

## 以 $[M(\text{DETA})_2]^{n+}$ ( $M=\text{Cu}^{2+}, \text{Ni}^{2+}, \text{Co}^{3+}$ ) 为客体的 $\text{MnPS}_3$ 夹层化合物的合成、结构表征与磁性研究

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**摘要:** 将过渡金属配合物阳离子 $[M(\text{DETA})_2]^{n+}$  ( $M=\text{Cu}^{2+}, \text{Ni}^{2+}, \text{Co}^{3+}$ ; DETA=Diethylenetriamine, 二乙烯三胺)作为客体插入层状  $\text{MnPS}_3$  层间得到了相应的 3 个夹层化合物。通过 X-射线粉末衍射、元素分析和红外光谱对夹层化合物的结构进行了表征。结果表明, 与主体  $\text{MnPS}_3$  0.65 nm 的层间距相比较, 夹层化合物 $(\text{Mn}_{0.88}\text{PS}_3[\text{Cu}(\text{DETA})_2]_{0.12})$ 的层间距扩大了 0.32 nm, 由此推测客体 $[\text{Cu}(\text{DETA})_2]^{2+}$  在层间以平面四方的配位形式存在, 而另 2 个夹层化合物 $(\text{Mn}_{0.79}\text{PS}_3[\text{Ni}(\text{DETA})_2]_{0.21})$  和  $\text{Mn}_{0.74}\text{PS}_3[\text{Co}(\text{DETA})_2]_{0.17})$ 的层间距扩大了 0.48 nm, 说明客体 $[M(\text{DETA})_2]^{n+}$  ( $M=\text{Co}^{3+}, \text{Ni}^{2+}$ ) 在主体层间以八面体配位形式存在。磁性测试结果表明过渡金属离子 $[M(\text{DETA})_2]^{n+}$  ( $M=\text{Cu}^{2+}, \text{Co}^{3+}$ )的插入能引起主体  $\text{MnPS}_3$  的磁性在 35~40 K 发生由顺磁向亚铁磁性的转变并表现自发磁化, 而客体 $[\text{Ni}(\text{DETA})_2]^{2+}$ 却使夹层化合物的反铁磁相互作用增强, 抑制了自发磁化的发生。

**关键词:** 夹层作用; 层状  $\text{MnPS}_3$ ; 二乙烯三胺; 配合物; 磁性

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## Intercalation of Cationic $[M(\text{DETA})_2]^{n+}$ ( $M=\text{Cu}^{2+}, \text{Ni}^{2+}, \text{Co}^{3+}$ ) into Layered $\text{MnPS}_3$ : Synthesis, Characterization and Magnetic Properties

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**Abstract:** Three intercalation compounds based on the insertion of cationic complex guests ( $[M(\text{DETA})_2]^{n+}$  ( $M=\text{Cu}^{2+}, \text{Ni}^{2+}, \text{Co}^{3+}$ ; DETA=Diethylenetriamine) into layered  $\text{MnPS}_3$  have been synthesized and characterized with X-ray powder diffraction, elemental analysis and infrared spectroscopy. Compared with pristine  $\text{MnPS}_3$  the lattice spacing of  $\text{Mn}_{0.88}\text{PS}_3[\text{Cu}(\text{DETA})_2]_{0.12}$  is expanded by about 0.32 nm suggesting that cationic  $[\text{Cu}(\text{DETA})_2]^{2+}$  guest exists in square geometry at the interlayer space of  $\text{MnPS}_3$ . But 0.48 nm of the lattice expansion for  $\text{Mn}_{0.79}\text{PS}_3[\text{Ni}(\text{DETA})_2]_{0.21}$  and  $\text{Mn}_{0.74}\text{PS}_3[\text{Co}(\text{DETA})_2]_{0.17}$  indicates that  $[M(\text{DETA})_2]^{n+}$  ( $M=\text{Co}^{3+}, \text{Ni}^{2+}$ ) adopts the octahedral geometry. The magnetic measurements indicate that the intercalation of  $[M(\text{DETA})_2]^{n+}$  ( $M=\text{Cu}^{2+}, \text{Co}^{3+}$ ) can induce the magnetic phase transition of  $\text{MnPS}_3$  slab from paramagnetism to ferrimagnetism at low temperature, but the insertion of  $[\text{Ni}(\text{DETA})_2]^{2+}$  strengthens antiferromagnetic interaction of the spins that suppresses the occurrence of spontaneous magnetization.

