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The intercalation reaction of 2,2′-bipyridine with layered compound $MnPS_3$

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Abstract

The intercalation process of 2,2′-bipyridine into layered $MnPS_3$ is studied with powder X-ray powder diffraction (XRD) technology as the monitoring tool. From the XRD results, it is found that the absence or presence of acid greatly influences the existing form and the arranged orientation of the guest. Two series of the reactions are carried out. In Series A, only $MnPS_3$ and 2,2′-bipyridine are present. While in Series B, a variety of acetic acid is added. During the intercalation of Series A, there coexist four phases: the $0\,0\,l$ phase (with lattice spacing of 6.47 Å) is pristine $MnPS_3$; the $0\,0\,l'$ phase (with lattice spacing of 9.81 Å), indicating the parallel orientation of the 2,2′-bipyridine molecular ring to the layer; the $0\,0\,l''$ phase (with lattice spacing of 12.20 Å), indicating the perpendicular orientation of the 2,2′-bipyridine molecular ring to the layer of the host, which is only an intermediate phase for the formation of the $0\,0\,l'''$ phase; the $0\,0\,l'''$ phase (with the lattice spacing of 15.33 Å), indicating the existence of the complex cation $[Mn(bipy)_3]^{2+}$ coming from the in situ coordination of the inserted guest with intralayered Mn^{2+} ions between the interlayer space of host. As the intercalation proceeds, the $0\,0\,l$, $0\,0\,l'$ and $0\,0\,l''$ phases finally disappear, and $0\,0\,l'''$ phase is intensified and a complete intercalate is obtained. In Series B, due to the presence of the acid, the formation of the complex cation $[Mn(bipy)_3]^{2+}$ is inhibited, and the amount of the acid in the intercalation plays a key role in the formation of the guest. With the increase of the acid, the protonated bipyridine becomes the main existing form of the guest, which is arranged in the perpendicular orientation of molecular ring to the layer. From the experimental evidences, the possible intercalation mechanisms are proposed and the novel intercalation phenomenon of in situ coordination of the inserted 2,2′-bipyridine with Mn^{2+} of the host is elucidated.

Keywords: Intercalation; $MnPS_3$; 2,2′-bipyridine; Mechanism

1. Introduction

Recently, much attention has been drawn to the organic–inorganic hybrid nanocomposites because it exhibits the great potential applications in many areas. Intercalation of organic species into layered inorganic solids represents one of the useful approaches to create ordered organic–inorganic nanocomposite materials with novel properties compared with the parent compounds [1].

The MPS_3 compounds, in which M is a divalent transition metal, should be considered as polynuclear coordination compounds, i.e., each slab can be seen as an array of M^{2+} ions assembled together by $P_2S_6^{2-}$ bridging ligands [2]. Since 1970s, the MPS_3 layered materials have received much attention due to their unusual reactivity as well as to the numerous properties of both the pure and intercalation compounds. Generally, the MPS_3 compounds undergo two types of intercalation. One is redox intercalation involving electron donation from guest to host [3]. But several MPS_3 (M = Mn, Fe, Cd, Zn) undergo a unique non-redox intercalation reaction based on cation exchange between host and guest, in which the electrical charge of the cationic guest species entering the host lattice is counterbalanced by the loss of interlayer M^{2+} ions [4]. Some inorganic, organic and organometallic cationic species have been intercalated into these systems by the above method and show a variety of interesting

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properties such as anisotropic electrical, low-dimensional magnetic, nonlinear optical and photomagnetic properties and even multifunctional properties [5–7]. These systems also undergo solvent exchange reactions wherein the water of hydration of interlamellar ion can be replaced by other solvating species, such as poly(ethyleneoxide), crown ethers, etc., through ion-dipole interactions [8,9].

Recently, considerable successes in the elucidation of the structural and physical properties of the intercalation compounds and some intercalation mechanism have been achieved using a combination of X-ray diffraction and neutron diffraction, solid-state NMR and theoretical simulation, etc. [10,11]. For example, the kinetics of the intercalation of some species into crystal $MnPS_3$ was studied using time-resolved in situ XRD by O'Hare et al. [12]. Qin et al. [13] studied the intercalation mechanism of 1,10-phenanthroline with $FePS_3$ through the X-ray powder diffraction (XRD) method to monitor the intercalation process. Joy and Vasudevan [14,15] proposed the intercalation mechanisms of Mn_xPS_3 $(pyridine)_y$ and $Cd_{0.75}PS_3K_{0.5}(H_2O)_y$. Result was obtained from multidimensional solid-state NMR to study the vacancy ordering and host–guest interactions in $CdPS_3$ intercalates [16].

