



## The Intercalation of 4-Aminopyridine into Layered FePS<sub>3</sub>

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### Abstract

A new intercalation compound, Fe<sub>0.81</sub>PS<sub>3</sub>(4-aminopyridineH)<sub>0.38</sub>, is synthesized by the direct reaction of 4-aminopyridine with layered FePS<sub>3</sub> in the presence of acetic acid. From the XRD results it was found that there are two phases (Phase I and Phase II) in this intercalation compound and that 4-aminopyridines as the guests adopt two different orientations between the interlayer region of the host (FePS<sub>3</sub>). In one of them with the lattice expansion ( $\Delta d$ ) of 6.0 Å the ring plane of the guest is perpendicular to the layer and in the other with  $\Delta d$  of 3.4 Å the ring plane of the guest is parallel to the layer of the host. The IR spectra imply that the inserted guests take the protonated form to maintain the charge balance of the intercalation compound. Magnetic measurements indicate that Fe<sub>0.81</sub>PS<sub>3</sub>(4-aminopyridineH)<sub>0.38</sub> exhibits paramagnetism in the range of measurement temperature (1.8 ~ 300 K), where the magnetic behavior is well in agreement with the Curie-Weiss Law above 55 K.

### Introduction

In recent years much interest has focused on the inorganic-organic hybrid compounds because this offers perspectives for the realization of molecular-based materials, especially those that can combine different properties such as metal-like conductivity and bulk ferromagnetic property in a single material [1]. Intercalation of organic species into layered inorganic solids represents one of the useful approaches to create the ordered molecular-based materials with some novel properties [2].

The MPS<sub>3</sub> compounds, in which M is a divalent transition metal, are a class of layered inorganic materials. They crystallize to space group C2/m, a monoclinic unit cell related to CdCl<sub>2</sub>-type structure with metal ions and phosphorus-phosphorus pairs occupying the cadmium positions and sulfur ions occupying the chloride positions, so M ions construct a honeycomb lattice in the *ab* plane and they are separated by Van der Waals gap between hexagonal layers of sulfur ions [3]. Some MPS<sub>3</sub> phases containing the paramagnetic M<sup>2+</sup> ions (Mn<sup>2+</sup>, *S* = 5/2; Fe<sup>2+</sup>, *S* = 2; Ni<sup>2+</sup>, *S* = 1) show the quasi-two-dimensional anti-ferromagnetism with a Néel temperature of 78 K, 120 K and 153 K, respectively [4]. When guest species are inserted into the interlayer space of MPS<sub>3</sub> (M = Mn, Fe), they can lead to the occurrence of some intralamellar M<sup>2+</sup> ion vacancies that makes the magnetic properties of the MPS<sub>3</sub> host lattice be changed and even dramatically altered [5–8]. In this paper, the synthesis, structural characteriza-

tion and magnetic property of the intercalation compound (Fe<sub>0.81</sub>PS<sub>3</sub>(4-aminopyridineH)<sub>0.38</sub>) are presented and a possible intercalation process is proposed for 4-aminopyridine into layered FePS<sub>3</sub>.

### Experimental

X-ray powder diffraction (XRD) patterns were obtained with Dmaxr A X-ray diffractometer using Cu K $\alpha$  radiation ( $\lambda$  = 1.5418 Å). Infrared spectrum was performed on a Nicolet SX Fourier transform spectrometer. Elemental analysis was performed with a Carlorba-1106 microanalyzer, and the magnetic property was studied by a SQUID-magnetometer (MPMS, Quantum Design).

Pure FePS<sub>3</sub> was synthesized as described by Taylor [9]. It was identified by means of XRD and indexed in a monoclinic unit cell (space group C2/m, *d* = 6.439 Å, *a* = 5.934 Å, *b* = 10.280 Å, *c* = 6.722 Å,  $\beta$  = 107.16°) [10]. 4-aminopyridine was purchased from Aldrich and 4-aminopyridine-HCl was synthesized by the reaction of 4-aminopyridine with chloride acid (HCl 36.5%, AR).