**Key words:** intercalation; layered  $\text{MnPS}_3$ ; diethylenetriamine; metal complex; magnetic property

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The intercalation of functional species into some layered inorganic solids is one of simple and effective approaches to build advanced functional materials, which has attracted considerable attention in recent years<sup>[1-6]</sup>. Through the synergic or complementary interaction between the guest and inorganic host the intercalation nanocomposites can exhibit some interesting properties<sup>[7-12]</sup>. And sometimes, they even can combine the different solid-state properties from the guest and the host to produce the multifunctional materials<sup>[13]</sup>.

The transition metal phosphorus trisulfides  $\text{MPS}_3$  ( $\text{M}=\text{Mn}, \text{Fe}, \text{Ni}, \text{Zn}, \text{Cd}$  etc.) are layered compounds made up of two dimensional arrays of  $\text{P}_2\text{S}_6^{4-}$  bridging ligand coordinated to the  $\text{M}^{2+}$  ions<sup>[14]</sup>. Among them  $\text{MnPS}_3$  shows antiferromagnetism with Neel temperature of 78 K<sup>[15-16]</sup>, which can undergo two types of intercalation reaction, the redox intercalation similar to that of the layered metal dichalcogenides<sup>[17]</sup> and the non-redox intercalation reaction based on exchange between  $\text{Mn}^{2+}$  ion of the host and cationic guest<sup>[18]</sup>. After non-redox intercalation some  $\text{Mn}^{2+}$  ions will leave the intralayer position of  $\text{MnPS}_3$  host and induce the dramatic change of magnetic properties<sup>[19-21]</sup>. For example, Clément and co-workers<sup>[22-23]</sup> reported that the intercalation of organic guests such as stilbazolium and Me-Mepepy into thin films of  $\text{MnPS}_3$  exhibited the photomagnetic effect through the structural photoisomerism by irradiation. In addition, some transition metal complexes have been chosen as the guests to be intercalated into layered  $\text{MPS}_3$  to elucidate the structure and mechanism of the intercalation<sup>[24-26]</sup> and also to explore physical properties<sup>[27-31]</sup>.

The transition metal complexes involving tridentate amines have attracted much attention in the past decades. Some metal complexes of diethylenetriamine (DETA) have been used as model compounds in bioinorganic systems or as building blocks in supramolecular assemblies<sup>[32]</sup>. Recently, Yu and co-workers reported that  $[\text{Co}(\text{DETA})_2]^{3+}$  as a guest into layered zirconium phosphate exhibited interesting photoluminescence in the UV-Vis spectra region<sup>[33]</sup>. Here we report a series of diethylenetriamine transition metal complexes intercalated into layered  $\text{MnPS}_3$ . The structural

characterization and magnetic properties of these intercalation compounds are studied and the cationic guests  $[\text{M}(\text{DETA})_2]^{n+}$  ( $\text{M}=\text{Cu}^{2+}, \text{Ni}^{2+}, \text{Co}^{3+}$ ) effects on magnetic properties of layered  $\text{MnPS}_3$  slab are discussed in this work.

## 1 Experimental

### 1.1 Materials and reagents

Pure  $\text{MnPS}_3$  was synthesized by the reaction of stoichiometric amounts of high-purity elements (>99.9%) in an evacuated quartz tube at 650 °C as described in the literature<sup>[34]</sup>. It was identified by means of XRD and indexed as a monoclinic unit cell (space group  $C2/m$ ), in which  $a=0.609\ 4\ \text{nm}$ ,  $b=1.058\ 9\ \text{nm}$ ,  $c=0.681\ 7\ \text{nm}$ ,  $\beta=107.23^\circ$ ,  $d=0.649\ 6\ \text{nm}$ .