In our previous research, we had reported a ferrimagnetic intercalation compound, $Mn_{0.86}PS_3(bipy)_{0.56}$, through direct intercalation of 2,2′-bipyridine with $MnPS_3$ in acetonitrile [7]. It was found that the guest mostly existed in the form of the complex cation $[Mn(bipy)_3]^{2+}$. This is an exotic and interesting intercalation phenomenon. However, little is known about its formation process. In this work we study the intercalation process of 2,2′-bipyridine into layered $MnPS_3$ in detail with powder XRD technology to follow the intercalation reaction in the absence or presence of acid, and propose the possible mechanisms to explain the different intercalation phenomena, especially for the in situ formation of the complex cation $[Mn(bipy)_3]^{2+}$ between the interlayer space of the host $MnPS_3$.

2. Experimental

2.1. Materials and measurements

XRD patterns were recorded on a Dmaxr A X-ray diffractometer using Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å). Infrared spectra were obtained on a Nicolet SX Fourier transform spectrometer. Elemental analysis of carbon, hydrogen, and nitrogen was performed on a VarioEL-III microanalyzer.

Pure $MnPS_3$ was synthesized by reaction of stoichiometric amounts of high-purity elements (>99.9%) in an evacuated quartz tube at 650°C as described in the literature [17]. It was identified by means of XRD and indexed as a monoclinic unit cell (space group $C2/m$), in which $a = 6.094$ Å, $b = 10.589$ Å, $c = 6.817$ Å, $\beta = 107.23°$, $d = 6.496$ Å [18]. Acetonitrile was used after dried and distilled over phosphorus pentoxide.

2.2. Synthesis of the intercalation compounds

Series A: 0.88 g (8 × 0.11 g) 2,2′-bipyridine was dissolved in 80 mL acetonitrile. The solution was divided into eight equal parts, and then each part was added into an ampoule containing 0.05 g $MnPS_3$ (No. A1–A8 in Table 1).

Series B: 0.66 g (6 × 0.11 g) 2,2′-bipyridine was dissolved in 60 mL acetonitrile, and it was divided into six equal parts, and then each part was added into an ampoule containing 0.05 g $MnPS_3$, in which different amounts of glacial acetic acid (HOAc) was used (No. B1–B6 in Table 2).

Series C: The intercalate $Mn_{1-x}PS_3\,[Mn(bipy)_3]_x$ was synthesized through the ion exchange reaction of preintercalate $Mn_{1-x}PS_3K_{2x}(H_2O)_y$ (0.6 g) with complex $[Mn(bipy)_3](PF_6)_2 \cdot 2H_2O$ (1.3 g) in 10 mL acetonitrile (No. C1). The complex $[Mn(bipy)_3](PF_6)_2 \cdot 2H_2O$ was prepared according to the method in the literature [19]. 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 as in Ref. [20]. About 0.05 g of sample A8 was added into an ampoule containing 0.2 mL glacial acetic acid (HOAc) in 10 mL of acetonitrile (noted as No. C2). About 0.05 g of sample B6 and 1.1 g 2,2′-bipyridine were placed into an ampoule containing 10 mL of acetonitrile (No. C3).

All the ampoules of series A were sealed under vacuum and the mixture was stirred at a constant temperature of 65°C for different periods, and the ampoules of series B and C were treated in the same condition for 15 days. After the reactions were finished, all samples were treated with the same procedure, in which the mixtures were filtered off, and the solids were washed with acetonitrile several times, and then dried in air. Powder solids were obtained. The elemental analysis

Table 1
Reaction period of experiment of Series A

Series A	A1	A2	A3	A4	A5	A6	A7	A8
Time (days)	0.5	1	2	3	5	9	11	15

Table 2
Amount of glacial acetic acid of Series B

Series B	B1	B2	B3	B4	B5	B6
Amount (mL)	0.02	0.05	0.1	0.3	0.5	1.0

Table 3
Elemental analysis of some full intercalates in Series A, B and C

Sample no.	Elements analysis (found and calculated)	Formula
A8	N: 5.24(5.23); C: 22.31(22.42); H: 1.68(1.50)	$Mn_{0.84}PS_3[Mn(bipy)_3]_{0.16}$
B1	N: 4.86(5.09); C: 21.95(21.85); H: 1.48(1.47)	$Mn_{0.84}PS_3(bipyH)_{0.04}[Mn(bipy)_3]_{0.14}$
B4	N: 4.71(4.68); C: 20.81(20.04); H: 1.56(1.48)	$Mn_{0.82}PS_3(bipyH)_{0.32}[Mn(bipy)_3]_{0.02}$
B6	N: 4.48(4.60); C: 20.30(19.73); H: 1.52(1.49)	$Mn_{0.81}PS_3(bipyH)_{0.38}$
C1	N: 5.53(5.68); C: 24.31(24.34); H: 1.71(1.63)	$Mn_{0.82}PS_3[Mn(bipy)_3]_{0.18}$

results of some full intercalation compounds are listed in Table 3.

