Organometallic Intercalates of some Lamellar Metal Phosphorus Trisulphides

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The lamellar compounds MPS_3 (M = Mn, Zn, Fe, or Ni) have been shown to react with neutral $[Co(\eta\text{-}C_5H_5)_2]$ and $[Cr(\eta\text{-}C_6H_6)_2]$ forming the intercalates of general stoicheiometry $MPS_3[Co(\eta\text{-}C_5H_5)_2]_x$ and $MPS_3[Cr(\eta\text{-}C_6H_6)_2]_x$. The role of the solvent is quite important. Thus, $MnPS_3$ intercalates $[Cr(\eta\text{-}C_6H_6)_2]$ together with benzene forming $MnPS_3[Cr(\eta\text{-}C_6H_6)_2]_{0.24}(C_6H_6)_{0.10}$. The compounds $MnPS_3$ and $ZnPS_3$ have also been shown to take up cationic species, giving the related intercalation products; this unexpected route to intercalation is briefly discussed.

PREVIOUS work has shown that transition-metal dichalcogenides were able to intercalate a number of neutral metallocenes, in particular those having a low first ionization potential and which oxidized to a cation stable to isolation.[1-3] In an attempt to explore the range and possible applications of organometallic intercalation compounds, we have studied the synthesis of intercalates with lamellar metal phosphorus trisulphides MPS_3, where M is a metal in the formal II oxidation state. These compounds have been shown [4] to have a structure related to that of cadmium chloride, with metal ions and P–P pairs occupying the cadmium positions and sulphur ions occupying the chloride positions. Some of these MPS_3 phases have already been shown to intercalate amines [5] and recently alkali metals, especially lithium.[6,7] The present work is concerned with the reaction of neutral or cationic metallocenes with MPS_3 phases where M is manganese, zinc, iron, or nickel. This series was chosen since there seem to be two different MPS_3 phases; thus the compounds with M = Mn or Zn are optically transparent, slightly coloured insulators with band gaps of 3.0 and 3.4 eV † respectively, whereas those with M = Fe or Ni are black semiconductors with band gaps of 1.5 and 1.6 eV respectively.[8]

EXPERIMENTAL

Pure layered MPS_3 phases were synthesized by heating the metal or its sulphide (ZnS) with a stoicheiometric amount of elemental sulphur and phosphorus (red or white) in evacuated silica ampoules, following the procedure described in ref. 9. The purity of the reagents was better than 99.5%. **CAUTION**: We note that the use of very finely divided metal may lead to explosions on heating the ampoules, even at temperatures as low as 150—200 °C. The MPS_3 compounds were identified by their *X*-ray diffractogram, using a Philips powder diffractometer fitted with a copper source. All the organometallic compounds quoted below were synthesized by reported methods.[10]

The following general experimental procedure for formation of new intercalates was used. A toluene or benzene solution (*ca.* 10 cm^3) of the neutral organometallic compound (1 mmol) was heated for 3—5 d at 130 °C with the MPS_3 compound (1 mmol) in an ampoule sealed under vacuum. The resulting solid was filtered off and washed with dry degassed toluene and ethanol.

The intercalates were characterized by their *X*-ray diffractogram, which essentially showed sharp intense 00*l* lines. The value of the basal spacing, *i.e.* the distance between adjacent MPS_3 layers, could thus be easily obtained. A few very weak additional lines were observed, but their restricted number and poor quality did not allow us to find the unit cell. Also the i.r. spectra of the intercalates were obtained (KBr discs) in the range 200—4 000 cm^{-1}. The intercalates were further characterized by carbon and hydrogen analysis; in several cases, the metal of the guest molecule has been analyzed by atomic absorption spectroscopy; in one case, a total analysis has been obtained.