### 1.2 Equipments

X-ray powder diffraction (XRD) patterns were recorded on a Shimadzu XRD-6000 X-ray diffractometer using  $\text{Cu K}\alpha$  radiation ( $\lambda=0.154\ 18\ \text{nm}$ ). Fourier transform infrared (FTIR) spectra were obtained on a Nicolet SX Fourier transform spectrometer in the region of  $4\ 000\sim 400\ \text{cm}^{-1}$  on KBr pellets. Elemental analysis of carbon, hydrogen, and nitrogen was performed on a Carlorba-1106 microanalyzer. Magnetic measurements were performed on polycrystalline samples with a SQUID-magnetometer (MPMS, Quantum Design) and the magnetic susceptibility was obtained in the temperature range of 1.8~300 K with an applied magnetic field of 500 Oe.

### 1.3 Synthesis

#### 1.3.1 Metal DETA complexes

General procedure for the preparation of  $[\text{M}(\text{DETA})_2]^{n+}\cdot n\text{X}^-$  ( $\text{M}=\text{Cu}^{2+}, \text{Co}^{3+}, \text{Ni}^{2+}$ ;  $\text{X}=\text{Cl}^-$  or  $\text{Br}^-$ )<sup>[35-36]</sup>: To a solution of  $\text{M}^{2+}$  ( $\text{M}=\text{Cu}, \text{Co}, \text{Ni}$ ) ion salt in water was added twofold amounts of diethylenetriamine. The mixture was stirred at room temperature for several hours, except that the solution of  $[\text{Co}(\text{DETA})_2]$  should be subject to blowing air for the other 36 hours to make sure that  $\text{Co}^{2+}$  ion is oxidized to  $\text{Co}^{3+}$  ion<sup>[36]</sup>. After filtration, the solution was evaporated to a small volume using rotary evaporator and the product was then precipitated from the solution by addition of ethanol. The product was filtered off and washed with ethanol

and acetone. The analysis results confirmed purification of the complexes.  $\text{Cu}(\text{DETA})_2\text{Br}_2 \cdot \text{H}_2\text{O}$ , calculated: C, 21.46; H, 6.30; N, 18.77. Found: C, 21.46; H, 5.85; N, 18.36.  $\text{Co}(\text{DETA})_2\text{Cl}_3 \cdot 1.5\text{H}_2\text{O}$ , calculated: C, 24.10; H, 7.33; N, 21.08. Found: C, 24.33; H, 7.23; N, 20.80.  $\text{Ni}(\text{DETA})_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ , calculated: C, 27.15; H, 7.97; N, 23.74. Found: C, 27.19; H, 7.54; N, 23.61.

### 1.3.2 Pre-intercalation compound $\text{Mn}_{1-x}\text{PS}_3\text{K}_{2x}(\text{H}_2\text{O})_y$ <sup>[37]</sup>

1.0 g of  $\text{MnPS}_3$  and 2.0 g of  $\text{KCl}$  in 10 mL  $\text{H}_2\text{O}$  were put into a 50 mL ampoule. After sealing under vacuum the mixture was stirred at 65 °C for 3 days and then filtered off. The obtained solid was washed with water and methanol for 3 times, respectively. The green powder was obtained by drying under vacuum.

### 1.3.3 Intercalation compounds $[M(\text{DETA})_2]^{n+}\text{-MnPS}_3$

General procedure: 0.15 g of pre-intercalate  $\text{Mn}_{1-x}\text{PS}_3\text{K}_{2x}(\text{H}_2\text{O})_y$  and 0.4 g of  $[M(\text{DETA})_2]^{n+} \cdot n\text{X}^-$  was put into an ampoule containing 20 mL methanol. It was sealed under vacuum and the mixture was stirred at 65 °C for one month. The powder was filtered off and washed with methanol and water, and then dried under vacuum. The analysis results suggest the formulae of the corresponding intercalation compounds.  $\text{Mn}_{0.88}\text{PS}_3[\text{Cu}(\text{DETA})_2]_{0.12}$ . Calculated: C, 5.55; H, 1.51; N, 4.85; Found: C, 5.48; H, 1.73; N, 4.69.  $\text{Mn}_{0.74}\text{PS}_3[\text{Co}(\text{DETA})_2]_{0.17}$ . Calculated: C, 7.67; H, 2.09; N, 6.71. Found: C, 7.75; H, 2.23; N, 6.58.  $\text{Mn}_{0.79}\text{PS}_3[\text{Ni}(\text{DETA})_2]_{0.21}$ . Calculated: C, 8.92; H, 2.43; N, 7.80. Found: C, 8.91; H, 2.72; N, 7.63.