3. Results and discussion

3.1. X-ray powder diffraction

Fig. 1 gives the XRD patterns of the eight samples in Series A. At the early stage, only those patterns corresponding to pure $MnPS_3$ (0 0 *l* phase) are observed (No. A1). After 1 day of reaction (No. A2), it is found that four phases appear. The *0 0 l* phase with the biggest lattice spacing of 6.47 Å is the pristine $MnPS_3$. The $0\,0\,l'$ phase, which shows the biggest lattice spacing of 9.81 Å, indicates that the arranged orientation of the 2,2′-bipyridine molecular ring is parallel to the layer of the host, and this phase almost coexists with 0 0 *l* and $0\,0\,l'''$ phase and finally disappear after 15 days in A8. The $0\,0\,l''$ phase showing the biggest lattice spacing of 12.20 Å indicates the perpendicular orientation of the 2,2′-bipyridine molecular ring to the layer. This phase is only obviously observed at the early stage of the intercalation and almost disappears at the late stage, so it can be considered as an intermediate phase for the formation of the $0\,0\,l'$ phase. The $0\,0\,l'''$ phase has the biggest lattice spacing of 15.33 Å corresponding to the lattice expansion (Δd) of ~8.9 Å, which is similar to that of the complex cation $[Ru(bipy)_3]^{2+}$ into MPS_3 (M = Mn, Cd) [21], and it exhibits almost the same XRD patterns to those of No. C1 in Series C. By comparison of the IR data of No. A8, No. C1 and complex cation $[Mn(bipy)_3]^{2+}$, it can be inferred that the guest in No. A8 is the complex cation $[Mn(bipy)_3]^{2+}$. This guest possibly comes from in situ coordination of the inserted guest (neutral 2,2′-bipyridine) with intralayered Mn^{2+} ions between the interlayer spaces of host. This is an exotic intercalation phenomenon that seldom observes in the intercalation chemistry. From the XRD results, it can be seen clearly as the intercalation proceeds, the 0 0 *l*, $0\,0\,l'$ and $0\,0\,l''$ phases finally disappear, and $0\,0\,l'''$ phase is intensified and a complete intercalate is obtained that only contains the $0\,0\,l'''$ phase (No. A8).

Series B is conducted in the presence of different amount of acetic acid. The XRD patterns of the six samples in series B are shown in Fig. 2. In this kind of intercalation, acetic acid is the source of protons for 2,2′-bipyridine and some protonated 2,2-bipyridine will be formed by proton exchange between acetic acid and 2,2-bipyridine in the solution. Therefore, the presence of acid can inhibit the formation of the complex cation

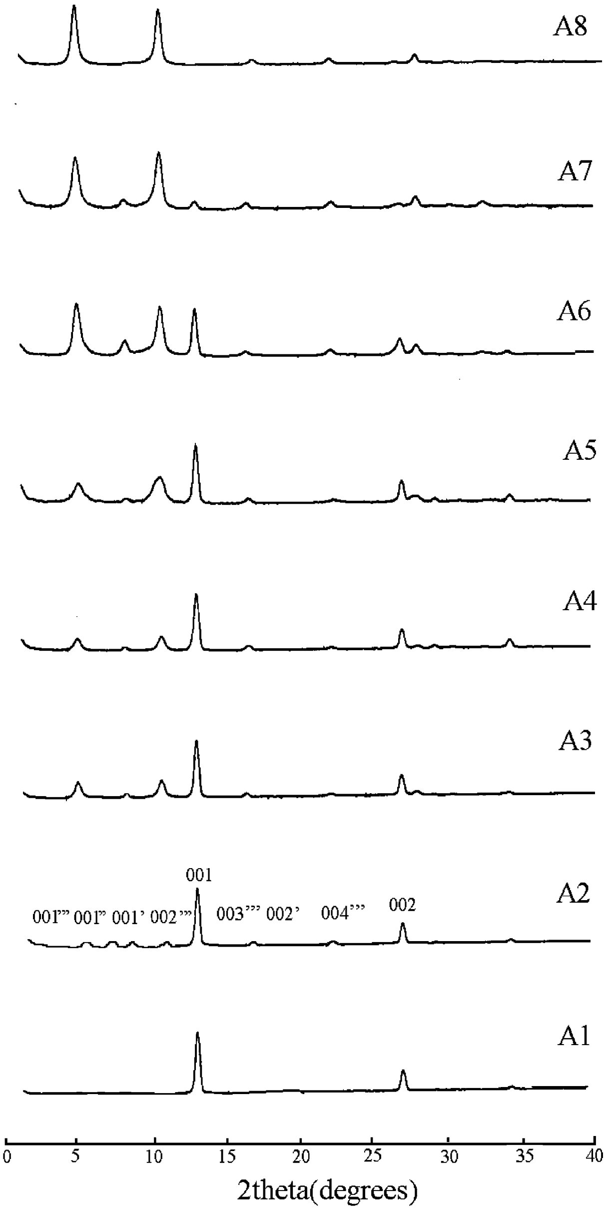


Fig. 1. XRD patterns of intercalates of Series A.

