



# Crystal structures and magnetic properties of the honeycomb-lattice antiferromagnet $M_2(\text{pymca})_3(\text{ClO}_4)$ , ( $M = \text{Fe}, \text{Co}, \text{Ni}$ )



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## ABSTRACT

We report on the syntheses, crystal structures, and magnetic properties of a series of transition metal coordination polymers  $M_2(\text{pymca})_3(\text{ClO}_4)$ , ( $\text{pymca} = \text{pyrimidine-2-carboxylic acid}$ ,  $M = \text{Fe}$  (1),  $\text{Co}$  (2), and  $\text{Ni}$  (3)). These compounds are found to crystallize in a trigonal crystal system, space group  $P\bar{3}1m$ , with the lattice constants  $a = 9.727 \text{ \AA}$  and  $c = 5.996 \text{ \AA}$  for 1,  $a = 9.608 \text{ \AA}$  and  $c = 5.996 \text{ \AA}$  for 2, and  $a = 9.477 \text{ \AA}$  and  $c = 5.958 \text{ \AA}$  for 3 at room temperature. In these compounds, each  $\text{pymca}$  ligand connects to two  $M^{2+}$  ions, forming a honeycomb network in the  $ab$  plane. The temperature dependences of magnetic susceptibilities in these compounds show broad maxima, indicating antiferromagnetic interactions within two-dimensional honeycomb layers. We also observed an antiferromagnetic phase transition at low temperatures by magnetic susceptibility and heat capacity measurements. From the crystal structures and magnetic properties, we conclude that the compounds 1, 2, and 3 are good realizations of honeycomb-lattice antiferromagnets.

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## 1. Introduction

In recent years, there has been considerable interest in the design, preparation and magnetic properties of coordination polymer based magnetic materials in which metal ion centers interact magnetically through bridging ligands [1]. In these systems, the bridging ligand seems to play a key role in determining the final structures and magnetic properties of the materials. Therefore, much attention has been focused on the exchange mechanism through the bridging ligands and the correlation between the crystal structures and magnetic properties of these systems. Oxalic acid have been widely used as bisbidentate bridging ligand, which can coordinate to transition metal ions yielding coordination polymer with interesting structural features (three-dimensional, layered, and chain structures) and magnetic properties that are useful in materials science [2]. For example, the bimetallic oxalate compound  $\text{N}(\text{C}_5\text{H}_{11})_4\text{MnFe}(\text{C}_2\text{O}_4)_3$  has a two-dimensional (2D) honeycomb structure of Mn and Fe ions

bridged by oxalate groups and behaves as a 2D ferrimagnet [3].  $\text{Pymca}$ , which is structurally analogous to the oxalate, is asymmetrical and includes two nitrogen atoms of a pyrimidine ring and one carboxylate group. Therefore,  $\text{pymca}$  has also been used as N,O-bisbidentate ligand to construct magnetic coordination polymers [4]. We reported on a copper coordination compound with this interesting ligand,  $\text{Cu}_2(\text{pymca})_3(\text{ClO}_4)$ , with focusing on its coordination structures and magnetic properties [5]. The  $\text{Cu}_2(\text{pymca})_3(\text{ClO}_4)$  consists of a 2D honeycomb  $\text{Cu}^{2+}$  network formed by bidentate  $\text{pymca}$  ligands, and its magnetic properties suggest that  $\text{Cu}_2(\text{pymca})_3(\text{ClO}_4)$  is a good realization of a spin-1/2 honeycomb lattice antiferromagnet. We also report on the absence of a magnetic ordering down to temperature  $T = 2 \text{ K}$  in  $\text{Cu}_2(\text{pymca})_3(\text{ClO}_4)$ . Since the honeycomb lattice has the smallest possible 2D coordination number ( $z = 3$ ), quantum fluctuation is expected to be larger than those in a square lattice ( $z = 4$ ) [6]. In such low dimensional systems, spin quantum number and anisotropy of magnetic ions play important roles in magnetic ordering, because they are significantly affected by quantum fluctuations which suppress the magnetic ordering. Therefore, we focused on the syntheses of various transition metal coordination polymers containing  $\text{pymca}$  ligand in order to study their coordination structures and magnetic

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ordering. In this paper, we report on the syntheses, X-ray crystallographic analyses, and magnetic properties of the title compounds,  $M_2(\text{pymca})_3(\text{ClO}_4)$ , ( $M = \text{Fe}$  (1),  $\text{Co}$  (2), and  $\text{Ni}$  (3)).