The intercalation compound Fe<sub>0.81</sub>PS<sub>3</sub>(4-aminopyridineH)<sub>0.38</sub> was prepared by stirring the mixture of FePS<sub>3</sub> (0.20 g, 1.1 mmol), 4-aminopyridine (0.60 g, 6.4 mmol) and acetic acid (HOAc) (1.0 mL) in a Pyrex ampoule containing 12 mL acetonitrile sealed under vacuum for two weeks at 70 °C. The black powder was filtered off, and washed with acetonitrile, ethanol and distilled water, and then dried in air. Elemental analysis led to the formula Fe<sub>0.81</sub>PS<sub>3</sub>(4-

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aminopyridineH)<sub>0.38</sub> (Found: C, 11.00; H, 1.05; N, 4.80 (%). Calculated: C, 10.94; H, 1.29; N, 5.10(%)).

## Results and discussion

### *X-ray powder diffraction*

The completion of intercalation was ascertained by X-ray powder diffraction (XRD). XRD reflection patterns show that the original *00l* reflection patterns of pure FePS<sub>3</sub> are totally absent and two new series of *00l* reflection patterns are observed in Fe<sub>0.81</sub>PS<sub>3</sub>(4-aminopyridineH)<sub>0.38</sub> (Figure 1(2)). This indicates that there are two phases (Phase I and Phase II) in this intercalation compound and the guest (4-aminopyridine) adopts two different orientations between the interlayer region of the host (FePS<sub>3</sub>). Phase I has the lattice spacing (*d*) of 12.44 Å corresponding to the lattice expansion ( $\Delta d$ ) of 6.0 Å indicating that the ring plane of the guest is perpendicular to the layer, which is in the similar case to that of mono-protonated 2,2'-pyridine (2,2'-pyridineH<sup>+</sup>) inserted into FePS<sub>3</sub> [11]. Phase II with lattice spacing (*d*) of 9.8 Å (expanded by 3.4 Å) corresponds to the pyridine ring plane parallel to the layer of the host, in which the guest is arranged in the similar orientation for protonated pyridine (pyridineH<sup>+</sup>) to be intercalated into FePS<sub>3</sub> [12] (Scheme 1 Equation (3)).

By comparison of the XRD reflection patterns of Fe<sub>0.81</sub>PS<sub>3</sub>(4-aminopyridineH)<sub>0.38</sub> with those of intercalation compounds 2,2'-bipyridineH/FePS<sub>3</sub> [11] and pyridineH/FePS<sub>3</sub> [12] in detail, it was found that the reflection patterns of two phases (Phase I and Phase II) in Fe<sub>0.81</sub>PS<sub>3</sub>(4-aminopyridineH)<sub>0.38</sub> can be readily indexed in the C2/m space group closely related to that of pristine FePS<sub>3</sub>, respectively. The calculated unit cell parameters are given in Table 1. Among them, the calculated *a*, *b* and  $\beta$  values are almost identical with that of pristine FePS<sub>3</sub> except the expansion of the unit parameter *c* and lattice spacing *d* in both phases. This means that the layered structure of the host is maintained after intercalation.

### *Infrared spectra*

In general, the intercalation compounds based on MPS<sub>3</sub> (M = Mn, Fe, Cd etc) have two or three sharp absorptions in the range 550~610 cm<sup>-1</sup>, which are assigned to the  $\nu(\text{PS}_3)$  asymmetric stretching band coming from the splitting of 570 cm<sup>-1</sup> in pure MPS<sub>3</sub> owing to departure of a fraction of metal ions into the solution during the intercalation. The occurrence of the intralamellar M<sup>2+</sup> vacancies makes the P-S bonds in the group of PS<sub>3</sub> unequivalent because some of PS<sub>3</sub> groups are surrounding the M<sup>2+</sup> vacancies and others are also coordinated to the M<sup>2+</sup> ions [13]. Therefore, the intense bands at 604 and 556 cm<sup>-1</sup> can be attributed to the  $\nu(\text{PS}_3)$  asymmetric stretching band, which reflects the occurrence of intralamellar Fe<sup>2+</sup> ion vacancies in Fe<sub>0.81</sub>PS<sub>3</sub>(4-aminopyridineH)<sub>0.38</sub>. There are numerous absorptions in the 700~3500 cm<sup>-1</sup> range that can be assigned to the guest.

