co(II) coordination polymers (CPs), namely, $\{[Co(IPT)_2(H_2O)_2] \cdot 2H_2O\}_n$ (**1**), $[Co(IPT)_2]_n$ (**2**), and $\{[Co_3(IPT)_2(CH_3COO)_2(OH)_2(H_2O)_2] \cdot 2H_2O\}_n$ (**3**). Compound **1** that obtained from $CoCl_2 \cdot 6H_2O$ at 120 °C is a 2D network based on Co(II) ions and μ_2 -IPT[−] ligands. Compound **2** that obtained from $CoCl_2 \cdot 6H_2O$ at 170 °C exhibits a 3D framework based on linear trinuclear Co(II) SBUs and features a **pcu** network topology. Compound **3**, which obtained by using $Co(Ac)_2$ as salt, displays a 2D network based on 1D SBUs. The structures of compounds **1–3** are dependent on the temperatures and inorganic anions. The magnetic properties of compounds **2–3** were also explored.

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Coordination polymers (CPs) have been attracted much attention due to their intriguing structures and diversity potential applications [1–4]. By choosing suitable metal ions and organic linkers, the possibility for obtaining such new metal-organic materials can be seen as numerous. In order to select special CPs with desirable properties from so many CPs, the coordination chemistry of organic ligands toward metal ions still need extensive explored. Ditopic ligands are one type of the most frequently used ligand, which are composed of two terminal coordination groups and a spacer between the groups. The type and number of donor atoms and the length and flexible/rigid of spacers play important role in the coordination behavior of organic ligand. Most N-donor ditopic ligands possess same terminal groups, while those with different N-donor terminal groups, are relatively less explored.

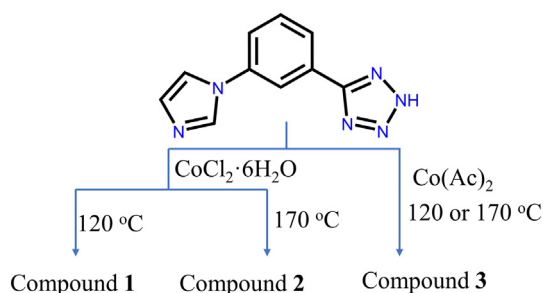
Tetrazolyl ligands have been widely used since the in situ syntheses of tetrazole ring from nitrile precursor were found [5–10]. Tetrazolyl group take on versatile coordination modes that ranging from monodentate to tetradentate have been used to assemble lots of well-defined multinuclear secondary building blocks in the related CPs [11–14]. On the other hand, imidazolyl ligands that display a rather simple coordination mode and relatively strong coordination ability were suitable to construct CPs based on simple inorganic nodes and organic linkers [15–17]. These two rings have similar size and geometry, but they exhibit very different coordination chemistry. Thus, it is reasonable to think that the combination of such two terminal groups in one ligand

may take advantages of both them and is beneficial for constructing new interesting CPs. However, although the pyridyl-tetrazole ligands are well studied [18–20], imidazole-tetrazole ligands are relatively less explored [21–24]. Recently, we have been firstly used 5-(3-(1H-imidazol-1-yl)phenyl)-1H-tetrazolate (HIPT) as organic ligand to react with Cd(II) ion and obtained series of CPs that exhibit interesting structural transformation behaviors [25]. As a continuous exploration, in the present work, the Co-center CPs based on HIPT were constructed. Their structural diversity is dependent on temperature and anions, as shown in Scheme 1. The crystal structures and magnetic properties were investigated.

