

## Syntheses, structures and properties of cobalt and manganese complexes based on pyridine-2,3,5,6-tetracarboxylic acid



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### ABSTRACT

Two new complexes based on pyridine-2,3,5,6-tetracarboxylic acid ( $H_4pdtc$ ) as ligand,  $\{[Co_2(pdtc)(H_2O)_4] \cdot H_2O\}_n$  (**1**) and  $\{Mn_2(pdtc)(H_2O)_4\}_n$  (**2**), have been obtained by hydrothermal syntheses and characterized by IR, elemental analysis, X-ray diffraction single crystal structure analysis, PXRD, thermal gravimetric analysis, and magnetic measurements. Complex **1** is 3D coordination polymer and complex **2** belongs to 2D grid structure by covalent bonds. In **1** and **2**, the metal ions show antiferromagnetic interactions.

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In the past few decades, design and synthesis of complexes with metals and organic ligands have been extensively studied for diverse topologies, aesthetic beauty, and potential applications in gas storage and separation, which allows for promising applications in functional materials such as catalysis, magnetism, chemical sensors, and luminescence [1–4]. Extensive efforts on such species have not only led to the creation of a huge number of coordination polymers, but also can provide a suitable strategy to build potential interaction sites for specific host–guest recognition and thus to tune their functional properties. A lot of researches are focused on N-donor ligand [5] or O-donor ligand [6] building blocks based on transition metal ions or rare-earth ions. Recently more and more transition metals have received increasing attention. For example, Zheng and co-workers have synthesized three complexes based on Co(II) and Mn(II) in 2012 [7]. They reported three new polymers which were synthesized by hydrothermal conditions. The  $pdtc^{4-}$  ligands bridged stair-like chains in the three polymers. In 2015, Zhang [8] reported a 3D network based on Co(II) clusters. It has a novel binodal (3,8)-connected *tfz-d* network and has good stability in high temperature. In the same year, our group has synthesized one robust metal-organic framework with  $[Mn_3]$  clusters [9]. The PXRD pattern data indicates that the polymer has excellent stability in various solvents. TGA also displays good thermal stability. As known, Co(II) ion and Mn(II) ion have different coordination geometries through the

bridges of carboxylic groups to form polynuclear complexes. At the same time, excellent magnetic properties are incorporated into the high-connected networks owing to the large molecular anisotropy of the Co(II) ion [8] and Mn(II) ion [7].

To obtain the desired networks, N-heterocyclic ligands are often applied. Our group previously has demonstrated that hetero-cyclic polycarboxylic acids, such as pyrazine-2,3,5,6-tetracarboxylic acid ( $H_4pztc$ ), 6-methyl-2,3,5-pyridine-tricarboxylic acid ( $H_3mptc$ ) and pyridine-2,3,5,6-tetracarboxylic acid ( $H_4pdtc$ ), which act as multidentate carboxylate ligands containing both N- and O-atoms, are good candidates to form multiple coordination modes. These have been proven to be excellent choices for the constructions of metal organic complexes [10–12]. In addition, the introduction of the polynuclear clusters into coordination polymers would lead to the construction of the resulting networks with magnetic properties and catalytic activities [13,14]. In recent years, with the aim of understanding coordination modes of  $H_4pdtc$  and properties of these coordination polymers, we continue our research on coordination polymers based on pyridine-2,3,5,6-tetracarboxylate with metal ions via different methods such as different solutions or hydrothermal synthesis. Our group has obtained a number of related results [12,15–17]. Herein, we report the details of syntheses and characterizations [18] of two new cobalt and manganese-based coordination polymers using pyridine-2,3,5,6-tetracarboxylic acid as chelating ligand, namely  $\{[Co_2(pdtc)(H_2O)_4] \cdot H_2O\}_n$  (**1**),  $\{Mn_2(pdtc)(H_2O)_4\}_n$  (**2**).

