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Synthesis, Characterization, and Magnetic Properties of Intercalation Compound of 1,10-Phenanthroline with Layered $MnPS_3$

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A new intercalation compound $Mn_{0.84}PS_3(phen)_{0.64}$ (phen = 1,10-phenanthroline) was synthesized in one step by direct reaction of host $MnPS_3$ with 1,10-phenanthroline, which was characterized by elemental analysis, X-ray powder diffraction, and infrared spectroscopy. As a result of intercalation, the lattice spacing of the intercalate expanded by 8.63 Å with respect to the pristine $MnPS_3$. For comparison, another new intercalation compound $Mn_{0.88}PS_3[Mn(phen)_4]_{0.12}(H_2O)$ was also prepared in two steps by means of ion exchange. The studies of magnetic properties with SQUID-magnetometer indicated that the two intercalates, $Mn_{0.84}PS_3(phen)_{0.64}$ and $Mn_{0.88}PS_3[Mn(phen)_4]_{0.12}(H_2O)$, exhibit bulk spontaneous magnetization below 36 and 33 K, respectively. © 2000 Academic Press

1. INTRODUCTION

Metal hexathiohypodiphosphates MPS_3, where M is a wide range of divalent metal ions (M = Mg, V, Mn, Cd, Fe, Co, Zn, Ni), have a layered structure made up of two dimensional arrays of $P_2S_6^{4-}$ bridging ligands coordinated to the M^{2+} ions. The MPS_3 phases containing paramagnetic M^{2+} ions (Mn^{2+}, S = 5/2; Fe^{2+}, S = 2; Ni^{2+}, S = 1) are described as two-dimensional antiferromagnets with Neel temperatures of 78, 120, and 253 K, respectively (1–4).

The MPS_3 lamellar compounds undergo two types of intercalation reaction. Redox intercalation involves electron donating from guest to host, resembling those of the metal dichalcogenides (5). In contrast, several MPS_3, especially $MnPS_3$, possess a unique nonredox intercalation reaction based on the cation exchange between host and guest (6). M^{2+} cations are able to leave their intralamellar sites to go into the solution, while guest cations in the solution can insert into the interlayer space to maintain the charge neutrality of the intercalation compounds. This direct cation exchange reaction often fails when the size of the guest species is over a critical value, such as in the case of $[Ru(2,2'\text{-bipy})_3]^{2+}$. However, this bulky species can be intercalated into $MnPS_3$ in two steps (7): (1) insertion of small cations, such as alkali metal ions or tetramethylammonium and (2) exchange of small cations of the preintercalate with the bulky species.

In the past decades there has been an increasing interest in molecular-based magnets. The strategy to design molecular-based compounds usually involves assembling ferromagnetic or ferrimagnetic chains or layers in three-dimensional space (8, 9). Recently, Clement's group reported that some MPS_3 (M = Mn, Fe) intercalation compounds show spontaneous magnetization (10–13), representing an alternative approach by modifying the antiferromagnetic layered materials to induce bulk magnetization. In our previous research, we also presented a new intercalate $Mn_{0.86}PS_3(bipy)_{0.56}$, which exhibits spontaneous magnetization below 40 K (14).

In this paper, a new intercalation compound $Mn_{0.84}PS_3(phen)_{0.64}$ was synthesized in one step by direct reaction of the host $MnPS_3$ with 1,10-phenanthroline. This material shows spontaneous magnetization below 36 K. In addition, we also present another new intercalate $Mn_{0.88}PS_3[Mn(phen)_4]_{0.12}(H_2O)$, which was prepared in two steps by means of ion exchange, for the purpose of comparison.

2. EXPERIMENT

X-ray powder diffraction (XRD) patterns were recorded on a Dmax rA X-ray diffractometer using CuKα radiation (λ = 1.5418 Å). Infrared spectrum was obtained on a Nicolet SX Fourier transform spectrometer. Elemental analysis of carbon, hydrogen, and nitrogen was performed on a Carlorba-1106 microanalyzer. The contents of manganese and phosphorus were measured by the method of ICP–AES on an Atomscan-2000 instrument. The magnetic properties

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were studied with a SQUID-magnetometer (MPMS, Quantum Design).

Pure $MnPS_3$ compound was synthesized by the reaction of the pure stoichiometric elements at 700°C described in literature (15). It was identified by means of XRD. The patterns of XRD were indexed in the monoclinic unit cell (space group $C2/m$). The calculated parameters are $a = 6.094$ Å (6.077 Å), $b = 10.589$ Å (10.524 Å), $c = 6.817$ Å (6.796 Å), and $\beta = 107.23°$ (107.35°). The numbers in parentheses are the lattice parameters reported in literature (16).

