The Characterization and Magnetic Properties of Inorganic-Organic Hybrid Nanocomposites, Stilbazoliums Inserted into Layered FePS₃

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Abstract

Five inorganic-organic intercalation compounds (**I–V**) with *N*-methylstilbazolium derivatives (i–v) inserted into the interlayer space of FePS₃, were synthesized, and characterized with X-ray diffraction (XRD), elemental analysis and infrared spectroscopy. The XRD results indicate that in all these intercalation compounds the molecular ring planes of the guests are almost perpendicular to the layers of the host FePS₃. From the lattice expansion of intercalates **IV** and **V** it can be inferred that a dipolar interaction may exist between the guests in the interlayer space of the host FePS₃. Their magnetic properties were measured with the SQUID technique. All these intercalation compounds show similar magnetic properties. At the Neel temperature of about 80 K they exhibit the antiferromagnetic transition, although the lattice spacing and the electron-accepting ability of the guest are different. It may imply that the lattice spacing expansion and an electron-effect of the guests have not altered their antiferromagnetic property of these FePS₃ intercalation compounds.

Introduction

There has been increasing interest in the past two decades in inorganic-organic hybrid materials due to their great significance in both theoretical and promising applications [1, 2]. Recently, it has been found that some layered compounds exhibit bulk ferromagnetic or ferrimagnetic properties after intercalation [3, 4]. For example, some intercalation compounds based on MPS₃ (M = Mn, Fe) [5, 6] and M₂(OH)₃A (M = Co, Cu; A = OAC⁻, NO₃⁻) [7, 8] show spontaneous magnetization and become magnets below the Curie temperature. This provides one of the useful routes to design and synthesize molecular-based magnetic materials by modifying the antiferromagnetic layered materials to induce the bulk magnetization through intercalation.

Metal hexathiohypodiphosphates (MPS₃), where M stands for a wide range of divalent transition metal ions (M = Mn, Cd, Fe, Co, Zn, Ni, etc), have the layered structure made up of two-dimensional arrays of $P_2S_6^{4-}$ bridging ligands coordinating to the M^{2+} ions. Some intercalation compounds based on MPS₃ (M = Mn^{2+}, S = 5/2; Fe^{2+}, S = 2) show low-temperature bulk ferrimagnetism [9]. This is much different from that of the related pure MPS₃ (M = Mn^{2+}, Fe^{2+}) which exhibit the normal two-dimensional antiferromagnetism with a Neel temperature of 78 K and 120 K, respectively [10]. In our previous research, we had also

reported some new ferrimagnetic intercalation compounds $Mn_{1-x}PS_3(G)_{4x}$ (G = 2,2′-bipyridine, 1,10-phenanthroline) [11, 12].

In order to explain the origin of the bulk magnetism, some studies on the MPS₃ intercalation compounds have been reported [13–16]. For some MnPS₃ intercalation compounds the bulk ferrimagnetism is attributed to the ordered intralayer Mn^{2+} vacancies that destroy the antiferromagnetic balance of the two sub-lattices of the host [17]. However, for some FePS₃ intercalation compounds, the reason for the ferrimagnetic transition from the antiferromagnetism of the pure FePS₃ has not been explained clearly. *N*-methylstilbazolium derivatives are one kind of organic second order nonlinear optical chromophore, whose structure can be easily changed through the substitution of different ortho- or para-groups of benzene, so their molecular size and electron-effect can be altered with the variety of the substituted group. Through ion exchange they can be intercalated into some layered materials. For instance, intercalation of 4′-dimethylamino-*N*-methylstilbazolium into MnPS₃ produced a multifunctional material combining a nonlinear optical property (with a second harmonic generation efficiency 300 times as strong as that of urea) and a ferrimagnetic property (with Tc = 40 K) [18]. Sawaki and his coworkers [19–21] had reported the intercalation of stilbazoliums into some clays, and the photochemical cycloaddition of stilbazoliums between the interlayer space of the host were mainly discussed. However, in this paper we select
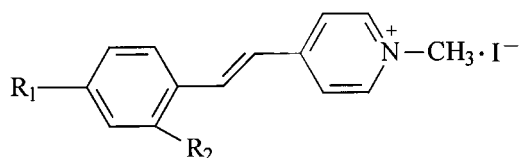
Figure 1. The structure of *N*-methylstilbazolium iodide.

a series of *N*-methylstilbazolium derivatives to be intercalated into lamellar $FePS_3$ for studying the electron-accepting ability of the guests and the different lattice spacing expansion to influence the magnetic properties of the $FePS_3$ intercalation compounds.

