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MAGNETIC BEHAVIOR OF LAMELLAR $MnPS_3$ AND $CdPS_3$ COMPOSITES WITH A PARAMAGNETIC MANGANESE(III) MACROCYCLIC GUEST

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ABSTRACT

Six new composites derived from the intercalation of the MPS_3 phases ($M = Mn^{II}, Cd^{II}$) with the macrocyclic manganese(III) complex $[MnL(H_2O)_2] \cdot NO_3 \cdot (H_2O)$ ($LH_2 =$ Schiff base macrocyclic ligand derived from the condensation of 2-hydroxy-5-methyl-1,3-benzene-dicarbaldehyde and 1,2-diamine-benzene) were obtained by two different synthetic procedures: a conventional and a microwave assisted method. The composites $[MnL]_{0.25}K_{0.15}Mn_{0.80}PS_3(H_2O)_{-1.0}$ (**1**), and $[MnL]_{0.25}K_{0.15}Cd_{0.80}PS_3(H_2O)_{-0.5}$ (**2**) were obtained by the conventional method, after stirring a suspension of the corresponding potassium precursor and the macrocyclic complex for two weeks, while $[MnL]_{0.35}K_{0.05}Mn_{0.80}PS_3(H_2O)_{-1.0}$ (**3**) and $[MnL]_{0.25}K_{0.15}Cd_{0.80}PS_3(H_2O)_{-0.5}$ (**4**) after stirring for four weeks at room temperature. Using a microwave assisted reaction permitted to obtain in a shorter period of time as compared with the conventional method, composites $[MnL]_{0.20}K_{0.20}Mn_{0.80}PS_3(H_2O)_{-1.0}$ (**5**) and $[MnL]_{0.15}K_{0.25}Cd_{0.80}PS_3(H_2O)_{-0.5}$ (**6**). All the Mn^{III}/Mn^{II} composites show a bulk antiferromagnetic behavior. However, the spontaneous magnetization present at low temperature in the potassium precursor $K_{0.40}Mn_{0.80}PS_3(H_2O)_{-1.0}$ is observable in composite $[MnL]_{0.20}K_{0.20}Mn_{0.80}PS_3(H_2O)_{-1.0}$ (**5**), while it is completely absent in composites $[MnL]_{0.25}K_{0.15}Mn_{0.80}PS_3(H_2O)_{-1.0}$ (**1**) and $[MnL]_{0.35}K_{0.05}Mn_{0.80}PS_3(H_2O)_{-1.0}$ (**3**).

Keywords: Intercalation; MPS_3 phases; Mn^{III} macrocyclic complex; microwave assisted synthesis; magnetic properties.

INTRODUCTION

Transition metal thiophosphates, MPS_3 , have a layered structure made up of two-dimensional arrays of $P_2S_6^{2-}$ bridging ligands, coordinating to the M^{II} cations^{1,2}. The interlayer array is held by van der Waals interactions and therefore many molecules and ions such as inorganic, organic, cationic metal complexes and organometallic cationic species can be intercalated in this space³⁻⁷. The obtained composites show a variety of interesting properties such as electrical^{8,9}, magnetic¹⁰⁻¹³, nonlinear optical and photomagnetic^{14,15}, and even multifunctional properties¹⁶. Especially, the observed magnetic change, from antiferromagnetism present in the $MnPS_3$ phase¹⁷ to ferrimagnetism in some of the intercalated species, is seldom observed among other similar layered inorganic solids obtained in the intercalation chemistry. This change arises from the unique ion-exchange intercalation process¹⁸⁻²⁰. However, this direct cation exchange reaction often fails when the size of the guest species is over a critical value. Bulky species can be intercalated into both $MnPS_3$ and $CdPS_3$ in two steps: i) the insertion into the interlamellar space of small cations such as alkali metal or tetramethylammonium ions by a cationic transfer processes, and then ii) exchange of these cations located in the interlamellar space of the pre-intercalate with the other cationic species²¹⁻²³.

The intercalation of coordination metal complexes with Schiff base ligands of salen type into lamellar MPS_3 host has been described in the literature. Among these, the $[Mn^{III}(\text{salen})]_{0.26}Mn^{II}_{0.87}PS_3 \cdot 0.5H_2O$ composite is reported to exhibit a magnetic transition from paramagnetism to ferrimagnetism at about 35 K¹³. Even though this Mn^{III}/Mn^{II} composite has been reported, to the best of our knowledge similar Mn^{III} macrocyclic complexes have not been intercalated into thiophosphate phases. The intercalation of macrocyclic complexes with magnetic and optical properties into the interlamellar space present in the thiophosphate phases can provide hybrid materials with new interesting properties.

