

## A New Inorganic-organic Nanocomposite, 4,4'-Bipyridine Intercalated into Lamellar FePS<sub>3</sub>

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**Abstract:** A new intercalation compound, Fe<sub>0.85</sub>PS<sub>3</sub>(4,4'-bipyH)<sub>0.30</sub> (4,4'-bipy = 4,4'-bipyridine), is obtained by the intercalation of 4,4'-bipyridine·2HCl with lamellar FePS<sub>3</sub>, which is characterized by elemental analysis, powder X-ray diffraction, infrared spectroscopy. By comparison with the pure FePS<sub>3</sub>, the lattice spacing of Fe<sub>0.85</sub>PS<sub>3</sub>(4,4'-bipyH)<sub>0.30</sub> is expanded by ~ 5.7 Å, indicating that the ring plane of the guest is perpendicular to the layer of the host. The magnetic property of Fe<sub>0.85</sub>PS<sub>3</sub>(4,4'-bipyH)<sub>0.30</sub> is studied with SQUID. It exhibits an antiferromagnetic phase transition with T<sub>N</sub> of about 70 K.

**Keywords:** Intercalation, lamellar FePS<sub>3</sub>, magnetic property.

Interest in nanocomposite materials is increased due to their great significance in both fundamental and applied research fields in the past two decades<sup>1</sup>. Intercalation of organic species into lamellar inorganic solids provides a useful approach to design and synthesize inorganic-organic nanocomposite materials with novel functional properties compared with the parent compounds<sup>2</sup>.

The transition metal phosphorous trisulfides, MPS<sub>3</sub> (M stands for a metal in +2 oxidation state), are lamellar compounds made up of two-dimensional arrays of the M<sup>2+</sup> cations coordinated to P<sub>2</sub>S<sub>6</sub><sup>4-</sup> bridging ligands (**Figure 1**). Some MPS<sub>3</sub> phases containing the paramagnetic M<sup>2+</sup> ions (Mn<sup>2+</sup>, S=5/2 and Fe<sup>2+</sup>, S=2, etc.) show the two-dimensional antiferromagnetism with Neel temperature of 78 and 120 K, respectively<sup>3</sup>. Sometimes, the magnetic property of some intercalates can be dramatically changed after intercalation<sup>4,6</sup>. In this paper, we present the synthesis, structural characterization and magnetic property of Fe<sub>0.85</sub>PS<sub>3</sub>(4,4'-bipyH)<sub>0.30</sub>.

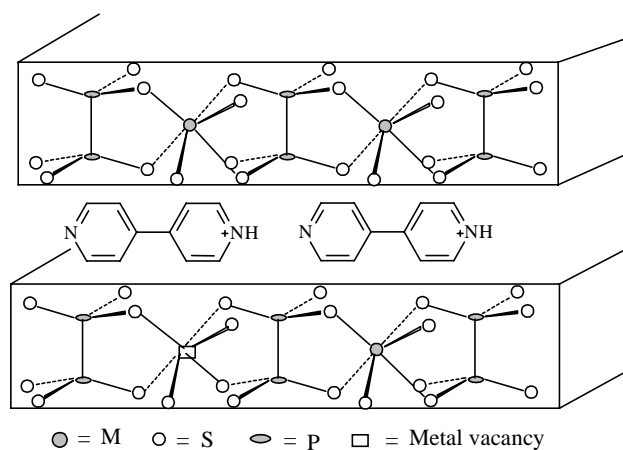
Pure FePS<sub>3</sub> was synthesized as described by Taylor<sup>7</sup>, which was identified by means of powder X-ray diffraction (XRD) and indexed as space group C<sub>2/m</sub> in a monoclinic unit cell (**Table 1**). The intercalate was prepared by stirring the mixture of FePS<sub>3</sub> (black powder, 0.25g) and 4,4'-bipyridine·2HCl (0.30 g) in the presence of 10 mL of 0.02 mol/L EDTA and the buffer solution of Na<sub>2</sub>CO<sub>3</sub> / NaHCO<sub>3</sub> sealed in an ampoule under vacuum for 15 days at 60°C. After cooling, the black powder was filtered off,

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and washed with distilled water and ethanol, and then dried in air. Elemental analysis led to the formula  $\text{Fe}_{0.85}\text{PS}_3(4,4'\text{-bipyH})_{0.30}$  (Found: C, 16.43; H, 1.04; N, 3.13(%). Calcd: C, 16.25; H, 1.23; N, 3.79 (%)).

