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Short communication

Solvent-controlled synthesis and reversible dynamic structural conversions of a series of iron(II) coordination complexes

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ABSTRACT

In this work, a versatile multi-dentate 1,2-bis(pyridin-4-ylmethylene)hydrazine (L) ligand has been employed to construct three novel iron(II) coordination complexes, $[Fe(L)_2(NCS)_2(H_2O)_2]\cdot 2H_2O$ (**1**), $[Fe(L)(NCS)_2(H_2O)_2]$ (**2**) and $\{[Fe(L)_2(NCS)_2]\cdot 2CH_3OH\}_n$ (**3**) (NH_4NCS = ammonium thiocyanate), which can be isolated under similar synthetic conditions, only different molar ratio of metal/ligand or different solvent systems are used. **1** is a mono-nuclear iron(II) coordination complex, and **2** is a one-dimensional (1D) iron(II) coordination complex, while **3** is a 2D micro-porous iron(II) framework with the channel dimensionality of 13.936(3) Å × 13.936(3) Å. PXRD patterns also confirm the purity of the bulky samples of **1**–**3**. For **1**–**3**, it represents the first example of solvent-induced drastic reversible dynamic conformation between different dimensional iron(II) coordination complexes **1** (0D), **2** (1D) and **3** (2D) (for **1**: water; for **2**: benzene; for **3**: methanol/acetone/acetonitrile), which are unambiguously confirmed by PXRD characterizations. Variable-temperature magnetic susceptibility data of **2**–**3** have been recorded in the 2–300 K temperature range, indicating weak antiferromagnetic interactions.

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In recent years, much work has been focused on the design and construction of coordination polymers with unusual structures and interesting properties such as optics, redox activity and magnetism owing to their potential as special functional materials [1,2]. The appropriate design of organic ligands is undoubtedly a key element in assembling coordination polymers with fantastic topologies [3]. Although a variety of metal coordination frameworks with beautiful topologies and interesting properties have been synthesized to date, rational control in the construction of polymeric networks remains a great challenge in crystal engineering [4]. In pursuit of synthesizing pre-designed architectures in general and dynamic MOFs in particular, neutral N-heterocycle ligands have shown the importance in the domain of dynamic MOFs both in terms of understanding structural dynamism and probing structure-property correlation [5,6]. For instance, the porous coordination polymers of 4,4′-bipyridine have relatively flexible frameworks based on the single site-binding of neutral pyridyl groups [7].

On the other hand, most coordination frameworks can be obtained from the solvent media [8]. Thus, the choice of solvents is an important parameter in the phase-pure synthesis of crystalline materials and is key to construct various diverse coordination networks. For example, the solvent-induced breathing effects of porous MOFs have been demonstrated, in which the sizes of solvents incorporated within the channels of coordination frameworks do play a key role in featuring "3D expanding and shrinking grids" networks [9,10]. These dynamic processes generally involve the formation and breakage of covalent or noncovalent interactions, by regulating the local binding features of individual ingredients and the overall structural extension/stacking in crystalline state. However it is noted that the examples of reversible dynamic conformation between different dimensional frameworks induced by different solvent systems are still scarcely reported [11].

We have been interested in constructing novel coordination polymers with N-heterocycle ligands [12]. In this work, a versatile multidentate 1,2-bis(pyridin-4-ylmethylene)hydrazine (L) ligand has been employed. Three iron(II) coordination complexes, namely $[Fe(L)_2(NCS)_2(H_2O)_2]\cdot 2H_2O$ (**1**), $[Fe(L)(NCS)_2(H_2O)_2]$ (**2**) and $\{[Fe(L)_2(NCS)_2]\cdot 2CH_3OH\}_n$ (**3**) (NH_4NCS = ammonium thiocyanate) can be isolated. It is noted that different molar ratio of metal/ligand or different solvent system is crucial for the preparation of these iron(II) crystalline complexes **1**–**3** under similar synthetic conditions. PXRD patterns also confirm the purity of the bulky samples **1**–**3**. To the best of our knowledge, for **1**–**3**, it represents the first example of solvent-induced drastic reversible dynamic conformation between different dimensional iron(II) coordination complexes **1** (0D), **2** (1D) and **3** (2D) (for **1**: water; for **2**: benzene; for **3**: ethanol/acetone/acetonitrile), which are also unambiguously confirmed by PXRD characterizations.