This work reports the syntheses and characterization of six new composites obtained from the intercalation of the MPS_3 phases with the $[Mn^{III}L]^+$ complex species, obtained by the conventional and the microwave assisted methods ($M = Mn^{II}$ and Cd^{II} ; LH_2 : macrocyclic ligand synthesized by the template condensation of 2-hydroxy-5-methyl-1,3-benzenedicarbaldehyde and 1,2-diaminebenzene). Furthermore, a comparison of the magnetic behavior of the $CdPS_3$ and $MnPS_3$ composites is given.

EXPERIMENTAL

Synthesis of the MPS_3 phases ($M = Mn, Cd$) and the potassium precursors

Pure MPS_3 were synthesized by the reaction of stoichiometric amounts of high purity elements in an evacuated quartz tube at 750 °C, as described in the literature^{24,25}.

$MnPS_3$: Anal. found(calcd.): Mn 30.8(30.2); P 17.7(17.0); S 52.5(52.8) %. IR (cm^{-1}): ν_{PS_3} 573(s); ν_{P-P} 447(w).

$CdPS_3$: Anal. found(calcd.): Cd 46.3(47.0); P 13.6(12.9); S 40.1(40.1) %. IR (cm^{-1}): ν_{PS_3} 563(s); ν_{P-P} 449(w).

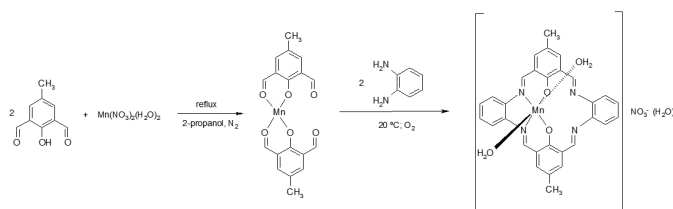
The potassium precursors were obtained by treatment of MPS_3 with a 2 M aqueous solution of KCl for 24 hours at room temperature using the conventional method, as described in the literature^{26,27}. In the case of the cadmium phase the intercalation was done in the presence of 0.1 M EDTA, pH ~ 10 (buffer $K_2CO_3/KHCO_3$).

$K_{0.40}Mn_{0.80}PS_3(H_2O)_{-1.0}$: Anal. found(calcd.): Mn 21.1(21.5); K 7.9(7.6); P 15.6(15.1); S 46.4(46.9); TGA: H_2O ; Dm % found(calcd.): 9.0(8.8). IR (cm^{-1}): ν_{PS_3} 607(s), 570(sh), 555(s); ν_{P-P} 447(w).

$K_{0.40}Cd_{0.80}PS_3(H_2O)_{-0.5}$: Anal. found(calcd.): Cd 36.5(37.2); K 6.7(6.5); P 13.1(12.8); S 39.5(39.8). TGA: H_2O ; Dm % found(calcd.): 4.2(3.7). IR (cm^{-1}): ν_{PS_3} 600(s), 555(s); ν_{P-P} 449(w).

Synthesis of the manganese complex $[MnL(H_2O)] [NO_3] \cdot H_2O$

The new macrocyclic manganese(III) complex was synthesized by a similar procedure to that previously reported by Paredes-García et al. for the preparation of a binuclear zinc(II) complex, $[Zn_2(L)](NO_3)_2$ ²⁸. The macrocyclic complex was obtained by a template reaction in two steps as shown in scheme 1.



Scheme 1

$[\text{MnL}(\text{H}_2\text{O})_2] \cdot \text{NO}_3(\text{H}_2\text{O})$: $\text{C}_{30}\text{H}_{28}\text{N}_5\text{O}_8\text{Mn}$ (PM: 641), Anal. found(calcd.): Mn 8.8(8.6); C 55.1(55.2); N 12.5(11.9); H 4.4(4.4) %. IR (cm^{-1}): $\nu \text{C}=\text{N}$ 1620(s), $\nu \text{C}=\text{C}$ 1590 (m), 1534 (s); νNO_3 1384(s); $\nu \text{C}-\text{O}_{\text{ph}}$ 1300(s); out of plane aromatic CH bending (ortho) 755 (s).