All the compounds are synthesized under hydrothermal conditions. Reaction of $CoCl_2 \cdot 6H_2O$ with HIPT at 120 °C result in compound **1**. Compound **1** crystallizes in the monoclinic system with space group $P2(1)/c$. The asymmetric unit of **1** consists of half of Co(II) ion, one IPT[−] ligand, one coordinated and one uncoordinated water molecule. Each Co(II) is surrounded by four nitrogen atoms from four tetrazolyl nitrogen (N_{Tz}) and two pyridyl nitrogen (N_{Py}) atoms, as well as two oxygen atoms from two coordination water molecules (Fig. 1a). The IPT[−] ligand adopts a μ_2 -coordination mode, in which the tetrazolyl group only use one N atom binds to one Co(II) ion and the imidazolyl group binds to another Co(II) ion. The combination of IPT[−] ligands and Co(II) ions lead to a 2D network with (4,4) topology (Fig. 1b). Although the coordination behaviors of tetrazolyl and imidazolyl are similar, they play different roles in the formation of hydrogen bonds. The uncoordinated N atoms on tetrazolyl group act as effective hydrogen bonding acceptors that form O—H...N hydrogen bonds with uncoordinated water molecules

* Corresponding author.

E-mail address: zhengsr@sncu.edu.cn (S.-R. Zheng).



Scheme 1. The reactions between HIPT and Co(II) ion.

(Fig. 1c). However, imidazolyl group are not involving in hydrogen bonding formation. Simultaneously, the uncoordinated water molecule are form O—H...N hydrogen bonds with coordinated water molecule. Thus, the combination of O—H...N and O—H...O hydrogen bonds link the 2D networks into 3D supramolecular framework, as shown in Fig. 1d.

Compound **2** was obtained when the temperature is increasing to 170 °C. The X-ray diffraction analyses reveal that there are two independent Co(II) ions with occupancy of 1/6 (for Co1) and 1/3 (for Co2), respectively, and one IPT[−] ligand in the asymmetrical unit. As shown in Fig. 2a, the Co1 is six-coordinated by six N_{tz} atoms, whereas Co2 is six-coordinated by three N_{tz} and three N_{im} atoms. Different from that in compound **1**, the IPT[−] ligands in **2** adopt μ_2 -coordination mode where the tetrazolyl and imidazolyl exhibit different coordination modes. The tetrazolyl group use its N2 and N3 atoms connects to two Co(II) ions, whereas the imidazolyl group connects to another Co(II) ion. Three Co(II) ions are connected by six tetrazolyl groups to form a linear trinuclear SBU [26], as shown in Fig. 2b. Such trinuclear SBUs are further connected by Co—N bond between Co(II) ion and imidazolyl N atom, give rise to a complicated 3D framework, as shown in Fig. 2c. On topological view, the trinuclear SBU that connects to six adjacent SBUs can

be seen as 6-connected node, thus the overall framework can be seen as a 6-connected **pcu** network topology [27], as shown in Fig. 2d.

Compound **3** was obtained when using Co(CH₃COOH)₂·4H₂O as salt. In compound **3**, there are one and a half of Co(II) ions, a IPT[−] ligand, one CH₃COO[−], one OH[−], one coordinated and one uncoordinated water molecules. As shown in Fig. 3a, Co1 is six-coordinated by one tetrazolyl N atom and one imidazolyl N atom, two O atoms from two OH[−], one O atom from coordinated water molecule, and one O atom from CH₃COO[−]. Co2 is six-coordinated by two tetrazolyl N atoms, as well as four O atoms from four OH[−]. The two adjacent Co1 ions are linked by two OH[−] anions, whereas the adjacent Co1 and Co2 are linked by one OH[−] anion, one tetrazolyl group, as well as one CH₃COO[−] group. Thus, a 1D SBU composed of Co(II) ions are formed, as shown in Fig. 3b. The coordination bond between Co1 and imidazolyl N atom link the 1D SBUs to a 2D network extending along *ac* plane, as shown in Fig. 3c. The O—H...O hydrogen bonds between coordinated water molecules and uncoordinated water molecules were formed between the 2D networks, which stabilized the whole 3D supramolecular framework, as shown in Fig. 3d.