Experimental

X-ray powder diffraction (XRD) patterns were obtained with a Dmaxr A X-ray diffractometer using Cu Kα radiation (λ = 1.5418 Å). Infrared spectroscopy was performed on a Nicolet SX Fourier transform spectrometer. Elemental analysis was performed with a CarloErba-1106 microanalyzer. The magnetic property was studied by a SQUID-magnetometer (MPMS, Quantum Design).

Pure $FePS_3$ was synthesized by the reaction of the pure stoichiometric elements at 700 °C as described in reference [22]. 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, β = 107.16°) [23]. *N*-methyl-4-picolinium iodide was obtained as in reference [24]. Stilbazoliums were synthesized as in reference [25], and their structure is shown as in Figure 1. Their formula were ascertained by elemental analysis (**i**, $R_1 = R_2$ = H, *N*-methylstilbazolium iodide, found (calcd): C, 51.92 (52.03), H, 4.23 (4.37), N, 3.98 (4.33); **ii**, R_1 = OH, R_2 = H, 4′-hydroxyl-*N*-methylstilbazolium iodide, found (calcd): C, 49.87 (49.58), H, 4.35 (4.16), N, 4.26 (4.13); **iii**, R_1 = NMe$_2$, R_2 = H, 4′-dimethylamino-N-methylstilbazolium iodide, found (calcd): C, 52.05 (52.47), H, 5.46 (5.23) N, 7.28 (7.65); **iv**, $R_1 = R_2$ = MeO, 2′,4′-dimethoxyl-*N*-methylstilbazolium iodide, found (calcd): C, 50.56 (50.15), H, 4.56 (4.73), N, 4.00 (3.65); **v**, $R_1 = R_2$ = Cl, 2′,4′-dichloro-*N*-methylstilbazolium iodide, found (calcd): C, 43.01 (42.89), H, 3.32 (3.08), N, 3.38 (3.57)).

The pre-intercalation compound, $Fe_{0.92}PS_3(Et_4N)_{0.16}$, was prepared as in reference [26] (Elemental analysis data, found (calcd): C, 7.56 (7.71), H, 1.85 (1.62), N, 1.30 (1.12)). The intercalation compounds were synthesized by stirring the mixture of a pre-intercalate, $Fe_{0.92}PS_3(Et_4N)_{0.16}$, with a solution of *N*-methylstilbazoliums (**i–v**) in ethanol in a sealed ampoule for half a month at 80 °C. The black powder was filtered off, and washed with DMF and ethanol several times, and then dried in air. Elemental analysis led to the formula $Fe_{1-x}PS_3$(*N*-methylstilbazoliums)$_{2x}$ (**I**, $Fe_{0.92}PS_3$(N-methyl-stilbazolium)$_{0.16}$, found (calcd): C, 12.75 (12.81), H, 0.98 (1.07), N, 1.35 (1.08); **II**, $Fe_{0.92}PS_3$(4′-hydroxyl-*N*-methylstilbazolium)$_{0.16}$, found (calcd): C, 12.38 (12.66), H, 1.00 (1.06), N, 1.15 (1.05); **III**, $Fe_{0.91}PS_3$(4′-dimethylamino-*N*-methylstilbazolium)$_{0.18}$,

Table 1. The lattice spacing (d) and calculated unit of the intercalation compounds

Compound	d (Å)	a (Å)	b (Å)	c (Å)	β (deg)
$FePS_3$	6.439	5.934	10.280	6.722	107.16
I	12.276	5.935	10.279	13.374	113.00
II	12.267	5.935	10.281	13.375	113.00
III	12.440	5.919	10.268	13.465	111.80
IV	21.020	6.018	10.278	22.550	111.59
V	19.619	5.923	10.288	20.546	108.87

Table 2. Indexation of XRD of Intercalate **I**

Spacing (Å)		*hkl*	Intensity
Obsd.	Calcd.		
12.2760	12.3113	001	100.0
6.1456	6.1556	002	39.0
4.0919	4.1038	003	6.0
3.1399	3.1303	11$\bar{4}$	2.0
3.0763	3.0778	004	6.0
2.8823	2.8749	122	3.0
2.7281	2.7316	200	3.0
2.6345	2.6400	210	5.0
2.4338	2.4375	132	1.0
2.2254	2.2266	221	2.0
1.9239	1.9220	134	1.0
1.7323	1.7341	204	11.0
1.6407	1.6390	11$\bar{8}$	2.0

found (calcd): C, 15.16 (15.65), H, 1.80 (1.56), N, 1.95 (2.28); **IV**, $Fe_{0.91}PS_3$(2′,4′-dimethoxyl-*N*-methylstilbazolium)$_{0.18}$, found (calcd): C, 15.05 (15.43), H, 1.23 (1.46), N, 0.95 (1.12); **V**, $Fe_{0.92}PS_3$(2′,4′-dichloro-*N*-methylstilbazolium)$_{0.16}$, found (calcd): C, 11.80 (12.18), H, 1.25 (0.88), N, 1.05 (1.01)).

