

# Synthesis, structural characterization and magnetic property of nanocomposite materials: Intercalation compounds of $\text{FePS}_3$ with 1,10-phenanthroline or 2,2'-bipyridine

CHEN, Xing-Guo<sup>a</sup> (陈兴国)    YANG, Chu-Luo<sup>a</sup> (杨楚罗)    QIN, Jin-Gui<sup>\*a</sup> (秦金贵)  
YAKUSHI, Kyuya<sup>b</sup>    NAKAZAWA, Yasuhiro<sup>b</sup>    ICHIMURA, Kenji<sup>c</sup>

<sup>a</sup> Department of Chemistry, Wuhan University, Wuhan, Hubei 430072, China

<sup>b</sup> Institute for Molecular Science, Okazaki, 444, Japan

<sup>c</sup> Department of Chemistry, Kumamoto University, Kumamoto 860, Japan

Two new intercalation compounds  $\text{Fe}_{0.90}\text{PS}_3(\text{phen})_{0.41}$  (1) (phen stands for 1,10-phenanthroline including a part of 1,10-phenanthroline  $\text{H}^+$ ) and  $\text{Fe}_{0.83}\text{PS}_3(\text{bipy})_{0.34}$  (2) (bipy stands for 2,2'-bipyridine $\text{H}^+$ ) were synthesized by the reaction of the layered  $\text{FePS}_3$  with 1,10-phenanthroline or 2,2'-bipyridine in the presence of anilinium chloride. They were characterized by elemental analyses, powder X-ray diffraction (XRD), infrared spectroscopy. The lattice spacing of the intercalate was expanded by 0.90 nm for  $\text{Fe}_{0.90}\text{PS}_3(\text{phen})_{0.41}$  and 0.57 nm for  $\text{Fe}_{0.83}\text{PS}_3(\text{bipy})_{0.34}$  with respect to the pristine  $\text{FePS}_3$ , indicating that the ring plane of the guests is perpendicular to the layer of the host. The UV-vis absorption spectra of the filtrate in preparation of the intercalates indicate that 1,10-phenanthroline or 2,2'-bipyridine also acts as a complexing agent to remove intralamellar  $\text{Fe}^{2+}$  ions into the solution during intercalation. The magnetic properties of 1 and 2 were studied.

**Keywords** Intercalation,  $\text{FePS}_3$ , 1,10-phenanthroline, 2,2'-bipyridine, magnetic property

## Introduction

Intercalation of organic species into layered inorganic solids provides a useful approach to create ordered organic-inorganic nanocomposite materials with novel properties compared with the parent compounds.<sup>1</sup> The transition metal phosphorus trisulfides  $\text{MPS}_3$ , where M stands for a metal in the 2+ oxidation state, are layered

compounds made up of two dimensional arrays of the  $\text{M}^{2+}$  cations coordinated to  $\text{P}_2\text{S}_6^{4-}$  bridging ligands. The  $\text{MPS}_3$  phases containing paramagnetic  $\text{M}^{2+}$  ions ( $\text{Mn}^{2+}$ ,  $S = 5/2$ ;  $\text{Fe}^{2+}$ ,  $S = 2$ ;  $\text{Ni}^{2+}$ ,  $S = 1$ ) show normal two-dimensional antiferromagnetism with Neel temperature of 78 K, 120 K and 153 K, respectively.<sup>2-4</sup> For these lamellar  $\text{MPS}_3$  compounds there are two types of intercalation reactions. One is the redox intercalation similar to that of the metal dichalcogenides involving electron donating from guest to host.<sup>5</sup> The other is a unique non-redox intercalation reaction based on the cation exchange between  $\text{M}^{2+}$  ions of the host and the guest cations, in which  $\text{M}^{2+}$  ions can leave their intralamellar sites into the solution, and the guest cations in the solution can be taken up into the interlayer space to maintain the charge balance.<sup>6</sup> After intercalation, the magnetic property of some intercalates can be dramatically changed.<sup>7-10</sup> In our previous research, we reported a new intercalate  $\text{Mn}_{0.86}\text{PS}_3(\text{bipy})_{0.56}$  which exhibited spontaneous magnetization with  $T_c$  at about 40 K.<sup>11</sup> In this paper, we present the synthesis, structural characterization and magnetic properties of two new intercalates,  $\text{Fe}_{0.90}\text{PS}_3(\text{phen})_{0.41}$  and  $\text{Fe}_{0.83}\text{PS}_3(\text{bipy})_{0.34}$ .

