

## Synthesis, crystal structure and magnetic properties of manganese(II) coordination polymer from isonicotinate and amino-tetrazole mixed-ligands

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### ABSTRACT

A new 3D coordination polymer,  $Mn_2(atz)(isonic)(OH)(Cl)_n$  (1), was synthesized hydrothermally from mixed-ligands of Hatz (Hatz = 5-amino-tetrazolate) and Hisonic (Hisonic = isonicotinate) and corresponding metal salts. It was characterized by IR spectra, elemental and thermal analysis, single crystal and powder X-ray diffraction. Variable temperature magnetic investigations indicate that compound 1 exhibits typical antiferromagnetic behaviors.

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Coordination polymers have drawn much attention because of their potential applications as functional materials as well as the intriguing molecular architectures and topologies during the past decades [1–9]. But the construction of polymers with fascinating architectures and novel properties still remains a long-term challenge [5,10]. Choosing multifunctional organic ligand and reasonable synthetic strategy will be a sempiternal principle. Judicious selection/design of organic ligands, which can efficiently mediate the magnetic coupling, will be a crucial step for desired structures and functions. Because of the suitable distance for transmitting efficiently magnetic couplings between spin carriers, the short bridge organic ligands, such as azide, [11–13] cyanide, [14,15] and formate, [16] have been extensively used to prepare molecular magnetic materials with metal ions. The other key step for novel structures and properties is synthetic strategy. The use of mixed-ligand may be one of the effective approaches to construct coordination polymer because it will combine the advantages of different types of coordination groups [17–22]. The combination of one or two different organic ligands and metal ions provides endless possibilities. The sum of physical properties of the inorganic and organic components and the possible synergistic effect between them provide intriguing properties for compounds. Recently, using azide ligand to combine the co-ligand carboxylate, various exotic and multidimensional molecular-based magnetic materials have been successfully built [23–27]. However, successful magnetic examples with simultaneous Hatz (Hatz = 5-amino-tetrazolate) and pyridyl-carboxylate were still rarely observed [28] because the simultaneous incorporation of the two negatively

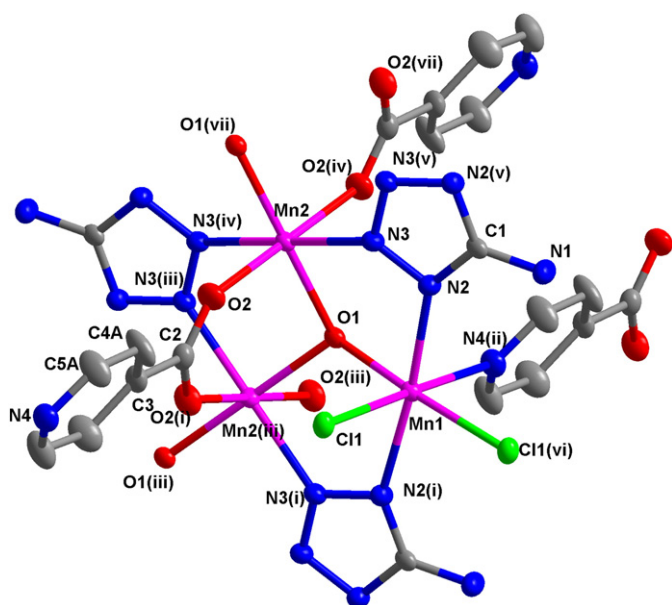
charged bridges is limited by their competition not only in binding metal ions but also in compensating the metal charge. Though it is a challenge, we believe that this combination would be hopefully expected because of the following two considerations: i) Structurally, both the tetrazoles and carboxylic acids exhibit a variety of coordination abilities and rich coordination modes, and there is a tendency of them forming architectures with multidimensional frameworks; ii) Magnetically, both the tetrazolyl and carboxylate groups can transmit efficiently different types of magnetic superexchange between the spin carriers. Based on the mentioned considerations, carboxylic acids and tetrazoles are appealing ligands for building new coordination compounds.