Conventional intercalation of the cationic manganese(III) macrocyclic complex

In a one-neck round bottom flask 300 mg of the preintercalated precursor and 380 mg of $[\text{MnL}(\text{H}_2\text{O})_2](\text{NO}_3)(\text{H}_2\text{O})$ for $\text{K}_{0.40}\text{Mn}_{0.80}\text{PS}_3(\text{H}_2\text{O})_{-1.0}$, or 320 mg for $\text{K}_{0.40}\text{Cd}_{0.80}\text{PS}_3(\text{H}_2\text{O})_{-0.5}$ were added to 25 mL of methanol, and stirred

at room temperature for two or four weeks. $[\text{MnL}]_{0.25}\text{K}_{0.15}\text{Mn}_{0.80}\text{PS}_3(\text{H}_2\text{O})_{-1.0}$ (**1**), and $[\text{MnL}]_{0.25}\text{K}_{0.15}\text{Cd}_{0.80}\text{PS}_3(\text{H}_2\text{O})_{-0.5}$ (**2**) were obtained after stirring for two weeks, and $[\text{MnL}]_{0.35}\text{K}_{0.05}\text{Mn}_{0.80}\text{PS}_3(\text{H}_2\text{O})_{-1.0}$ (**3**) and $[\text{MnL}]_{0.25}\text{K}_{0.15}\text{Cd}_{0.80}\text{PS}_3(\text{H}_2\text{O})_{-0.5}$ (**4**) after stirring for four weeks (Table 1). The dark red powders were filtered off, washed with methanol, and dried in an oven at 50 °C for two days. In order to eliminate any adsorbed complex, the composite was further purified by washing it several times with dimethylformamide, until the solvent remained colorless.

IR (cm^{-1}): $\nu_{\text{C}=\text{N}}$ 1655(s), ν_{PS_3} 610(m), 590(m), 557(s), $\nu_{\text{P}-\text{O}}$ 447 for the Mn phase, and $\nu_{\text{C}=\text{N}}$ 1655(s), ν_{PS_3} 600(m), 585(m), 552(s), $\nu_{\text{P}-\text{O}}$ 449 for the Cd phase.

Table 1. Analytical results for the obtained composites.

Conventional method						
Sample	Mn %	K %	Cd %	P %	S %	H ₂ O Δm %
$[\text{MnL}]_{0.25}\text{K}_{0.15}\text{Mn}_{0.80}\text{PS}_3(\text{H}_2\text{O})_{-1.0}$ (1)	30.0 (30.2)	3.2 (3.1)		16.8 (16.3)	50.5 (50.4)	5.7 (5.4)
$[\text{MnL}]_{0.25}\text{K}_{0.15}\text{Cd}_{0.80}\text{PS}_3(\text{H}_2\text{O})_{-0.5}$ (2)	5.3 (5.8)	2.3 (2.5)	38.8 (38.0)	13.7 (13.1)	41.9 (40.6)	2.2 (2.4)
$[\text{MnL}]_{0.35}\text{K}_{0.05}\text{Mn}_{0.80}\text{PS}_3(\text{H}_2\text{O})_{-1.0}$ (3)	33.1 (32.9)	1.2 (1.1)		16.7 (16.1)	49.7 (49.9)	4.5 (4.7)
$[\text{MnL}]_{0.25}\text{K}_{0.15}\text{Cd}_{0.80}\text{PS}_3(\text{H}_2\text{O})_{-0.5}$ (4)	5.9 (5.8)	2.4 (2.5)	37.1 (38.0)	13.8 (13.1)	40.8 (40.6)	2.3 (2.4)
Microwave assisted method						
Sample	Mn %	K %	Cd %	P %	S %	H ₂ O Δm %
$[\text{MnL}]_{0.20}\text{K}_{0.20}\text{Mn}_{0.80}\text{PS}_3(\text{H}_2\text{O})_{-1.0}$ (5)	28.9 (29.0)	4.0 (4.1)		16.7 (16.3)	50.4 (50.6)	6.0 (5.8)
$[\text{MnL}]_{0.15}\text{K}_{0.25}\text{Cd}_{0.80}\text{PS}_3(\text{H}_2\text{O})_{-0.5}$ (6)	3.4 (3.5)	4.0 (4.2)	37.8 (38.3)	13.0 (13.2)	41.3 (40.8)	2.7 (2.6)

* Anal. Found (calcd)

Intercalation of the cationic manganese(III) macrocyclic complex assisted by microwave irradiation

Identical reaction mixtures, as used for the conventional method, were irradiated for twelve minutes using microwave radiation of 800 Watts. After this period of time the methanol solutions start to boil, so the time of irradiation was limited by the boiling point of the solvent. $[\text{MnL}]_{0.20}\text{K}_{0.20}\text{Mn}_{0.80}\text{PS}_3(\text{H}_2\text{O})_{-1.0}$ (**5**) and $[\text{MnL}]_{0.15}\text{K}_{0.25}\text{Cd}_{0.80}\text{PS}_3(\text{H}_2\text{O})_{-0.5}$ (**6**) were obtained (Table 1), and purified by a similar procedure as described in the previous section. For both methods the non-existence of adsorbed macrocyclic complex salt was verified by the absence of the vibration band of the ionic nitrate anion in the infrared spectrum. For the composites obtained by the intercalation process assisted by microwave radiation (**5**) and (**6**), the infrared spectra showed the same pattern as the one for the composites obtained by stirring at room temperature.

