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of alternate positions, one involving Cl(1) and Cl(2) and the other involving Cl(3) and Cl(4), were allowed to refine with an occupancy of *k* assigned to the first set and 1 − *k* assigned to the second set. The chloride ligands were given equivalent isotropic *U* values of 0.04 Å^2. Refinement yielded *k* = 0.548 (7). Since the disorder in atoms Cl(1), Cl(2), Cl(3), and Cl(4) corresponded to approximately 50% occupancy for these atoms, the possibility that the noncentrosymmetric space group *P*1 could resolve this disorder was investigated. However, a difference map computed in *P*1 clearly revealed the presence of all four chlorines in both of the triiridium complexes. Thus, we conclude that the disorder results from a distribution of the two forms of the molecule in a lattice site that does not discriminate between these two forms. Final cycles of refinement were made with anisotropic thermal parameters for iridium, arsenic, and phosphorus and isotropic thermal parameters for all remaining atoms. Hydrogen atoms were refined with use of a riding model in which an idealized C–H vector of 0.96-Å length is recalculated with each cycle of refinement. Isotropic hydrogen thermal parameters were fixed at 1.2 times the equivalent isotropic thermal parameter of the bonded carbon. Scattering factors and corrections for anomalous dispersion were taken from a standard source.[22] An absorption correction (XABS) was applied.[23] The atoms of four dichloromethane molecules were assigned equivalent isotropic *U* values of 0.07 Å^2 and were allowed to refine with variable occupancy. The final occupancies were 0.643 (12) for Cl(5)···Cl(6), 0.654 (12) for Cl(7)···Cl(8), 0.425 (13) for Cl(9)···Cl(10), and 0.373 (12) for Cl(11)···Cl(12). Carbon atoms for the last two dichloromethanes were not located due to the low occupancy and disorder. Two low-angle reflections suffering from extinction were removed from the data set for the final cycles of refinement. A conventional *R* factor of 0.083 was obtained. The final difference map showed some residual electron density in the vicinity of the dichloromethane molecules, but otherwise no significant features were present.

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Registry No. **2**, 84774-74-3; **3**, 100700-65-0; **4**, 86372-61-4; $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-CO})_2(CO)_2(\mu\text{-Cl})Cl][BPh_4]$, 100700-67-2; $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-CO})_2(CO)_2(\mu\text{-Br})Br][BPh_4]$, 100700-69-4; $[Rh_3(\mu\text{-dpmp})_2(\mu\text{-CO})_2(CO)_2(\mu\text{-I})I][BPh_4]$, 100700-71-8; $[Rh_3(\mu\text{-dpma})_2(\mu\text{-CO})_2(CO)_2(\mu\text{-I})I][BPh_4]$, 100700-73-0; $[Ir_3(\mu\text{-dpma})_2(\mu\text{-CO})_2(CO)_2(\mu\text{-Cl})Cl][BPh_4]$, 100700-76-3; $[Ir_3(\mu\text{-dpma})_2(\mu\text{-CO})_2(CO)_2(\mu\text{-Br})Br][BPh_4]$, 100700-78-5; $[Ir_3(\mu\text{-dpma})_2(\mu\text{-CO})_2(CO)_2(\mu\text{-I})I][BPh_4]$, 100700-80-9; $Ir(CO)_2Cl(p\text{-tld})$, 14243-22-2; $[Rh_3(\mu\text{-dpma})_2(\mu\text{-CO})(CO)_2(\mu\text{-I})_2][BPh_4]$, 100700-82-1.

Supplementary Material Available: Listings of hydrogen atom positions, bond lengths, bond angles, anisotropic thermal parameters, and structure factor amplitudes (55 pages). Ordering information is given on any current masthead page.

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[22] "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4.

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Coordination Chemistry of the Lamellar MPS_3 Materials: Metal–Ligand Cleavage as the Source of an Unusual "Cation-Transfer" Intercalation Process

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Several MPS_3 lamellar materials exhibit a very unusual intercalation chemistry based on a "cation-transfer" process between the solid and a solvent. This contrasts with the electron-transfer process that governs the intercalation chemistry of the layered dichalcogenides MX_2. Although the MPS_3 layers are made up of infinite arrays of $P_2S_6^{4-}$ units coordinated to the M^{2+} cations, the metal–ligand (M–S) bonding still exhibits enough lability to allow the M^{2+} cations to jump, under very mild conditions, from intra- toward interlamellar sites (or the opposite) and even to be removed from the material, provided a suitable cation is available to intercalate the lattice and maintain electrical neutrality. Depending on the metal, the solvent, and the guest species, the reaction may take place spontaneously or require an assist, usually by complexing the leaving M^{2+} cations (EDTA). Small inserted ions (Na^+, K^+, ...) are strongly solvated and mobile, and they can in turn be exchanged. To rationalize this behavior, we suggest that the intercalation chemistry of the MPS_3 involves a chemical transformation of the whole of the material, rather than a diffusional process of the guest species within the host lattice. The MPS_3 layered materials are considered as polynuclear complexes that can undergo heterogeneous equilibrium with their constitutive species M^{2+} and $P_2S_6^{4-}$ and other species present in solution. In support of this mechanism, MPS_3 materials have been successfully prepared by mixing aqueous solutions of $Na_4P_2S_6$ and transition-metal salts. Some implications of this mechanism are discussed.