Complex **1** displays a 3D architecture and crystallizes in a triclinic system, space group  $P\bar{1}$ . The asymmetric unit contains two Co(II)

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atoms (one Co1, half Co2 and half Co3), one  $\text{pdtc}^{4-}$  anion, four coordinated water molecules, and one free water molecule, as shown in Fig. 1a. As shown in Fig. 1b, Co1 atom shows a distorted octahedral geometry bonding three oxygen (O1, O5C, O8) atoms from two  $\text{pdtc}^{4-}$  anions and one nitrogen atom (N1) from one of  $\text{pdtc}^{4-}$  anions in the equatorial plane, the axial positions are occupied by two oxygen atoms (O3B, O6D) from other two  $\text{pdtc}^{4-}$  anions. Co2 and Co3 atoms also adopt distorted octahedral geometries. But they are coordinated by four oxygen atoms from four water molecules in the equatorial plane, the axial positions are occupied by two oxygen atoms from two  $\text{pdtc}^{4-}$  anions.

The  $\text{pdtc}^{4-}$  anion links six Co(II) atoms (four Co1, one Co2 and one Co3), only one Co1 exhibits tridentate chelating coordination mode and others exhibit monodentate coordination modes. Complex **1** forms a 3D network without any non-covalent bond as shown in Fig. 1c through the above coordination. The Co–N bond length is 2.042 (2) Å and the Co–O bond lengths range from 2.024(2) to 2.184(2) Å, which are all in great agreement with the reported lengths [19]. The bond lengths and angles of the complex **1** are given in Table S2.

In order to obtain a better insight of the 3D structure of complex **1**, the topological structure of **1** was analyzed by the application of topology analysis using the program TOPOS. When Co1 and the  $\text{pdtc}^{4-}$  anion are treated as 4- and 6-connected node, respectively, the topology analysis suggests that the coordination framework can be simply demonstrated as a bimodal (4,6)-connected node nets with Schläfli symbol of  $(4^4 \cdot 6^{10} \cdot 8) \cdot (4^4 \cdot 6^2)$ . (see Fig. 1d)

Complex **2** was crystallized in triclinic system, space group  $P\bar{1}$ . The asymmetric unit contains two Mn(II) centers, one  $\text{pdtc}^{4-}$  anion, and

four coordinated water molecules (Fig. 2a). The Mn1 adopts a distorted octahedral geometry and is directly coordinated by four oxygen atoms (O1, O9, O10, O11) from one  $\text{pdtc}^{4-}$  anion and three different coordinated water molecules in the equatorial plane; two oxygen atoms (O4A, O5B) from other two  $\text{pdtc}^{4-}$  anions in the axial positions. The Mn2 center is hepta-coordinated and shows a distorted pentagonal bipyramidal geometry, bonding four oxygen atoms (O2B, O3B, O6D, O12) from two  $\text{pdtc}^{4-}$  anions, one coordinated water molecule, and one nitrogen atom (N1B) from one of the  $\text{pdtc}^{4-}$  anions in the equatorial plane. The axial positions are occupied by two oxygen atoms (O7, O8C) from other two  $\text{pdtc}^{4-}$  anions in Fig. 2b. Interestingly, the oxygen atoms and nitrogen atom in the same  $\text{pdtc}^{4-}$  anion are all coordinated with Mn(II) ions, which is reported the first time. The ligands adopt a novel coordination mode: each  $\text{pdtc}^{4-}$  links seven Mn(II) atoms (three Mn1 and four Mn2), only one Mn2 exhibits tridentate chelating mode and others exhibit monodentate coordination modes displayed in Fig. S1a. The Mn–N bond length is 2.296 (19) Å and the Mn–O bond lengths range from 2.134(17) to 2.371(15) Å. Bond lengths and angles of the complex **2** are given in Table S3.