RESULTS

Using Toluene as a Solvent.—The compounds $MnPS_3$ and $ZnPS_3$ were treated with a toluene solution of the following neutral sandwich compounds: bis(η-cyclopentadienyl)-iron, -nickel, -cobalt, and -chromium, bis(η-benzene)-chromium, -molybdenum, and -vanadium, and finally bis(η-cyclopentadienyl)dihydridomolybdenum. Only cobaltocene $[Co(\eta\text{-}C_5H_5)_2]$ was found to give rise to intercalates. They had the stoicheiometries $MPS_3[Co(\eta\text{-}C_5H_5)_2]_x$ where M = Zn, $x = 0.28$, or M = Mn, $x = 0.33$. The increase (by *ca.* 5.30 Å) of the basal spacings compares with the value observed when cobaltocene intercalates into ZrS_2 (5.35 Å) [1] and it clearly shows the formation of a 'first-stage' compound, *i.e.* that there is one layer of guest molecules per layer of the host lattice. The data are collected in Table 1. The i.r. spectra of both intercalates exhibit bands which may be assigned to $Co(\eta\text{-}C_5H_5)_2$ systems. Furthermore, the frequencies of these bands are closer to those of the cobalticenium cation $[Co(\eta\text{-}C_5H_5)_2]^+$ than to those of neutral cobaltocene; in particular, both intercalates show a strong band at 860 cm^{-1}, which coincides with the band of the cobalticenium cation, whereas neutral cobaltocene is known to absorb at 828 and 778 cm^{-1}.[11] Both intercalates also show two bands at 495 and 455 cm^{-1} which are characteristic of the cobalticenium cation.[11] Besides, the absorption lines of the host lattice are somewhat modified. Thus, the strong band at 570 cm^{-1} of pure $MnPS_3$ is split into two bands at 555 and 605 cm^{-1} for the corresponding intercalate, which might indicate a distortion of the $[P_2S_6]^{4-}$ groups. Both intercalates are stable in air for months; they may be dissolved in dilute HCl, yielding a yellow solution which contains the cobalticenium cation. It has not been possible to recover the starting $ZnPS_3$ or $MnPS_3$ phases by hydrolysis of the intercalates; this presumably reflects the low stability of the phases towards hydrolysis.

The compounds $FePS_3$ and $NiPS_3$ were treated with $[M(\eta\text{-}C_5H_5)_2]$ (M = Ni, Cr, or Co), $[Cr(\eta\text{-}C_6H_6)_2]$, and

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† Throughout this paper: 1 eV ≈ 1.60×10^{-19} J.

TABLE 1

Intercalation in MPS_3 phases using neutral metallocenes

Host lattice	Metallocene and solvent	Stoicheiometry [a] (±0.01)	Basal spacing (±0.03 Å)	Lattice expansion [b] (±0.03 Å)	Analytical data of the intercalate in wt. %
$MnPS_3$	$[Co(\eta\text{-}C_5H_5)_2]$ Toluene	0.33	11.82	5.32	Co, 7.6; C, 16.0
	$[Co(\eta\text{-}C_5H_5)_2]$ Benzene	0.24 [c]	12.05	5.55	Co, 6.0; C, 15.8
	$[Cr(\eta\text{-}C_6H_6)_2]$ Toluene		no intercalation		
	$[Cr(\eta\text{-}C_6H_6)_2]$ Benzene	0.24 [c]	12.42	5.92	Cr, 5.2; C, 17.4
$ZnPS_3$	$[Co(\eta\text{-}C_5H_5)_2]$ Toluene	0.28	11.74	5.31	Co, 6.7; C, 13.7
	$[Cr(\eta\text{-}C_6H_6)_2]$ Toluene		no intercalation		
	$[Cr(\eta\text{-}C_6H_6)_2]$ Benzene		very slow intercalation		
$FePS_3$	$[Co(\eta\text{-}C_5H_5)_2]$ Toluene [d]	0.39	11.74	5.32	Co, 9.0; C, 18.25
	$[Cr(\eta\text{-}C_6H_6)_2]$ Toluene	0.32	12.38	5.96	C, 18.45
$NiPS_3$	$[Co(\eta\text{-}C_5H_5)_2]$ Toluene [d]	0.37	11.68	5.33	Co, 8.55; C, 17.4
	$[Cr(\eta\text{-}C_6H_6)_2]$ Toluene	0.34	12.26	5.92	C, 19.1

[a] The number of organometallic guest molecules per MPS_3 group. [b] The difference between the basal spacing of the intercalate and that of the pure host lattice. [c] Benzene is intercalated too (see text). [d] The corresponding experiment in benzene gave the same results.