I. Introduction

Transition-metal hexathiohypodiphosphates MPS_3, where M stands for a metal in the II oxidation state, form a class of lamellar semiconductors first described by Klingen.[2] The structure of these materials (Figure 1) is closely related to that of the well-known transition-metal dichalcogenides MX_2 and for this reason, the MPS_3 compounds have been merely considered in the beginning as an exotic appendix of this wide class. Indeed, the early chemistry carried out in the series supported this analogy: as well as the MX_2 compounds, several MPS_3 compounds have been shown to react with electron-donor species (butyllithium, cobaltocene) to form intercalation compounds and to behave as good cathode materials in secondary lithium batteries.[3-5]

A few years ago, one of us discovered that $MnPS_3$ could spontaneously react at room temperature with aqueous solutions of certain salts, such as KCl and NH_4Cl and salts of small organometallic cations such as cobaltocenium;[6] this reaction led to compounds of the type $Mn_{1-x}PS_3[G]_{2x}(H_2O)_y$, where the positive charge of the guest cation G^+ was counterbalanced by the removal of an equivalent amount of intralayer Mn^{2+} cations. The host structure was observed to remain solid throughout the reaction process, and therefore such an exchange process appeared rather unusual, as no similar reaction had been described in any other layered system. Furthermore, small inserted cations such as K^+ or NH_4^+ were found to be strongly solvated and highly mobile,

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[1] LURE: CNRS laboratory for synchrotron radiation, associated with the Université de Paris Sud.

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Table I. Summary of General Conditions Allowing Intercalation by Cation Transfer in the MPS_3 Phases

$MnPS_3$	$MnPS_3 + 2xK^+Cl^- \xrightarrow[20\ °C,\ 1h]{water} Mn_{1-x}K_{2x}PS_3 \cdot nH_2O + xMn^{2+}{}_{aq} + 2xCl^-{}_{aq}$	
	$MnPS_3 + 2xCoCp_2{}^+I^- \xrightarrow[20\ °C,\ 1\ day]{water} Mn_{1-x}(CoCp_2)_{2x}PS_3 \cdot nH_2O + xMn^{2+}{}_{aq} + 2xI^-{}_{aq}$	
$CdPS_3$	$CdPS_3 + 2xCoCp_2{}^+I^- \xrightarrow[60°C,\ 1\ day]{ethanol} Cd_{1-x}(CoCp_2)_{2x}PS_3 \cdot n(solv) + xCd^{2+} + 2xI^-$	$Cd^{2+} + excess\ I^- \rightleftarrows CdI_4{}^{2-}$
	$CdPS_3 + 0.5KCl \xrightarrow[20\ °C,\ 2\ days]{water + EDTA} Cd_{0.75}K_{0.5}PS_3 \cdot H_2O + 0.25Cd^{2+}\ 0.5Cl^-$	$Cd^{2+} \rightleftarrows [CdEDTA]$
$ZnPS_3$	reaction in water + EDTA leading to amorphous powders impossible to characterize	
	$ZnPS_3 + 2xCoCp_2{}^+I^- \xrightarrow[60°C,\ 1\ day]{ethanol} Zn_{1-x}(CoCp_2)_{2x}PS_3 \cdot n(solv) + xZn^{2+} + 2xI^-$	$Zn^{2+} + excess\ I^- \rightleftarrows ZnI_4{}^{2-}$
$FePS_3$	no intercalation in water of C_2H_5OH up to 100 °C	
	$FePS_3 + 2xCoCp_2{}^+I^- \xrightarrow{water + EDTA} Fe_{1-x}(CoCp_2)_{2x}PS_3 \cdot nH_2O + xFe^{2+} + 2x2I^-$	$Fe^{2+} \rightleftarrows [FeEDTA]$
$NiPS_3$	no exchange	

Table II. Data for Representative Intercalates Obtained by Cation Transfer[a]

intercalate formula	interlayer expansion, Å	anal. data, % Cd	Fe	P	S	H	C	Co	other
$Cd_{0.84}PS_3(CoCp_2)_{0.32}(solv)_{\sim 0.3}$[b]	5.32	33.0		10.9	33.7	1.4	13.6	6.5	
$Cd_{0.75}PS_3K_{0.5}(H_2O)_{1.0}$ (I)	2.93	33.9		12.2	39.0	0.8			K, 7.8
$Cd_{0.5}PS_3Na_{1.0}(H_2O)_{\sim 4.0}$	5.58	20.5		11.4	34.8	2.6			Na, 8.5
$Cd_{0.75}PS_3Sr_{0.25}(H_2O)_{\sim 3.0}$	5.42	29.5		10.9	33.6	2.1			Sr, 7.2
$Fe_{0.83}PS_3(CoCp_2)_{0.34}(H_2O)_{\sim 0.3}$ (II)	5.32		19.3	12.65	39.6	1.6	16.7	8.3	
$Fe_{0.85}PS_3(Et_4N)_{0.3}(H_2O)_{\sim 0.5}$	4.78		21.6	14.1	43.5	2.9	12.8		N, 2.0

[a] The amount of solvent retained in the material has been determined by thermogravimetric analyses. The figures given are only approximate, as this amount depends on the temperature and the hygrometry. [b] Although this intercalate was obtained in 96% ethanol, the solvent retained seems to be a mixture of water and ethanol.

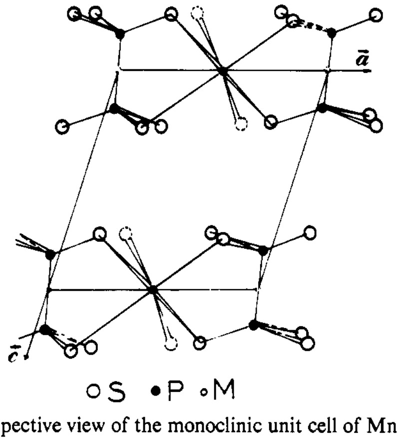

Figure 1. Perspective view of the monoclinic unit cell of $MnPS_3$, showing the coordination of the metal to the $P_2S_6{}^{4-}$ ligands.

