

Synthesis, structural characterization and ferrimagnetic property of $MnPS_3$ intercalated with nickel(II) cyclopolyamine complex cations

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Abstract

Two new intercalation compounds were prepared by the reactions of Ni(II) cyclopolyamine complex cations with a preintercalate $Mn_{1-x}PS_3K_{2x}(H_2O)_y$, respectively, through “ion exchange” process. Their structures were characterized by elemental analysis, X-ray powder diffraction and infrared spectroscopy. The lattice spacing increased 0.567 and 1.093 nm with respect to the pristine $MnPS_3$. Ferrimagnetism of the intercalates was confirmed by SQUID experiment with T_c at 40 and 33 K, respectively.

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1. Introduction

In the last decades, intercalation chemistry has received great and rapid development for its promising application in catalysis, electrochemical batteries and functional materials [1,2]. Among them, magnetic interactions observed in many two-dimensional lamellar materials have drawn much attention because the inserting of guests may cause profound modifications of the host in their magnetic properties and induce previously non-existent magnetization. Recently, it has been found that some layered compounds, such as MPS_3 ($M = Mn, Fe$) and $M_2(OH)_3A$ ($M = Co, Cu$; $A = OAc^-, NO_3^-$) showed spontaneous magnetization and became magnets after intercalation [3–7]. So it provides a unique approach to obtain molecular-based magnetic materials by inserting functional guest into some inorganic host.

The transition metal phosphorus trisulfides MPS_3 , where M stands for a metal in the +2 oxidation state, form a class of insulating layered compounds whose structure is similar to $CdCl_2$ [8]. Generally, the MPS_3 compounds undergo a unique ion exchange intercalation process in which cations can be inserted into MPS_3 interlayer van der Waals gaps with M^{2+} cations of the host leaving their intralamellar sites and going into the solution to maintain the charge balance [9]. Over the past 20 years, a wide range of guests were known to be inserted into MPS_3 , such as inorganic, organic cations, organometallic molecules and biomolecules, and some intercalation compounds of MPS_3 have shown interesting physical properties [10–14].

On the other hand, the coordination chemistry of the macrocyclic ligands including crown ethers and macrocyclic polyamines has attracted increasing attention and has been extensively studied for their unique chelate ability to metal cations [15]. Their metal complexes have a wide range of application such as biochemical simulation [16], catalysis [17] and low-dimensional conductors [18]. Intercalation of such complexes into the charged layer of host

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structures often leads to efficient catalytic properties comparable to those of the homogeneous solution [19,20]. However, no any cyclopolyamine has formed intercalation compound with MnPS_3 until we have done it in 2003 when a dioxomacrocyclic polyamine was inserted into MnPS_3 and the intercalate showed spontaneous magnetization below 40 K [21]. This prompts us to further investigate the possibility to intercalate a metal cyclopolyamine complex into MPS_3 , since it is very rare in the literature that a metal complex has been inserted into MPS_3 lattice. Our interest is to search for a MPS_3 intercalation system where there is more or less interaction between the host and the guest. We are also interested in the intercalation compound in which the host and the guest are, respectively, responsible for the spontaneous magnetization and another property such as electrical conduction. Therefore, in this study we have selected two cyclopolyamine ligands, one is a medium sized hydroxyl mesocyclic diamine (*A*) and the other is a larger sized 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-*trans*-diene (*B*). Both ligands formed the coordination compounds with Ni^{2+} ion first (structures are shown in Fig. 1), and then were intercalated into MnPS_3 . This paper describes the synthesis, structural characterization and magnetic property of these two new intercalation compounds. To the best of our knowledge, they are the first two examples of metal cyclopolyamine complex to be intercalated into MPS_3 family.