Equipment

The microwave assisted syntheses were carried out with a microwave oven, LAVIS-1000 Multi-Quant of frequency 2459 MHz. Infrared spectra of the powder samples were recorded in the 4000–400 cm^{-1} range at room temperature on a Bruker-IFS 28 spectrometer, as KBr pellets. The powder X-ray diffraction analysis was carried out using a diffractometer with $\text{Cu}-K\alpha$, radiation, with an Imaging Plate Guinier Camara G 670, in the $5^\circ < 2\theta < 80^\circ$ range. The samples were dispersed on polyethylene using a mixture of vaseline and ethanol. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDXS) analyses were done using a Joel Jem 6400 equipment. The analysis of Mn was also done with a ICP-OES Vista RL (Varian) analyzer, while the analyses of C, H and N were done with a Leco Micro-CHNS-932 Analyzer. Thermogravimetric analyses were done with an equipment model Q50 TA Instruments. The samples were heated in a nitrogen atmosphere, at a rate of 10 ° per min in the range between 20 to 700 °C. The stoichiometry of the obtained composites was calculated from the experimental analyses given by the above mentioned techniques.

The magnetic properties were recorded with a SQUID-magnetometer (MPMS XL7, Quantum Design); for the measurement a polycrystalline sample was filled into a precalibrated quartz tube. Susceptibility data were taken at 0.4, 1.0 and 10 kOe in a temperature range of 1.8 to 400 K. All the magnetic data were corrected by temperature independent paramagnetism (TIP).

RESULTS AND DISCUSSION

Synthesis of the Mononuclear Macrocyclic Manganese(III) Complex

The synthesis of the manganese macrocyclic complex was achieved by the template reaction of 1,2-diaminebenzene and 2-hydroxy-5-methyl-1,3-benzenedicarbaldehyde in the presence of manganese(II) nitrate. The isolated compound analyzed well for $[\text{MnL}(\text{H}_2\text{O})_2][\text{NO}_3] \cdot \text{H}_2\text{O}$, where LH_2 is the corresponding macrocyclic Schiff base. The aerial oxidation during the reaction of the manganese(II) salt accounts for the final oxidation state of the metal center in the obtained complex. A similar oxidation process for manganese(II) has been reported by several authors in the formation of Mn^{III} Schiff base complexes²⁹⁻³³. For example, the crystal structure of a mononuclear complex $[\text{Mn}^{\text{III}}\text{L}'\text{Cl}(\text{H}_2\text{O})_4]$, isolated from the aerial oxidation reaction of MnCl_2 in the presence of $\text{L}'\text{H}_2$ (macrocyclic ligand obtained by the condensation reaction of 2-hydroxy-5-methyl-1,3-benzenedicarbaldehyde and 1,2-diaminecyclohexane) was reported³³.

Syntheses of the Composites

The intercalation of the manganese(III) macrocyclic complex was done in two steps. First the potassium precursor was obtained by the cationic transfer process. Then, using the cationic exchange process^{11,12,34}, the monovalent potassium cations were replaced by the new monocationic manganese(III) macrocyclic complex guest. This last process is actually not a true intercalation reaction, but rather an ion exchange reaction between the interlamellar potassium and the complex ions. Since the host-guest interactions

are electrostatic in nature, the stability of the intercalated species depends on the coulombic forces between the negatively charged polyanions, $(M_{1-x}PS_3)^{2x-}$, and the positive potassium and/or manganese(III) mononuclear macrocyclic complex $[MnL]^+$. The increase of the interlamellar distance from 9.4 Å in the potassium precursor to 10 Å in the final composites confirmed the existence of a cationic exchange process (Figure 1(a) and 1(b)).

