A Novel Route to Intercalation into Layered $MnPS_3$

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Summary The layered $MnPS_3$ reacts with a wide range of 'guest' cations G^+, leading to new intercalation compounds of the type $Mn_{1-x}PS_3,G_{2x},(H_2O)_y$.

TRANSITION metal phosphorus trisulphides MPS_3, where M is a divalent metal cation, form a class of lamellar materials[1,2] structurally related to the transition metal dichalcogenides. Similar chemical properties accompany this structural analogy; for instance, $NiPS_3$ has been shown to intercalate lithium either chemically upon reduction with butyl-lithium or electrochemically.[3,4] Reduction of several MPS_3 compounds by organometallic species such as cobaltocene or dibenzenechromium also leads to intercalation compounds,[5,6] and spectroscopic studies of these organometallic intercalates have shown that the guest species are cationic.[7] However the location of the negative charge which must have been given to the layers remains an open question. We have found that $MnPS_3$ will react with various cations to form intercalation compounds through a different route which does not involve any electron transfer.

$MnPS_3$ was treated with aqueous solutions of a number of ionic salts G^+X^- (typically over 24 h at room temperature). The Table shows that a wide range of cations, including organometallic species and ammonium and alkali metal cations, intercalate into the host lattice. Elemental analysis gives $Mn_{1-x}PS_3,G_{2x},(H_2O)_y$ as the formula for the resulting compounds. Analysis of the aqueous solution

Table Intercalates obtained by reaction of $MnPS_3$ with aqueous solutions of some G^+X^- salts

Reacting G^+X^- salt (in water)	Interlayer distance /Å	Intercalate formula[a]
$[Co(\eta\text{-}C_5H_5)_2]^+I^-$	11.82	$Mn_{0.84}PS_3[Co(\eta\text{-}C_5H_5)_2]_{0.32}[H_2O]_{0.3}$[b,c]
$[Cr(\eta\text{-}C_6H_6)_2]^+I^-$	12.26	$Mn_{0.86}PS_3[Cr(\eta\text{-}C_6H_6)_2]_{0.28}[H_2O]_{0.3}$[b]
$NH_4^+Cl^-$	9.38	$Mn_{0.81}PS_3[NH_4]_{0.38}[H_2O]_{1.0}$
$(CH_3)_4N^+Cl^-$	11.45	$Mn_{0.85}PS_3[Me_4N]_{0.30}[H_2O]_{0.9}$
$(C_2H_5)_4N^+I^-$	11.18	$Mn_{0.86}PS_3[Et_4N]_{0.28}[H_2O]_{0.3}$
pyH^+Cl^-[d]	9.65	$Mn_{0.86}PS_3[pyH]_{0.28}[H_2O]_{0.7}$
$CH_3(CH_2)_7NH_3^+Cl^-$	10.38	$Mn_{0.90}PS_3[C_8H_{17}NH_3]_{0.23}[H_2O]_{0.4}$
Cs^+Cl^-	9.57	$Mn_{0.81}PS_3[Cs]_{0.38}[H_2O]_{0.9}$
Rb^+Cl^-	9.40	$Mn_{0.81}PS_3[Rb]_{0.38}[H_2O]_{0.9}$
K^+Cl^-	9.37	$Mn_{0.81}PS_3[K]_{0.38}[H_2O]_{0.9}$
$MnPS_3$	6.50	—

[a] All formulae were obtained from a full elemental analysis (except for oxygen). [b] This formula corrects a result previously given (ref. 5) which is now known to have been in error owing to a faulty chemical analysis. [c] The cobalticenium intercalate has even been obtained in the form of thin, quasi-monocrystalline platelets which are currently being studied by i.r. spectroscopy. [d] pyH^+ = pyridinium.

after the reactions confirmed that the intercalation of $2x$ mol of G^+ was accompanied by the dissolution of x mol of Mn^{2+} from the reacting solid $MnPS_3$. The reaction can then be written as equation (1). The intercalates have

$$MnPS_3 + 2xG^+_{aq} \rightarrow Mn_{1-x}PS_3,G_{2x},(H_2O)_y + xMn^{2+}_{aq} \qquad (1)$$

been further characterized by their *X*-ray powder diffraction patterns which exhibit sharp *hkl* reflections indicating good crystallinity; although the patterns have not been yet fully indexed, the presence of strong 001 reflections renders the calculation of the interlayer distance easy and the data are summarized in the Table. The interlayer distance (6.5 Å for $MnPS_3$) increases upon intercalation by an amount close to the 'van der Waals bulk' of the guest species.

The intercalates are transparent, slightly coloured materials and their i.r. spectra were obtained by routine methods. They show bands which can be readily assigned either to the guest species or to the host lattice. In addition, two broad bands around 3500 and 1600 cm^{-1} reveal that the intercalates contain a small amount of water, especially when the guest species is small and hygroscopic; thermogravimetry shows that these H_2O molecules are easily lost upon heating (between 20 and 100 °C) and subsequently reabsorbed upon cooling. The water content thus measured is consistent with the estimation of oxygen derived from the analytical data.

$MnPS_3$ has been shown by Klingen[1,2] to be isostructural with $FePS_3$. Thus, each layer is built up by stacking sulphur octahedra with Mn^{2+} cations occupying 2/3 of the centres of the octahedra. The intercalation process must therefore involve the departure of Mn^{2+} from inside the layers, resulting in the creation of 'intralayer' vacancies, whereupon an 'interlayer' uptake of a corresponding amount of guest cations occurs. Such a process, although similar to cation exchange, is quite different from the mechanism commonly found in ion exchangers such as the silicates, where ions already in the interlayer space are exchanged against other ions. Preliminary studies indicate that the process reported here also takes place with $ZnPS_3$ and $CdPS_3$, but not with $FePS_3$ or $NiPS_3$. An important factor for this process could be the crystal field stabilisation energy corresponding to the (MS_6) octahedral units. Ions such as Zn^{2+}, Cd^{2+}, and Mn^{2+} (which do not induce any crystal field stabilization) would be 'labile,' but Fe^{2+}, Ni^{2+}, *etc.*, which induce a crystal field stabilisation, would not.

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