The intercalate $Mn_{0.84}PS_3(phen)_{0.64}$ (**1**) was prepared by stirring the mixture of $MnPS_3$ (1.01 g) and 1,10-phenanthroline (3.63 g) in a solution of dry acetonitrile (10 ml) for 12 days at 80°C. The yellow–brown powder was filtered, washed with acetonitrile, and dried in air. Elemental analysis led to the formula $Mn_{0.84}PS_3(phen)_{0.64}$ (calculated: Mn, 15.64; P, 10.95; C, 31.95; H, 1.78; N, 6.21(%); found: Mn, 16.00; P, 10.75; C, 31.20; H, 1.99; N, 7.00(%)).

The complex $[Mn(phen)_4](PF_6)_2 \cdot 2H_2O$ was prepared according to the method in the literature (17, 18). A solution of $MnCl_2 \cdot 4H_2O$ (0.5 g) and phenanthroline monohydrate (1.5 g) in 100 ml hot water was treated with a solution of NH_4PF_6 (0.7 g) in water. A white precipitate immediately appeared. White needles were obtained after recrystallization of the precipitate from acetonitrile (found: C, 51.76; H, 3.49; N, 9.68; calculated: C, 52.32; H, 3.27; N, 10.17(%)). Infrared data of this complex is listed in Table 3. The preintercalate $Mn_{1-x}PS_3K_{2x}(H_2O)_y$ was obtained by treating $MnPS_3$ with a large excess of 0.1 M aqueous KCl solution. Then the yellow–brown intercalate $Mn_{0.88}PS_3[Mn(phen)_4]_{0.12}(H_2O)$ (**2**) was synthesized by treating the above potassium preintercalate (0.4 g) with a solution of the complex $[Mn(phen)_4](PF_6)_2 \cdot 2H_2O$ (0.8 g) in 15 ml of acetonitrile for 2 days at 50°C, followed by filtration and washing with acetonitrile. Stoichiometry of this intercalate was established by the elemental analysis (calculated: Mn, 19.62; P, 11.06; C, 26.97; H, 1.80; N, 6.29(%). found: Mn, 20.05; P, 11.29; C, 27.23; H, 2.01; N, 6.04(%)).

3. RESULTS AND DISCUSSION

3.1. *X-Ray Powder Diffraction*

The X-ray powder diffraction (XRD) of intercalate $Mn_{0.84}PS_3(phen)_{0.64}$ exhibits a new series of sharp $00l$ reflections (up to 005), while the original patterns of pure $MnPS_3$ completely disappeared. This reveals full intercalation and good crystallinity. All reflections could be readily indexed in a monoclinic unit cell (Table 1) closely related to that of pristine $MnPS_3$. The calculated unit cell parameters are given in Table 2. Among them, a, b, and β values are almost identical with that of pristine $MnPS_3$. As a result of intercalation, the lattice spacing increased to 15.121 Å, corresponding to a lattice expansion (Δd) of ca. 8.63 Å with respect to pure $MnPS_3$. Generally, such large lattice expansion in the $M PS_3$-based intercalation compounds can only be obtained in two steps by ion exchange. However, in this case it was achieved in one step by the direct reaction of the host $MnPS_3$ with 1,10-phenanthroline.

TABLE 1
Indexation of XRD of $Mn_{0.84}PS_3(phen)_{0.64}$

Spacing (Å)			
Observed	Calculated	*hkl*	Intensity
15.121	15.177	001	1000
7.609	7.609	002	676
5.075	5.077	003	18
3.805	3.809	004	45
3.046	3.049	005	39
2.994	2.989	115	8
2.834	2.839	131	16
2.621	2.617	040	19
2.539	2.540	223	7
2.379	2.377	221	11
2.158	2.158	044	6
1.954	1.955	152	7

3.2. *Infrared Spectrum*

The IR spectrum absorptions of the intercalate attributed to the $\nu(PS_3)$ asymmetric stretching band occur at 610, 592, and 559 cm^{-1}, coming from the splitting of 570 cm^{-1} in pure $MnPS_3$. This reflects the presence of intralayer Mn^{2+} ion vacancies (19, 20).