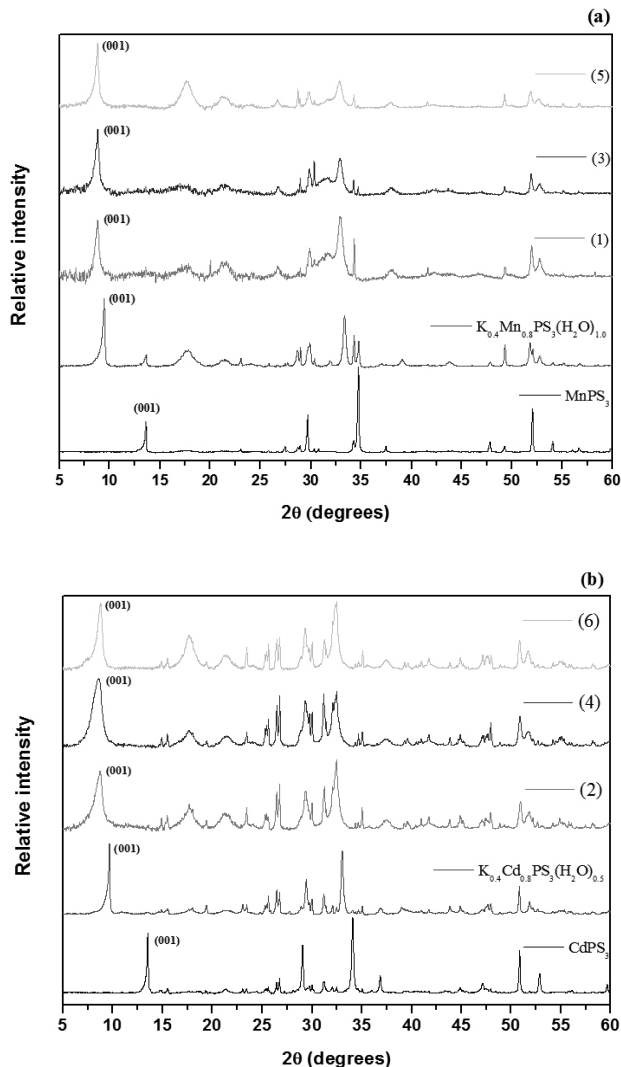


Figure 1.- (a) Powder diffractograms for MnPS₃, potassium precursor, and composites (1), (3), and (5). (b) Powder diffractograms for CdPS₃, potassium precursor, and composites (2), (4), and (6).

During the exchange process it is necessary to assume that the octahedral manganese(III) complex loses the axial ligand molecules, and enters as a planar species into the interlamellar space. This conclusion is drawn out from powder diffraction data, since all the composites show the same interlamellar distance of ca. 10 Å, which can only permit a parallel position of a square planar complex with an aromatic ring, as would be the case of the macrocyclic manganese(III) complex. The final environment of the manganese(III) cations can be inferred as distorted octahedral, due to the interactions with the protruding sulphur atoms of the layers.

The time dependence of the cationic exchange process was tested by obtaining the composites through reactions of two and four weeks. In the case of the cadmium thiophosphate phase a composite with a unique stoichiometric formulae was obtained $[MnL]_{0.25}K_{0.15}Cd_{0.80}PS_3(H_2O)_{-0.5}$ for (2) and (4), independently of the time the conventional reaction was carried out. However, the manganese thiophosphate phase permitted to isolate two species, $[MnL]_{0.25}K_{0.15}Mn_{0.80}PS_3(H_2O)_{-1.0}$ (1) (two weeks of reaction) and $[MnL]_{0.35}K_{0.05}Mn_{0.80}$

$PS_3(H_2O)_{-1.0}$ (3) (four weeks of reaction). Thus, the Mn^{III}/Mn^{II} composite (3) shows an almost complete exchange of potassium ions by the monocationic macrocyclic complex.

The manganese thiophosphate phase is known to be more ionic in nature than the cadmium one^{35,36}. Besides, the K⁺ ions have been shown to be weakly interacting with the sulphur atoms of the (P₂S₆)⁴⁻ clusters in the interlamellar space in the MnPS₃ phase, as inferred from XPS spectra³⁷. With respect to the K⁺ ions that intercalate into the interlamellar space in the CdPS₃ phase, some of these tend to migrate into the layers occupying the vacancies left during the intercalation process. This is concluded by comparing the solid state ³¹P-NMR spectrum of a freshly intercalated CdPS₃ phase, with that of an aged one³⁸. The appearance of a new maximum in the spectrum with the aging effect is associated with the migration process of K⁺ into the vacancies of the K_{0.4}Cd_{0.8}PS₃ intercalate. This decreases the existence of negatively charged zones in the lamellae. Therefore, two types of potassium ions can be identified, presenting different exchange abilities, the interlamellar and intralamellar ones. The above mentioned facts will affect the exchange process in the cadmium phase of K⁺ with the cationic macrocyclic guest, thus explaining the observation that the exchange process is more favorable for the manganese phase than that for the cadmium one.

The microwave assisted exchange process gave a different stoichiometry for the obtained composites, depending on the phase used. For the same period of twelve minutes of irradiation, the composition in macrocyclic complex is lower for the cadmium thiophosphate composite, $[MnL]_{0.15}K_{0.25}Cd_{0.80}PS_3(H_2O)_{-0.5}$ (6), as compared to $[MnL]_{0.20}K_{0.20}Mn_{0.80}PS_3(H_2O)_{-1.0}$ (5).