## 2. Experimental section

Single crystals of the compounds 1, 2, and 3 were obtained by heating mixtures of  $M\text{Cl}_2 \cdot n\text{H}_2\text{O}$  ( $M = \text{Fe}$ ,  $\text{Co}$ ,  $\text{Ni}$ ) (0.8 mmol), 2-cyanopyrimidine (1.2 mmol),  $\text{NaClO}_4$  (0.4 mmol), and  $\text{H}_2\text{O}$  (10 mL) in a 25 mL Teflon-lined autoclave at  $T = 393$  K for 12 h under autogenous pressure, followed by slow cooling to room temperature. Dark brown fine crystals of 1, orange fine crystals of 2, and blue-green fine crystals of 3 were collected after drying in air overnight. The X-ray powder diffraction data of these compounds at room temperature were collected with a Bruker D8 ADVANCE ECO diffractometer using  $\text{Cu K}\alpha$  radiation. Profile matching and Rietveld refinement of the X-ray powder diffraction patterns for 1, 2, and 3 were done by using RIETAN 2000 software [7]. The final reliable factor ( $R_{\text{wp}}$ ) and goodness of fitting ( $S$ ) of refinement were  $R_{\text{wp}} = 13.0$  and  $S = 2.8$  for 1,  $R_{\text{wp}} = 4.0$  and  $S = 1.7$  for 2, and  $R_{\text{wp}} = 4.3$  and  $S = 2.3$  for 3, respectively. The magnetization ( $M$ ) of crystalline samples of 1, 2, and 3 was measured with a SQUID magnetometer (Quantum Design MPMS XL). The  $M$  versus  $T$  measurements were performed at  $T = 2$ – $300$  K in a magnetic field of  $H = 1$  kOe under the field-cooled condition. The heat capacity of pelletized powder of the compounds 1 and 3 were measured by using a microcalorimeter (Quantum Design PPMS).

## 3. Results and discussion

The hydrothermal reaction of 2-cyanopyrimidine with  $M\text{Cl}_2 \cdot n\text{H}_2\text{O}$  causes hydrolysis of 2-cyanopyrimidine to pymca and the formation of pymca bridging between  $M^{2+}$  ions. Single crystals of the compounds 1, 2, and 3 were formed in consequence of the hydrothermal reaction. Fig. 1 shows the X-ray diffraction patterns for the randomly oriented fine crystalline sample of 1, 2, 3, and  $\text{Cu}_2(\text{pymca})_3(\text{ClO}_4)$  [5]. The X-ray diffraction patterns for these compounds were consistent with trigonal crystal system (space group  $P\bar{3}1m$ ), with lattice constants of  $a = 9.727$  Å and  $c = 5.996$  Å for 1,  $a = 9.608$  Å and  $c = 5.996$  Å for 2, and  $a = 9.477$  Å and  $c = 5.958$  Å for 3. While the lattice constant  $c$  does not depend on  $M$ , lattice constant  $a$  decreases with increasing the atomic number of  $M$ . The crystal structures of 1, 2, and 3 are isomorphic with  $\text{Cu}_2(\text{pymca})_3(\text{ClO}_4)$  reported by us previously. Based on their analogous crystal structures to  $\text{Cu}_2(\text{pymca})_3(\text{ClO}_4)$ , we suggest that each pymca ligand connects to two  $M^{2+}$  ions, and a honeycomb cationic

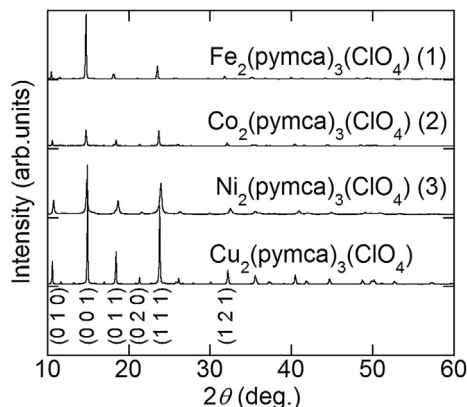


Fig. 1. XRD patterns for  $\text{Fe}_2(\text{pymca})_3(\text{ClO}_4)$  (1),  $\text{Co}_2(\text{pymca})_3(\text{ClO}_4)$  (2),  $\text{Ni}_2(\text{pymca})_3(\text{ClO}_4)$  (3), and  $\text{Cu}_2(\text{pymca})_3(\text{ClO}_4)$ .

network  $[\text{M}_2(\text{pymca})_3]_n^{n+}$  is formed in the  $ab$  plane of the compounds 1, 2, and 3 (Fig. 2(a)). The  $[\text{M}_2(\text{pymca})_3]_n^{n+}$  honeycomb layers are separated by a unit cell length along the  $c$ -direction (Fig. 2(b)). In each hexagonal ring in the 2D honeycomb network, the pyrimidine rings of the pymca ligands are alternatively tilted from the normal direction to the ring, and three of them point to the center of the ring. The  $\text{ClO}_4^-$  anions are encapsulated inside the voids in the hexagonal rings. The O and N atoms in the pymca ligand form an octahedral surrounding with  $C_3$  symmetry around the  $M^{2+}$  ion.