We also measured the spectra of 4-aminopyridine and 4-aminopyridine-HCl. By comparison of the IR spectra of Fe<sub>0.81</sub>PS<sub>3</sub>(4-aminopyridineH)<sub>0.38</sub>, 4-aminopyridine and 4-aminopyridine-HCl [14] (Table 2 and Figure 2), the spectrum of Fe<sub>0.81</sub>PS<sub>3</sub>(4-aminopyridineH)<sub>0.38</sub> exhibits some characteristic absorption bands at 3319, 3196, 2964, 2934, 1651, 1589, 1526, 1198, 997, 816 and 501 cm<sup>-1</sup> etc., which is similar to those of 4-aminopyridine-HCl but different from 4-aminopyridine. This suggests that the inserted guests are the protonated 4-aminopyridine cations formed by proton exchange between acetic acid and 4-aminopyridine in the solution.

### *Magnetic properties*

The magnetic properties of Fe<sub>0.81</sub>PS<sub>3</sub>(4-aminopyridineH)<sub>0.38</sub> were studied with SQUID. The antiferromagnetic transition at 120 K in pure FePS<sub>3</sub> no longer exists. Figure 3 displays the molar susceptibility ( $\chi$ ) and the inverse of the molar susceptibility ( $1/\chi$ ) versus temperature (*T*) of Fe<sub>0.81</sub>PS<sub>3</sub>(4-aminopyridineH)<sub>0.38</sub> and Figure 4 shows the plot of  $\chi T$  versus *T*. From Figure 3 it was found that Fe<sub>0.81</sub>PS<sub>3</sub>(4-aminopyridineH)<sub>0.38</sub> exhibits the paramagnetism in the range of the measured temperature (2~300 K). And the curve of  $\chi T$  vs. *T* in Figure 4 shows that the  $\chi T$  value monotonically decreases as the temperature decreases in the whole temperature range indicating that the magnetic interaction between the localized Fe<sup>2+</sup> ions is antiferromagnetic one in the paramagnetic range. This behavior is confirmed by the inverse of the paramagnetic susceptibility as a function of temperature of Fe<sub>0.81</sub>PS<sub>3</sub>(4-aminopyridineH)<sub>0.38</sub> displayed in Figure 3. The inverse of the paramagnetic susceptibility is well in agreement with Curie-Weiss Law above 55 K. The Curie constant is 3.20 cm<sup>3</sup>·K·mol<sup>-1</sup> and the effective magnetic moment per Fe<sup>2+</sup> ion is evaluated as 5.0 BM, which is closed to that of the spin-only value of high spin Fe<sup>2+</sup> ion (4.94 BM) [15]. This suggests that the Fe<sup>2+</sup> ion is still in the +2 oxidation state after intercalation. Weiss constant ( $\theta$ ) is about -173 K that also reflects the strong localized antiferromagnetic coupling interaction between the Fe<sup>2+</sup> ions. However, its antiferromagnetic coupling interaction between the Fe<sup>2+</sup> ions is much different from that of pure FePS<sub>3</sub> that shows the ferromagnetic coupling interaction in paramagnetic range ( $\theta = +104$  K) [4]. Due to the intercalation the existence of the intralayered the Fe<sup>2+</sup> ion vacancies may change the magnetic interaction of the localized Fe<sup>2+</sup> ions of the host layer.

From the above magnetic behavior, it is found that the magnetic property of Fe<sub>0.81</sub>PS<sub>3</sub>(4-aminopyridineH)<sub>0.38</sub> is different from either its similar intercalation compounds such as pyridinium-FePS<sub>3</sub>, N-methylpyridinium-FePS<sub>3</sub> that exhibit spontaneous magnetization at low temperature [12] or Fe<sub>0.90</sub>PS<sub>3</sub>(phen)<sub>0.41</sub> showing antiferromagnetic transition with *T*<sub>N</sub> at about 75 K [11]. It is also different from the pristine FePS<sub>3</sub> with the antiferromagnetic transition at *T*<sub>N</sub> of about 120 K [4]. Why does Fe<sub>0.81</sub>PS<sub>3</sub>(4-aminopyridineH)<sub>0.38</sub> exhibits the paramagnetism? The main reason is that the occurrence of the intralayered Fe<sup>2+</sup> ion vacancies in the intercalation compound dilutes the magnetic