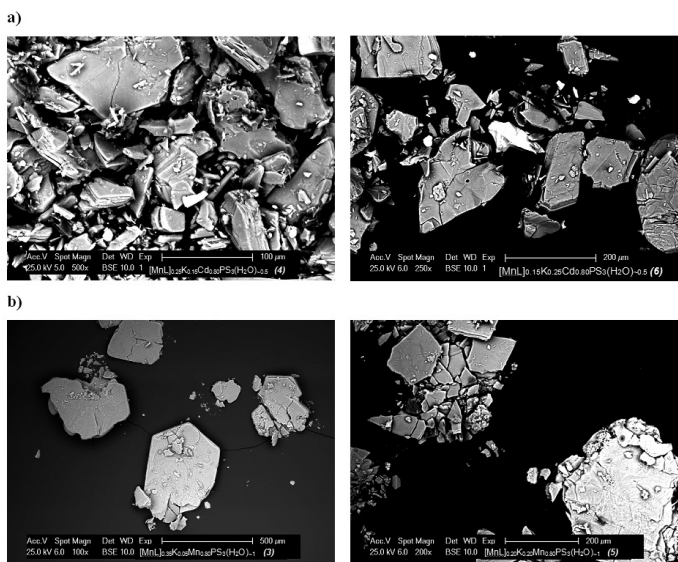


Figure 2.- SEM images of the composites corresponding to Mn^{II} and Cd^{II} phases. (a) $[MnL]_{0.25}K_{0.15}Cd_{0.80}PS_3(H_2O)_{-0.5}$ (4) and $[MnL]_{0.15}K_{0.25}Cd_{0.80}PS_3(H_2O)_{-0.5}$ (6); (b) $[MnL]_{0.35}K_{0.05}Mn_{0.80}PS_3(H_2O)_{-1}$ (3) and $[MnL]_{0.20}K_{0.20}Mn_{0.80}PS_3(H_2O)_{-1}$ (5).

From a synthetic point of view, it is important to emphasize that even though the microwave assisted process permits a faster exchange, the conventional synthetic method gives a more complete exchange of the interlamellar potassium ions by the macrocyclic Mn^{III} complex. Furthermore, it is important to remark that the products obtained by microwave assisted synthesis, (5) and (6), retain the lamellar structure which is observed for the composites prepared by the conventional synthesis, (1) to (4). Figure 2a and 2b show the comparison of the morphological characteristics of the composites.

Magnetic Properties

The magnetic behavior of the composites was analyzed taking into account the magnetic properties of the corresponding precursor for the two phases, K_{0.40}Cd_{0.80}PS₃(H₂O)_{-0.5} and K_{0.40}Mn_{0.80}PS₃(H₂O)_{-1.0}. While the cadmium precursor is diamagnetic, the manganese one presents both antiferromagnetism and spontaneous magnetization at low temperatures. Therefore, for the composites derived from the cadmium precursor the observed magnetic behavior is due to the Mn^{III} intercalated complex, while for the composites obtained with the manganese precursor the observed magnetic behavior corresponds to both the

Mn^{III} intercalated complex and the Mn^{II} present in the lamellar structure.

Figure 3 presents the magnetic behavior of $[\text{MnL}]_{0.25}\text{K}_{0.15}\text{Cd}_{0.80}\text{PS}_3(\text{H}_2\text{O})_{-0.5}$ (**2**) for different magnetic fields. The χT product results to be temperature independent till ca. 100 K, while at low temperatures a decrease in the values of the χT product is observed. This behavior is typical for a magnetically dilute high spin Mn^{III} ion, whose magnetic moment decreases at low temperature due to the orbital coupling constant. The mixing of the 3E_g ground state with the higher lying ${}^5T_{2g}$ state generates the orbital component that is reflected in the magnetic behavior of the manganese(III) composite³⁹. Composites $[\text{MnL}]_{0.25}\text{K}_{0.15}\text{Cd}_{0.80}\text{PS}_3(\text{H}_2\text{O})_{-0.5}$ (**4**), and $[\text{MnL}]_{0.15}\text{K}_{0.25}\text{Cd}_{0.80}\text{PS}_3(\text{H}_2\text{O})_{-0.5}$ (**6**), exhibit similar behavior.

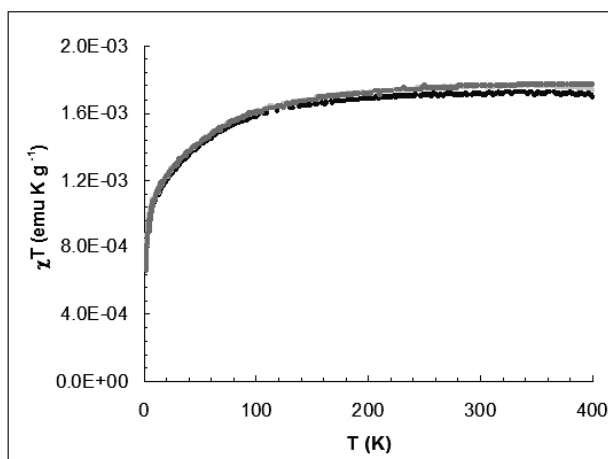


Figure 3.- Temperature dependence of the magnetic behavior for $[\text{MnL}]_{0.25}\text{K}_{0.15}\text{Cd}_{0.80}\text{PS}_3(\text{H}_2\text{O})_{0.5}$ (**2**). Blue: 400 Oe; green: 1 kOe; grey: 10 kOe.