As a part of our investigations of the mixed-ligand strategy for design of hybrid materials, [28–32] we introduced Hisonic (Hisonic = isonicotinate) coligand into the metal/tetrazolate system, and a new 3D compound,  $[Mn_2(atz)(isonic)(OH)(Cl)]_n$  (1), was successfully isolated under hydrothermal conditions at 130 °C for 3 days [33]. The crystalline phase purity was confirmed by the powder X-ray diffraction (PXRD) patterns of the bulk solid (Fig. S1), and the compositions were further defined from single crystal X-ray diffraction and elemental analysis. Additionally, the variable temperature magnetic behaviors of 1 were also investigated.

Single crystal X-ray analysis [34] shows that complex 1 is a 3D framework network with strip-shaped chains and trinuclear triangular  $[Mn_3(\mu_3-OH)]^{5+}$  clusters. It crystallizes in monoclinic space group  $C2/m$ . There are two halves of six-coordinated Mn(II) atoms, half of an atz ligand, half of an isonic ligand and half of a hydroxyl group in the asymmetric unit, of which the Mn(II) atoms, atz ligand, isonic ligand and hydroxyl group are all sited on the two-fold axis positions (Fig. 1). As illustrated in Fig. 1, the two unique metal centers (Mn1 and Mn2) adopt distorted-octahedral coordination geometry. Three

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**Fig. 1.** View of the coordination environment of Mn(II) in 1 at 50%, Hydrogen atoms are omitted for clarity. Symmetry codes: (i)  $x, -y, z$ ; (ii)  $x, y, 1 + z$ ; (iii)  $0.5 - x, -0.5 + y, -z$ ; (iv)  $0.5 - x, 0.5 - y, -z$ ; (v)  $x, 1 - y, z$ ; (vi)  $-x, y, -z$ ; (vii)  $0.5 - x, 0.5 + y, -z$ .

nitrogen atoms (N2, N2(i) and N4(ii) from two atz ligands and an isonic ligand, respectively) and a chloride atom (Cl1) define an equatorial quasi-plane, and the axial positions are completed by the other chloride atom (Cl1vi) and a hydroxyl oxygen atom (O1) for Mn1 center to form a slightly distorted octahedron. For Mn2 center, four oxygen atoms (two pairs of symmetry-related oxygen atoms, O1 from hydroxyl group and O2 from isonic ligand, respectively) define an equatorial plane, and the axial positions are occupied by two symmetry-related N3 atoms from two atz ligands. The bond distances of Mn–O, Mn–N and Mn–Cl are 2.138(3) – 2.167(4), 2.262(3) – 2.308(6) and 2.505(3) – 2.575(6) Å, respectively, which are all normal [28,32,35,36].

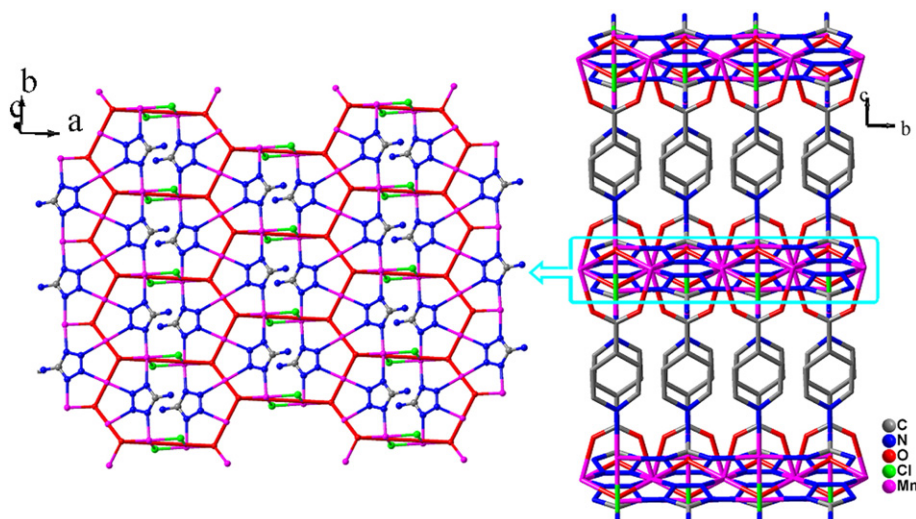
In this compound, the hydroxyl acts as a  $\mu_3$ -bridge to link one Mn1 atom and two equivalent Mn2 atoms, generating an isosceles triangle with Mn–Mn separation of 3.713(1) and 3.384(2) Å. The Mn–O1–Mn angle is about 104–119.2°, so the OH group is displaced out of the Mn1–Mn2–Mn2(iii) plane, which results in the formation of a noncoplanar  $[\text{Mn}_3(\mu_3\text{-OH})]$  triangular cluster (Fig. 1). The triangular cationic clusters  $[\text{Mn}_3(\mu_3\text{-OH})]^{5+}$  are linked together by sharing the Mn2 ions and