As shown in Scheme S1, all the iron(II) coordination complexes are synthesized under similar hydrothermal conditions, only different molar ratio of metal/ligand or different reaction solvent systems are used [13–15]. The crystallographic data is listed in Table S1, and selected bond lengths and angles are listed in Table S2. Hydrogen bonds analysis was carried out using the PLATON program [16], all the hydrogen bonds

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distances and angles are listed in Table S3. Power X-ray diffraction (PXRD) patterns determined for the crystal materials of the title complexes and their calculated pattern deduced from single-crystal X-ray data are shown in Fig. S1–Fig. S3. They are in good agreement with PXRD patterns simulated from the sharpness of the lines but also the position of the peaks. The result reveals that single-crystal structures are representative of the bulk of the corresponding samples. The differences in reflection intensities between the simulated and the experimental patterns are due to the variation in the crystal orientation of the powder sample.

A view of the coordination complex $[Fe(L)_2(NCS)_2(H_2O)_2]\cdot 2H_2O$ (**1**) (L = 1,4-di-3-pyridyl-2,3-diaza-1,3-butadiene) is shown in Fig. 1(a). The fundamental structural unit of **1** contains one crystallographic independent Fe^{II} ion, two mono-dentate coordinated L, two NCS^- atoms, two coordinated aqua molecules and two lattice water molecules. The central iron(II) atom lies in a distorted octahedral geometry with two nitrogen atoms of NCS^- (N5, N5 A) occupying the axial positions and two nitrogen atoms of L (N1, N1A), two oxygen atoms of auqa molecules (O1, O1A) building the basal plane. The band lengths of Fe1-O1, Fe1-N1 and Fe1-N5 are 2.0848(19), 2.256(2) and 2.127(3) Å, respectively. The band angle of O1-Fe1-N1 is 89.40(8)°.

There are intermolecular hydrogen bonds in complex **1**. In the crystal structure, the oxygen atoms of two coordinated aqua molecules in per mononuclear unit are associated with the mono-dentate coordinated ligands L from neighboring units through O1-H1⋯N4 hydrogen bonds (distance is 2.734(3) Å; angle is 176°). Additionally these lattice water molecules (O2 or O2A), coordinated water molecules water molecules (O1 or O1A) and N3 or N3A atoms from L ligand are also inter-linked through these hydrogen bonds (O1-H1B⋯O2, 2.761(3) Å; O2-H2A⋯N3, 2.920(3) Å). Complex **1** is extended into a 3D supramolecular network through these hydrogen bonds and also stabilized by these intermolecular interactions (Fig. S4).

Further, when similar synthetic method as preparation of **1** is used, only the reaction molar ratio of corresponding iron(II) salts and L change from 1:2 to 1:1, one-dimensional (1D) iron(II) $[Fe(L)(NCS)_2(H_2O)_2]$ (**2**) can be isolated. For **2**, the fundamental structural unit contains one crystallographic independent Fe^{II} ion, one bi-dentate bridging coordinated L, two NCS^- atoms and two coordinated aqua molecules (Fig. 1(b)). The central Fe^{II} ion is located on an inversion center and is situated in a distorted N_4O_2 octahedral coordination geometry. The axial positions are occupied by two oxygen atoms from two aqua molecules. The equatorial positions are occupied by four nitrogen atoms, two from equivalent pairs of L molecules and two N atoms from equivalent pairs of mono-dentate NCS^- ligands. L adopts the bi-dentate bridging coordination mode and link two neighboring Fe^{II} centers, which ultimately form one dimensional chain coordination complex (Fig. 2(a)). The neighboring $Fe^{II}\cdots Fe^{II}$ distance within the 1D chain is 13.027(17) Å.

Complex **3** $\{[Fe(L)_2(NCS)_2]\cdot 2CH_3OH\}_n$ crystallizes in the monoclinic $P2_1/c$ crystal system. The fundamental structural unit of Complex **3** consists of one crystallographic independent Fe^{II} ion, two bi-dentate bridging coordinated L, two NCS^- atoms and two lattice coordinated CH_3OH molecules. At 296(2) K, for complex **3**, Fe-N(L) bond lengths are 2.262(4) Å-2.265(4) Å, whereas the Fe-N(NCS^-) bond lengths are somewhat shorter and are 2.101(4) Å, which indicates that all the Fe^{II} ions are in the high-spin state. As shown in Fig. 1(c), L adopts the bi-dentate bridging coordination mode and link four neighboring Fe^{II} centers, which ultimately form the two-dimensional grid-like metal-organic framework. All the neighboring $Fe^{II}\cdots Fe^{II}$ distance within the 2D grid-like network are 13.936(3) Å. For complex **3**, guest methanol solvent molecules are encapsulated in the 1D channel of the 2D framework, as calculated by PLATON, the 1D channel without guest molecules accounts for 12.4%.