## 2 Results and discussion

$\text{Mn}_{1-x}\text{PS}_3\text{K}_{2x}(\text{H}_2\text{O})_y$  was used as a pre-intercalate to react with different metal DETA complexes ( $[M(\text{DETA})_2]^{n+} \cdot n\text{X}^-$ ,  $M=\text{Cu}^{2+}$ ,  $\text{Co}^{3+}$ ,  $\text{Ni}^{2+}$ ;  $\text{X}=\text{Cl}^-$  or  $\text{Br}^-$ ) and the corresponding intercalation compounds were obtained. X-ray powder diffraction (XRD) patterns shown in Fig.1 confirm that they are the full intercalation compounds. As can be seen, the 001 reflections of  $\text{Mn}_{1-x}\text{PS}_3(\text{K})_{2x}$  are disappeared, instead, a series of new 00l reflections are observed. Compared with pristine  $\text{MnPS}_3$  ( $2\theta=13.60^\circ$ ,  $d=0.65$  nm), the 001 reflection peak of  $\text{Mn}_{0.74}\text{PS}_3[\text{Co}(\text{DETA})_2]_{0.17}$  and  $\text{Mn}_{0.79}\text{PS}_3[\text{Ni}(\text{DETA})_2]_{0.21}$  is located at  $2\theta=7.80^\circ$ , corresponding to the greatest

lattice spacing of 1.13 nm. The lattice expansion of 0.48 nm indicates that cationic complexes ( $[M(\text{DETA})_2]^{n+}$ ,  $M=\text{Ni}^{2+}$ ,  $\text{Co}^{3+}$ ) exists in octahedral geometry with six coordination numbers<sup>[16,18]</sup>. The possible existing form and geometry of  $[M(\text{DETA})_2]^{n+}$ ,  $M=\text{Ni}^{2+}$  and  $\text{Co}^{3+}$  are proposed as in Fig.2. Different from  $\text{Mn}_{0.74}\text{PS}_3[\text{Co}(\text{DETA})_2]_{0.17}$  and  $\text{Mn}_{0.79}\text{PS}_3[\text{Ni}(\text{DETA})_2]_{0.21}$ , the lattice spacing of  $\text{Mn}_{0.88}\text{PS}_3[\text{Cu}(\text{DETA})_2]_{0.12}$  is only increased to 0.97 nm and the corresponding spacing expansion is about 0.32 nm ( $\Delta d=0.97\sim 0.65$  nm). This suggests that  $\text{Cu}^{2+}$  ion adopts 4 coordination numbers to form cationic  $[\text{Cu}(\text{DETA})_2]^{2+}$  complex at the interlayer region of  $\text{MnPS}_3$  and its square geometric plane is parallel to the  $\text{MnPS}_3$  layer (shown in Fig.2). In addition, the less loaded cationic  $[\text{Cu}(\text{DETA})_2]^{2+}$  than  $[M(\text{DETA})_2]^{n+}$  ( $M=\text{Ni}^{2+}$  and  $\text{Co}^{3+}$ ) into interlayer space of  $\text{MnPS}_3$  is also an indirect evidence to support that  $[\text{Cu}(\text{DETA})_2]^{2+}$  is in square geometry with 4 coordination numbers. Thus, it occupies much more interlayer area than octahedral geometry with 6 coordination numbers.