2. Experimental

X-ray powder diffraction patterns were obtained on a Shimadzu XRD-6000 X-ray diffractometer using $\text{CuK}\alpha$

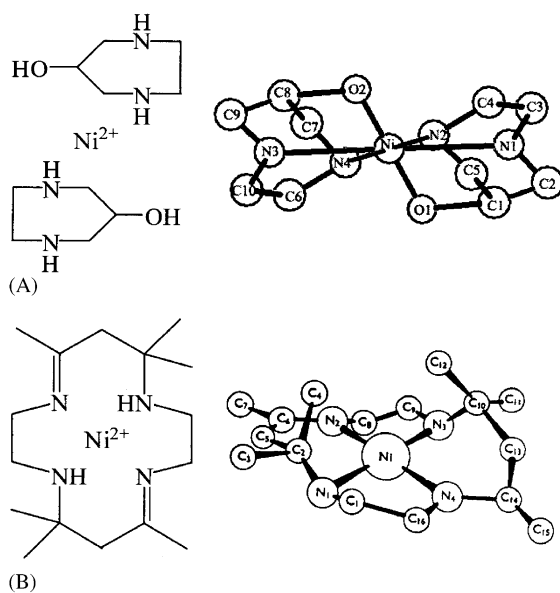


Fig. 1. Structural formula (left) and stereo configurations (right) of Ni(II) complex cations *A* and *B*.

radiation ($\lambda = 0.15418$ nm). The infrared (IR) spectra of KBr discs were recorded on a Nicolet SX Fourier transform spectrometer. Elemental analysis of C, H, N was performed on a Carloerba-1106 microanalyzer. The contents of manganese and nickel were obtained on an Atomscan-2000 instrument by the method of ICP-AES. The magnetic properties were determined by a SQUID-magnetometer (MPMS, Quantum Design).

Pure MnPS_3 was synthesized by heating stoichiometric amount of pure element (>99.9%) in sealed evacuated quartz tube at 700 °C, with the reported method [8]. The purity of the host was identified by means of XRD. It was indexed as a monoclinic unit cell (space group $C2/m$), in which $a = 0.6094$ nm, $b = 1.0589$ nm, $c = 0.6817$ nm [22].

Hydrobromate salt of guest *A* and perchlorate salt of *B* were synthesized according to the literature [19,23].

The intercalates were obtained by a two step “ion exchange” reaction. Firstly, MnPS_3 was treated with a 5 mol dm^{-3} aqueous KCl solution, and a preintercalate $\text{Mn}_{1-x}\text{PS}_3\text{K}_{2x}(\text{H}_2\text{O})_y$ was obtained [9]. Then, it was reacted with the aqueous solution of the guests at about 60 °C for 10 days, followed by filtration and thoroughly washing with water. The formula of the two intercalates were established by the elemental analysis: (1) $\text{Mn}_{0.82}\text{PS}_3(\text{A})_{0.18}$ (Calcd: Mn, 20.10; Ni, 4.71; C, 9.62; H, 1.92; N, 4.49. Found: Mn, 19.89; Ni, 4.58; C, 9.35; H, 2.05; N, 4.32), and (2) $\text{Mn}_{0.87}\text{PS}_3(\text{B})_{0.13}$ (Calcd: Mn, 21.82; Ni, 3.48; C, 11.21; H, 1.46; N, 3.32. Found: Mn, 21.60; Ni, 3.32; C, 11.21; H, 1.80; N, 3.24).

3. Result and discussion

3.1. X-ray powder diffraction

Fig. 2 gives the XRD results of the two intercalates. Complete intercalation was confirmed by the total disappearance of the 00*l* reflection of the pre-intercalate. Instead, the new sharp 00*l* reflections of the intercalates were observed, suggesting the expansion of the interlayer distances were 0.567 nm for $\text{Mn}_{0.82}\text{PS}_3(\text{A})_{0.18}$ and 1.093 nm for $\text{Mn}_{0.87}\text{PS}_3(\text{B})_{0.13}$, compared with the pure MnPS_3 . The orientation of the guests can be suggested by comparing the increase of the lattice spacing and the molecular size of the guests. In the crystal structure of guest *A*, the two mesocycles adopt chair-like conformations and the four nitrogen atoms coordinate Ni (II) cation with an approximately planar structure [23]. Using the Diamond program, the molecular size of cation *A* can be calculated by its crystal structure with dimension of 0.78 nm × 0.48 nm × 0.62 nm, and the shortest dimension (0.48 nm) is parallel to the plane formed by four nitrogen and Ni (II) atoms. Since the interlayer distance increase is 0.567 nm, it is proposed that this plane is