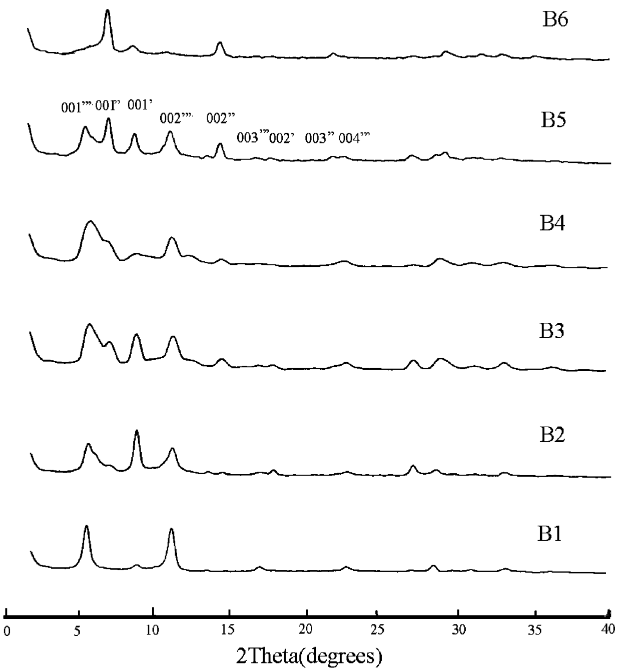


Fig. 2. XRD patterns of intercalates of Series B.

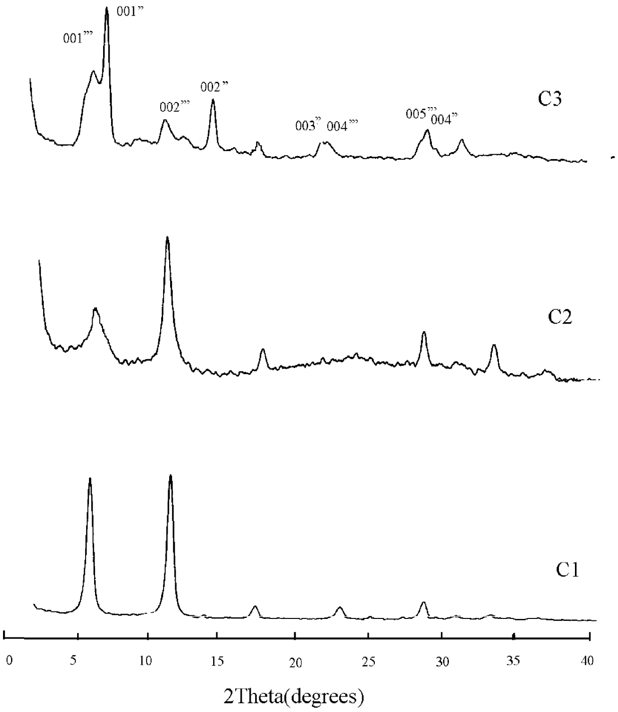


Fig. 3. XRD patterns of intercalates of Series C.

$[Mn(bipy)_3]^{2+}$. If the amount of the acid is not enough, some bipyridine exist in the neutral form, so the inhibition is not complete. For example, in Experiment B1 the amount of acid used is so little (0.2 mL) that the XRD patterns of B1 show little difference with those of A8. However, with the increase of acid, three phases ($0\,0\,l'$, $0\,0\,l'''$ and $0\,0\,l'''$ phases) appear and coexist in sample B2–B5. When the amount of the acid increases enough to form the protonated bipyridine completely, the formation of the complex cation $[Mn(bipy)_3]^{2+}$ will be fully inhibited and the protonated bipyridine becomes the only existing guest. So we can see with the increase of the amount of the acid, the reflections of $0\,0\,l'''$ phase gradually diminish, and finally almost disappear. The $0\,0\,l'$ phase is intensified at first, then diminishes, and finally disappears. At the same time, the $0\,0\,l''$ phase appears, then is gradually strengthened, and eventually becomes the main phase of the final sample of this series (No. B6). It is clear that the amount of the acid plays a key role to the formation of the guest.

In order to confirm the existence of the complex cation $[Mn(bipy)_3]^{2+}$ in Series A, we also perform the experiments of Series C. No. C1 is the intercalation of the complex cation $[Mn(bipy)_3]^{2+}$ with pre-intercalate $Mn_{1-x}PS_3K_{2x}(H_2O)_y$. Intercalate C1 exhibits almost same XRD reflection patterns as those of No. A8, which supports that the guest in intercalate A8 is $[Mn(bipy)_3]^{2+}$ ions. No. C2 is the treatment of the product of No. A8 with acetic acid in acetonitrile. The XRD pattern of C2 still exhibits a similar result to that of intercalate A8, although the crystallinity of product is poor due to the presence of the acid. It is clear that the presence of acetic acid does not alter the existing form of the guest in No. A8. If the intercalate B6 further reacts with 2,2′-bipyridine (No. C3), it is found that the $0\,0\,l'''$ phase appears indicating that more neutral 2,2′-bipyridine can be inserted into interlayer of host of sample B6 to form the $[Mn(bipy)_3]^{2+}$ ions as the guest. All of XRD patterns of Series C are shown in Fig. 3.