## Experimental

X-ray powder diffraction (XRD) patterns were ob-

\* Received August 11, 1999; accepted March 2, 2000.

Project supported by the National Natural Science Foundation of China (No. 29582001) and the Education Ministry of China (No. 96048610).

tained with Dmaxr A X-ray diffractometer using  $\text{CuK}\alpha$  radiation ( $\lambda = 0.15418 \text{ nm}$ ). Infrared spectrum was performed on a Nicolet SX Fourier transform spectrometer. UV-vis spectrum was conducted on Shimadzu UV-1206 spectrometer. Elemental analysis of carbon, hydrogen and nitrogen was performed with a Carlorba-1106 micro-analyzer. The content of iron was measured by the method of ICP-AES with an Atomscan-2000 instrument, and the magnetic property was studied by SQUID-magnetometer (MPMS, Quantum Design).

Pure  $\text{FePS}_3$  was synthesized as described by Taylor.<sup>2</sup> It was identified by means of XRD and indexed in a monoclinic unit cell (space group  $C2/m$ ,  $d = 0.6439 \text{ nm}$ ,  $a = 0.5934 \text{ nm}$ ,  $b = 1.0280 \text{ nm}$ ,  $c = 0.6722 \text{ nm}$ ,  $\beta = 107.16^\circ$ ).

The intercalates  $\text{Fe}_{0.90}\text{PS}_3(\text{phen})_{0.41}$  (1) and  $\text{Fe}_{0.83}\text{PS}_3(\text{bipy})_{0.34}$  (2) were prepared by stirring the mixture of  $\text{FePS}_3$  (0.20 g, 1.1 mmol), anilinium chloride (0.50 g, 3.9 mmol) and 1,10-phenanthroline monohydrate (0.66 g, 3.3 mmol) or 2,2'-bipyridine (0.52 g, 3.3 mmol) in a Pyrex ampoule containing 10 mL of ethanol sealed under vacuum for two weeks at about  $65^\circ\text{C}$ , in which anilinium chloride played a key role for this intercalation. The black powder was filtered off, and washed with ethanol and water, and then dried in air. Elemental analysis led to the formula  $\text{Fe}_{0.90}\text{PS}_3(\text{phen})_{0.41}$  (Calcd: Fe, 19.98; C, 23.49; H, 1.71; N, 4.57. Found: Fe, 19.55; C, 23.92; H, 1.53; N, 4.50), and  $\text{Fe}_{0.83}\text{PS}_3(\text{bipy})_{0.34}$  (Calcd: Fe, 20.43; C, 17.99; H, 1.36; N, 4.22. Found: Fe, 19.20; C, 17.64; H, 1.34; N, 3.99), respectively.

## Results and discussion

### X-ray powder diffraction

The XRD results show that the  $00l$  reflections of pure  $\text{FePS}_3$  are totally absent in the intercalates, and a new series of  $00l$  reflections are observed with the lattice spacing increased to 1.549 nm for  $\text{Fe}_{0.90}\text{PS}_3(\text{phen})_{0.41}$  and 1.210 nm for  $\text{Fe}_{0.83}\text{PS}_3(\text{bipy})_{0.34}$ , corresponding to a lattice expansion ( $\Delta d$ ) of ca. 0.90 nm and 0.57 nm compared with pure  $\text{FePS}_3$ , respectively (Fig. 1). This indicates that the pyridine ring plane is perpendicular to the layer of the host. The reflection patterns of the intercalates could be readily indexed in the  $C2/m$  space

group closely related to that of pristine  $\text{FePS}_3$ , in which the calculated  $a$ ,  $b$  and  $\beta$  values are almost identical with those of pristine  $\text{FePS}_3$  (Tables 1 and 2).