Contrary to the cadmium precursor, $\text{K}_{0.40}\text{Cd}_{0.80}\text{PS}_3(\text{H}_2\text{O})_{-0.5}$, the layers of the manganese precursor $\text{K}_{0.40}\text{Mn}_{0.80}\text{PS}_3(\text{H}_2\text{O})_{-1.0}$ are formed by paramagnetic Mn^{II} ions. Therefore, the Mn^{III} composites of the Mn^{II} phase will present magnetic phenomena due to the presence of two different spin carriers, the high spin manganese(III) mononuclear macrocyclic complex and the high spin manganese(II) ions present in the layers of the phases. These latter ions in the MnPS_3 phase are known to show intralamellar antiferromagnetic interactions. This magnetic behavior is present in a lesser degree in the potassium precursor, due to the existence of vacancies generated by the removal of some of the manganese(II) ions during the intercalation process²⁰. Besides, these vacancies are responsible for a spontaneous magnetization at low temperatures for the potassium precursor $\text{K}_{0.40}\text{Mn}_{0.80}\text{PS}_3(\text{H}_2\text{O})_{-1.0}$. Joy and Vasudevan²⁰ have explained the observed increase in χT below 50 K for the potassium precursor proposing two models, i) the first assuming that the canting angle is different for the different sublattices, so no complete cancellation of the moments occurs; ii) the second being related to the loss of the center of symmetry, due to the removal of part of the manganese(II) ions. This implies that the structure can support a canted antiferromagnetic state due to the Dzyaloshinsky-Moriya antisymmetric exchange.

Figure 4 presents the temperature dependence of the magnetic behavior of $[\text{MnL}]_{0.35}\text{K}_{0.05}\text{Mn}_{0.80}\text{PS}_3(\text{H}_2\text{O})_{-1.0}$ (**3**) for different magnetic fields. Composites $[\text{MnL}]_{0.25}\text{K}_{0.15}\text{Mn}_{0.80}\text{PS}_3(\text{H}_2\text{O})_{-1.0}$ (**1**) and $[\text{MnL}]_{0.20}\text{K}_{0.20}\text{Mn}_{0.80}\text{PS}_3(\text{H}_2\text{O})_{-1.0}$ (**5**) have a similar temperature dependence in the 400 to 60 K range. A decrease in the value of χT as the temperature is lowered till 60 K is observed for (**1**), (**3**) and (**5**). When the magnetic behavior of (**1**) and (**3**) is compared with that of the composite obtained by microwave assisted intercalation, (**5**), it is possible to state that the spontaneous magnetization observed in the potassium precursor is still present in this latter composite as a remnant magnetization. A similar phenomenon was observed for Zn^{II}/Mn^{II} composites as reported previously⁴⁰. Nevertheless, the observed spontaneous magnetization at low temperatures is field dependent, being suppressed at high field (Figure 5a). Composites (**1**) and (**3**) as mentioned above, only present the normal decrease in χT corresponding to the manganese(III) cations, and the antiferromagnetic interactions of the lamellar manganese(II) structure (Figure 5b).

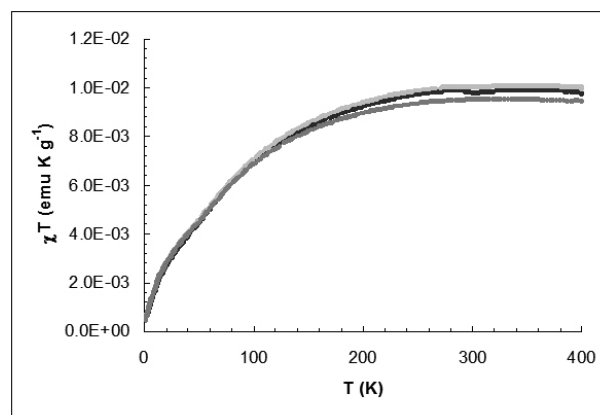


Figure 4.- Temperature dependence of the magnetic behavior for $[\text{MnL}]_{0.35}\text{K}_{0.05}\text{Mn}_{0.80}\text{PS}_3(\text{H}_2\text{O})_{-1.0}$ (**3**) for different magnetic fields. Blue: 400 Oe; light grey: 1 kOe; red: 10 kOe.