Four oxygen atoms in each  $\text{pdtc}^{4-}$  anion (O4, O5, O7, O8) coordinate with four Mn(II) ions respectively in complex **2**. Among the oxygen atoms, O4, O8 from the  $\text{pdtc}^{4-}$  anion and O4', O8' from the second  $\text{pdtc}^{4-}$  anion connect two ligands together by coordinating with Mn(II) ions; O5, O7 and O5'', O7'' from the third  $\text{pdtc}^{4-}$  anion connect two ligands in the same way. The adjacent two  $\text{pdtc}^{4-}$  anions connect with each other, which makes the structure into 1D chain as shown in Fig. S1b. The 1D chain is connected to the 2D lattice structure by Mn(II) ions and the O6 in each  $\text{pdtc}^{4-}$  anion as shown in Fig. 2c. The

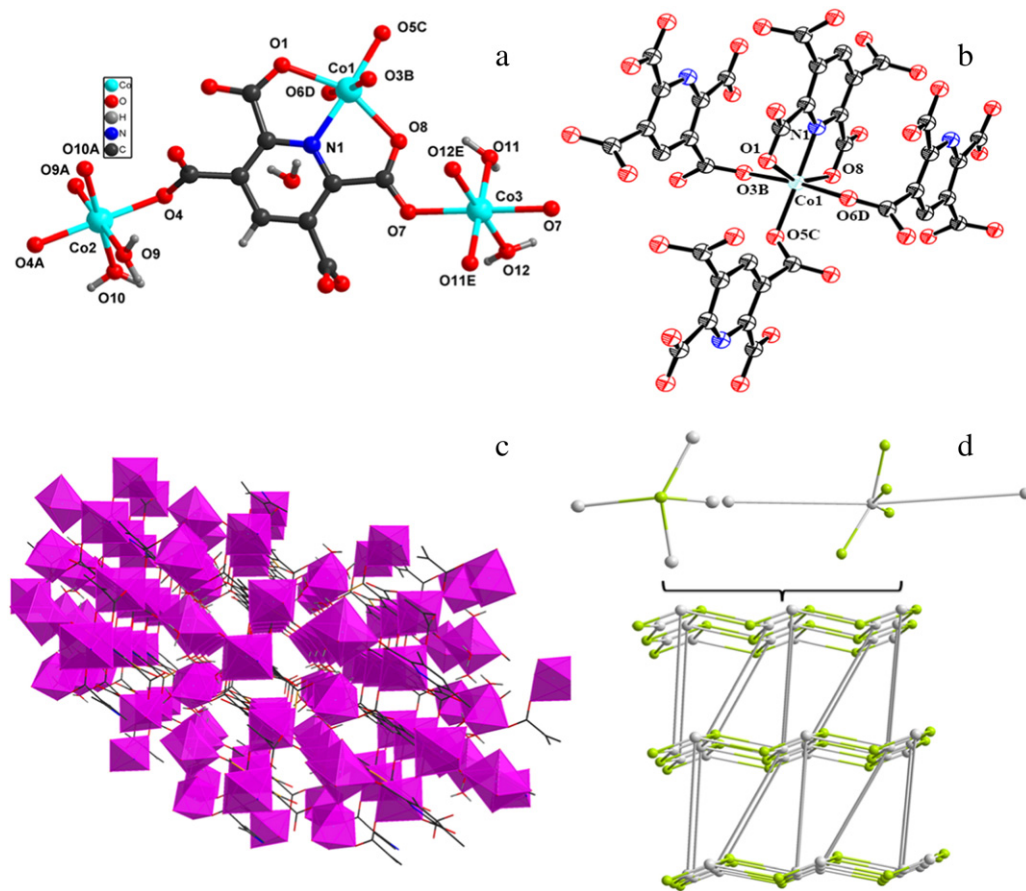


Fig. 1. (a) The crystal structure of complex **1**. (b) The coordination environments of Co1 showing at the 50% probability level. Symmetry code: A:  $-x + 1, -y + 1, -z$ ; B:  $-x, -y + 1, -z + 1$ ; C:  $x - 1, y, z$ ; D:  $-x, -y + 2, -z + 1$ ; E:  $-x, -y + 2, -z + 2$ . (c) The 3D structure of complex **1**. (d) The (4,6)-connected network with Schläfli symbol of  $(4^4 \cdot 6^{10} \cdot 8) \cdot (4^4 \cdot 6^2)$ .

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