Table III. Indexation of $Cd_{0.75}PS_3K_{0.5}(H_2O)$ at Room Temperature

Cell Dimensions

$a = 6.254$ Å $c = 9.632$ Å

$b = 10.743$ Å $\beta = 107.36°$

spacing, Å obsd	calcd	*hkl*	intens
9.20[a]	9.19	001	m
4.598	4.596	002	w
3.077	3.072	130	s
3.066	3.064	003	w
3.057	3.057	$13\bar{1}$	w
2.698[b]	2.686	040	m
2.614	2.618	201	w
1.790	1.790	060	s
1.758	1.757	061	m
1.542	1.546	063	m
1.492	1.492	400	m

[a] It should be noted that the interlamellar distance depends on temperature and hygrometry for this particular compound. [b] This reflection is somewhat broad, possibly due to the overlap of two lines.

and they could in turn be exchanged against much bigger species such as large organometallic cations unable to be inserted in pure $MnPS_3$ directly.[7] Therefore, a very large number of species can be inserted in $MnPS_3$, and it was interesting to examine whether such an unusual intercalation process was a general property of the whole series. MPS_3 compounds with M = Cd, Zn, where the M–S bond is fairly ionic, were thought to be good candidates, while cathode materials such as $FePS_3$ or $NiPS_3$ seemed a priori to be unfavorable cases because of more covalent M–S bonds. Besides, the easy removal of intralamellar M^{2+} ions from the solid MPS_3 has not yet been explained, and therefore our goal was also to find support for a reasonable mechanism.

II. Experimental Section

Pure $MnPS_3$ (M = Mn, Cd, Zn, Fe, Ni) compounds were synthesized by heating stoichiometric mixtures of the 99.9% pure elements in sealed evacuated quartz ampules, under the same conditions as those described in ref 2. After grinding and reheating, homogeneous materials were obtained. Intercalation reactions were performed simply by contact of the powdered MPS_3 with solutions of the desired cation. In a typical experiment, 200 mg of MPS_3 was stirred with 20 mL of a ~5 M aqueous solution of the appropriate salt. When a complexing agent was required, about 10 mL of 0.1 M EDTA in a 1 M $K_2CO_3/KHCO_3$ buffer was added. Other particular conditions are listed in Table I. Reactions were carried out under inert atmosphere in the case of $FePS_3$ to avoid oxidation of the removed Fe^{2+} cations. Full insertion was ascertained by X-ray powder diffraction. The obtained materials are quite well ordered, as they exhibit sharp *hkl* reflections. Indexation of a representative intercalate is given in Table III. Samples sedimented on a holder show preferential orientation, which results in an enhanced intensity of the 00*l* reflections. This fact allows a straightforward derivation of the interlamellar distance of all the materials described in this paper. Infrared spectra were obtained in the range 4000–200 cm^{-1} by using the KBr disk technique. Total elemental analyses were obtained for all compounds described in the paper. Magnetic data were recorded by the Faraday method using a magnetometer previously described.[8] X-ray absorption

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spectra at the iron K edge were run at LURE, the French synchrotron radiation laboratory, using the X-ray absorption spectrometer of the DCI storage ring, already described in ref 9. Raman spectra were obtained with a Coderg T800 instrument equipped with an ionized argon laser (5145 Å) between 525 and 25 cm^{-1}. EPR spectra were recorded at room temperature with a Bruker ER 200D spectrometer operating at X-band frequency. The $Na_4P_2S_6 \cdot xH_2O$ salt used in this work was prepared by treating an aqueous solution of Na_2S by PCl_3, as described in ref 10.

III. Results

III.1. Intercalation in $CdPS_3$. In contrast to $MnPS_3$ no reaction was observed upon treatment of $CdPS_3$ with an aqueous solution of KCl or cobaltocenium iodide ($CoCp_2I$). However, treatment of $CdPS_3$ with an ethanolic solution of $CoCp_2I$ (1 day, 60 °C) led to a yellow intercalate $Cd_{1-x}PS_3(CoCp_2)_{2x}(\text{solvent})_n$, where $x = 0.16$ and $n \sim 0.3$ (Tables I and II). The presence of the guest species in its cationic form was ascertained by IR and UV–visible spectroscopy. Interestingly, yellow needles were observed to crystallize from the mother liquor, in the above experiment. These needles could be identified as the cobaltocenium salt of the CdI_4^{2-} complex $(CoCp_2)_2CdI_4$. This led to the idea that complexation of the leaving Cd^{2+} was an important factor for a successfull intercalation. In an attempt to achieve intercalation in an aqueous medium, $CdPS_3$ was therefore treated with a concentrated ($\sim$5 M) aqueous solution of KCl in the presence of EDTA at pH $\sim$10 (for instance, the $KHCO_3/K_2CO_3$ buffer can be conveniently used). Intercalation of the K^+ ions occurred within 1–2 days at room temperature. According to the elemental analysis, the white material obtained can be formulated as $Cd_{1-x}PS_3K_{2x}(H_2O)_{\sim 1.0}$ (I), where $x \simeq 0.25 \pm 0.01$. The interlamellar distance depends slightly on the temperature and hygrometry, and it has been found in the range 9.2–9.45 Å. This range of values shows that the K^+ ions are loosely solvated by a monolayer of water molecules. Heating I to 80 °C gives an anhydrous material with a much smaller interlamellar distance (8.0 Å), but water is reversibly retaken upon cooling. The solvated K^+ ions in I are highly mobile and they can be readily exchanged, in water or in methanol, with a number of other cations, including alkali-metal and alkaline-earth-metal cations (Table II) or transition-metal compounds such as $Ru(bpy)_3^{2+}$ or even larger organometallic cationic compounds. All compounds are air-stable insulators with optical characteristics suitable for IR and UV–visible studies. Infrared spectra show that the $\nu(PS_3)$ asymmetric stretching band, which occurs at 570 cm^{-1} in pure $CdPS_3$, is split into two components at 555 and 605 cm^{-1} in most of its intercalates. The same feature had already been noted for $MnPS_3$ intercalates.[11] The amount of cadmium vacancies in the layers may exceed 0.25 if a cation smaller than potassium is inserted. Thus, while treatment of I with an aqueous NaCl solution simply results in the K → Na replacement, addition of EDTA at pH $\sim$9–10 causes further removal of cadmium. The compound $Cd_{0.5}PS_3Na_{1.0}(H_2O)_{\sim 4}$ is thus obtained in which the sodium ions are solvated by a bilayer of water molecules (interlamellar distance 12.1 Å).