3.2. Infrared spectra

Fig. 4 gives the IR spectra of some samples (partial and full intercalates) of Series A, B and C. Also listed are those of 2,2′-bipyridine, bipyridium and $[Mn(bipy)_3]^{2+}$ cation for comparison in Table 4 [7,22]. The absorptions of the (partial or complete) intercalates occurring at around 610 and 557 cm^{-1} originate from the splitting of 570 cm^{-1} of pure host, which reflects the presence of intralamellar Mn^{2+} ion vacancies [23]. The IR spectra also provide evidences for the presence of guest species and their existing forms. For series A, B and C, all of the spectra exhibit analogous characteristic absorptions that can be assigned to the bipyridine ring frequencies in the 700–2000 cm^{-1} range. However, there are still some nuances between different samples, which imply that the existence of guests are different in different samples.

For series A, the spectrum of No. A8, which is the full intercalate only containing $0\,0\,l'''$ phase in series A, exhibits some different absorption from neutral bipyridine and protonated bipyridine (Table 4). But it shows

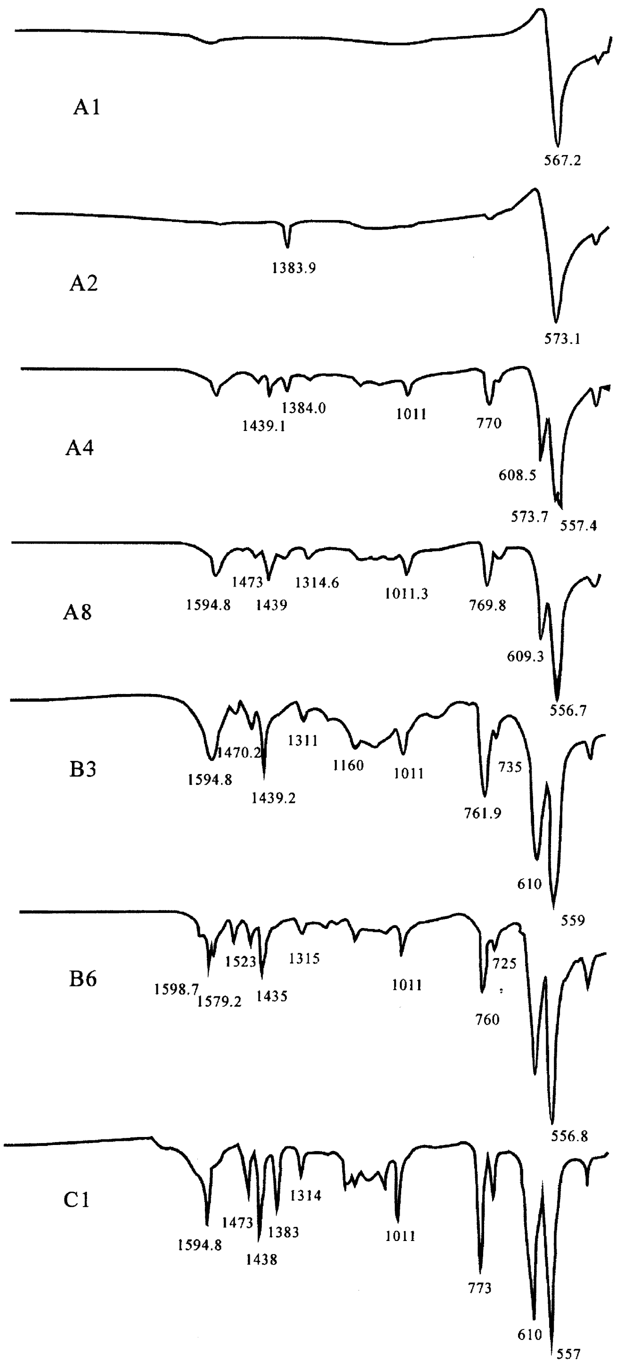


Fig. 4. IR spectra of some samples of Series A, B and C.

almost identical IR absorptions with those of No. C1 and some absorption bands such as 1595, 1473, 1439, 1315, 1011 and 770 cm^{-1}, etc., are the characteristic absorption bands of cation $[Mn(bipy)_3]^{2+}$. Combining the XRD results and IR spectra, it can be concluded that the inserted guest is $[Mn(bipy)_3]^{2+}$ for intercalate A8. Its formation will be explained in the possible mechanism of Series A.