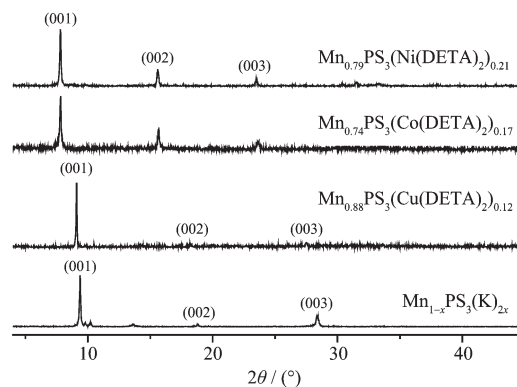


Fig.1 XRD patterns of pre-intercalate  $\text{Mn}_{1-x}\text{PS}_3(\text{K})_{2x} \cdot y\text{H}_2\text{O}$ ,  $\text{Mn}_{0.88}\text{PS}_3[\text{Cu}(\text{DETA})_2]_{0.12}$ ,  $\text{Mn}_{0.74}\text{PS}_3[\text{Co}(\text{DETA})_2]_{0.17}$  and  $\text{Mn}_{0.79}\text{PS}_3[\text{Ni}(\text{DETA})_2]_{0.21}$

The characteristic IR absorption of guest molecules and the related intercalation compounds are listed in Table 1. Three intercalation compounds exhibit analogous characteristic IR absorptions to the related  $[M(\text{DETA})_2]^{n+}$  cationic complexes in the range of 700~2 000  $\text{cm}^{-1}$ . As an example, Fig.3 gives the IR spectra of  $\text{Ni}(\text{DETA})_2\text{Cl}_2 \cdot \text{H}_2\text{O}$  and  $\text{Mn}_{0.79}\text{PS}_3[\text{Ni}(\text{DETA})_2]_{0.21}$  for comparison. The absorptions at about 1 622, 1 590, 1 456, 1 108 and 1 069  $\text{cm}^{-1}$  are the characteristic vibrations for  $[\text{Ni}(\text{DETA})_2]^{2+}$  complex, that is similar to

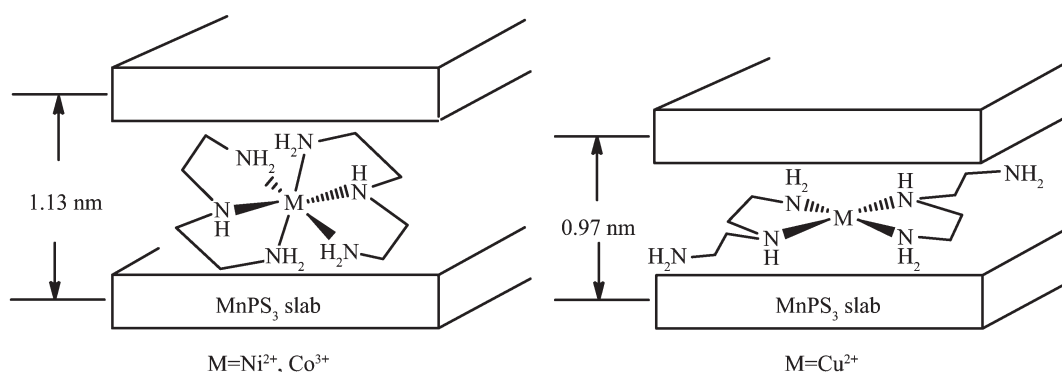


Fig.2 Possible geometry and arrangement of the cationic  $[M(\text{DETA})_2]^{n+}$  ( $M=\text{Ni}^{2+}$ ,  $\text{Co}^{3+}$ ,  $\text{Cu}^{2+}$ ) guest in the interlayer space of  $\text{MnPS}_3$  slab

**Table 1 Comparison of IR spectra of the guest molecules with the related intercalation compounds ( $\text{cm}^{-1}$ ):**  
 **$\text{Mn}_{0.88}\text{PS}_3[\text{Cu}(\text{DETA})_2]_{0.12}$ ,  $\text{Mn}_{0.74}\text{PS}_3[\text{Co}(\text{DETA})_2]_{0.17}$  and  $\text{Mn}_{0.79}\text{PS}_3[\text{Ni}(\text{DETA})_2]_{0.21}$**