III.2. Deintercalation of $Cd_{1-x}PS_3K_x(H_2O)$. A Mild Route to Heterometallic $Cd_{1-x}M_xPS_3$ Layers (M = Ni, Mn). Treating I with an aqueous $\sim$1 M solution of $NiCl_2$ results in an interesting reaction, which proceeds in two steps. The K^+ ions in I are first replaced by $Ni(H_2O)_6^{2+}$ cations, whereupon the basal spacing of the material increases from $\sim$9.45 to $\sim$16.0 Å. The powder is then decanted, washed with water, and dried. A brown material $Cd_{0.75}Ni_{0.25}PS_3$ is obtained, which has nearly the same interlamellar distance ($\sim$6.45 Å) as pure $CdPS_3$ (6.52 Å) and which no longer contains any solvent. Besides, the $\nu(PS_3)$ absorption band in the IR spectrum of $Cd_{0.75}Ni_{0.25}PS_3$ is no longer split. A strong single band is observed at 570 cm^{-1}, as in pure $CdPS_3$ or $NiPS_3$. These experimental facts are identical with those observed when $Mn_{1-x}PS_3K_{2x}(H_2O)$ is treated with aqueous $NiCl_2$. In the latter case, an EXAFS study[12] has unambiguously demonstrated that the resultant $Mn_{1-x}Ni_xPS_3$ contains anhydrous intralayer Ni^{2+} cations. The nickel ions in $Cd_{0.75}Ni_{0.25}PS_3$ are therefore very likely to occupy also *intra*lamellar sites. Detailed studies of a structural study of this compound, as well as of its optical and magnetic properties, will be published later by our group.[13]

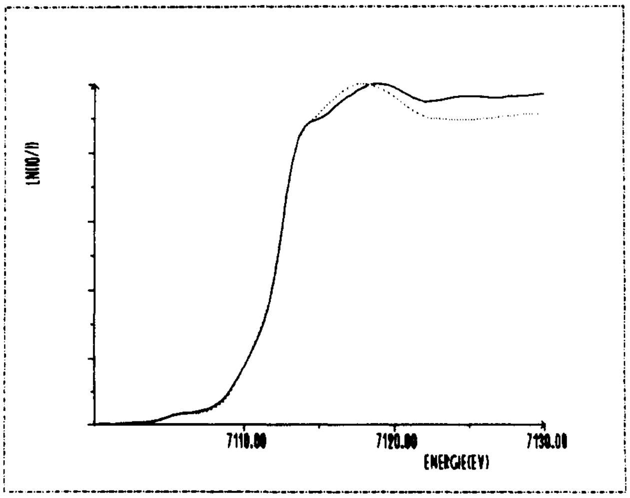

Figure 2. X-ray absorption at the Fe-K edge of pure $FePS_3$ (solid line) and $Fe_{0.83}PS_3(CoCp_2)_{0.34}(H_2O)_{0.3}$ (dotted line).

III.3. Cation Transfer in $ZnPS_3$. As described above for $CdPS_3$, $ZnPS_3$ does not react with an aqueous solution of KCl. Addition of EDTA at pH $\simeq$ 10 results in the removal of zinc from the material. However, whereas $CdPS_3$ yields a well-crystallized solid compound, $ZnPS_3$ only leads to quasi-amorphous sludges, which have not been studied in detail. Nevertheless, it is worthwhile to recall here that reaction of $ZnPS_3$ with $CoCp_2I$ in EtOH at $\sim$60 °C has been previously shown by one of our group[14] to yield $Zn_{1-x}PS_3(CoCp_2)_{2x}(\text{solv})_y$. Similarly, $ZnPS_3$ reacts with ethanolic solutions of Et_4NI and $CrPh_2I$. Therefore, $ZnPS_3$ clearly undergoes cation-transfer processes, but aqueous media cause further reactions, probably due to hydrolysis of the Zn(II) species.

III.4. Cation Transfer in $FePS_3$. In contrast to the slightly colored, fairly ionic MPS_3 (M = Mn, Zn, Cd) compounds, $FePS_3$ is an optically opaque semiconductor (optical gap around 1.6 eV), which acts as a good cathodic material in lithium batteries.[4] This property corresponds to more covalent metal–sulfur bonds,[15] and therefore $FePS_3$ did not appear a priori to be a good candidate for an intercalation process involving cation removal from the slabs. Indeed, treatment of $FePS_3$ with an aqueous or ethanolic solution of $CoCp_2I$ did not give any reaction, even after refluxing for 1 day at the boiling temperature of the solvent.

However, treatment of $FePS_3$ with an aqueous solution of $CoCp_2I$ at 20 °C in the presence of EDTA at pH $\sim$10 results in iron removal from the material and subsequent insertion of cobaltocenium cations. Analyses of the compound give a formulation $Fe_{1-x}PS_3(CoCp_2)_{2x}(H_2O)_y$ (II). Other cationic species such as Et_4N^+ and $CrBz_2^+$ have been successfully inserted in the same manner, and some data on these new materials are gathered in Table II. Infrared spectra of these intercalates also show that the $\nu(PS_3)$ band is split into two components at 605 and 555 cm^{-1}. Hydrated Na^+ or K^+ ions could not be intercalated into $FePS_3$, but no explanation can yet be given for this fact.