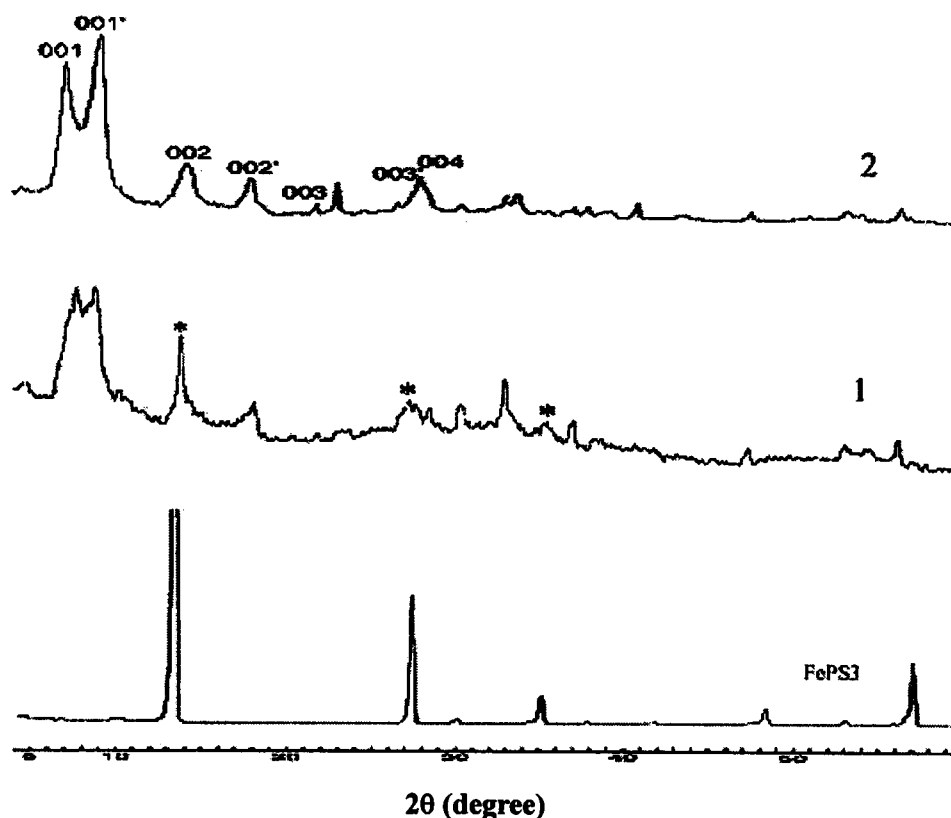


Figure 1. The XRD reflection patterns of different intercalation products and pure  $\text{FePS}_3$  for comparison **1** – partial intercalation of 4-aminopyridine with  $\text{FePS}_3$  (\* Represents the reflection patterns of pristine  $\text{FePS}_3$ ); **2** full intercalation of 4-aminopyridine with  $\text{FePS}_3$ .

Table 1. Lattice spacing (d) and calculated unit cell parameters

Compound		d (Å)	a (Å)	b (Å)	c (Å)	$\beta$ (deg)
$\text{FePS}_3$		6.439	5.934	10.280	6.722	107.16
$\text{Fe}_{0.81}\text{PS}_3(4\text{-aminopyridineH})_{0.38}$	Phase I	12.44	5.935	10.280	13.510	113.00
	Phase II	9.82	5.940	10.300	16.660	113.10

coupling interaction between the  $\text{Fe}^{2+}$  ions. It was reported that  $\text{Fe}_{0.83}\text{PS}_3(2,2\text{-bipyH})_{0.34}$  [11] also exhibited paramagnetism in the range of its measured temperature (2~300 K). In these two intercalation compounds  $\text{Fe}_{1-x}\text{PS}_3(\text{G})_{2x}$  (G stands for the guest with +1 positive charge), the intralayered  $\text{Fe}^{2+}$  ion vacancies are equal or more than 0.17. It is clear that the dilution of the  $\text{Fe}^{2+}$  ion vacancies is much stronger than that of other related intercalation compounds such as  $\text{Fe}_{0.88}\text{P}_{0.99}\text{S}_3(\text{pyridinium})_{0.24}$ ,  $\text{Fe}_{0.89}\text{P}_{0.99}\text{S}_3(4\text{-picolinium})_{0.20}$  and  $\text{Fe}_{0.90}\text{PS}_3(1,10\text{-phenanthroline})_{0.41}$ , in which the intralayered  $\text{Fe}^{2+}$  ion vacancies is less than 0.12. It is anticipated that the more the  $\text{Fe}^{2+}$  ion vacancies, the stronger the dilution in the host of  $\text{FePS}_3$ , which may drastically alter the magnetic properties of the intercalation compound and make an antiferromagnet of pure  $\text{FePS}_3$  become a paramagnet after intercalation.

