Novel Tetrathiafulvalene–MPS$_3$ (M = Mn, Cd) Layered Composite Materials

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Hydrated potassium intercalates $M_{1-x}PS_3K_{2x}(H_2O)_y$ (M = Mn, Cd) derived from MPS$_3$ lamellar materials react with $(TTF)_3(BF_4)_2$ in MeCN to yield lamellar composites in which tetrathiafulvalene (TTF) species are intercalated between $M_{1-x}PS_3$ slabs.

We have shown previously that the MPS$_3$ layered materials, where M is a transition metal in the +2 oxidation state, give rise to a unique intercalation chemistry,[1,2] due to the ability of the MPS$_3$ slabs to lose a variable amount of M^{II} intralayer cations. This chemistry should provide a route for the insertion of organic radical cations such as TTF$^+$ and related species using ion exchange processes, in contrast to the redox processes involved in the intercalation chemistry of TTF into FeOCl and some silicates.[3—6]

Pure MPS$_3$ (M = Mn, Cd) materials were synthesized by reaction of the elements at 700 °C.[7] A sample of the potassium intercalate $Mn_{1-x}PS_3K_{2x}(H_2O)_y$ (x ~0.17) was obtained by ion exchange,[1] treating MnPS$_3$ with a large excess of ~1 M aqueous KCl solution. A cadmium analogue $Cd_{1-x}PS_3K_{2x}(H_2O)_y$ (x ~0.16) was obtained similarly, but in the presence of a complexing reagent [0.1 M ethylenediamine-tetra-acetic acid (EDTA) at pH ~10 fixed by a KHCO$_3$/ K$_2$CO$_3$ buffer]. Synthesis of the final composite materials was then achieved by treating the potassium intercalates (100 mg) with a solution of 100 mg of $(TTF)_3(BF_4)_2$[8] in dry acetonitrile (50 ml). Dark crystalline powders were eventually obtained, the reaction rate being obviously higher when M = Mn (duration 12 h at 40 °C) than when M = Cd (2 days at 60 °C). These materials appear substantially different from each other and they will be described separately.

For composite (1) (obtained from MnPS$_3$) the X-ray powder diffraction pattern exhibits sharp *hkl* reflections which reveal a high crystallinity. Among them, a set of 00*l* reflections (up to 006) afford a value of 12.15 Å for the basal spacing, which thus indicates an overall increase by *ca.* 5.65 Å with respect to pure MnPS$_3$. This value is very close to the increase (5.70 Å) observed upon insertion of TTF into FeOCl,[3] and comparison with this case suggests that the molecular planes of the TTF species are essentially perpendicular to the MPS$_3$

slabs, with the C=C binary axis parallel to the layers. Elemental analysis (Table 1) shows that (1) can be formulated $Mn_{0.83}PS_3(TTF)_{0.42}K_{0.10}(H_2O)_{~0.4}$. Electrical charge balance implies that TTF species are in a mixed valence state, roughly $[TTF^+]_{0.24}[TTF^0]_{0.18}$ [Note that $(TTF)_3(BF_4)_2$ contains two TTF$^+$ for one TTF^0]. The conductivity, σ, has been measured using a monocrystalline platelet of (1) fitted with two gold electrodes, deposited by evaporation *in vacuo*. The value found for σ at 300 K was 2.3 × 10^{-3} Ω^{-1} cm^{-1}. Under the same conditions, we have found 3 × 10^{-9} Ω^{-1} cm^{-1} and 1.0 × 10^{-8} Ω^{-1} cm^{-1} for the conductivity of MnPS$_3$ and $Mn_{1-x}PS_3K_{2x}(H_2O)_y$ respectively. Preliminary tests have shown that the conductivity of (1) is strongly thermally activated.

I.r. spectra of (1) in KBr pellets showed bands (Table 1) which could be attributed either to the TTF species or to the P$_2$S$_6$ units of the slabs. Interestingly, the $\nu_{as}(PS_3)$ absorption band, which occurs at 570 cm^{-1} in pure MnPS$_3$,[1] is split into three components in (1). This band is usually split into only two components in the $Mn_{1-x}PS_3G_{2x}(solv)_n$ intercalates (where G denotes a monovalent cation), this splitting being related to the occurrence of intralamellar vacancies.[1,2,9] The more complex splitting scheme exhibited by (1) may indicate partial reoccupation of the intralayer vacancies in material (1) by the remaining potassium ions. The fact that some K$^+$ ions are able to stay in the lattice is certainly an important degree of freedom to favour mixed valency as the number of TTF$^+$ cations necessary to balance the electrical charge is reduced.

The magnetic susceptibility of (1) was studied between ~30 K and 300 K using a Faraday magnetometer. Results are consistent with localised spins (due to Mn^{2+} ions) coupled antiferromagnetically. A transition leading to a magnetically ordered state occurs over the range 40—50 K, as already observed in other MnPS$_3$ intercalates.[10]

Table 1. Main characteristic data of the composite materials described in the text.

Material	(1)	(2)
Composition	$Mn_{0.83}PS_3(TTF)_{0.42}K_{0.10}(H_2O)_{\sim0.4}$	$Cd_{0.84}PS_3(TTF)_{0.36}(H_2O)_{\sim0.4}$
Analytical data	C, 11.42; H, 0.64; S, 55.26; P, 11.57; Mn, 16.77; K, 1.39	C, 9.26; H, 0.73; S, 45.86; P, 10.89; Cd, 30.85; K, <0.1
I.r. (cm^{-1})[a]		
Assigned to TTF species	1380 w, 1310 s, br, 1080 m, 830 w, 740 m	1380 w, 1320 s, br, 1080 m, 830 w, 740 m
Assigned to PS$_3$ units	610 m, 590 m, 550 s	600 m, 550 s
σ at 300 K	$2.3 \times 10^{-3} \, \Omega^{-1} cm^{-1}$	$<10^{-5} \, \Omega^{-1} cm^{-1}$
Basal spacing	12.15 Å	Diphasic: 12.15 Å; 11.35 Å (predominant)

[a] s = strong, m = medium, w = weak, br = broad.

With composite (2) (obtained from CdPS$_3$), in contrast to (1), the X-ray diffraction pattern shows that this material is diphasic. The existence of two distinct basal spacings is obvious from the appearance of two sets of 00*l* reflections: 12.15 Å, as in (1), and 11.35 Å, the intensity of the latter set being predominant. Elemental analysis yields an overall composition $Cd_{0.84}PS_3(TTF)_{0.36}(H_2O)_{\sim0.4}$. In contrast to (1), no potassium ions remain in the material. This formula suggests that nearly all TTF species are cationic. The i.r. spectrum of (2) supports this idea: the $\nu_{as}(PS_3)$ band is split into only two components (Table 1), as usual in the intercalates $Cd_{1-x}PS_3G_{2x}$ (solv)$_n$.[2,9] No further data will be given yet owing to the diphasic nature of (2). The existence of a cadmium analogue to material (1) is nevertheless interesting because it illustrates the fact that the approach can be generalised.

In conclusion, the synthetic approach described in this communication suggests a strategy to develop a class of new materials merging the fields of layered inorganic materials MPS$_3$ and organic metals. Indeed, the method should apply in a quite general way to various derivatives of TTF and other radical cations. In particular, it is hoped to control the TTF$^+$/TTF^0 ratio in the composites either by partial reduction of TTF$^+$ cations or by controlling the amount of the remaining potassium ions.

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