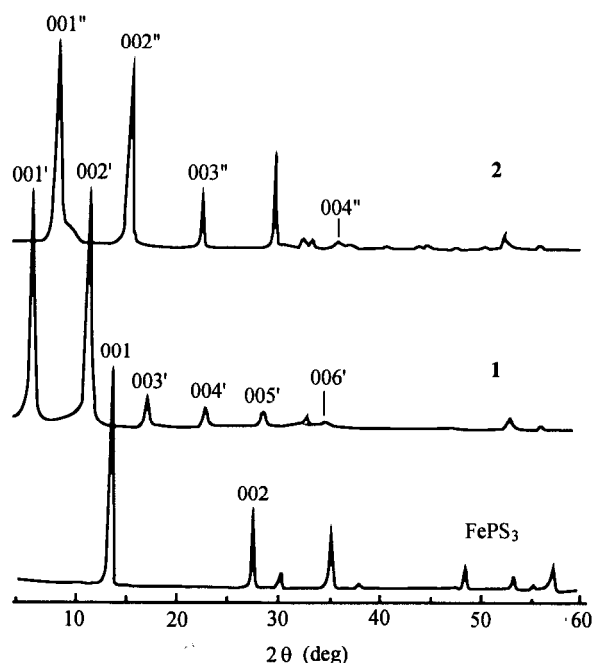


Fig. 1 X-ray powder diffraction patterns of pure  $\text{FePS}_3$ , intercalates 1 and 2.

Table 1 Indexation of XRD of the intercalate  $\text{Fe}_{0.90}\text{PS}_3(\text{phen})_{0.41}$

Spacing (nm)		$hkl$	Intensity
Obsd.	Calcd.		
1.5490	1.5560	001	vs
0.7755	0.7785	002	vs
0.5211	0.5190	003	m
0.3897	0.3892	004	m
0.3129	0.3114	005	w
0.2720	0.2722	133	w
0.2597	0.2595	006	w
0.2427	0.2420	224	w
0.2220	0.2224	007	w
0.1916	0.1917	300	w
0.1726	0.1727	332	w
0.1635	0.1636	029	w

Table 2 Lattice spacing ( $d$ ) and calculated unit cell parameters

Compound	$d$ (nm)	$a$ (nm)	$b$ (nm)	$c$ (nm)	$\beta$ (deg)
$\text{FePS}_3$	0.6439	0.5934	1.0280	0.6722	107.16
1	1.549	0.6050	1.0090	1.6380	108.10
2	1.210	0.6076	1.0133	1.3292	113.36

## UV-vis and infrared spectra

The UV-vis absorption spectrum of the filtrate in preparation of the intercalate **1** exhibits almost the same absorption to that of  $[\text{Fe}(\text{phen})_3]_2$  in ethanol with a strong broad band around 510 nm, which is the characteristic absorption of  $\text{Fe}(\text{phen})_3^{2+}$  indicating the occurrence of  $\text{Fe}(\text{phen})_3^{2+}$  in the filtrate<sup>13</sup> (Fig. 2). It is clear that 1, 10-phenanthroline acts as a complexing agent to remove intralamellar  $\text{Fe}^{2+}$  ions into the solution during the intercalation.