Comparing the IR spectra of Series B with bipyridine, bipyridium and $[Mn(bipy)_3]^{2+}$ cation in Fig. 4 and Table 4 it can be seen that the intercalates of series B exhibit the characteristic absorptions of all of three species or two of them. Especially for the spectrum of No. B6 only containing $0\,0\,l''$ phase, we can see that it is much similar to that of bipyridium than neutral bipyridine as well as the complex cation, so it can be inferred that the inserted guest in No. B6 is protonated bipyridine. These results are well in agreement with the data of the elemental analyses in Table 3. From the data in Table 3 we can also infer that with the increase of acid, the amounts of the guests in the form of complex cation $[Mn(bipy)_3]^{2+}$ gradually diminish, while the amounts of the guests in the form of the protonated bipyridine increase. When the amount of the acid increases enough, the protonated bipyridine becomes the only existing guest as shown in B6. Obviously, due to the presence of the acid the in situ formation of $[Mn(bipy)_3]^{2+}$ between the interlayer spaces of the host can be inhibited in Series B.

3.3. *Possible intercalation mechanism*

Why do four phases coexist in Series A? How is the guest $[Mn(bipy)_3]^{2+}$ formed in Series A? And which is the main existing form of the guest in Series B? In order to explain these intercalation phenomena, the possible intercalation mechanisms are proposed for 2,2′-bipyridine intercalated into layered $MnPS_3$ as Scheme 1 for Series A and Scheme 2 for Series B based on the experimental results.

Scheme 1 shows the possible mechanism (Mechanism A) for Series A. From the XRD results, it is found that $0\,0\,l''$ phase is only obviously observed at the early stage of the intercalation and almost disappears at the late stage, but the other three phases coexist for a long time. As the period of intercalation is prolonged, XRD reflections of the $0\,0\,l'''$ phase are strengthened and the $0\,0\,l$ and $0\,0\,l'$ phases are gradually weakened. Finally, a full intercalate (A8) only showing the $0\,0\,l'''$ phase is obtained. So it can be tentatively suggested that the initial intercalation is the parallel insertion of neutral 2,2′-bipyridine into the layer of $MnPS_3$ to form the $0\,0\,l'$ phase (Eq. (1) in Scheme 1), which may be a slow reaction. Therefore, this phase almost exists during the whole intercalation process. After the van der Waals forces holding the layers of the host together are destroyed, 2,2′-bipyridine should be easily inserted into the interlayer space, in which the guest is arranged perpendicular to the layer ($0\,0\,l''$ phase). The reason for this orientation may be due to the restriction of limited interlayer space of the host and to the favorable arrangement for the in situ coordination of bipyridine with Mn^{2+} ions from the intralayered position of the host (Eq. (2) in Scheme 1). Once the guest is arranged in the perpendicular orientation to the layer, it can readily coordinate with Mn^{2+} ions to form the complex cation

Table 4
Comparison of the IR absorption (cm^{-1}) of intercalates of Series A, B and C with those of 2,2′-bipyridine, bipyridium and $[Mn(bipy)_3]^{2+}$

Assignment	A8	B6	C1	2,2′-bipy[a]	Bipy · HCl[a]	$[Mn(bipy)_3]^{2+}$[b]
Ring structure (C=C, C=N)	1595	1599	1595		1600	1597
		1579		1579	1578	1574
		1523		1553	1530	1562
					1500	1491
	1473	1471	1473		1470	1473
		1454			1452	
Ring structure + H bond	1439	1435	1438	1448	1432	1439
				1410	1410	1425
					1390	
$N–H^+$ out of planar bend	1315	1315	1314		1315	1315
Res. Deformation ring structure	1247	1240	1247	1240	1230	1249
H in planar bend		1171	1177	1210	1172	1176
	1155	1162	1155		1165	1154
				1138	1152	
	1100	1102	1100		1105	1098
Ring structure + bend	1058	1066	1060	1063	1070	1060
Ring breathing mode	1011	1011	1011	991	1010	1011
		991			1005	
Ring structure + H bond					980	911
H out of planar bend	898			890	875	895
	770	760	773	753	760	774
	737	725	737	738	725	737
Ring bend	647	652	645	651	660	644
					640	621

[a] Ref. [22].
[b] Ref. [7].