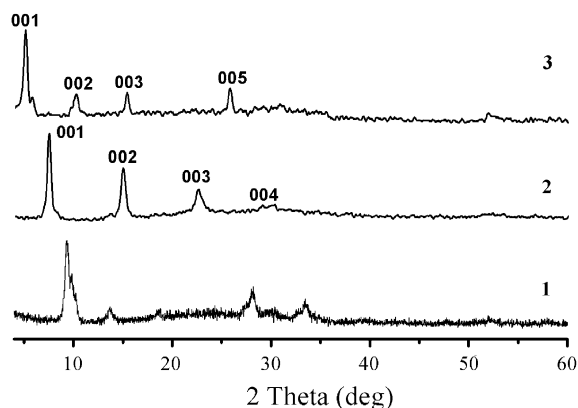


Fig. 2. Powder X-ray diffraction (XRD) of: (1) $\text{Mn}_{1-x}\text{PS}_3\text{K}_{2x}(\text{H}_2\text{O})_y$, (2) $\text{Mn}_{0.82}\text{PS}_3(A)_{0.18}$, and (3) $\text{Mn}_{0.87}\text{PS}_3(B)_{0.13}$.

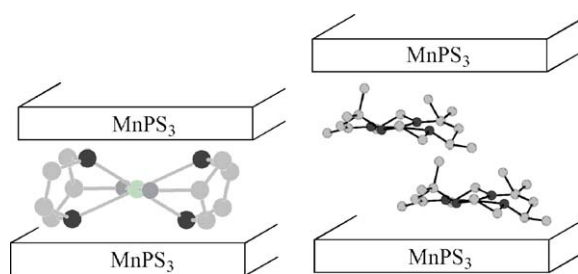


Fig. 3. Possible arrangement of guest *A* (left) and *B* (right) cations in the interlayer space of MnPS_3 .

located perpendicular to the layers, as illustrated in Fig. 3. The nearly planar complex cation *B* has a molecular size of $0.86 \text{ nm} \times 0.50 \text{ nm} \times 0.74 \text{ nm}$ [24] calculated in the same way. The large expansion of 1.093 nm seems to allow the cation to form a bimolecular arrangement parallel to the layer (Fig. 3). Further evidences are needed to confirm the structural arrangement.

3.2. Infrared spectra

The IR spectra of the intercalates and pure guests are shown in Fig. 4. The $\nu(\text{PS}_3)$ asymmetric stretching band located at 570 cm^{-1} in the pure MnPS_3 is split into two components at 557 and 606 cm^{-1} in both two intercalated compounds, reflecting the presence of intralaminar metal vacancies [25]. A number of peaks assigned to the guest complex cations are obviously observed in the spectra of intercalates. The spectrum of $\text{Mn}_{0.82}\text{PS}_3(A)_{0.18}$ intercalate shows bands at 3278 and 1431 cm^{-1} attributable to $\nu(\text{OH})$ stretching mode and $\delta(\text{OH})$ deformation mode of guest *A*. The band at 1646 cm^{-1} attributed to N–H bending mode and 1132 cm^{-1} to C–N stretching mode in $\text{Mn}_{0.82}\text{PS}_3(A)_{0.18}$ are consistent with the free guest [23]. The peak due to the C=N vibration is located at 1664 cm^{-1} for guest *B* and at 1646 cm^{-1} for $\text{Mn}_{0.87}\text{PS}_3(B)_{0.13}$ [26].