Results and discussion

X-ray powder diffraction (XRD)

From XRD results it is found that the original 00*l* patterns of the pre-intercalate, $Fe_{0.92}PS_3(Et_4N)_{0.16}$, as well as the pure $FePS_3$ completely disappeared. Instead, a new series of sharp 00*l* reflections are exhibited for five intercalation compounds. This implies that these intercalation compounds, $Fe_{1-x}PS_3$(*N*-methylstilbazoliums)$_{2x}$ (**I–V**), are the fully intercalated and well crystallized products. All reflections can be indexed in a monoclinic unit cell closely related to that of pure $FePS_3$. The calculated a, b and β values are almost identical with that of pure $FePS_3$ (Table 1) except for the expansion of the unit parameter c and lattice spacing d, which indicates the layered structure of the host is maintained after intercalation. Tables 2 and 3 give the indexation of intercalate **I** and **IV** as examples.

From the results of XRD, it was found that the lattice spacing is increased by 5.8–6.0 Å for Intercalates **I**, **II** and

Table 3. Indexation of XRD of Intercalate **IV**

Spacing (Å)		*hkl*	Intensity
Obsd.	Calcd.		
21.0200	20.9674	001	100.0
10.5171	10.4837	002	263.0
6.9642	6.9891	003	74.0
5.1510	5.1392	020	66.0
4.1295	4.1404	023	15.0
3.4901	3.4946	006	19.0
3.3857	3.3813	031	50.0
2.9568	2.9621	20$\bar{4}$	39.0
2.7281	2.7280	20$\bar{6}$	63.0
2.4338	2.4311	11$\bar{9}$	8.0
2.2202	2.2212	23$\bar{1}$	9.0
1.9278	1.9283	24$\bar{1}$	6.0
1.7293	1.7298	302	62.0
1.7054	1.7058	312	15.0
1.6407	1.6394	322	13.0
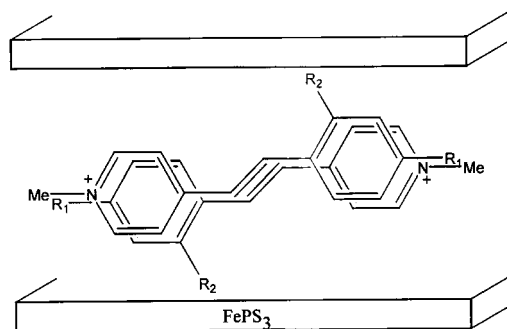
Figure 2. The possible arrangement of the guests between the interlayer space of $FePS_3$.

Table 4. The infrared data of the intercalation compounds (cm^{-1})

	$Fe_{0.92}PS_3(Et_4N)_{0.16}$	I	II	III	IV	V
$\nu_{C=N}$		1639	1645	1636	1643	
or		1618			1593	1624
$\nu_{C=C}$		1593	1591	1566	1562	1578
		1514	1514	1518	1514	1516
	1475	1461	1472	1470	1464	1470
	1445	1447				
	1430		1435	1425	1413	
δ_{C-H}		1388	1385	1366	1362	1385
in		1327	1342	1323		1327
plane					1288	
				1205	1207	
	1167	1184	1167	1153	1180	1186
					1150	
	1080	1078	1082	1086	1082	1088
		978		941		972
ν_{C-H}		978		878		
out of		831	835	823	823	825
plane	789	754	799			789
		712				736
	689	689				685
ν_{PS3}	608	604	608	608	608	606
		584	580	580		
	554	554	556	554	556	557

III compared with pure $FePS_3$ ($d = 6.439$ Å). This indicates that the molecular ring plane of the guests is perpendicular to the layer of the host similar to that of molecular pyridine inserted into the $MnPS_3$ interlayer space [14]. For Intercalates **IV** and **V**, the lattice spacing of **IV** and **V** may be only expanded by about 8.5–10.0 Å if the ortho-group of OMe in **iv** and of the Cl atom in **v**, are considered for one molecule to be arranged perpendicular to the layer of the host as in Intercalates **I**, **II** and **III**. However, the lattice spacing expansion (Δd) of Intercalates **IV** and **V** are 14.6 Å and 13.2 Å, respectively, which is much larger than expected. This means that the guest molecule is not randomly located, and it can be possibly suggested that there exists a dipolar interaction between the guests in the interlayer space of the host, adopting the arrangement as in Figure 2.