	A	B	C	D	E	F
$\nu_{\text{N-H}}$	3 378, 3 329, 3 253, 3 136	3 268	3 172, 3 055	3 217, 3 084	3 324, 3 265, 3 186, 3 171	3 309, 3 270
$\nu_{\text{C-H}}$	2 919, 2 872	2 961, 2 917	2 958, 2 883	2 923, 2 870	2 917, 2 869	2 920, 2 878
$\nu_{\text{N-H}}$	1 618, 1 568	1 633, 1 572	1 608, 1 552	1 633	1 622, 1 563	1 625, 1 590
$\nu_{\text{C-N}}$	1 470, 1 446	1 461	1 482, 1 453	1 469	1 450	1 456
$\nu_{\text{C-N}}$	1 093, 1 025, 978	1 124	1 097, 1 058, 1 041	1 120, 1 075, 1 033	1 087, 1 009, 977	1 108, 1 069
$\nu_{\text{PS}}$		617, 589, 563		619, 605, 553		608, 557

Note: A:  $[\text{Cu}(\text{DETA})_2]\text{Br}_2$ ; B:  $\text{Mn}_{0.88}\text{PS}_3[\text{Cu}(\text{DETA})_2]_{0.12}$ ; C:  $[\text{Co}(\text{DETA})_2]\text{Cl}_3$ ; D:  $\text{Mn}_{0.74}\text{PS}_3[\text{Co}(\text{DETA})_2]_{0.17}$ ; E:  $[\text{Ni}(\text{DETA})_2]\text{Cl}_2$ ; F:  $\text{Mn}_{0.79}\text{PS}_3[\text{Ni}(\text{DETA})_2]_{0.21}$ .

those results reported by some references<sup>[36]</sup>. The small difference for some IR absorption vibrations between guest molecule and the related intercalation compounds can be attributed to the interlayer region environment of the host as well as the interaction of host and guest. Similar phenomenon has been observed in some other  $\text{MnPS}_3$  intercalation compounds<sup>[39-40]</sup>.

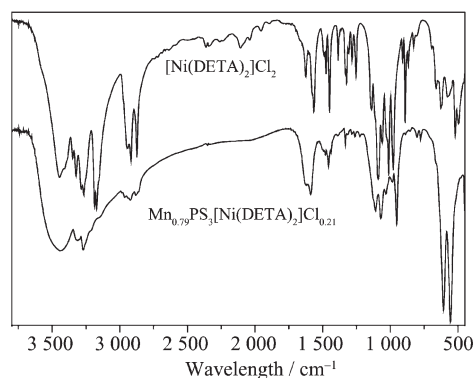


Fig.3 IR spectra of  $[\text{Ni}(\text{DETA})_2]\text{Cl}_2$  and  $\text{Mn}_{0.79}\text{PS}_3[\text{Ni}(\text{DETA})_2]_{0.21}$

In addition, there are two or three characteristic IR absorptions occurring at around  $620\sim 550\text{ cm}^{-1}$  for these intercalation compounds, which originates from the

splitting of  $570\text{ cm}^{-1}$  of pure  $\text{MnPS}_3$ . This is the evidence of the presence of intralayered  $\text{Mn}^{2+}$  vacancies<sup>[41-42]</sup>. Obviously, the inserted guest exists in the cationic form to compensate positive charge of  $\text{Mn}^{2+}$  ions leaving from the intralayer position and also to maintain charge balance of the intercalation compound.

The curves of magnetic susceptibility ( $\chi$ ) versus temperature ( $T$ ) for three intercalation compounds are shown in Fig.4~6. As can be seen, they show similar magnetic behaviour above 50 K, where  $\chi$  gradually increases with the decrease in temperature. The Curie-Weiss law can be applied to fit  $1/\chi-T$  curve well above 50 K and the Weiss constant ( $\theta$ ) is obtained for  $\text{Mn}_{0.88}\text{PS}_3[\text{Cu}(\text{DETA})_2]_{0.12}$  ( $\theta=-33\text{ K}$ ),  $\text{Mn}_{0.74}\text{PS}_3[\text{Co}(\text{DETA})_2]_{0.17}$  ( $\theta=-51\text{ K}$ ) and  $\text{Mn}_{0.79}\text{PS}_3[\text{Ni}(\text{DETA})_2]_{0.21}$  ( $\theta=-83\text{ K}$ ), respectively. The negative  $\theta$  value indicates that the localized magnetic interaction between the intralayer  $\text{Mn}^{2+}$  spins is antiferromagnetic. However, the difference of negative  $\theta$  value indicates that the strength of interaction for three intercalation compounds is different. For example,  $\text{Mn}_{0.79}\text{PS}_3[\text{Ni}(\text{DETA})_2]_{0.21}$  shows the largest

negative Weiss constant ( $\theta = -83 \text{ K}$ ) indicating that its antiferromagnetic interaction is stronger than that of the other two intercalation compounds. As the temperature further decreases to about 40 K, an obvious rise-up of the magnetic susceptibility is observed for all the intercalation compounds. This is an evidence for the occurrence of magnetic phase transition.