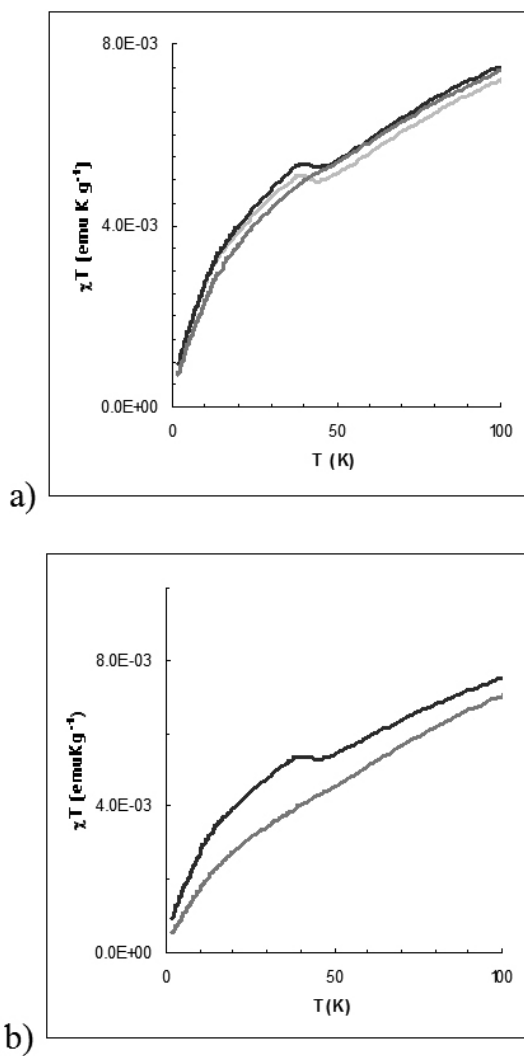


Figure 5. a) Dependence of the magnetic behavior for $[\text{MnL}]_{0.2}\text{K}_{0.2}\text{Mn}_{0.8}\text{PS}_3(\text{H}_2\text{O})_{-1.0}$ (**5**) at low temperatures at: Blue: 400 Oe, Green: 1 kOe, Red: 10 kOe. b) Dependence of the magnetic behavior at low temperatures at 1kOe. Red: $[\text{MnL}]_{0.35}\text{K}_{0.05}\text{Mn}_{0.80}\text{PS}_3(\text{H}_2\text{O})_{-1.0}$ (**3**); black: $[\text{MnL}]_{0.2}\text{K}_{0.2}\text{Mn}_{0.8}\text{PS}_3(\text{H}_2\text{O})_{-1.0}$ (**5**)

The obtained composites (**1**) and (**3**), and (**5**) must have the same amount of vacancies as the potassium precursor $K_{0.40}Mn_{0.80}PS_3(H_2O)_{-1.0}$. This is due to the fact that the final composites were obtained by cationic exchange, and the vacancies are previously generated during the formation of the potassium precursor. Assuming that this is valid for both the conventional and microwave assisted intercalation methods, it becomes necessary to conclude that composites (**1**) and (**3**) would need to have their different sublattices modified, with such canting angles that would permit the cancellation of the moments, and would lead to the absence of the spontaneous magnetization. Therefore, the long periods of stirring of two and four weeks, necessary to obtain composites (**1**) and (**3**) give rise to the thermodynamic products, which present an antiparallel ordering of the dipoles of the sublattices, while composite (**5**) obtained by the microwave assisted procedure is isolated before the magnetic sublattices reorder.

It is important to remark that all the studied Mn^{III}/Mn^{II} composites show a bulk antiferromagnetic behavior, with differences in the low temperature range, depending on the used synthetic method to obtain the composite.

CONCLUSIONS

The microwave irradiation induces the exchange process at very short times. This exchange leads to composites which also maintain the lamellar morphology, but with a composition in the manganese(III) complex slightly lower than the product obtained by the conventional method.

The magnetic behavior of the composite $[MnL]_{0.20}K_{0.20}Mn_{0.80}PS_3(H_2O)_{-1.0}$ (**5**) obtained by microwave assisted method presents a remnant spontaneous magnetization at low temperature, magnetization which is present in the potassium precursor. In contrast, this magnetization is completely absent in the composites obtained by the conventional exchange process $[MnL]_{0.25}K_{0.15}Mn_{0.80}PS_3(H_2O)_{-1.0}$ (**1**) and $[MnL]_{0.35}K_{0.05}Mn_{0.80}PS_3(H_2O)_{-1.0}$ (**3**). These facts demonstrate the importance of the experimental conditions on the magnetic properties of the obtained composites.

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