$[Mo(\eta\text{-}C_5H_5)_2H_2]$. Both layer phases were found to incorporate $[Co(\eta\text{-}C_5H_5)_2]$ and $[Cr(\eta\text{-}C_6H_6)_2]$ (see Table 1 for details). Again we note that the 'lattice expansion' associated with the uptake of $[Cr(\eta\text{-}C_6H_6)_2]$ is very close to the value reported for the intercalation of this compound into ZrS_2.[2] The high stoicheiometry of the compound $FePS_3[Co(\eta\text{-}C_5H_5)_2]_{0.39}$ is consistent with the guest molecules being essentially close-packed within the layers. Infrared spectra of all these intercalates have been obtained: as above, the observed lines support the idea of the organometallic molecule being cationic, once inside the layers. Finally, treatment of the intercalates with boiling dilute HCl in air gives the pure starting $FePS_3$ or $NiPS_3$ phases and the corresponding organometallic cation.

Using Benzene as a Solvent.—When $MnPS_3$ is treated with a solution of $[Cr(\eta\text{-}C_6H_6)_2]$ in benzene intercalation occurs, in contrast to the experiment performed in toluene which gave a negative result. The value of the lattice expansion is 5.92 Å, and the i.r. spectrum of the intercalate exhibits bands which may be assigned to a $Cr(\eta\text{-}C_6H_6)_2$ system, more precisely to the $[Cr(\eta\text{-}C_6H_6)_2]^+$ cation. Thus, bands were observed at 3 060, 1 430, 1 000, 970, 788, 461, and 411 cm^{-1}; their relative intensity parallels that of the corresponding bands of $[Cr(\eta\text{-}C_6H_6)_2]^+$. Besides, two bands at 608 and 553 cm^{-1} were attributed to the host lattice, as discussed above. Finally, two additional bands at 685m and 1 470w cm^{-1} may probably be attributed to a small amount of intercalated benzene. According to chromium and carbon analysis (Table 1), the intercalate may be then formulated as $MnPS_3[Cr(\eta\text{-}C_6H_6)_2]_{0.24}(C_6H_6)_{0.10}$.

A comparative study of the reaction of $MnPS_3$ with cobaltocene either in toluene or in benzene gave the followings results: intercalation of cobaltocene occurs in both cases, but the basal spacing of the obtained intercalate is greater in the benzene experiment (12.05 Å) than in the toluene one (11.82 Å), the difference being significant and reproducible. The presence of intercalated benzene (in the corresponding experiment) is evidenced by i.r. spectroscopy and by vapour-phase chromatography after dissolving the intercalate in concentrated HCl. Finally, according to cobalt and carbon analysis, the intercalate prepared in the presence of benzene may be formulated as $MnPS_3[Co(\eta\text{-}C_5H_5)_2]_{0.24}(C_6H_6)_{0.12}$.

The reaction of $[Cr(\eta\text{-}C_6H_6)_2]$ with $ZnPS_3$ has been performed using benzene as a solvent; intercalation occurred, but only partially after 1 week at 130 °C. Comparative studies of the intercalation of cobaltocene into $FePS_3$ and $NiPS_3$ using either benzene or toluene did not give significantly different results.

Intercalation using Organometallic Salts.—In an at first sight surprising reaction it was observed that stirring $MnPS_3$ for 1 d at room temperature with an excess of the salt $[Co(\eta\text{-}C_5H_5)_2]I$ in water or dry ethanol gave a compound with identical characteristics to the intercalate obtained from $MnPS_3$ and neutral cobaltocene in toluene (the data are collected in Table 2). A full elemental analysis shows