For  $\text{Fe}_{0.90}\text{PS}_3(\text{phen})_{0.41}$ , the intense bands of infrared spectrum containing three sharp absorptions at 606, 582 and 556  $\text{cm}^{-1}$  in the range 550–610  $\text{cm}^{-1}$  are assigned to the  $\nu(\text{PS}_3)$  asymmetric stretching band coming from the splitting of 570  $\text{cm}^{-1}$  in pure  $\text{FePS}_3$ , which

reflects the occurrence of intralamellar  $\text{Fe}^{2+}$  ion vacancies due to the departure of a fraction of intralamellar  $\text{Fe}^{2+}$  ions removed by 1, 10-phenanthroline into the solution during the intercalation.<sup>14</sup> There are numerous absorptions in the 700–2000  $\text{cm}^{-1}$  range that can be assigned to the guests. By comparison of the infrared spectra of  $\text{Fe}_{0.90}\text{PS}_3(\text{phen})_{0.41}$ , 1, 10-phenanthroline monohydrate<sup>15</sup> and 1, 10-phenanthroline  $\cdot \text{HClO}_4$ <sup>16,17</sup> (Table 3), the infrared spectrum of  $\text{Fe}_{0.90}\text{PS}_3(\text{phen})_{0.41}$  combines some characteristic absorption bands of the neutral 1, 10-phenanthroline and protonated phenanthroline ( $\text{phenH}^+$ ). This suggests that the inserted guests are the neutral phenanthroline and the protonated phenanthroline cations formed by proton exchange between anilinium and phenanthroline in the solution.

**Table 3** Comparison of the IR absorptions ( $\text{cm}^{-1}$ ) of intercalate  $\text{Fe}_{0.90}\text{PS}_3(\text{phen})_{0.41}$  with those of  $\text{phen} \cdot \text{H}_2\text{O}$ <sup>15</sup> and  $\text{phen} \cdot \text{HClO}_4$ <sup>16, 17</sup> as well as comparison of the IR absorptions ( $\text{cm}^{-1}$ ) of intercalate  $\text{Fe}_{0.83}\text{PS}_3(\text{bipy})_{0.34}$  with that of  $\text{bipy} \cdot \text{HCl}$ <sup>18</sup>

Assignment	$\text{phen} \cdot \text{H}_2\text{O}$	$\text{phen} \cdot \text{HClO}_4$	$\text{Fe}_{0.90}\text{PS}_3(\text{phen})_{0.41}$	$\text{Fe}_{0.83}\text{PS}_3(\text{bipy})_{0.34}$	$\text{bipy} \cdot \text{HCl}$
ring stretching	1615m	1618w	1615w		
				1601s	1600s
	1585w	1599w	1592m	1575m	1578m
		1544s	1539m	1525m	1530m
	1502s	1502m	1507w	1498w	1500s
	1492m	1473s	1494w		
				1468m	1470w
				1439	1452
	1422s	1419s	1419s		1432s
		1370w	1371w		
	1345w	1340w	1340w	1408w	1410w
				1319w	1315
				1270m	
H in planar deformation	1217w	1228w	1235w	1230w	1230s
			1213w	1215m	
	1186w	1192w	1185w	1168m	1172m
	1137m	1145m	1142m	1155m	1165sh
	1092m	1088s	1089m	1080m	1105w
				1065s	1070m
			1024s	1010w	
				1005w	
H out of planar bend				940w	980w
	853vs				
	840s			875w	
	779m	847s	839s		
	738vs	782m	766w	764s	760vs
	724m		730w	725m	
		717s	715s		
				670w	660w
				640w	

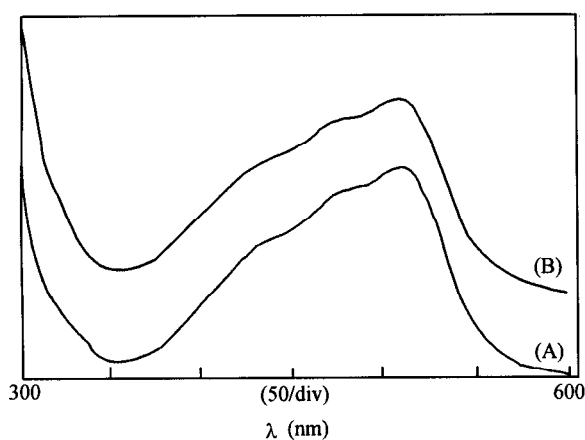


Fig. 2 UV-vis spectra of  $[\text{Fe}(\text{phen})_3]\text{I}_2$  in ethanol (A) and the filtrate in preparation of intercalate 1 (B).