It is worthwhile noting that misleading analytical data may be obtained. For instance, $FePS_3$ is able to take up $CoCp_2^+$ cations from an aqueous solution of cobaltocenium hydroxide even in the absence of EDTA. Analysis of the solid obtained then leads to a formulation $FePS_3(CoCp_2)_{0.34}(H_2O)_n$, which apparently does

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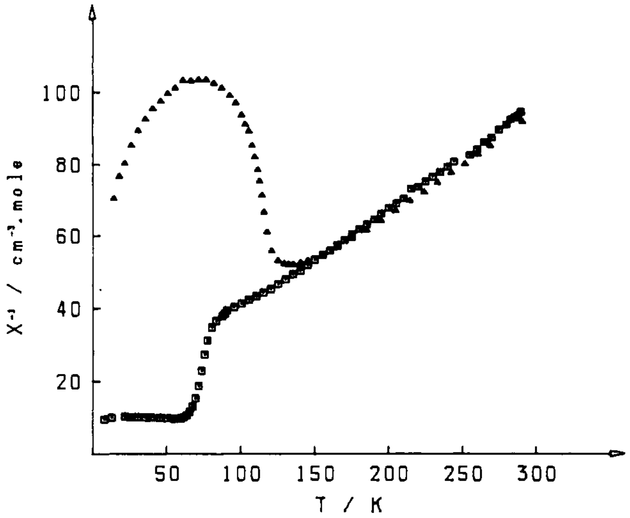

Figure 3. Reciprocal magnetic susceptibility of pure $FePS_3$ (▲) and $Fe_{0.83}Ps_3(CoCp_2)_{0.34}(H_2O)_{0.3}$ (□).

not show any iron deficit. However, this turns out to be the overall formulation of a diphasic solid. If the latter is treated by dilute (~0.1 N) HCl, the residual material turns out to have a formulation $Fe_{1-x}PS_3(CoCp_2)_{2x}(H_2O)_y$ with $x \simeq 0.18$. Our interpretation of the successful intercalation is that OH^- ions help xFe^{2+} ions to be removed from $FePS_3$ because solid iron hydroxide is formed. The latter is not separated from the intercalate by the washing treatment, hence the confusing analytical data.

Further characterization of the $Fe_{1-x}PS_3(CoCp_2)_{2x}(H_2O)_y$ compound has been attempted:

(i) The X-ray absorption of II at the iron K edge has been studied and compared to that of pure $FePS_3$. As shown in Figure 2, both absorption curves are identical with each other from 7105 to 7115 eV, that is throughout the preedge and the edge regions. This result strongly supports the fact that the iron ions have the same electronic structure in both compounds. The curves in the region above 7115 eV (XANES) are slightly different from each other, but it is extremely difficult to give a clear explanation of the features observed in this region. Small ligand field changes and effects of disorder (increased upon intercalation, as already demonstrated for $MnPS_3$[9]) might possibly account for such small differences.

(ii) The temperature dependence of the reciprocal magnetic susceptibility χ^{-1} of II is shown in Figure 3. Previous results for pure $FePS_3$ are also recalled for comparison. The following qualitative conclusions can be drawn:

(a) The maximum at ~135 K of the susceptibility of pure $FePS_3$ is not longer observed on the curve of intercalate II. This indicates that the antiferromagnetic exchange between the Fe^{2+} spins is weakened in the intercalate, a difference that may simply reflect the existence of vacancies in the Fe^{+II} sublattice.

(b) A rather abrupt transition takes place around 65 K, below which the susceptibility seems to be almost temperature-independent, indicating the occurence of a magnetically ordered state in the material. This behavior strongly recalls that of $Mn_{1-x}PS_3(CoCp_2)_{2x}(H_2O)_n$, where a strong spontaneous magnetization has been evidenced. Also it must be underlined that the $\chi = f(T)$ curve of the cation-exchanged $Fe_{0.83}PS_3(CoCp_2)_{0.34}(H_2O)_{0.3}$ is very similar to the one previously obtained for $FePS_3(CoCp_2)_{0.37}$ obtained by the electron-transfer route,[17] i.e. by treatment of $FePS_3$ with a toluene solution of neutral cobaltocene. In particular, the latter also exhibits an identical transition at the same temperature.[17] As the magnetic ordering temperature strongly depends on the coupling constant,[18] our results can be taken as evidence that both compounds have the same geometrical and electronic structure. This implies that, despite its apparent formulation, the intercalate $FePS_3(CoCp_2)_{0.37}$ in fact contains metal vacancies in the layers; of course this conclusion means that the formula given so far is somewhat inappropriate. Further work is in progress on this problem.

III.5. Reaction of $NiPS_3$. In contrast to the MPS_3 studied so far in this work, $NiPS_3$ does not react at all upon treatment with an aqueous solution of $CoCp_2I$ or KCl, even with concentrated EDTA solution up to pH ~12. Under still harder conditions, $NiPS_3$ is found to incorporate sodium ions upon treatment with aqueous 1 M solutions of NaOH or Na_2S. However, no nickel departure can be observed and analysis of the solid compound gives the formulation $NiPS_3Na_{0.5}(H_2O)_n$. Further work is in progress on this reaction.