The temperature dependences of the magnetic susceptibilities  $\chi$  of randomly oriented fine crystalline samples of the compounds 1, 2, and 3 are shown in Figs. 3–5, respectively. The susceptibilities of all three compounds show round maxima, which is characteristic of low-dimensional antiferromagnets. The  $\chi$  versus  $T$  curves show maximum values at  $T_{\text{max}} = 26.0$  K for 1, 24.0 K for 2, and 65.0 K for 3. The susceptibility data above 150 K for all three compounds obey the Curie-Weiss law, and their antiferromagnetic natures of the dominant interactions are confirmed by negative signs of the Weiss temperatures. The Weiss temperatures  $\theta$  were found to be  $-50.1$  K,  $-74.1$  K, and  $-120.2$  K for the compounds 1, 2, and 3, respectively. Since  $\text{Ni}^{2+}$  ion in an octahedral coordination environment with  $C_3$  symmetry shows magnetic behavior with small zero-field splitting ( $D/k_B \sim 0.8$  K) [8], the large Weiss temperature for 3 can be interpreted as the presence of strong antiferromagnetic superexchange interaction between  $\text{Ni}^{2+}$  ions through the pymca ligands. The Curie constant is  $C = 2.43$  emu K/mol for 3 which is consistent with the spin ( $S$ ) only value (2.42 emu K/mol) expected for  $\text{Ni}^{2+}$  ( $d^8$ ) ions with  $S = 1$  and  $g = 2.2$  under an octahedral crystalline field. The Curie constants are  $C = 7.30$  emu K/mol for 1 and  $C = 6.44$  emu K/mol for 2. They are much higher than the spin-only values expected for high-spin  $\text{Fe}^{2+}$  ( $d^6$ ) ions (6.00 emu K/mol)

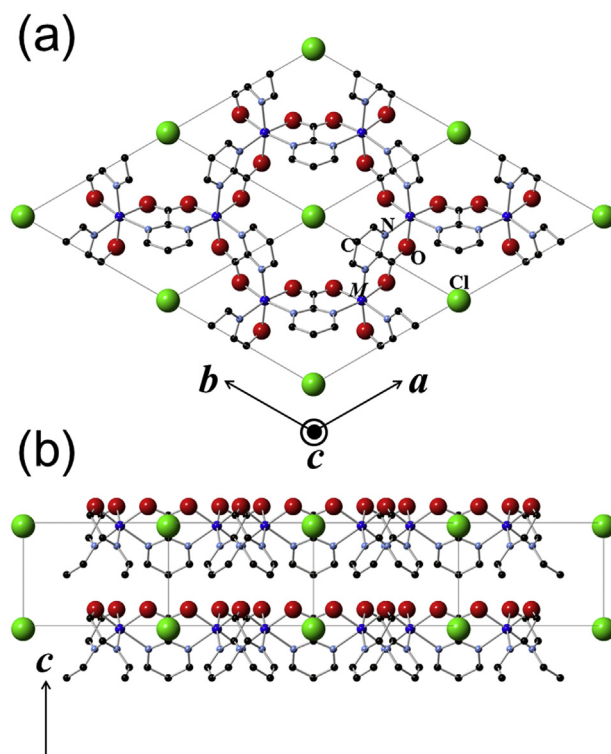


Fig. 2. (a) Top view of the  $[\text{M}_2(\text{pymca})_3]_n^{n+}$  honeycomb layer of  $\text{M}_2(\text{pymca})_3(\text{ClO}_4)$  from the  $c$  axis. Hydrogen atoms are omitted for clarity. (b) Side view of three adjacent  $[\text{M}_2(\text{pymca})_3]_n^{n+}$  honeycomb layers in  $\text{M}_2(\text{pymca})_3(\text{ClO}_4)$  from the  $[110]$  direction. Hydrogen atoms and oxygen atoms on  $\text{ClO}_4^-$  are omitted for clarity.

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