#### Synthesis and the possible intercalation process

In the study of the intercalation of 4-aminopyridine with  $\text{FePS}_3$  it was found that in the absence of acetic acid this

intercalation did not occur, which was confirmed by XRD results where the product shows the same x-ray reflection patterns to those of pristine  $\text{FePS}_3$ . This is because there does not exist 4-aminopyridine $\text{H}^+$  in this intercalation. In order to obtain the intercalation compound containing only one phase (phase I or phase II), the synthesis of 4-aminopyridine with layered  $\text{FePS}_3$  has been tried three times through changing the amount of HOAc used. It was also found if the amount of HOAc is less than 0.5 mL in the reaction only the partial intercalation compound is obtained, and the XRD measurement showed that patterns of Phase I and Phase II do exist and some  $\text{FePS}_3$  still remained in this case of 0.5 mL HOAc (Figure 1 in 1). Obviously, the amount of HOAc plays a key role in the intercalation of 4-aminopyridine with  $\text{FePS}_3$ .

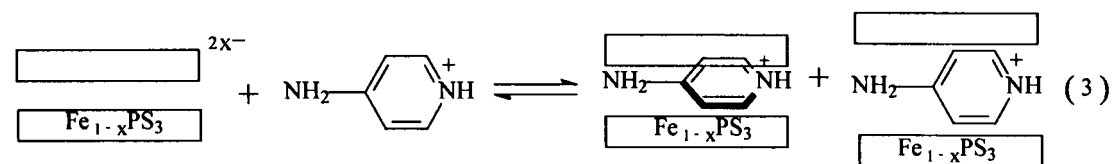
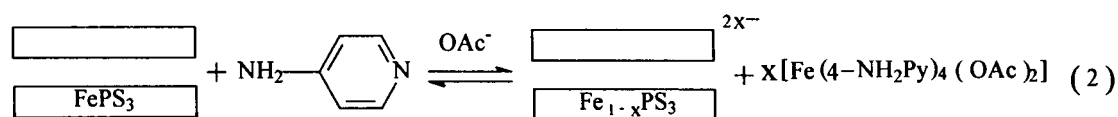
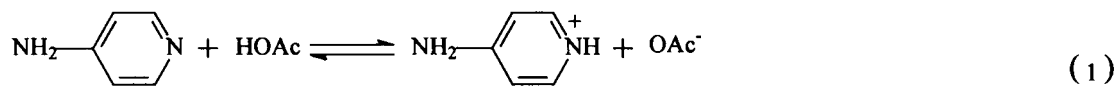
From the experimental results, a possible intercalation process is proposed for 4-aminopyridine intercalated into layered  $\text{FePS}_3$  as Scheme 1.

As discussed, the infrared spectrum indicates that the inserted guest is the protonated 4-aminopyridine and there are some intralamellar  $\text{Fe}^{2+}$  ion vacancies in the host. How does

Table 2. The IR data of 4-aminopyridine, 4-aminopyridine·HCl and Fe<sub>0.81</sub>PS<sub>3</sub>(4-amino pyridineH)<sub>0.38</sub>