The similar results of UV-vis and infrared spectra are obtained for  $\text{Fe}_{0.83}\text{PS}_3(\text{bipy})_{0.34}$ . The infrared spectrum of  $\text{Fe}_{0.83}\text{PS}_3(\text{bipy})_{0.34}$  exhibits the similar characteristic infrared absorption band to that of  $\text{bipy} \cdot \text{HCl}^{18}$  (Table 3). It indicates that the guest of insertion in this intercalate is mono-protonated bipyridine, which is consistent with the view of the charge neutrality of the intercalate.

#### Magnetic properties

The magnetic properties of the two intercalates were studied with SQUID magnetometer. The antiferromagnetic transition at 120 K in pure  $\text{FePS}_3$  no longer exists for both the intercalates. Fig. 3 shows the plot of  $\chi_T$  vs.  $T$  and the magnetization curve at several temperatures of  $\text{Fe}_{0.90}\text{PS}_3(\text{phen})_{0.41}$  (1). Fig. 4 shows the temperature dependence of magnetic moment (in the unit of Bohr magneton), and the inset of the figure displays the molar susceptibility and the inverse of the molar susceptibility versus temperature of intercalate 1. From the curve of  $\chi_T$  vs.  $T$  in Fig. 3, the  $\chi_T$  value decreases from 300 K to 100 K indicating that the interaction is antiferromagnetic one in the paramagnetic range. This behavior is confirmed by the inverse of the paramagnetic susceptibility of intercalate 1 displayed as a function of temperature (shown in above inset of Fig. 4), where the solid line shows the Curie-Weiss behavior between 100 K and 300 K and the Weiss constant is about  $-100$  K. And then it exhibits upward increase at 100 K (Fig. 3) as if it is

ferromagnetic transition around this temperature. However, the temperature dependence of magnetic moment (Fig. 4) shows that the increase of magnetization is too

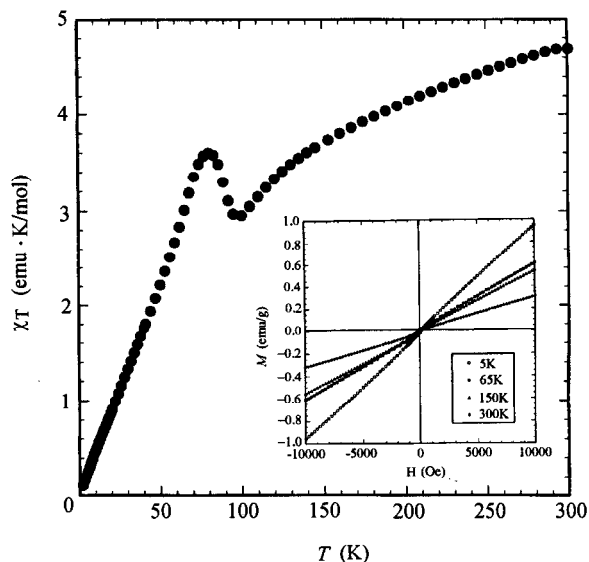


Fig. 3 Plot of  $\chi_T$  vs.  $T$  of intercalate 1. The inset shows the field dependence of magnetization at different temperatures.