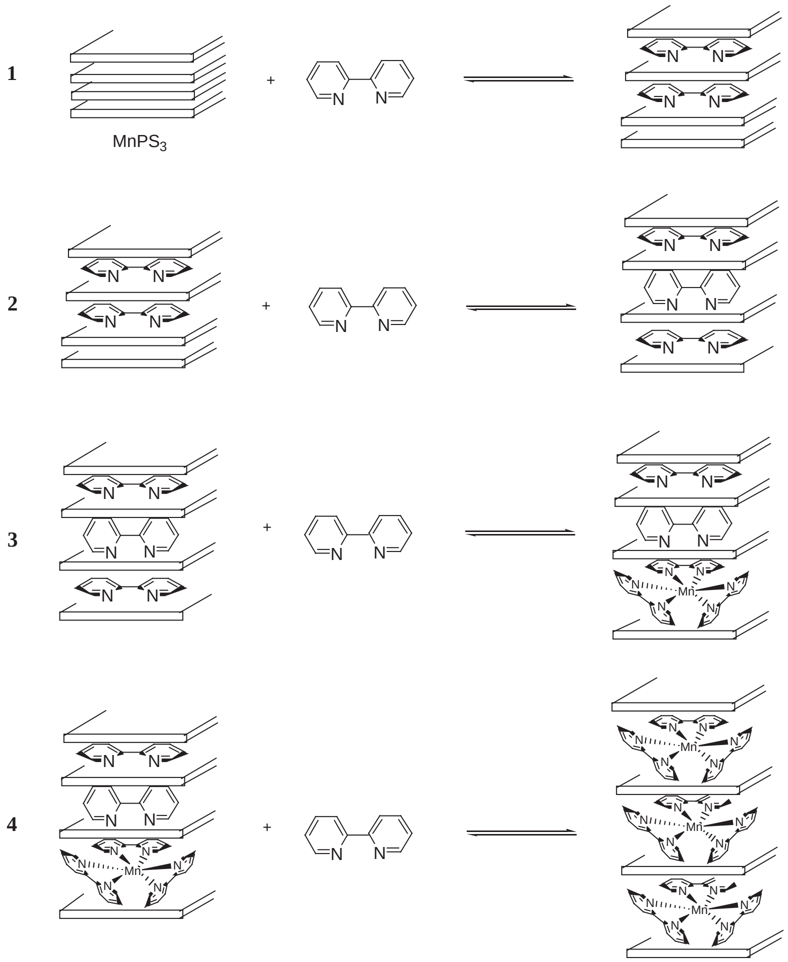
$[Mn(bipy)_3]^{2+}$ and the $0\,0\,l'''$ phase appears, which is a fast reaction. So $0\,0\,l''$ phase seems to exist for a transient period from the XRD spectra because the XRD reflection intensity of $0\,0\,l'''$ phase increases rapidly that greatly suppresses the intensity of $0\,0\,l''$ phase. As far as we know, this is an exotic intercalation phenomenon that is seldom observed in the research of the intercalation chemistry.

During this intercalation, the reaction is a multiphase reaction and the rate of the intercalation is slow, so several phases in XRD spectra coexist for a long time (Eq. (3) in Scheme 1). As the intercalation is going on, the $0\,0\,l'''$ phase is rapidly intensified and becomes the main phase owing to the strong inclination of coordination of bipyridine with Mn^{2+} ions, and finally other three phases disappear and the full intercalate (No. A8) only exhibiting $0\,0\,l'''$ phase is obtained (Eq. (4) in Scheme 1).

For Series B, due to the presence of acetic acid, the XRD results show the different reflection patterns from those of Series A. In Series B, acetic acid provides the proton for bipyridine to form the protonated bipyridine in the solution. If the acid is not enough to form the protonated bipyridine fully, the neutral bipyridine also exists in the solution. And the intercalation of the neutral bipyridine with $MnPS_3$ will follow the same mechanism as that of Series A. But the intercalation of the protonated bipyridine will adopt another intercalation mechanism (Mechanism B) as in Scheme 2.

Firstly, bipyridine obtains the proton to form the protonated bipyridine in the solution (Eq. (1) in Scheme 2). This is a reversible reaction, so some bipyridine will still exist in neutral form even in the presence of acetic acid. It can remove the little amount of Mn^{2+} ions to form the complex cation $[Mn(bipy)_3]^{2+}$ into the solution and make the host intralayer to be of negative charge (Eq. (2) in Scheme 2). Then, some protonated bipyridine will insert into the interlayer space in a parallel orientation to maintain the charge balance (Eq. (3) in Scheme 2). Once much more protonated bipyridine inserts into the host, it will be arranged in perpendicular orientation to the layer due to the limited interlayer space of the host, so the XRD reflection intensity of $0\,0\,l''$ phase of Series B is gradually intensified (Eq. (4) in Scheme 2). This is different from Series A that only observes in the early stage because the guest (2,2′-bipyridine) exists in different form, although the biggest lattice spacing is the same. If there is excessive amount of the acid in the solution, most of bipyridine becomes the protonated form, and the intercalation will completely follow Mechanism B.