From the XRD results, it was found that the  $00l$  reflections of pure  $\text{FePS}_3$  have totally disappeared and a new series of  $00l$  reflections are observed with the lattice spacing expansion ( $\Delta d$ ) of ca. 5.7 Å in  $\text{Fe}_{0.85}\text{PS}_3(4,4'\text{-bipyH})_{0.30}$ . This indicated that 4,4'-bipyH ring plane is almost perpendicular to the layer of the host (as shown in **Figure 1**) similar to that of pyridine intercalated into  $\text{MnPS}_3$ <sup>5</sup>. The XRD reflection patterns can be readily indexed in the space group closely related to that of pristine  $\text{FePS}_3$ , in which the calculated  $a$ ,  $b$  and  $\beta$  values are almost identical with that of pure  $\text{FePS}_3$  (**Table 1**).

**Figure 1** The possible orientation of the guest (4,4'-bipyH) between the interlayered space of the host ( $\text{FePS}_3$ )



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

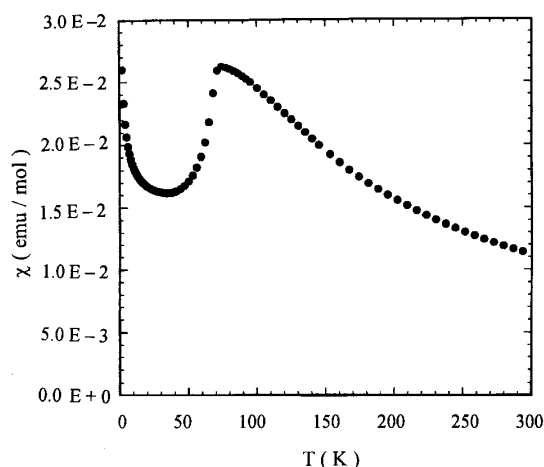
Compound	$d$ (Å)	$a$ (Å)	$b$ (Å)	$c$ (Å)	$\beta$ (deg)
$\text{FePS}_3$	6.439	5.934	10.280	6.722	107.16
$\text{Fe}_{0.85}\text{PS}_3(4,4'\text{-bipyH})_{0.30}$	12.13	6.076	10.133	13.292	113.36

The intense bands of IR spectrum at 602 and 552  $\text{cm}^{-1}$  of  $\text{Fe}_{0.85}\text{PS}_3(4,4'\text{-bipyH})_{0.30}$  are assigned to the  $\nu(\text{PS}_3)$  asymmetric stretching band from the splitting of 570  $\text{cm}^{-1}$  in  $\text{FePS}_3$ <sup>6</sup>, which reflects the occurrence of intralamellar  $\text{Fe}^{2+}$  ion vacancies formed by the coordination of  $\text{Fe}^{2+}$  ions with EDTA during the intercalation<sup>6</sup>. The IR absorption in the 700~3500  $\text{cm}^{-1}$  range can be assigned to the guests. By comparison of the infrared spectra of  $\text{Fe}_{0.85}\text{PS}_3(4,4'\text{-bipyH})_{0.30}$ , 4,4'-bipy<sup>8</sup>, 4,4'-bipy·HX, 4,4'-bipy·2HX (X = I, Br, Cl,  $\text{ClO}_4$  etc.)<sup>9,10</sup> and 4,4'-bipy·Y (Y =  $\text{AgNO}_3$ , 2ICl)<sup>11</sup>, it was found that the absorption bands of  $\text{Fe}_{0.85}\text{PS}_3(4,4'\text{-bipyH})_{0.30}$  at 1599, 1498, 1074, 855, 806  $\text{cm}^{-1}$  etc. are similar to the bands exhibited by neutral 4,4'-bipyridine, which belongs to the characteristic absorption of the 4,4'-bipy ring. However, the bands at around 1619, 1506, 1475, 1394, 1005, 725  $\text{cm}^{-1}$  etc. are different from those related absorption bands of 4,4'-bipy and

4,4'-bipy·2HCl but similar to those of 4,4'-bipy·HX. This result is in agreement with the elemental data, which indicated that the inserted guest is the mono-protonated 4,4'-bipy to maintain the charge balance of the intercalate.

The temperature dependence of the magnetic susceptibility of Fe<sub>0.85</sub>PS<sub>3</sub>(4,4'-bipyH)<sub>0.30</sub> is shown in **Figure 2**. Fe<sub>0.85</sub>PS<sub>3</sub>(4,4'-bipyH)<sub>0.30</sub> exhibits paramagnetic behavior above 90 K, which is in agreement with Curie-Waiss law. At around 70 K it exhibits an antiferromagnetic phase transition. It is obvious that its antiferromagnetic transition temperature is much lower than that of pure FePS<sub>3</sub> (T<sub>N</sub> = 120 K). This is derived from the dilution of the coupling interaction between the Fe<sup>2+</sup> ions caused by the intralamellar Fe<sup>2+</sup> ion vacancies.

**Figure 2** The temperature (T) dependence of the molar magnetic susceptibility ( $\chi$ ) of Fe<sub>0.85</sub>PS<sub>3</sub>(4,4'-bipyH)<sub>0.30</sub>



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