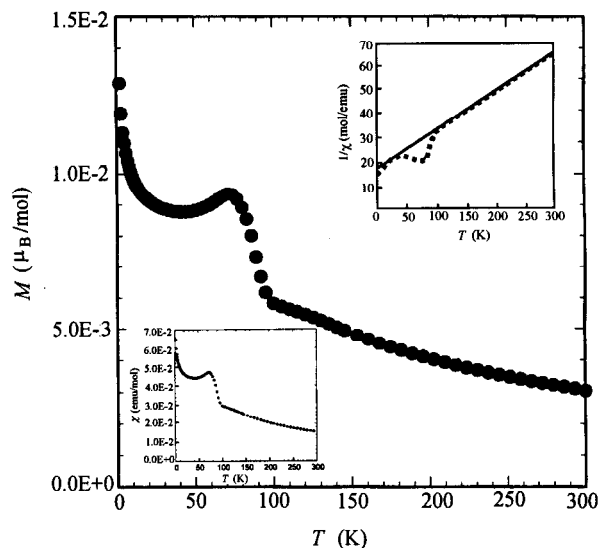


Fig. 4 Temperature dependence of magnetic moment (in the unit of Bohr magneton) of intercalate 1. The inset shows a temperature dependence of mole magnetic susceptibility (below) and a plot of inverse of magnetic susceptibility (above) versus temperature.

small (about  $0.004 \mu_B/\text{mol}$  at 1000 Oe) to state that this is a ferromagnetic phase transition (In general, the magnetic moment in the order of  $1 \mu_B/\text{mol}$  is observable for ferromagnetic order). In addition, the magnetization curve at several temperatures also does not suggest the ferromagnetic order at low temperatures (the inset of Fig. 3). This exotic magnetic behavior possibly derives from the spin glass transition produced by the competition between original antiferromagnetic interaction and ferromagnetic interaction induced by intercalation around the peak temperature. The further study is necessary and in progress. Below 75 K the  $\chi_T$  value decreases rapidly, indicating the occurrence of strong antiferromagnetic interaction.

For  $\text{Fe}_{0.83}\text{PS}_3(\text{bipy})_{0.34}$  (2), the temperature dependence of the magnetic susceptibility at an applied magnetic field of 1 KOe is shown in Fig. 5. In the inset of the figure, the inverse of the paramagnetic susceptibility versus temperature is displayed, in which the solid line also shows the Curie-Weiss behavior between around 120 K and 300 K. The slope of the straight line is about  $0.32 \text{ emu}^{-1} \cdot \text{mol} \cdot \text{K}^{-1}$ , close to the value of expected for  $\text{Fe}^{2+}$  ions ( $8/[g^2 S(S+1)] = 0.30$  if  $g = 2.1$ ), which is consistent with localized iron ions with localized 2 spins coupled antiferromagnetically.<sup>19</sup> However, below 120 K it deviates from the Curie-Weiss law, which per-

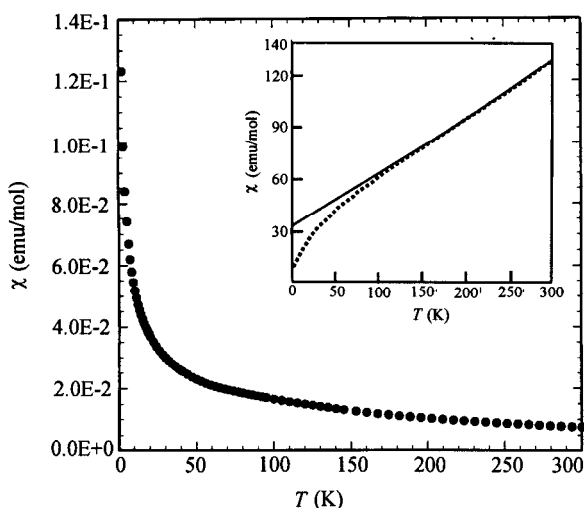


Fig. 5 Temperature dependence of magnetic susceptibility of intercalate 2. The inset shows the plot of inverse of magnetic susceptibility versus temperature.

haps derives from the strengthened short-range localized couple interaction.