Assignments	4-NH <sub>2</sub> Py	4-NH <sub>2</sub> Py·HCl	Fe <sub>0.81</sub> PS <sub>3</sub> (4-NH <sub>2</sub> PyH) <sub>0.38</sub>
ν(NH)	3437 (3433)		
	3303 (3302)	3314 (3313)	3319
ν(CH)		3200 (3195)	3196
		3140 (3143)	3144
		3089 (3091)	3088
ν(NH <sup>+</sup> )		3039 (3042)	
		2966 (2968)	2964
δ(NH <sub>2</sub> or NH <sub>2</sub> <sup>+</sup> )		2934 (2936)	2934
	1649 (1645)	1652 (1650)	1651
ν(C=N <sup>+</sup> or C=C)	1601 (1596)	1638 (1636)	
	1557 (1555)	1595 (1592)	1589
	1523 (1523)	1525 (1527)	1526
	1507 (1508)		
δ(C-H)	1474 (1479)		
	1435 (1435)		1440
		1406 (1402)	1414
		1375 (1375)	
		1367 (1364)	
		1333 (1334)	
		1270 (1270)	
		1266(1262)	
		1218 (1219)	
		1191 (1189)	1198
		1102	1051
		1053 (1052)	1049 (1050)
			1022
		991 (990)	995 (991)
	885	920	
ν(PS <sub>3</sub> )	842 (842)	847 (846)	
	822 (824)	805 (801)	816
	737	715	
	681 (680)	587	
	536	526	
		500	501
			604
		556	

Note: The data in parentheses are cited from reference 14.



Scheme 1. The possible intercalation process of FePS<sub>3</sub> with 4-aminopyridin.

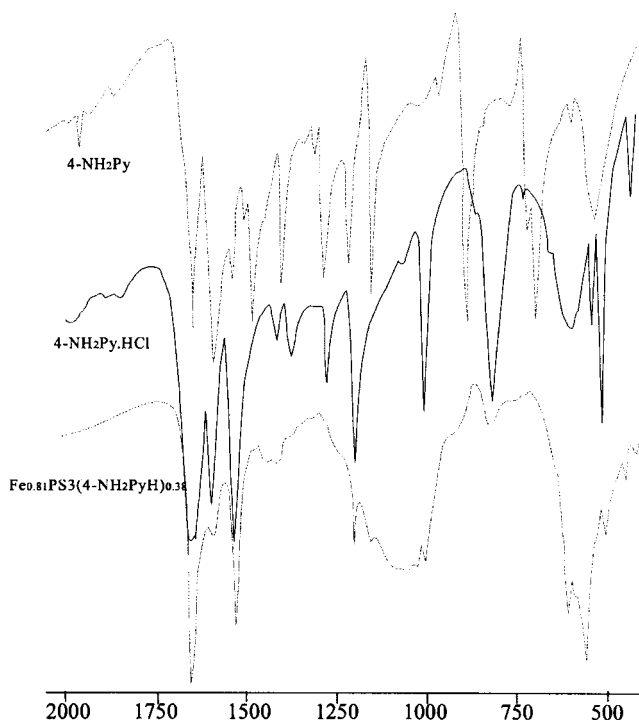


Figure 2. The infrared spectra of 4-aminopyridine, 4-aminopyridine·HCl and  $\text{Fe}_{0.81}\text{PS}_3(4\text{-aminopyridineH})_{0.38}$ .

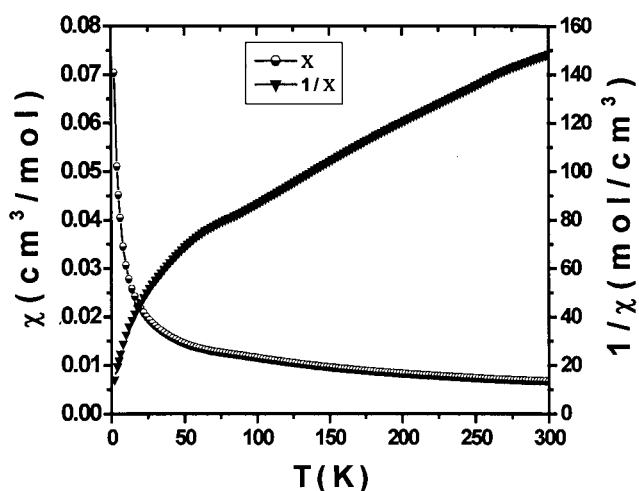


Figure 3. Temperature dependence of magnetic susceptibility ( $\chi$ ) and the inverse of magnetic susceptibility ( $1/\chi$ ) of  $\text{Fe}_{0.81}\text{PS}_3(4\text{-aminopyridineH})_{0.38}$  (the plot of  $1/\chi$ -T above 55 K is in good agreement with the Curie-Weiss Law).