III.6. Synthesis of MPS_3 Materials (M = Mn, Cd) from Aqueous Solutions of M^{2+} Cations and $P_2S_6^{4-}$ Anions. The MPS_3 structure can be described as $P_2S_6^{4-}$ units coordinated to M^{II} ions. This description is not a formal one, as $P_2S_6^{4-}$ is actually a molecular species that can be readily available in solution in the form of the sodium salt $Na_4P_2S_6{\cdot}xH_2O$.[10] In an attempt to find some support for the mechanism that will be suggested in the discussion (see below), we have undertaken to synthesize materials by mixing aqueous solutions of $Na_4P_2S_6$ (~0.1 M) with a large excess of a concentrated ~5 M solution of $MnCl_2$ or $CdCl_2$ (or the sulfates). Precipitation occurred immediately; the solid was centrifugated and washed several times with distilled water. After drying, nearly amorphous powders were obtained (green with Mn, white with Cd). Seeman–Bohlin photographs only show two broad reflections centered at the same positions as the 001 and 002 reflections of crystalline $MnPS_3$ and $CdPS_3$. Chemical analysis gives a formulation of $MPS_3{\cdot}xH_2O$. Anal. Found for $CdPS_3{\cdot}xH_2O$: Cd, 44.7; P, 12.5; S, 37.4. Found for $MnPS_3{\cdot}xH_2O$: Mn, 28.4; P, 16.2; S, 48.1. A little water seems to be retained in the samples ($x \sim 0.5$). The IR spectra of the manganese and cadmium samples show a strong band at 570 cm^{-1}, which appears at the same frequency as the $\nu(PS_3)$ stretching modes in the crystalline MPS_3 materials, although it is significantly broader. The ν(P–P) band is also present at ~450 cm^{-1}. Measurements of the room-temperature magnetic susceptibility of the $MnPS_3{\cdot}0.5H_2O$ material gave a value of 9100 × 10^{-6} cm^3 mol^{-1} identical with that for crystalline $MnPS_3$. This implies an antiferromagnetic coupling of the same strength in both cases, which in turn implies a similar structural arrangement.

In addition, the precipitated materials take up cationic species from aqueous solution of ionic salts such as $CoCp_2I$ etc. under the same conditions as the crystalline materials, but with much higher rates. Compounds such as $Mn_{1-x}PS_3(CoCp_2)_{2x}(H_2O)_y$ ($x = 0.19$; $y \sim 0.7$) (III) are obtained, which have characteristics very close to the those of intercalates prepared from the crystalline materials, except for a lower crystallinity. Anal. Found for III: Mn, 17.5; P, 12.2; S, 37.7; Co, 8.8; C, 17.9; H, 1.5. Thus, the $\nu(PS_3)$ band in the IR spectrum of III is split into two components at 605 and 555 cm^{-1}. The magnetic susceptibility of III at 293 K is ~11 200 × 10^{-6} cm^3 mol^{-1}, a slightly higher value than that obtained for the related crystalline material (~10 200 × 10^{-6}). This is consistent with a slightly higher rate of vacancies in III, which causes antiferromagnetic interactions to be weaker. Finally, Seeman–Bohlin patterns of III show two broad reflections centered at positions corresponding to the 001 and 002 reflections of the crystalline materials. Therefore, it may be reasonably assumed that the MPS_3 materials prepared by aqueous chemistry are structurally very close to those prepared by high-temperature solid-state chemistry. EXAFS studies are being pursued to obtain a better picture of the manganese and cadmium environments.

III.7. Colloidal Dispersion and Dissolution of $MnPS_3$ Crystals. We have shown in section III.6 that the molecular species $M^{2+}{}_{aq}$ and $P_2S_6^{4-}{}_{aq}$ could react to yield MPS_3 materials. To demonstrate further that these solvated molecular species play an essential role in the exceptional reactivity of MPS_3, we have tried to show that the $MnPS_3$ crystals could be dispersed and even dissolved. Thus, treatment of the $Mn_{0.8}PS_3K_{0.4}(H_2O)$ compound with an aqueous 1 M solution of LiCl results in a rapid K^+–Li^+ exchange, accompanied by a further removal of Mn^{2+} ions. This leads to the

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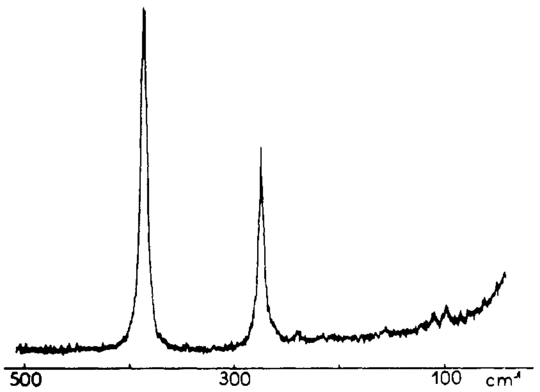

Figure 4. Raman spectrum of the green colloidal dispersion obtained from $Mn_{1-x}PS_3$ $Li_{2x}(H_2O)_n$ (10^{-2} M).

lamellar material $Mn_{1-x}PS_3Li_{2x}(H_2O)_y$ where x reaches a value of about 0.5, as noted previously for sodium.[7] The interlamellar distance in this compound is still well-defined, and it is found from X ray diffractograms to be about 12.0 Å, indicating the occurrence of a double layer of water molecules. However, when the centrifuged greenish crystals are shaken in a large amount of distilled water, the solid is readily dispersed and a colloidal suspension is formed. If EDTA is now added at pH ~10 into the suspension, the suspension even completely dissolves after a few minutes and a transparent colorless solution is obtained. These experiments strongly suggest that $MnPS_3$ can be progressively dissociated into its molecular species.

Further characterization of the dissociation steps is described below.

