

# Formation of surfactant intercalates of MnPS<sub>3</sub> as observed by real time *in situ* powder X-ray diffraction

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Time-resolved, *in situ* energy-dispersive X-ray diffraction is used to monitor the intercalation of long-chain ammonium surfactants in MnPS<sub>3</sub>; the initial rate of intercalation appears to independent of the chain length, but for the longer chain length guest ions the new intercalate phases are short lived and start to decompose before the reaction is complete.

Manganese hexathiophosphate, MnPS<sub>3</sub>, is a layered semiconducting material which has a monoclinic structure (space group *C2/m*) related to the CdCl<sub>2</sub> type.<sup>1</sup> This material displays a unique, ion-transfer intercalation reaction whereby cationic species are intercalated into the van der Waals interlayer region at the expense of Mn<sup>2+</sup> ions vacating the MnPS<sub>3</sub> layers to maintain charge balance.<sup>2</sup> Examples of cations which undergo this type of intercalation include K<sup>+</sup>, NR<sub>4</sub><sup>+</sup>, Hpy<sup>+</sup>, [Co(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>]<sup>+</sup>, tetrathiofulvene (TTF), *N,N*-dimethylamino-*N*-methylstilbazolium (DAMS), and poly(ethylene oxide) (PEO) to give compounds of the general formula Mn<sub>1-x</sub>PS<sub>3</sub>(G)<sub>2x</sub>(H<sub>2</sub>O)<sub>y</sub> (G = guest cation; 0 ≤ x ≤ 0.2).<sup>3-6</sup> Many of these intercalates have been shown to exhibit a range of remarkable multifunctional optical and magnetic properties.<sup>7</sup> For example, both Mn<sub>1-x</sub>PS<sub>3</sub>(G)<sub>2x</sub>(H<sub>2</sub>O)<sub>y</sub> {G = NMe<sub>4</sub><sup>+</sup>, [Co(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>]<sup>+</sup>} exhibit a spontaneous magnetisation below 40 K.<sup>8</sup> The powder neutron diffraction data show magnetic scattering below T<sub>c</sub>, which is consistent with an ordered array of Mn<sup>2+</sup> vacancies.<sup>9</sup> The intercalation of DAMS in both CdPS<sub>3</sub> and MnPS<sub>3</sub> gives materials which have large efficiencies for the doubling of laser radiation at 1340 nm.<sup>10</sup>

Given the recent interest in the preparation of inorganic materials with regular pore sizes in the mesoscopic domain we have investigated the intercalation of a range of amine surfactants into MnPS<sub>3</sub>. Owing to the complexity of many of these reactions we have investigated them using real time, *in situ* energy-dispersive synchrotron X-ray powder diffraction in our environmental cell.<sup>11,12</sup> Here we report on the synthesis of a range of new surfactant intercalates of MnPS<sub>3</sub> and the observation of transient crystalline intermediates.

The intercalation of dodecyltrimethylammonium bromide (C<sub>12</sub>TMABr) into MnPS<sub>3</sub> at 120 °C in water was monitored *in situ* in a medium-pressure Pyrex reaction vessel by energy-dispersive X-ray powder diffraction. The reaction proceeds smoothly and affords a stable crystalline compound. The X-ray diffraction pattern of the product can be indexed on a hexagonal unit cell with a *c* lattice parameter of 11.26 Å. Integration of the 001 Bragg reflection with respect to time is shown in Fig. 1. The half-life for the reaction at 120 °C is *ca.* 400 s with the reaction essentially complete in 700 s. The increase in the interlamellar spacing of 4.77 Å is consistent with the packing of the dodecyltrimethylammonium ions parallel to the planes of the host lattice (Scheme 1). Elemental analysis is consistent with the formulation of this intercalate as Mn<sub>0.92</sub>PS<sub>3</sub>(C<sub>12</sub>TMA)<sub>0.16</sub>.