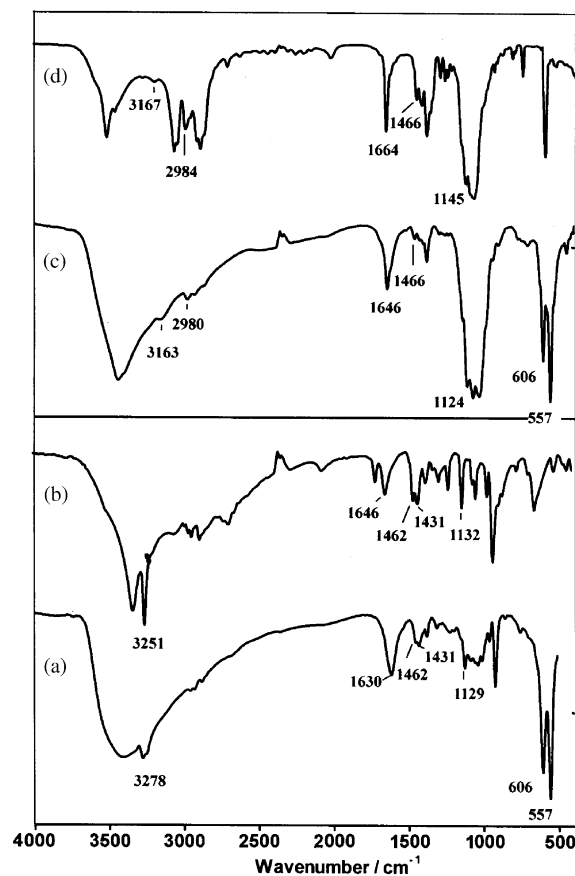


Fig. 4. IR spectra of: (a) $\text{Mn}_{0.82}\text{PS}_3(A)_{0.18}$, (b) *A*, (c) $\text{Mn}_{0.87}\text{PS}_3(B)_{0.13}$ and (d) *B*.

The frequencies at 2980 and $1300\text{--}1470 \text{ cm}^{-1}$ in $\text{Mn}_{0.87}\text{PS}_3(B)_{0.13}$ are assigned to the C–H stretching mode and C–H bending mode, respectively. The N–H and C–N stretching bands of guest *B* appeared at 3167 and 1145 cm^{-1} can also be found in the spectrum of the corresponding intercalate at 3163 and 1124 cm^{-1} .

3.3. Magnetic properties

The magnetic properties of the two intercalates were studied with SQUID magnetometer. The temperature dependence of the magnetic susceptibility of $\text{Mn}_{0.82}\text{PS}_3(A)_{0.18}$ at the applied magnetic field 500 Oe was measured in a temperature range from 1 to 300 K , as shown in Fig. 5. As may be seen from the figure, intercalation causes a drastic difference in the susceptibility behavior. The antiferromagnetic transition in pure MnPS_3 no longer exists and instead an abrupt increase of magnetic susceptibility occurs at about 40 K , which is consistent with the plot of $\chi T/T$ curve in the set of Fig. 6. In the set of Fig. 5, the inverse of the paramagnetic susceptibility is displayed as a function of temperature. As shown in the figure, the high-temperature paramagnetic region conforms the Curie–Weiss law

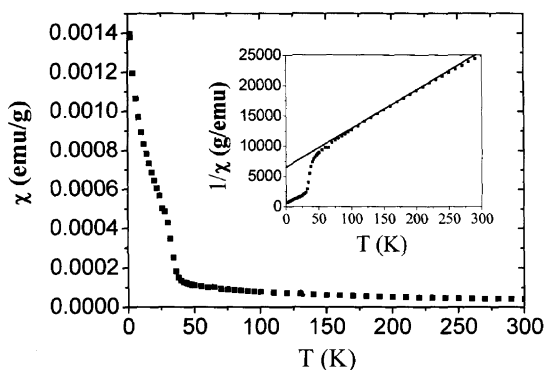


Fig. 5. Temperature dependence of the magnetic susceptibility of MnPS_3/A intercalate. The inset shows a plot of inverse of magnetic susceptibility vs. temperature.

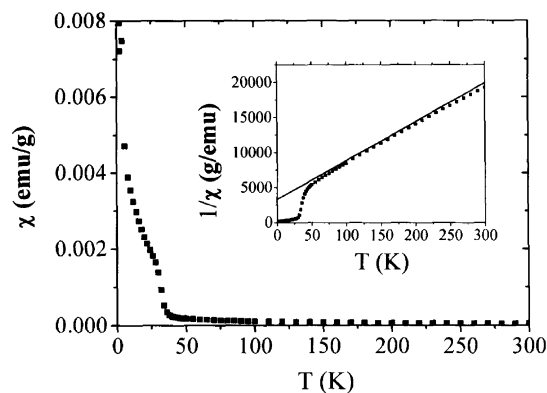


Fig. 7. Temperature dependence of the magnetic susceptibility of MnPS_3/B intercalate. The inset shows a plot of inverse of magnetic susceptibility vs. temperature.