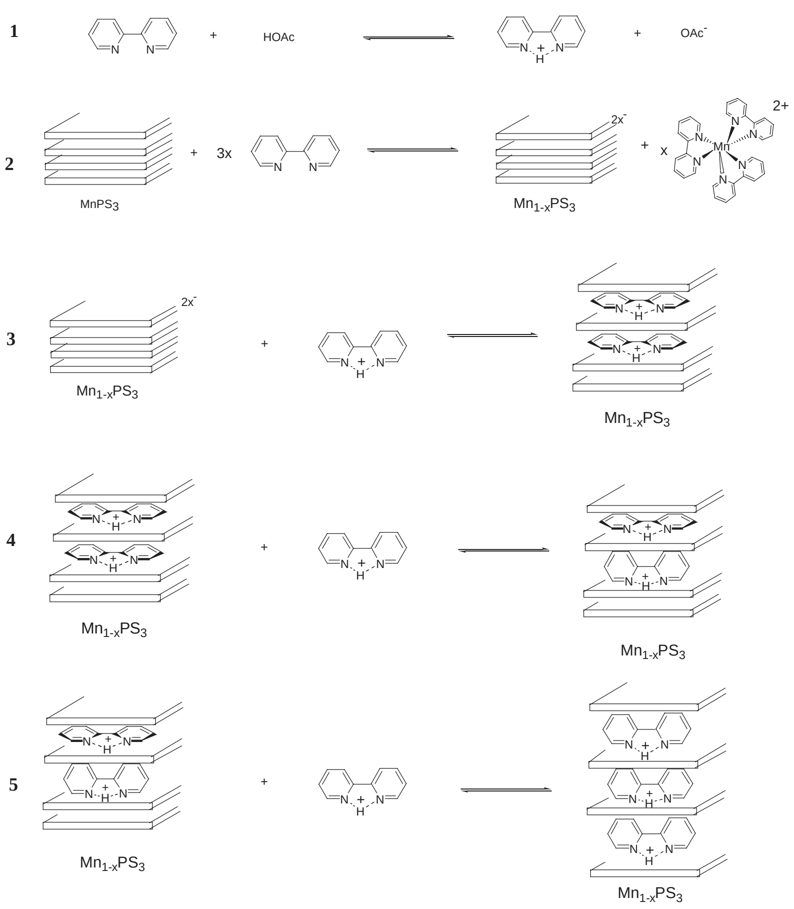
From XRD results, it is found that all of the samples in Series B are full intercalation compounds. However, most of them (No. B2–B5) show three coexisting phases ($0\,0\,l'$, $0\,0\,l''$ and $0\,0\,l'''$ phases). As the amount of the



Scheme 1. Possible intercalation mechanism for Series A.

acid increases, the reflection intensity of $0\,0\,l'$ and $0\,0\,l'''$ phases gradually diminishes, and finally disappears. But the $0\,0\,l''$ phase is gradually strengthened, and eventually becomes the main phase of the final sample of this series (No. B6). Why does Series B exhibit this intercalation phenomenon? In the presence of acid, two kinds of forms of bipyridine (neutral and protonated) exist in the solution, neutral bipyridine follows Mechanism A, which will produce the $0\,0\,l'''$ phase, and the protonated bipyridine obeys Mechanism B that gives the $0\,0\,l'$ and $0\,0\,l''$ phases. If the amount of the acid is small, most of bipyridine will act as the neutral form and $0\,0\,l'''$ phase becomes the main phase. At the same time, the small amount of protonated bipyridine mainly produce the $0\,0\,l'$ phase because no more protonated bipyridine is inserted in the host to form the $0\,0\,l''$ phase. Therefore, at early stages, the intensities of XRD patterns of $0\,0\,l'$ and $0\,0\,l'''$ phases show much stronger than those of $0\,0\,l''$ phase. With the increase of amount of the acid, the protonated bipyridine becomes the main existing form, so the $0\,0\,l'''$ phase that is related to neutral bipyridine is inhibited gradually, and much more protonated bipyridine are inserted into the host that intensify the $0\,0\,l''$ phase and weaken the $0\,0\,l'$ phase owing to the limited interlayer space of the host. Finally, when the acid is greatly excessive, the neutral bipyridine is overwhelmed by protonated bipyridine, the $0\,0\,l'''$ phase (in situ formation of complex cation $[\mathrm{Mn(bipy)_3}]^{2+}$) is fully suppressed, and $0\,0\,l'$ phase is also replaced by $0\,0\,l''$ phase, which produces a full intercalation compound only containing the $0\,0\,l''$ phase.

In addition, some evidences in Series C are provided to further confirm the intercalation mechanism for Series A and Series B. No. C1 supports the existence of the in situ formation of complex cation $[\mathrm{Mn(bipy)_3}]^{2+}$ ($0\,0\,l'''$ phase) in Series A. From No. C2, it can be seen that the presence of acetic acid does not alter the existing form of the guest in No. A8. In No. C3, it is found that the $0\,0\,l$ phase appears indicating that neutral 2,2′-bipyridine can be inserted into interlayer of host to follow Mechanism A to form the $[\mathrm{Mn(bipy)_3}]^{2+}$ ions as the guest.



Scheme 2. Possible intercalation mechanism for Series B.

4. Conclusion

The intercalation reaction of 2,2′-bipyridine with layered $MnPS_3$ has been studied in detail using power XRD technology to monitor the intercalation process. In light of the XRD results, the possible intercalation mechanisms, which are also supported by the results of IR spectra and elemental analysis, are proposed to explain the different intercalation phenomena for the intercalation of 2,2′-bipyridine with layered $MnPS_3$ in the different reaction conditions. It is found that the presence of acid or not greatly influences the intercalation process of 2,2′-bipyridine with $MnPS_3$ and the existing form of the guest. An interesting intercalation phenomenon of in situ coordination of the inserted 2,2-bipyridine with Mn^{2+} of the host is observed and elucidated.

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