(i) The Raman spectrum below 500 cm^{-1} of the green colloidal dispersion mentioned above is shown in Figure 4. Comparison with previous results obtained for $MnPS_3$[11] shows that the very strong bands at found at 385 and 274 cm^{-1} for the green dispersion can be unambiguously assigned to internal modes of the P_2S_6 groups, $\nu_s(PS_3)$ and $\nu_d(PS_3)$, respectively. In contrast, two intense bands, which were found at 244 (vs) and 225 cm^{-1} (m) in the spectrum of pure solid $MnPS_3$,[11] only appear as very weak bands in the spectrum of the green dispersion, at 237 and 217 cm^{-1}. Interestingly, these latter bands have been assigned[11] to the translational T'_{xy} and rotational R'_{xy} motions of the PS_3 groups. These results therefore suggest that the green dispersion is still made up of P_2S_6 units, but that these units are bound together in a somewhat different way with respect to pure $MnPS_3$. Since the xy (in the plane of the layers) external motions are considerably affected by the dispersion process, one may even think that the structure of the dispersed particles is not longer truly lamellar.

(ii) The EPR spectrum of the above ~10^{-2} M colloidal dispersion is shown in Figure 5a. The broad intense absorption is identical with that given by pure $MnPS_3$, and it indicates the existence of magnetically coupled Mn^{2+} ions. However, four weak lines are present on the sides of the intense line, which may be readily attributed to the hyperfine structure of magnetically isolated $Mn(H_2O)_6^{2+}$ species. Indeed the spectrum of a more diluted (~0.5×10^{-3} M) dispersion clearly exhibits six lines (Figure 5b) at the same field as those given by a 10^{-3} M aqueous $MnCl_2$ solution. Dissolution of both dispersions upon addition of EDTA yields solutions that are EPR silent. We have checked that an aqueous $MnCl_2$ solution also becomes EPR silent upon addition of EDTA. We can therefore conclude that dispersed $MnPS_3$ particles are partially dissociated into hexaaquamanganese(II) species and probably $P_2S_6^{4-}$ ions; however, no $MnPS_3$ microdomains subsist any longer once the dispersion has been dissolved.

Note: Intercalates can be instantaneously reobtained by ion exchange from the colloidal suspension, even with very bulky organometallic cations such as $Rh(PPh_3)_4^+$.

IV. Discussion

The crucial point of this work is the exceptional ability for M^{II} ions to be removed from the MPS_3 slabs or to be reintroduced, at least when M = Mn, Zn, Cd, and Fe. This is a matter of surpise, as no similar phenomena have ever been reported in the field of other layered materials. In fact, we suggest that the "intercalation chemistry" of the MPS_3 series must be thought of in terms of chemical reactivity, involving a chemical transformation of the whole of the materials, rather than a diffusional process of guest species within a host lattice.

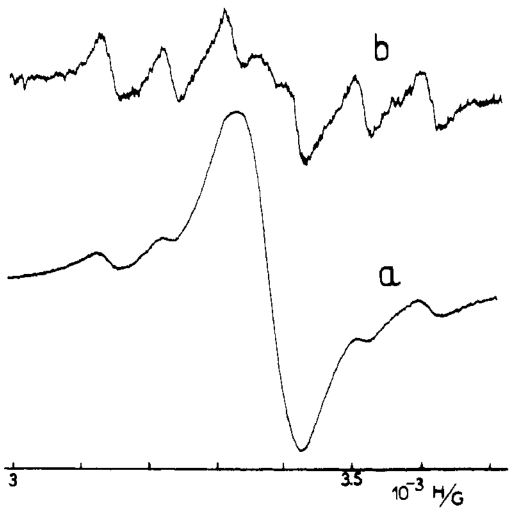

Figure 5. EPR spectra of the colloidal dispersion obtained from $Mn_{1-x}PS_3$ $Li_{2x}(H_2O)_n$: (a) concentration 10^{-2} M; (b) concentration 0.5×10^{-3} M.

Each MPS_3 slab is constituted of an array of $P_2S_6^{4-}$ units coordinated to the metal ions by sulfur atoms. If we consider the $P_2S_6^{4-}$ units as rigid entities (they are stable in solution), then the cohesion within the slabs is based on the bonding within MS_6 pseudooctahedra. Therefore we suggest that the MPS_3 compounds should be considered as polynuclear complexes to which the usual concepts of molecular coordination chemistry should apply. Now the metal M is in the II oxidation state, which is often characterized by a high lability of the metal–ligand bonding. In addition, the large size of the $P_2S_6^{4-}$ ions certainly results in a rather weak lattice energy.

Therefore, when an MPS_3 unit is in contact with an aqueous solution, a heterogeneous equilibrium can occur between $MnPS_3$, Mn^{2+} species (hexaaqua or complexed with EDTA), and solvated $P_2S_6^{4-}$. This equilibrium is then displaced by the other "intercalatable" (K^+, $CoCp_2^+$, ...) moiety present in the solution, according to the ability of these ions to give an increase of the lattice energy. Thus, although the MPS_3 materials apparently remain solid during the intercalation reaction, the microscopic process would involve a locally highly solvated transition state, which then readily accounts for the high rate of ion exchange even at room temperature. Of course the same mechanism can also explain the reverse process, i.e. when Ni^{2+} ions are transferred from the solution into the intralayer vacancies via the interlayer space.

In support of this suggested mechanisms, we have shown that $MnPS_3$ can be progressively dissociated into its constituting species in aqueous medium and also that $MnPS_3$ and $CdPS_3$ could be spontaneously re-formed from M^{2+} and $P_2S_6^{4-}$ species. Such a dissociation–condensation process would also explain the experimental fact than crystals are observed to stick to each other when an intercalation reaction is left running over several days in the total absence of stirring, in the same manner as small ice pieces stick to each other when they are in equilibrium with liquid water.