The IR spectrum also provides evidence for the presence of guest species. Table 3 lists the characteristic IR absorptions of this intercalate. Also listed are those of phenanthroline monohydrate, phen.$HClO_4$ and the complex $[Mn(phen)_4](PF_6)_2 \cdot 2H_2O$ for comparison. The spectrum of free phenanthroline shows characteristic ring frequencies at 1505 cm^{-1} (21, 22), however, these absorption bands of the intercalate $Mn_{0.84}PS_3(phen)_{0.64}$ (**1**) show a remarkble shift of 17 cm^{-1}, like in the case of the complex $[Mn(phen)_4](PF_6)_2 \cdot 2H_2O$, indicating the coordination of phenanthroline with Mn^{2+} ion (17, 18). This suggests the presence of the complex cation $[Mn(phen)_4]^{2+}$ formed by

TABLE 2
Lattice Spacing (*d*) and Calculated Unit Cell Parameters

Compound	*d* (Å)	*a* (Å)	*b* (Å)	*c* (Å)	*β* (deg)
$MnPS_3$	6.496	6.094	10.589	6.817	107.23
$Mn_{0.84}PS_3(phen)_{0.64}$	15.121	6.023	10.476	16.038	107.94
$Mn_{0.88}PS_3[Mn(phen)_4]_{0.12}(H_2O)$	15.018	5.967	10.689	16.539	111.32

TABLE 3
Comparison of the IR Absorptions (cm^{-1}) of Intercalates with Those of phen·H_2O[21], phen·$HClO_4$[17,22], and [Mn(phen)$_4$](PF_6)$_2$·$2H_2O$

Assignment	Phen·H_2O	Phen·$HClO_4$	[Mn(phen)$_3$](PF_6)$_2$·$2H_2O$	Intercalate **1**	Intercalate **2**
Ring structure	1642m	1635m	1623m	1623m	1621m
	1615m	1618w		1606w	
	1585w	1599w	1591m	1588w	1591w
		1544s		1542w	
	1502s	1502m	1518s	1519s	1515s
	1492m		1494m	1495m	1494m
	1422s	1419s	1427s	1420vs	1423vs
		1370w		1371w	
	1345w	1340w	1342w	1344w	1344w
H in pl. deformation	1217w	1228w	1222w	1225w	1224w
	1186w	1192w		1198w	
	1137m	1145m	1143m	1144m	1141m
			1102m	1101m	1103m
H out of pl. bend	853vs	847s	839vs	853s	845vs
	779m	782m	764m	781m	773m
	738vs		727vs	729vs	726vs
	724m	717s		722s	

the Mn^{2+} ion and the phenanthroline ligand between the layers.

In order to gain further evidence of the existence of the complex cation, we synthesized another new intercalate $Mn_{0.88}PS_3[Mn(phen)_4]_{0.12}(H_2O)$ (**2**) using the ion exchange reaction of preintercalate $Mn_{1-x}PS_3K_{2x}(H_2O)_y$ with complex [Mn(phen)$_4$](PF_6)$_2$·$2H_2O$; this was also characterized by elemental analysis, X-ray powder diffraction, and infrared spectrum. Table 4 lists the indexed results of XRD reflections of this intercalate. Table 3 also lists its characteristic IR absorptions. It is obvious that Intercalate **2** exhibits almost identical IR absorptions with Intercalate **1**. Especially, the two intercalates show almost equal expansion of lattice spacing (Table 2). These facts imply that the existing forms of guest species between the layers of Intercalate **1** may include the complex cation $[Mn(phen)_4]^{2+}$, which was formed *in situ* between the layers by the reaction of Mn^{2+} (having left the intralamellar sites) with large excess phenanthroline. Similar phenomenon was also observed in the case of the intercalate $Mn_{0.86}PS_3(bipy)_{0.56}$ (14). Based on the balance of electrical charge and elementary analysis results, it was believed that the existing forms of guest species of Intercalate **1** also include protonated phenanthroline ($phenH^+$) (23, 24). In fact, the IR spectrum of Intercalate **1** shows some characteristic absorptions of $phenH^+$.

TABLE 4
Indexation of XRD of $Mn_{0.88}PS_3[Mn(phen)_4]_{0.12}(H_2O)$

Spacing (Å)			
Observed	Calculated	*hkl*	Intensity
15.018	15.020	001	1000
7.728	7.664	002	794
3.074	3.075	005	194
2.992	2.994	130	319
2.974	2.978	202	185
2.925	2.922	201	136
2.841	2.840	133	298
2.603	2.603	222	197