Infrared spectra

Table 4 gives the infrared data of these intercalation compounds as well as the pre-intercalation compound, $Fe_{0.92}PS_3(Et_4N)_{0.16}$, for comparison. There are two or three strong infrared absorption bands around 555–610 cm^{-1} for these intercalation compounds. These characteristic bands can be assigned to the asymmetric stretching absorption of the PS_3^- anion group. They come from the splitting of 570 cm^{-1} in pure $FePS_3$ reflecting the presence of some intralamellar Fe^{2+} ion vacancy [26]. Infrared absorption at 650 to 2000 cm^{-1} can be attributed to the *N*-methylstilbazolium derivative cations guest species. Especially, the ring stretching bands above 1500 cm^{-1} strongly support the existence of *N*-methylstilbazoliums.

Magnetic properties

The magnetic properties of the materials were studied with a SQUID magnetometer. Figures 3 and 4 give the curves of χ (magnetic susceptibility) vs. T (temperature) and χT vs. T of Intercalate **II** as an example. Figure 3 clearly shows the weak antiferromagnetic transition at about 80 K that is lower than that of pure $FePS_3$ ($T_N = 120$ K). From the curve of χT vs. T in Figure 4, the χT value decreases as the temperature decreases. This means that the Fe^{2+} ion interaction is antiferromagnetic. Above 120 K, the inverse of the paramagnetic susceptibility fitted to the Curie–Weiss law very well and the solid line shows the Curie–Weiss law (Figure 3 inset). The Curie constant is about 2.92 cm^3 K mol^{-1}. The effective magnetic moment per iron ion is evaluated as 4.83 BM, which is closed to that of the spin-only value of high spin Fe^{2+} ion (4.90 BM) [27]. This suggests that the iron ion is still in the +2 oxidation state in Intercalate **II** after intercalation. The Weiss constant is about −121 K that also supported the existence of the antiferromagnetic coupling between Fe^{2+} ions in the paramagnetic range.
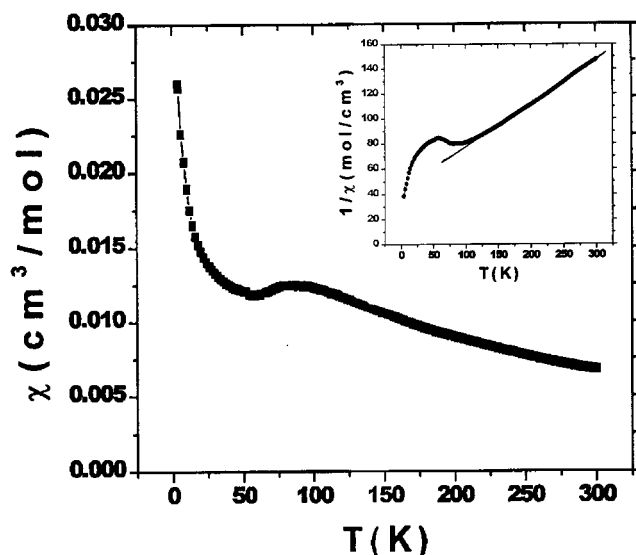
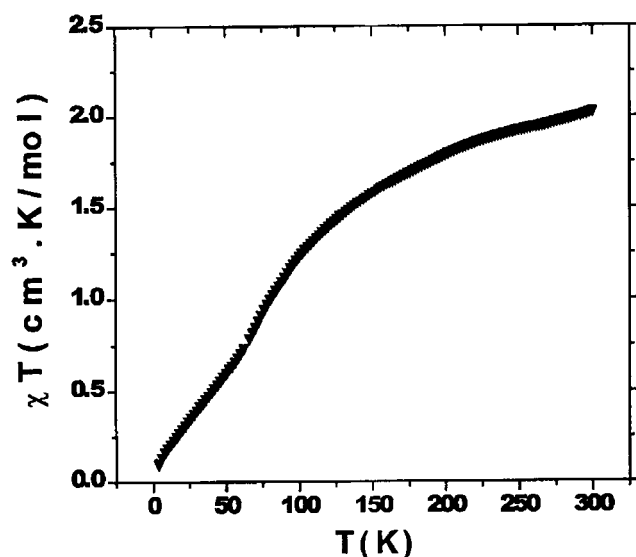Figure 3. The plot of χ-T of Intercalate II (The inset is the curve of $1/\chi$-T).
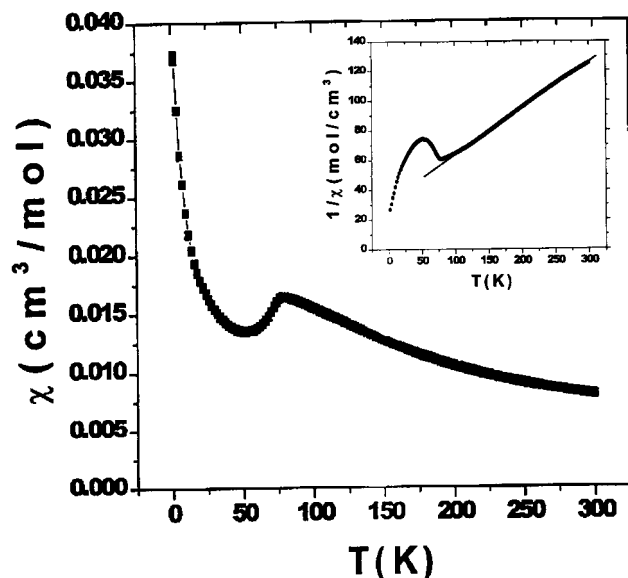