Therefore, the MPS_3 layered materials should no longer be considered as "exotic" compounds structurally similar to the layered dichalcogenides MX_2. They are much better described as a series of polynuclear solid-state complexes, capable of reacting under very mild conditions, much as low molecular weight coordination compounds would do. This point of view opens interesting perspectives for a mild solid-state chemistry leading to materials that have already been shown to possess useful properties (electrode materials,[4] electronic[19] and ionic conductivity,[20] ferromagnetism[16]). It is easy to understand why the dichalcogenides MX_2 cannot give the same type of chemistry. In the latter, the metal is in the IV oxidation state, so that the lability of the $[MS_6]$ units must exceedingly low. In addition, the lattice energy is certainly higher than in MPS_3 because of the small size of the S^{2-} ligand with respect to $P_2S_6^{4-}$.

The view of MPS_3 as polynuclear complexes could also be useful to understand how the intercalation reaction of neutral cobaltocene (dissolved in toluene) into MPS_3 (M = Zn, Mn, Cd, Fe, Ni) occurs[3]. So far, it has been reported that cobaltocene reacts by giving an electron to the layers, as in the chemistry of the transition-metal dichalcogenides. As the $MPS_3(CoCp_2)_{\sim 0.35}$ intercalates obtained remained insulating, the electron was supposed to be localized, but no evidence has ever been found for a particular location.[17] On the basis of magnetic properties, we have shown evidence in this work that the layers of $FePS_3(CoCp_2)_{0.37}$ (electron-donation route) were in fact intrinsically identical with those of $Fe_{0.83}PS_3(CoCp_2)_{0.34}(H_2O)_y$ (ion-exchange route). The same remark is also true for the intercalates of $MnPS_3$. Therefore, the electron-donation route would also create metal vacancies in the layers,e ven though the reaction is carried out in the absence of any water. Such a process seems very unlikely if thermal diffusion was the driving force. For instance, tantalum ions embedded in the octahedral sites of the TaS_2 layers require highly energetic irradiation to overcome the barriers imposed by the sulfur atoms and jump into the interlamellar space at room temperature.[21] In contrast, a reaction process involving dissociation and reconstruction of the MPS_3 material would easily lead to a material containing vacancies in the layers. Now such a process can easily be imagined, once we consider the MPS_3 as polynuclear complexes. Indeed, we know from coordination and organometallic chemistry that ligand exchange and redox phenomena take place in a variety of organic media. More details on this electron-transfer route will be published later, as further work is still in course. Finally, preliminary results concerning the reaction of dibenzene chromium with $FePS_3$[19] are also best understood from a coordination chemistry point of view.

For solid state chemists, the word "intercalation" is usually reserved to describe topochemical reactions, in which the integrity of the layers is preserved. We have clearly demonstrated that this is not the case for the MPS_3 series, at least for the reactions studied. Nevertheless, it is very convenient to call "intercalate" a lamellar solid made up of molecular species lying between infinite layers. Since this terminology has been the one used in all the literature on MPS_3 for 10 years, we have chosen to keep it in this paper.

In conclusion, we wish to emphasize that the MPS_3 series constitutes a very promising bridging area between coordination chemistry and solid-state chemistry in the field of the transition-metal sulfides.

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Registry No. $MnPS_3$, 20642-09-5; $CdPS_3$, 28099-03-8; $ZnPS_3$, 29331-38-2; $FePS_3$, 20642-11-9; K^+Cl^-, 7447-40-7; $CoCp_2^+I^-$, 11087-17-5; $Cd_{0.75}K_{0.5}PS_3\cdot H_2O$, 89045-92-1; $Cd_{0.5}PS_3Na_{1.0}$, 89045-93-2; $Cd_{0.75}PS_3Sr_{0.25}$, 101199-86-4.

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Bonding Mode of Axial NCS⁻ Ligands of Iron Macrocyclic Complexes. Crystal Structure of $[Fe(TIM)(SCN)_2]PF_6$

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The mode of thiocyanate bonding has been studied in four *low-spin* iron complexes of TIM (2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene). A solid phase of $[Fe(TIM)(SCN)_2]PF_6$ can be obtained that exclusively exhibits Fe–S bonding as shown by a single-crystal X-ray diffraction study of monoclinic crystals, space group *I*2/*a*, with $a = 14.846$ (5) Å, $b = 10.458$ (4) Å, $c = 14.974$ (6) Å, $\beta = 97.75$ (2)°, and $Z = 4$. The bonding modes of NCS^- in the solids $[Fe(TIM)(NCS)_2]$, $[Fe(TIM)(NCS)(CO)]PF_6$, and $[Fe(TIM)(SCN)Cl]PF_6$ have been assigned by using intensity data taken from infrared spectra. The first two are N-bonded, and the third is S-bonded. EPR spectra of frozen solutions of $[Fe(TIM)(SCN)_2]PF_6$ are interpreted in terms of an equilibrium mixture of the possible linkage isomers. The addition of water to acetone solutions is shown to favor the formation of the S,S-bonded isomer.

Introduction

The class of six-coordinate complexes $Fe(TIM)(X)(Y)^n$ (where the 14-membered tetraimine macrocycle TIM invariably occupies four equatorial coordination sites[1–7]) can be prepared containing formal Fe(II) and Fe(III) centers[1–6,8–16] depending on the nature of X and Y. The bis(thiocyanato) complex is of particular interest because it can be readily isolated and easily maintained in both oxidation states of iron. The electronic structures of bis(thiocyanato) complexes, including $[Fe(TIM)(NCS)_2]$ and the linkage isomers $[Fe(TIM)(NCS)_2]^+$ and $[Fe(TIM)(SCN)_2]^+$, have been investigated by using SCF-Xα-SW calculations.[17] Although a small Jahn–Teller preference (about 4 kcal/mol) for the S-bonded isomer was predicted, it was concluded that "other factors may be significant in the relative stability."[17] In this work, we include experimental evidence bearing on the mode of SCN^- binding in low-spin Fe(II)- and Fe(III)–TIM species, including the bis-

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