As shown in Fig. S3, when **3** were heated for 24 h for 120 °C, the desolvated sample **3** is obtained. PXRD patterns also confirm the structure of desolvated sample **3** remains unchanged. TGA curves of desolvated sample **3** were also determined indicating the 2D micro-porous framework can remain stable until 200 °C (Fig. S5). When the desolvated samples **3** were immersed into different solvent systems such as Methanol/Acetone/Acetonitrile for three days, PXRD patterns indicated the structure of 2D micro-porous framework **3** still remains unchanged (Fig. S6).

As shown in Scheme S1, it can be seen that water molecules can be used as terminal coordination co-ligands in **1**–**2** while methanol molecules are employed as guest solvent molecules in the 2D micro-porous framework of **3**, solvent are quite important for the self-assembly of these iron(II) coordination frameworks. Further when the bulky samples of **1** (0D) was immersed in the benzene for 24 h, **1** (0D) can be completely converted into the structure of **2** (1D). While the bulky samples of **1** (0D) or **2** (0D) are immersed in the Ethanol/Acetone/Acetonitrile solvent systems for 24 h, **1** (0D) or **2** (0D) can be completely converted into the structure of **3** (2D). On the other hand, when the

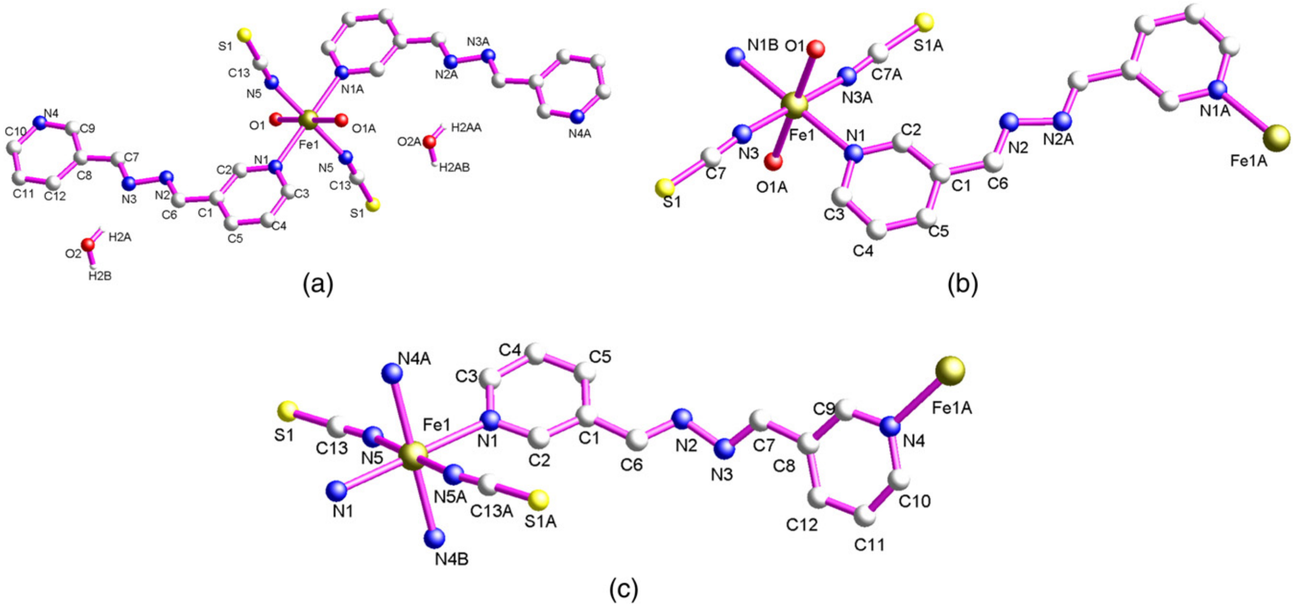

Fig. 1. The fundamental structural unit of (a) **1**. (b) **2**. (c) **3**.

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