3.3. Magnetic Properties

The temperature dependence of the magnetic susceptibility of Intercalate **1** at an applied magnetic field of 1 KOe is shown in Fig. 1. The correction of Pascal diamagnetic contribution has been performed. In the inset of the figure, the inverse of the paramagnetic susceptibility is displayed as a function of temperature. The solid line shows the Curie–Weiss fitting of the data between 100 and 300 K, which exhibits $C = 3.93$ emu/K mol and $\theta = -65.9$ K. The antiferromagnetic transition at 78 K in pure $MnPS_3$ no longer exists and instead an abrupt increase of magnetic susceptibility indicating a spontaneous magnetization occurs at about 40 K. The transition to the spontaneous magnetization is also confirmed by the hysteric behavior in the magnetization curve at 5 K and a temperature dependence of magnetization is obtained in a weak external field of 3 Gauss as shown in the inset of Fig. 2. The Curie temperature is defined to be 36 K, at which the M–T curve shows a distinct kink. The effective magnetic moment per Mn ion is evaluated as 6.1 μ_B for Intercalate **1**, which demonstrates that the valence of the Mn ion is divalent in this material

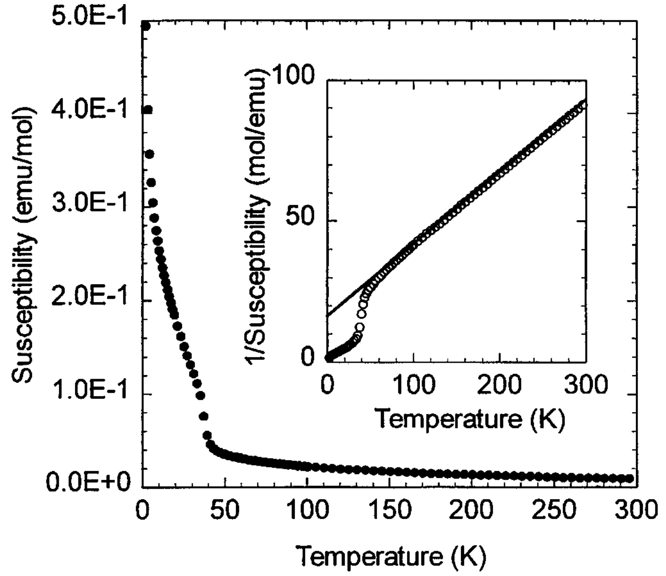

FIG. 1. Temperature dependence of magnetic susceptibility of Intercalate **1**. The inset shows a plot of inverse of magnetic susceptibility vs temperature.

just like in the case of $Mn_{0.86}PS_3(bipy)_{0.56}$ (14). However, different from the $Mn_{0.86}PS_3(bipy)_{0.56}$ case, the saturation behavior of the magnetization curve is not so remarkable up to 1 T. The coercive force and remnant magnetization are 220 Oe and 0.02 μ_B, respectively.

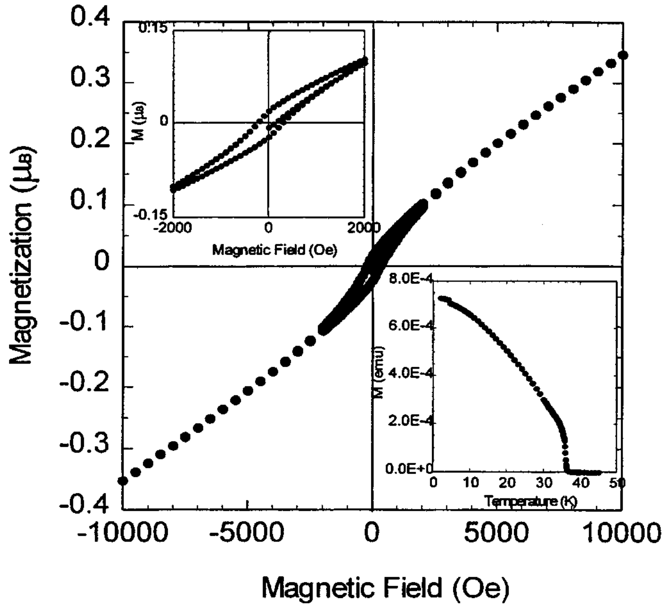

FIG. 2. Field dependence of magnetization of Intercalate **1** at 5 K. The top inset shows an expanded view of the low-field region of the magnetization curve. The bottom inset shows a temperature dependence of the magnetization obtained in H = 3 Gauss.