However, dramatically different behaviour was observed when we monitored the intercalation of the larger hexadecyl- and octadecyl-trimethylammonium bromides (C<sub>16</sub>TMABr and C<sub>18</sub>TMABr) in MnPS<sub>3</sub>. For both reactions, we observed the growth of a series of Bragg reflections which can be indexed to unit cells with *c* lattice parameter of 33.80 and 36.20 Å for the

hexadecyl- and octadecyl-trimethylammonium reactions respectively. These large *c* lattice parameters correspond to interlayer expansions of *ca.* 27.3 and 29.7 Å for the hexadecyl- and octadecyl-trimethylammonium intercalates respectively. A plot of the time dependence of the integrated intensities of the Bragg reflections due to these intercalate phases shows that the initial rates of intercalation of all three ammonium cations are essentially equal suggesting that the rate determining step in each of these reactions is the separation of the MnPS<sub>3</sub> layers (Fig. 2). However, for both reactions involving the intercalation of C<sub>16</sub>TMA<sup>+</sup> and C<sub>18</sub>TMA<sup>+</sup> the peak intensities of the intercalate phases start to decrease gradually after *ca.* 600 s and after approximately 30 min no reflections are observed in the energy window of the detector. The resulting grey powder which can be collected from the reaction mixtures is identical from both reactions and is poorly crystalline. Both elemental microanalysis and X-ray microprobe analysis suggest that it has the composition MnPO<sub>4</sub>·xH<sub>2</sub>O although the unit cell dimensions do not match any of the known manganese phosphates or hydrogen phosphates.

Intercalation of the intermediate length tetradecyltrimethylammonium bromide (C<sub>14</sub>TMABr) in MnPS<sub>3</sub> gives rise to a complex reaction. Different behaviour has been observed when the reaction was monitored *in situ* on three different occasions. The first attempt showed the transient formation of a new phase which could be indexed with a *c* lattice parameter of 31.6 Å, on a second occasion a different phase was observed with a *c* lattice parameter of 11.5 Å, which co-formed with a small amount of the previous phase. On another occasion only the phase with an 11.5 Å lattice parameter could be detected. A plot of the unit cell dimension *vs.* the number of carbon atoms for the guest molecule, C<sub>*n*</sub>TMA<sup>+</sup> (*n* = 14, 16, 18) is linear. The gradient of this plot is 1.15 Å per C. Assuming the guests molecules form a monolayer between the MnPS<sub>3</sub> layers, this suggests that the guests ions are oriented at *ca.* 65° to the host layers (Scheme 1).

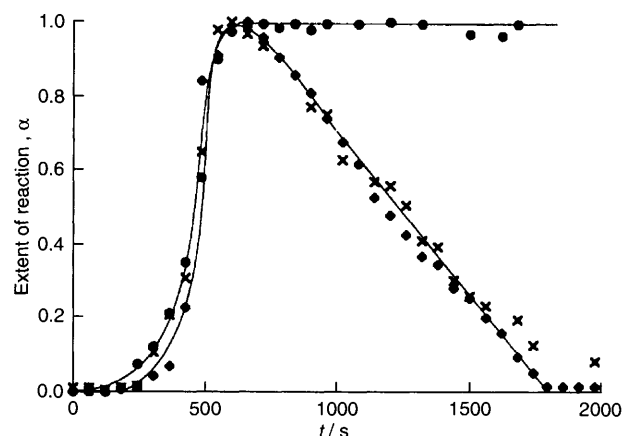
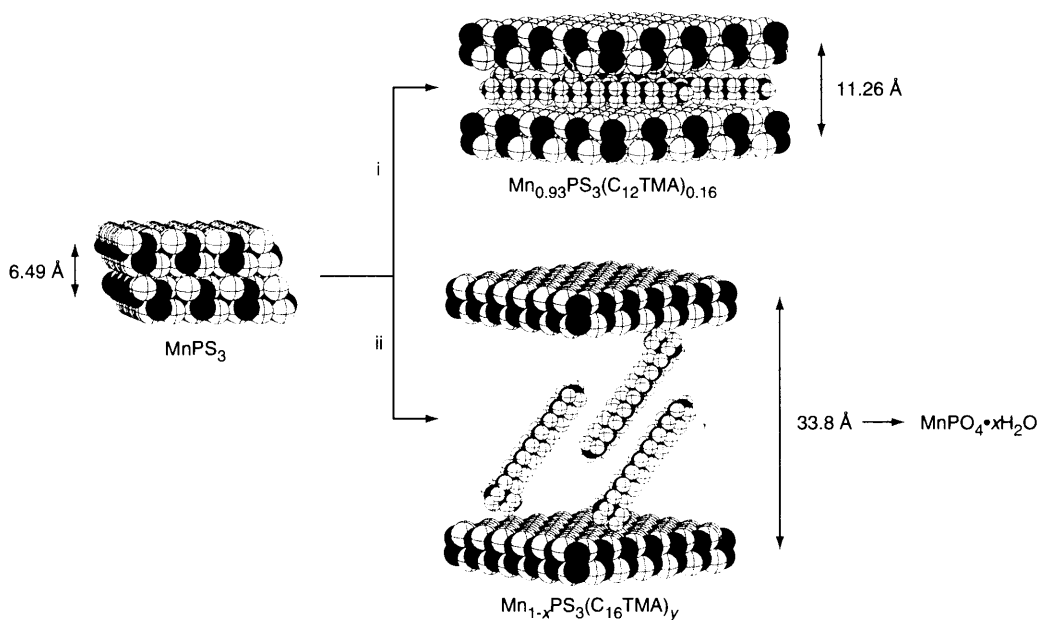
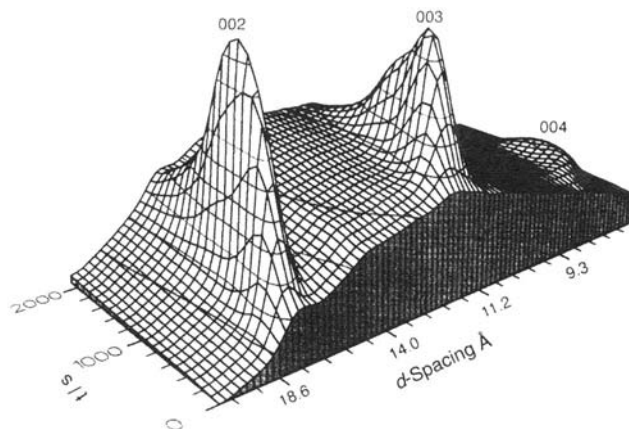