Figure 4. The plot of χT-T of Intercalate II.

Figure 5. The plot of χ-T of Intercalate V (The inset is the curve of $1/\chi$-T).

Table 5. The magnetic data of the intercalation compounds

	FePS$_3$	I	II	III	IV	V
T_N (K)	~120	~80	~80	~80	~80	~80
θ (K)	+104	−75.5	−101.2	−86.90	−75.5	−121.3
μ_{eff} (BM)		4.74	4.83	4.56	5.22	4.89

Figure 5 gives the curve of χ vs. T and $1/\chi$ vs. T of another intercalation compound **V**. It shows a similar antiferromagnetic transition to Intercalate **II** at around 80 K, although the electron-accepting ability of the guest is stronger than that of **II** and its lattice space is expanded to 19.62 Å which is 7.35 Å larger than that of Intercalate **II**. The Curie constant is 2.99 cm^3 K mol^{-1} and the effective magnetic moment per iron ion is evaluated as 4.89 BM. The Weiss constant is about −101 K.

For the other three intercalation compounds (**I**, **III**, **IV**), they exhibited similar magnetic properties, although the electron-accepting ability of the guests and the lattice spacing in these intercalates are different from each other.

The magnetic data of these five intercalation compounds are gathered in Table 5. Due to the dilution of the intralamellar Fe^{2+} ion vacancies in the host, the Neel temperature is decreased compared with pure FePS$_3$ (T_N = 120 K). At the range of the paramagnetic temperature, the negative Weiss constant reflects the short-range antiferromagnetic coupling interaction between the Fe^{2+} ions. However, their antiferromagnetic coupling interaction between the Fe^{2+} ions is different from that of pure FePS$_3$ that shows the ferromagnetic coupling interaction in the paramagnetic range [11]. Perhaps, the intercalation of the stilbazoliums into the intralayer space of layered FePS$_3$ could change the magnetic structure of the host.

From the magnetic results, it seems that the lattice spacing expansion and the electron-effect of the substitution group in the guests have little influence on the antiferromagnetic properties of these intercalation compounds.

Conclusions

A series of inorganic-organic hybrid nanocomposites, *N*-methylstilbazolium derivatives intercalated into layered FePS$_3$, were synthesized, whose structures are characterized with XRD, IR and elemental analysis. The lattice spacing expansion (Δd) of 5.8–6.0 Å for Intercalates **I**, **II** and **III**, 14.6 Å for Intercalate **IV** and 13.2 Å for Intercalate **V** compared with FePS$_3$ indicates that the molecular ring planes of the guests are almost perpendicular to the layers of the host. From the lattice expansion of Intercalates **IV** and **V** it can be inferred that a dipolar interaction may exist between the guests in the interlayer space of the host FePS$_3$. All these intercalation compounds exhibited similar antiferromagnetic properties with a Neel temperature at around 80 K, although the lattice space of the intercalates and the

electron-accepting ability of the guest are different. It may imply that the lattice spacing expansion and the electron-effect of the substitution group of the guest have not altered the antiferromagnetic property of these $FePS_3$ intercalation compounds.

Acknowledgements

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