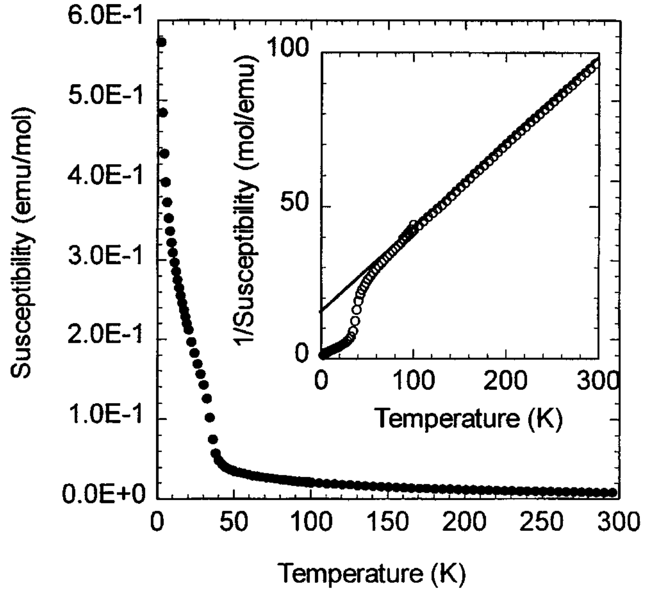

FIG. 3. Temperature dependence of magnetic susceptibility of Intercalate **2**. The inset shows a plot of the inverse of magnetic susceptibility vs temperature.

Similar magnetic behavior is also observed for Intercalate **2** as shown in Figs. 3 and 4. The Curie temperature of this material is defined as 33 K, which is slightly lower than that of Intercalate **1**. The Curie–Weiss fitting results shown in the inset of Fig. 3 gives values of C = 3.61 emu/K mol and

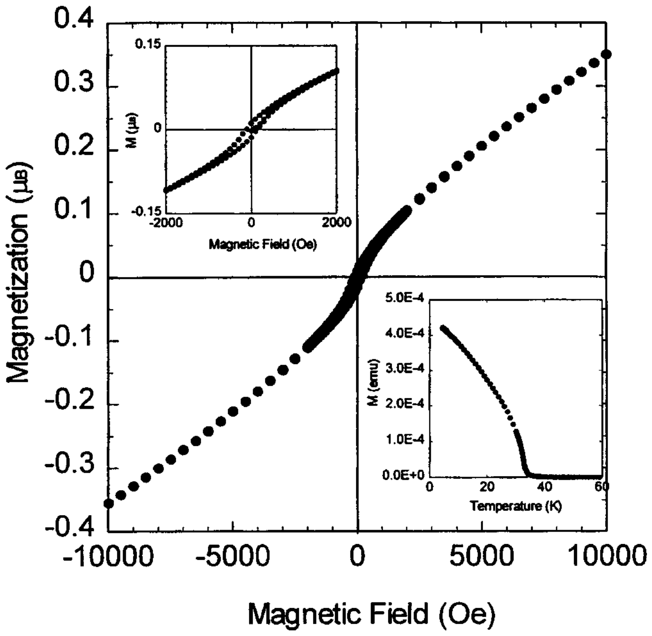

FIG. 4. Field dependence of magnetization of Intercalate **2** at 5 K. The top inset shows an expanded view of the low-field region of the magnetization curve. The bottom insets shows a temperature dependence of the magnetization obtained in H = 3 Gauss.

$\theta = -55.6$ K. These value correspond to the paramagnetic moment of 5.4 μ_B per Mn ion. Except for the relatively smaller coercive force of 160 Oe and remnant magnetization of 0.012 μ_B, the character and shape of the magnetization curve presented in Fig. 4 is almost identical with those of Intercalate **1**.

4. CONCLUSIONS

A new intercalation compound of 1,10-phenanthroline with layered $MnPS_3$ was synthesized in one step by a direct reaction. Elemental analysis led to its formula $Mn_{0.84}PS_3(phen)_{0.64}$ (**1**). X-ray power diffraction reveals a complete intercalation and a well-crystallized product. All reflections can be readily indexed in a monoclinic unit cell. As a result of intercalation, the lattice spacing of the intercalate has expanded by 8.63 Å with respect to the pristine $MnPS_3$. It is unique that such a large lattice expansion was achieved in one step in the MPS$_3$-based intercalation compounds. Infrared spectrum shows evidence of the presence of coordinated phenanthroline ligands and protonated phenanthroline between the host layers. For comparison, another new intercalation compound $Mn_{0.88}PS_3[Mn(phen)_4]_{0.12}(H_2O)$ (**2**) was also synthesized in two steps by ion exchange reaction of hydrated potassium preintercalate $Mn_{1-x}PS_3K_{2x}(H_2O)_y$ with the complex $[Mn(phen)_4](PF_6)_2 \cdot 2H_2O$. Intercalate **2** shows almost the same IR spectrum and almost equal expansion of lattice spacing to Intercalate **1**, suggesting the presence of the guest species $[Mn(phen)_4]^{2+}$ in Intercalate **1**. The magnetic properties of the two intercalates were studied using a SQUID-magnetometer. The results indicate that both exhibit similar magnetic properties, showing bulk spontaneous magnetization below 36 and 33 K, respectively.

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