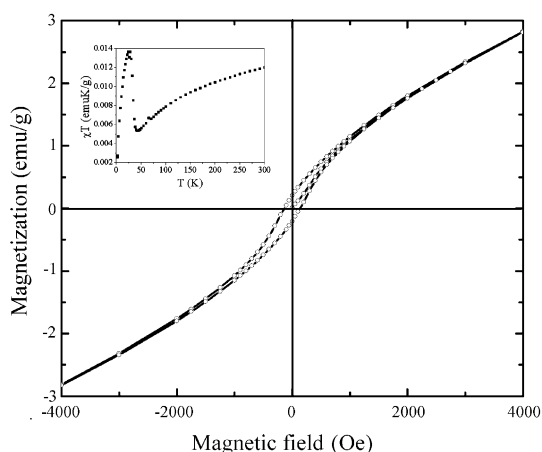


Fig. 6. Field dependence of magnetization of MnPS_3/A intercalate at 1.85 K. The inset is the curve of $\chi T - T$.

with $C = 0.0156 \text{ emu K/g}$ and $\theta = -96 \text{ K}$. The ferromagnetism of the intercalate is further confirmed by the hysteric behavior in the magnetization curve at 1.85 K shown in Fig. 6. The coercive force and remnant magnetization are 132 Oe and 0.21 emu/g, respectively.

Similar magnetic behavior is also observed for the B intercalate as shown in Figs. 7 and 8. The Curie temperature is defined as 33 K, which is slightly lower than that of A intercalate. The Curie–Weiss fitting results shown in inset of Fig. 7 gives values of $C = 0.0181 \text{ emu K/g}$ and $\theta = -53 \text{ K}$. Except for the relatively larger coercive force of 200 Oe and remnant magnetization of 1.29 emu/g, the character and shape of the magnetization curve presented in Fig. 8 is almost identical with those of A intercalate.

4. Conclusion

Cyclopolyamines are the interesting guests for the intercalation chemistry of MnPS_3 for their nearly planar configuration of the cycles and unique complexation

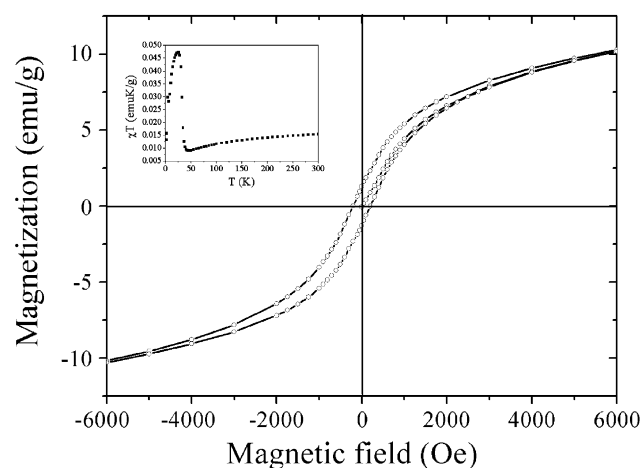


Fig. 8. Field dependence of magnetization of MnPS_3/B intercalate at 1.85 K. The inset is the curve of $\chi T - T$.

properties toward metal cations. As a result of intercalation, the lattice distance increased 0.567 and 1.093 nm, respectively, compared with the pure MnPS_3 . By calculating the molecular size and the interlayer expansion, the possible arrangement of the guests was proposed. The SQUID measurement results indicated that both exhibited bulk spontaneous magnetization below 40 and 33 K, respectively. In our opinion, this work not only presents two new members of the magnetic intercalates of MPS_3 , but also provide with first two examples of metal–cyclopolyamine complex/ MPS_3 system. In addition, they may represent a new step toward the new approach for the double-action multifunctional molecular materials.

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