Fig. 1 Plot of extent of reaction ( $\alpha$ ) *vs.* time for the reactions of: (●) C<sub>12</sub>TMABr with MnPS<sub>3</sub> in water at 120 °C, (×) C<sub>16</sub>TMABr with MnPS<sub>3</sub> in water at 120 °C, (◆) C<sub>18</sub>TMABr with MnPS<sub>3</sub> in water at 120 °C [ $\alpha = I(t)/I_{\max}$  for the strongest Bragg reflection in each case]. The solid line is not a mathematical fit to the data but a guide for the eye.



**Scheme 1** Reagents and conditions: i,  $\text{MnPS}_3$  (150 mg) +  $\text{C}_{12}\text{TMA}$ Br (1 mmol) in  $5 \text{ cm}^3$  water at  $120^\circ\text{C}$ ; ii,  $\text{MnPS}_3$  (150 mg) +  $\text{C}_{16}\text{TMA}$ Br (1 mmol) in  $5 \text{ cm}^3$  water at  $120^\circ\text{C}$



**Fig. 2** Time-resolved energy-dispersive X-ray diffraction of the reaction of  $\text{C}_{16}\text{TMA}$ Br with  $\text{MnPS}_3$  in  $\text{H}_2\text{O}$  at  $120^\circ\text{C}$

In addition, it seems reasonable to postulate that the  $\text{C}_{14}\text{TMA}$  cation is just at the critical length where the energy difference between the lying down or the  $65^\circ$  tilted arrangements of the guests are very small.

Given the current interest in template-assisted crystallisation, these experiments clearly demonstrate the power of time-resolved, *in situ* diffraction measurements to monitor and help unravel the complex interactions of surfactant molecules with inorganic lattices. In this example, we have not only determined the kinetics of these reactions but also observed novel transient metastable phases that would probably have gone undetected using conventional laboratory procedures.

We would like to thank DRAL for a CASE studentship (R. J. F.) and the use of the Synchrotron Radiation Source

facility, and Dr S. M. Clarke, and the technical staff at Daresbury Laboratory for helping in the design and construction of the experimental cell.

#### Footnote

† Dermot O'Hare is the Royal Society of Chemistry Sir Edward Frankland Fellow.

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Received, 22nd August 1996; Com. 6/05854J