bridged by  $\mu_4$ -atz ligands to form a strip-shaped metal  $\Delta$ -chain along the b axis direction. Then the strip-shaped metal  $\Delta$ -chains were connected into a 2D layer structure (Fig. 2, left). The  $\mu_3$ : $\eta^1$ : $\eta^1$ : $\eta^1$ -bridge isonic ligand is sited on twofold axis and acts as bridging-ligand to link the adjoining layers. On one end, two carboxylate O atoms of the isonic anion monodentated two Mn2 atoms of the  $[\text{Mn}_3(\mu_3\text{-OH})]^{5+}$  cluster of one layer, and on the other end, one N atom of the isonic anion was linked to the Mn1 atom of the other strip-shaped metal  $\Delta$ -chain of the other layer, resulting in a 3D framework (Fig. 2, right).

Alternatively, the structure of 1 can be described in terms of strip-shaped chains of oxocentred trinuclear manganese clusters,  $[\text{Mn}_3(\mu_3\text{-OH})]^{5+}$ , which were connected by the  $\mu_2$ -Cl into an inorganic layer (Fig. 3), and the inorganic layers were further stabilized by organic  $\mu_4$ -atz bridges (Fig. 2, left). The 2D layers were pillared by the  $\mu_3$ -isonic ligands into a 3D framework (Figs. 2, right and 4). Topologically, when we take atz,  $\mu_2$ -Cl and  $\mu_3$ -OH as linkers, isonic ligand as 3-connected node, and Mn1 and Mn2 ions as two 6-connected nodes, respectively, the 3D compound represents a (3,6) $\Delta$ -connected 3-nodal topological net with the Schläfli symbol [37] of  $(3 \cdot 6^2) (3 \cdot 4^4 \cdot 5^2 \cdot 6^7 \cdot 8) (3^4 \cdot 4^4 \cdot 5^2 \cdot 6^4 \cdot 7)$  (Fig. 5). It is an unprecedented topological net, which has never been reported in the 3D network.

It is noticeable that the  $\Delta$ -chain topology of compound 1 consists of scalene triangles which may be expected to lead to different ratios between the three magnetic exchange interactions corresponding to the triangle's edges, for deviation from equality is likely to lead to suppression of the frustration [38,39]. Additionally, the Mn atoms in the  $\Delta$ -chain were further bridged by  $\mu_2$ -Cl atoms except for the  $\mu_4$ -atz and  $\mu_3$ -isonic bridges. These will enhance the magnetic coupling interactions between the spin carriers and will be detailed as follows.

The magnetic susceptibilities of 1 were measured in the 1.8–300 K temperature range at 2 kOe, and are shown as  $\chi_m T$  and  $\chi_m$  versus  $T$  plots (Fig. 6). As depicted in Fig. 6, the experimental  $\chi_m T$  value of 1 at room temperature is 8.42 emu K mol $^{-1}$ , which is a little lower than the spin-only value (8.75 emu K/mol) expected for two magnetically isolated high-spin Mn(II) ions considering  $g = 2.00$  and  $S = 5/2$ . The  $1/\chi_m$  vs  $T$  plot above 50 K is exactly linear following the Curie–Weiss law with  $C = 11.09$  emu K/mol and  $\theta = -91.76$  K (Fig. S2). The  $C$  value corresponds to  $g = 2.00$ , being normal for the spin only coupling of an octahedral Mn(II) ions. Upon cooling from room temperature,  $\chi_m T$  value of 1 steadily decreases until it reaches a minimum at 1.8 K, suggesting antiferromagnetic behavior. A round peak was observed in the  $\chi_m$  versus  $T$  curve, indicating strong antiferromagnetic nature. The antiferromagnetic ordering was further confirmed by the field-cooled and zero field-cooled (ZFC) magnetizations measurement: At low-



**Fig. 2.** Left) View of the layer bridged by the atz ligands; Right) View of the packing diagram of 1, along a axis direction, neighboring layer was pillared by the isonic ligands.

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