Above all, it is obvious that their magnetic properties are different either from their corresponding intercalates of  $\text{MnPS}_3$ ,  $\text{Mn}_{1-x}\text{PS}_3(\text{G})_{4x}$  ( $\text{G} = \text{bipy}, \text{phen}$ ),<sup>11</sup> or from their similar intercalates of pyridine— $\text{FePS}_3$ , methyl viologen— $\text{FePS}_3$  and *N*-methylpyridinium— $\text{FePS}_3$ ,<sup>10</sup> all of which exhibit spontaneous magnetization at low temperature, or from the pristine  $\text{FePS}_3$  that shows antiferromagnetic behavior with  $T_N$  at around 120 K.<sup>4</sup> What are the main factors to affect the magnetic properties of the intercalates? One is the occurrence of the intralayer  $\text{Fe}^{2+}$  ion vacancies in the intercalates that dilutes the couple interaction of the  $\text{Fe}^{2+}$  ions. Thus, the Neel temperature of  $\text{Fe}_{0.90}\text{PS}_3(\text{phen})_{0.41}$  is much lower than that of pristine  $\text{FePS}_3$ , and  $\text{Fe}_{0.83}\text{PS}_3(\text{bipy})_{0.34}$  only shows paramagnetic behavior owing to the greater content of the  $\text{Fe}^{2+}$  ion vacancies. The other possible factor is the structure of the intercalates. It is known that  $\text{FePS}_3$  and  $\text{MnPS}_3$  have the different magnetic structure. For  $\text{MnPS}_3$  any  $\text{Mn}^{2+}$  ion is antiferromagnetically coupled with its three nearest neighbors, but in  $\text{FePS}_3$  each  $\text{Fe}^{2+}$  ion is ferromagnetically coupled with two of the three nearest neighbors, and antiferromagnetically with the third.<sup>4</sup> Thus, for some  $\text{MnPS}_3$  intercalates the bulk magnetization originates from the destroying their antiferromagnetic balance of  $\text{MnPS}_3$  layers after intercalation.<sup>20</sup> For the intercalates of  $\text{FePS}_3$  such as pyridine, methyl viologen and *N*-methylpyridinium the bulk magnetization possibly derives from the interaction between the electron-accepting guest and the sulfur atoms of the host that causes a slight geometry change favoring the ferromagnetic interaction at the expense of the antiferromagnetic ones.<sup>10</sup> It should be noted that the lattice expansion ( $\Delta d$ ) of the intercalates such as pyridine— $\text{FePS}_3$ , methyl viologen— $\text{FePS}_3$  and *N*-methylpyridinium— $\text{FePS}_3$  is about 0.34—0.35 nm, indicating the pyridine ring plane is parallel to the layer of the host, which favors the overlapping between the  $\pi$ -electron orbital of pyridine ring and the sulfur atoms. But in the intercalates of  $\text{Fe}_{0.90}\text{PS}_3(\text{phen})_{0.41}$  and  $\text{Fe}_{0.83}\text{PS}_3(\text{bipy})_{0.34}$ , the pyridine ring plane is perpendicular to the layer, which does not favor the overlapping of the  $\pi$ -electron orbital of pyridine ring and the sulfur atoms. Therefore, it can be tentatively suggested that the orientation of the guest may affect the magnetic property of the interca-

lates. The further study on the relationship between the orientation of the guest and the magnetic property of the intercalates is still in progress.