the protonated 4-aminopyridine come from? Because acetic acid is present in this intercalation, some 4-aminopyridine can obtain the protons from acetic acid to form the protonated 4-aminopyridine (4-aminopyridineH<sup>+</sup>) and acetic anion (Scheme 1 Equation 1). And how does the intralamellar Fe<sup>2+</sup> ion vacancies occur? It is known that pyridine and its derivatives such as  $\beta$ - or  $\gamma$ -picoline etc., have the strong ability to coordinate with Fe<sup>2+</sup> salts to form a series of complexes  $\text{FePy}_4\text{L}_2$  (Py = pyridine and its derivatives, L = HCOO, OAc, Cl, Br, I, SCN etc.) [16–20]. Therefore, in this intercalation it may be inferred that 4-aminopyridine (4-NH<sub>2</sub>Py) and acetic anion (OAc<sup>-</sup>) can remove some intralamellar Fe<sup>2+</sup> ions to form the similar complex [Fe(4-

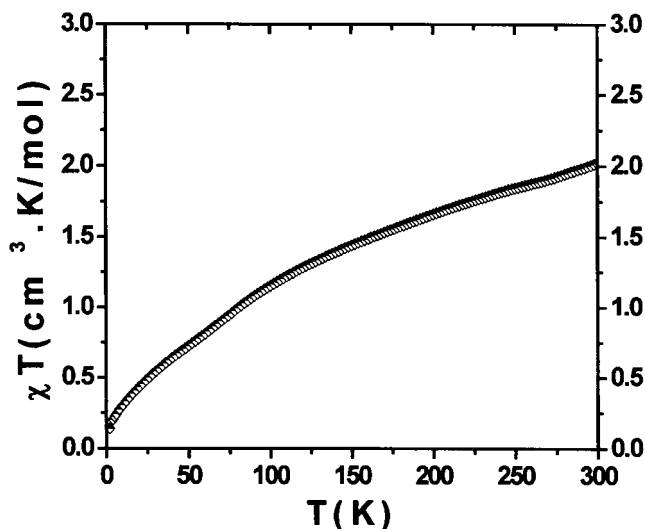


Figure 4. The plot of  $\chi T - T$  of  $\text{Fe}_{0.81}\text{PS}_3(4\text{-aminopyridineH})_{0.38}$ .

NH<sub>2</sub>Py)<sub>4</sub>(OAc)<sub>2</sub>] into the solution. Thus, there are some intralamellar Fe<sup>2+</sup> ion vacancies that makes the host have negative charges (as in Scheme 1 Equation 2) and at the same time the protonated 4-aminopyridine will insert into the interlayer space of the host to maintain the charge balance. So the driving force for this intercalation may be the static-charge attraction between the layered cluster anion of the host and the cation of the protonated 4-aminopyridine (Scheme 1 Equation 3). In this process the initial intercalation is the parallel insertion of protonated 4-aminopyridine into the interlayer region of FePS<sub>3</sub> (Phase I). And then the guest may be easily inserted into the interlayer space of the host because the van der Waals force holding the layers of the host together is destroyed, where protonated 4-aminopyridine will be arranged perpendicular to the layer (Phase II) due to the limited interlayer space of the host. Therefore, there coexist two phases during the intercalation.

## Conclusion

A new intercalation compound,  $\text{Fe}_{0.81}\text{PS}_3(4\text{-aminopyridineH})_{0.38}$ , is synthesized by the direct reaction of 4-aminopyridine with layered FePS<sub>3</sub>. The XRD results indicate that the guest (4-aminopyridineH) is arranged in two orientations between the interlayer region of the host (FePS<sub>3</sub>), in which one arrangement with the lattice expansion ( $\Delta d$ ) of 6.0 Å indicates that the molecular ring plane of the guest is perpendicular to the layer of the host and the other with 3.4 Å means that the ring plane of the guest is perpendicular to the layer. The IR spectra imply that the inserted guest of 4-aminopyridine exists in the protonated form to maintain the charge balance of the intercalation compound. Magnetic measurement indicate that  $\text{Fe}_{0.81}\text{PS}_3(4\text{-aminopyridineH})_{0.38}$  exhibits paramagnetism in the range of measured temperature (2~300K), where the magnetic behavior is well in agreement with the Curie-Weiss Law above 55 K. A possible intercalation process was proposed for 4-aminopyridine inserted into layered FePS<sub>3</sub>.

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