TABLE 2

Intercalation in MPS_3 phases using a metallocene salt

Host lattice	Salt (in water or ethanol)	Stoicheiometry (±0.01)	Basal spacing (±0.03 Å)	Lattice expansion (±0.03 Å)	Analytical data of the intercalate in wt. %
$MnPS_3$	$[Co(\eta\text{-}C_5H_5)_2]I$	0.33	11.82	5.32	Mn, 22.25; Co, 8.05 P, 12.95; S, 39.3 C, 16.4; H, 0.95
	$[Cr(\eta\text{-}C_6H_6)_2]I$	0.33	12.26	5.76	Cr, 6.8; C, 18.9
	$[Cr(\eta\text{-}C_6H_6)_2][PF_6]$	0.33	12.26	5.76	Cr, 6.6; C, 18.5
	$[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)][PF_6]$	0.30	12.05	5.55	C, 16.4
$ZnPS_3$	$[Co(\eta\text{-}C_5H_5)_2]I$	0.28	11.72	5.29	Co, 6.7; C, 13.7
	$[Cr(\eta\text{-}C_6H_6)_2]I$	0.21 *	12.25	5.82	C, 12.8
	$[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)][PF_6]$	0.2 *	12.08	5.65	C, 11.3

* Intercalation was not complete (from *X*-ray diagrams) after stirring for 1 month.

that the compound may be formulated as $MnPS_3[Co(\eta\text{-}C_5H_5)_2]_{0.33}$. Also we found that the cation $[Cr(\eta\text{-}C_6H_6)_2]^+$ is capable of intercalating into $MnPS_3$ using the same procedure. Similarly, $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_6H_6)]^+$ could be incorporated into $MnPS_3$. The values of the 'lattice expansion' measured for the three intercalates parallel the size of the related intercalated cations. The same intercalation reactions of these cations also occur with $ZnPS_3$, but at a much slower rate. However, the cations are not observed to react with $FePS_3$ or $NiPS_3$.

DISCUSSION

The fact that metallocenes with a low first ionization potential intercalate into MPS_3 phases would seem to indicate that the driving force to the reaction is a charge transfer from the guest molecules to the host layers. The MPS_3 phases would then behave as layer systems such as the transition-metal dichalcogenides or MoO_3.[12] From this point of view the intercalation of $[Co(\eta\text{-}C_5H_5)_2]$ or $[Cr(\eta\text{-}C_6H_6)_2]$ into $FePS_3$ and $NiPS_3$ is consistent with the observation that lithium may intercalate in these phases. However, the intercalation of cobaltocene into $ZnPS_3$ is more surprising, since lithium is not intercalated by $ZnPS_3$.[7] Although further studies are necessary to understand this point, it may be that a purely ionic model is not sufficient and that interactions between the cyclopentadienyl ligands and the sulphur layers might play an important role as suggested in a similar system.[3]

The reaction of $MnPS_3$ with a cobalticenium salt yielding an intercalate has been firmly established, but raises some problems: the basic reaction may be written as below and we thus have to account for the origin of

$$MnPS_3 + 0.33\ [Co(\eta\text{-}C_5H_5)_2]^+ + 0.33\ e \longrightarrow MnPS_3[Co(\eta\text{-}C_5H_5)_2]_{0.33}$$

the electrons. We have experimentally observed that some $MnPS_3$ dissolves during the reaction; for example, Mn^{2+} ions have been shown to be formed and the mass of the product is lower than that expected by a factor of 6—8%. Thus the mechanism of the reaction might involve a dismutation of $MnPS_3$, of which a key step would be hydrolysis and oxidation of the dissolved $[P_2S_6]^{4-}$ anions; these anions have been shown to hydrolyse, but the exact reaction is not known.[13] Further analytical studies are being carried out to confirm this suggestion.

Further questions which arise are why does $[Cr(\eta\text{-}C_6H_6)_2]^+$ intercalate into $MnPS_3$ whereas $[Cr(\eta\text{-}C_6H_6)_2]$ requires the presence of benzene to intercalate, and does not react at all if toluene is used. Such irregularities may reflect the importance of kinetic factors in intercalation processes, as previously observed in the case of TaS_2.[2] An interesting effect of the intercalated benzene is that it causes an increase of the basal spacing of the products. A reasonable explanation of this fact, using an ionic model, is that the presence of benzene reduces the organometallic content of the intercalate, thus reducing the packing forces between the cationic guest molecules and the negatively charged layers.

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