## Conclusions

Two new intercalates,  $\text{Fe}_{0.90}\text{PS}_3(\text{phen})_{0.41}$  (1) and  $\text{Fe}_{0.83}\text{PS}_3(\text{bipy})_{0.34}$  (2), are synthesized. X-ray powder diffraction results reveal that they are complete intercalates and well crystallized products. All reflections can be readily indexed as a monoclinic unit cell. As the result of intercalation, the lattice expansion ( $\Delta d$ ) of 0.90 nm for  $\text{Fe}_{0.90}\text{PS}_3(\text{phen})_{0.41}$  and 0.57 nm for  $\text{Fe}_{0.83}\text{PS}_3(\text{bipy})_{0.34}$  with respect to the pure  $\text{FePS}_3$  indicates that the ring plane of the guest is perpendicular to the layer of the host. Infrared spectra provide the evidences to support the presence of the phenanthroline and protonated phenanthroline or protonated bipyridine between layers, and UV-vis spectra indicate that phenanthroline or bipyridine also has acted as a complexing agent during the intercalation. The magnetic measurements with SQUID-magnetometer indicate that  $\text{Fe}_{0.90}\text{PS}_3(\text{phen})_{0.41}$  shows paramagnetism above 100 K, an exotic magnetic transition around 100 K and antiferromagnetic transition at  $T_N$  of 75 K, but  $\text{Fe}_{0.83}\text{PS}_3(\text{bipy})_{0.34}$  exhibits paramagnetism above 100 K.

## References

1. Schollhorn, R., *Chem. Mater.*, **8**, 1747(1996).
2. Taylor, B. E.; Steger, J.; Wold, A., *J. Solid State Chem.*, **7**, 461(1973).
3. Jernberg, P.; Bjarman, S.; Wappling, R., *J. Magn. Mater.*, **46**, 178(1984).
4. Brec, R., *Solid State Ionics*, **22**, 3(1986).
5. Johnson, J. W., in "Intercalation Chemistry", Eds. Whittingham, M. S.; Jacobson, A. J., Academic, New York, 1982, p.267.
6. Clement, R., *J. Chem. Soc., Chem. Commun.*, 647(1980).
7. Clement, R.; Cirerd, J. J.; Morgenstern-Badarau, I., *Inorg. Chem.*, **19**, 2852(1980).
8. Joy, P. A.; Vasudevan, S., *J. Am. Chem. Soc.*, **114**, 7792(1992).
9. Lacroix, P. G.; Clement, R.; Nakatani, K.; Zyss, J.; Ledaux, I., *Science*, **263**, 658(1994).
10. Leautic, A.; Audiere, J. P.; Cointereau, D.; Clement, R.; Lomas, L.; Varret, F.; Constant-Machado, H., *Chem. Mater*, **8**, 1954(1996).
11. Qin, J.; Yang, C.; Yakushi, K.; Nakazawa, Y.; Ichimura, K., *Solid State Commun.*, **100**, 427(1996).
12. Klingen, Von W.; Eulenberger, G.; Hahn, H., *Z. Anorg. Allg. Chem.*, **401**, 97(1973).
13. Harvey, A. E., Jr.; Smart, J. A.; Amis, E. S., *Anal. Chem.*, **27**, 26(1955).
14. Coradin, T.; Clement, R.; Lacroix, P. G.; Nakatani, K., *Chem. Mater*, **8**, 2153(1996).
15. Thornton, D. A.; Watkins, G. M., *Spectrochim. Acta*, **47A**, 1085(1991).
16. Schilt, A. A.; Taylor, R. C., *J. Inorg. Nucl. Chem.*, **9**, 211(1959).
17. Dega-Szafran, Z., *Rocz. Chem.*, **43**, 823(1969).
18. Strukl, J. S.; Walter, J. L., *Spectrochim. Acta*, **27A**, 223(1971).
19. Leautic, A.; Audiere, J. P.; Lacroix, P. G.; Clement, R.; Lomas, L.; Michalowicz, A.; Dunham, W. R.; Francis, A. H., *Chem. Mater.*, **7**, 1103(1995).
20. Evans, J. S. O.; O'Hare, D.; Clement, R.; Leautic, A.; Thuery, P., *Adv. Mater.*, **7**, 735(1995).

(E9908095 SONG, J. P.; DONG, L. J.)