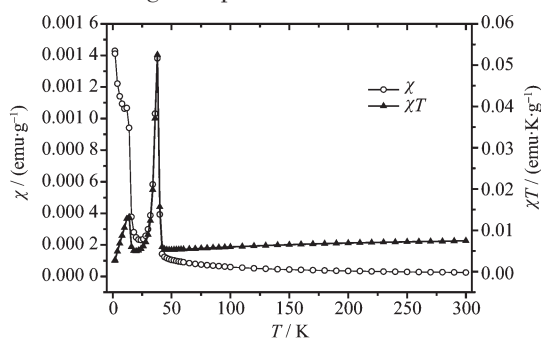


Fig.4  $\chi$ - $T$  and  $\chi T$ - $T$  curves of  $\text{Mn}_{0.88}\text{PS}_3[\text{Cu}(\text{DETA})_2]_{0.12}$

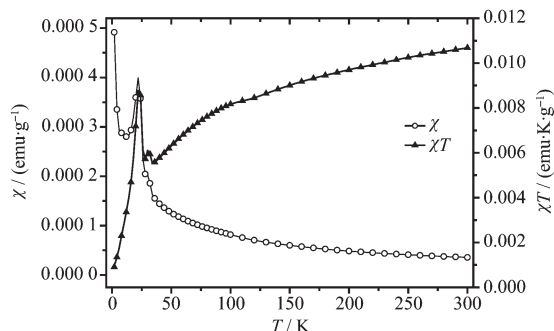


Fig.5  $\chi$ - $T$  and  $\chi T$ - $T$  curves of  $\text{Mn}_{0.74}\text{PS}_3[\text{Co}(\text{DETA})_2]_{0.17}$

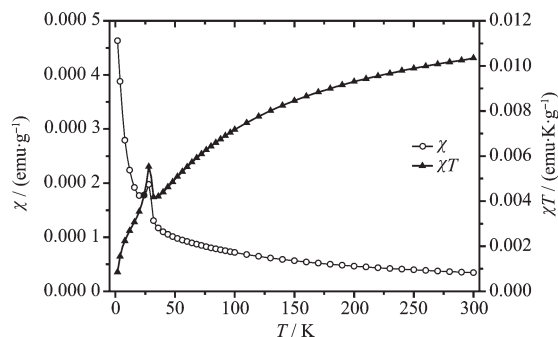


Fig.6  $\chi$ - $T$  and  $\chi T$ - $T$  curves of  $\text{Mn}_{0.79}\text{PS}_3[\text{Ni}(\text{DETA})_2]_{0.21}$

Fig.7~9 show the relationship of magnetization ( $M$ ) versus applied magnetic field ( $H$ ) measured at 1.85 K for three intercalation compounds. It can be seen that  $\text{Mn}_{0.88}\text{PS}_3[\text{Cu}(\text{DETA})_2]_{0.12}$  and  $\text{Mn}_{0.74}\text{PS}_3[\text{Co}(\text{DETA})_2]_{0.17}$  show the hysteresis with remnant magnetization of 251 and 57  $\text{emu} \cdot \text{mol}^{-1}$  and coercive field of 200 and 300 Oe, respectively. This confirms that both of them are low-temperature ferrimagnets. However,  $\text{Mn}_{0.79}\text{PS}_3[\text{Ni}$

$(\text{DETA})_2]_{0.21}$  does not show obvious hysteresis loop, indicating that spontaneous magnetization does not occur at low temperature.