From the above discussion, we can see that the structural diversity of compounds **1–3** is largely dependent on the inorganic anions [28–29] and temperature [30–31]. When using Cl[−] anion, the anion is not observed in the structures and compounds **1–2** were obtained at 120 °C and 170 °C, respectively. This means that the temperature may play a more vital role in the assemble process than inorganic anions. At relatively lower temperature (120 °C), the water molecules tend to coordinate to Co(II) ion, thus generate lower-dimensional 2D network of compound **1**. When at higher temperature (170 °C), the water molecule is relatively hard to coordinate, thus the 3D framework of compound **2** may be favor. When using CH₃COO[−] anion, the anion is involved in coordination due to the strong coordination ability of carboxylate group, thus produce a structure that totally different from that in compounds **1–2**. In addition, the structure of compound **3** retained not matter what the temperatures used in our experimental conditions.

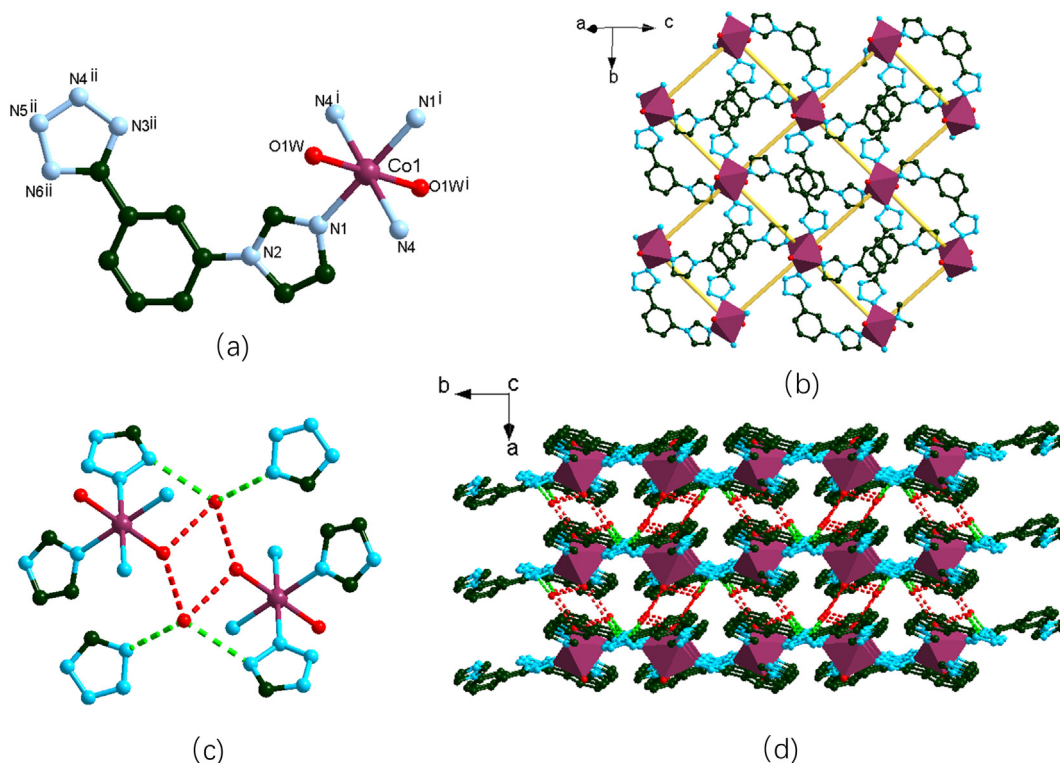


Fig. 1. (a) The coordination environment of Co(II) ion in compound **1**. Symmetric code: (i) $-x, -1 - y, 1 - z$; (ii) $-x, -1/2 + y, 1/2 - z$. (b) The 2D network in compound **1**. (c) The hydrogen bonds in **1**. (d) The 3D supramolecular framework in compound **1**.

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