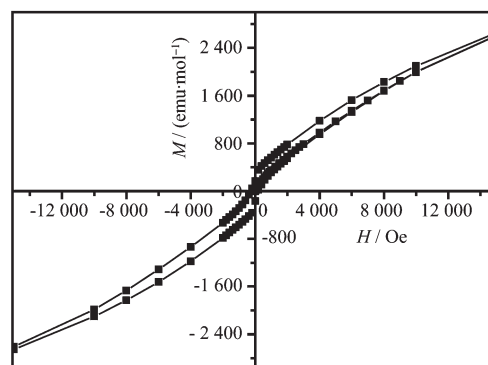


Fig.7  $M$ - $H$  curve of  $\text{Mn}_{0.88}\text{PS}_3[\text{Cu}(\text{DETA})_2]_{0.12}$  at 1.85 K

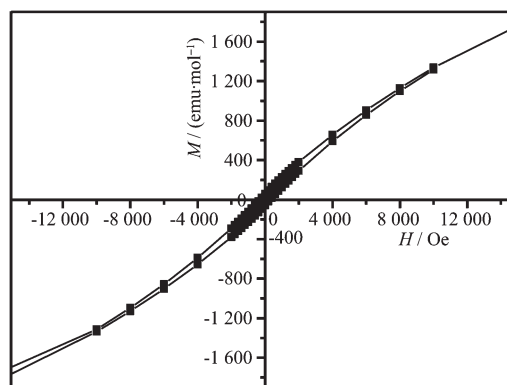


Fig.8  $M$ - $H$  curve of  $\text{Mn}_{0.74}\text{PS}_3[\text{Co}(\text{DETA})_2]_{0.17}$  at 1.85 K

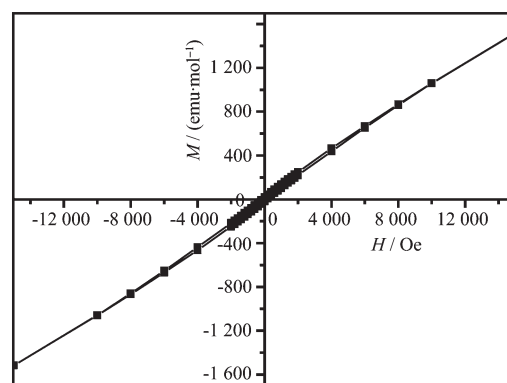


Fig.9  $M$ - $H$  curve of  $\text{Mn}_{0.79}\text{PS}_3[\text{Ni}(\text{DETA})_2]_{0.21}$  at 1.85 K

The origin of magnetism for  $\text{MnPS}_3$  intercalation compounds had been investigated by O' Hare and Clément et al.<sup>[43]</sup> It was proposed that the ferrimagnetism arises from parts of  $\text{Mn}^{2+}$  ions leaving  $\text{MnPS}_3$  lattice to form the ordered  $\text{Mn}^{2+}$  vacancies during the ion-exchange process. According to this proposition it can be inferred that the insertion of cationic  $[M(\text{DETA})_2]^{n+}$  makes  $\text{Mn}^{2+}$  ions leave the  $\text{MnPS}_3$  lattice and result in



the incomplete compensation of antiferromagnetically coupled  $\text{Mn}^{2+}$  spins. Among them, intercalation of  $[\text{M}(\text{DETA})_2]^{n+}$  ( $\text{M}=\text{Cu}^{2+}$ ,  $\text{Co}^{3+}$ ) into  $\text{MnPS}_3$  induces spontaneous magnetization at low temperature. However, the intercalation of  $[\text{Ni}(\text{DETA})_2]^{2+}$  seems to strengthen antiferromagnetic interaction of the intralayer  $\text{Mn}^{2+}$  spins that suppresses the occurrence of low-temperature spontaneous magnetization.

### 3 Conclusions

Via the insertion of cationic complexes  $[\text{M}(\text{DETA})_2]^{n+}$  ( $\text{M}=\text{Cu}^{2+}$ ,  $\text{Co}^{3+}$ ,  $\text{Ni}^{2+}$ ) into layered  $\text{MnPS}_3$  three intercalation compounds are obtained. XRD results confirm the occurrence of full intercalation and infrared spectra support the presence of cationic complex guests located at the interlayer space of  $\text{MnPS}_3$ . The magnetic measurements indicate that the intercalation of cationic complexes with different metal ions can influence the magnetic properties of the layered  $\text{MnPS}_3$  slab.

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