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Observation of a thermally induced spin crossover in a $CdPS_3$ intercalate

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Magnetic susceptibility measurements of the layered intercalate $Cd_{1-x}PS_3\,[Fe^{III}(SalEen)_2]_{2x}$ ($x=0.14$) reveal that the trapped species undergo a gradual thermally induced spin crossover.

There has been in recent years a renewed interest in the high-spin (HS) ↔ low-spin (LS) crossover phenomenon exhibited by transition metal complexes.[1–3] Besides progress in the understanding of thermally induced spin crossovers, light-induced spin switching has opened up perspectives in optical information technology.[4,5] There are several reasons to investigate intercalation of spin-transition complexes in layered systems. The environment of the active complex (solvent,[2,6] counterion,[2,7,8] intermolecular interactions,[9] packing defects[1]) is well known to exert a dramatic influence on the transition. Therefore the effect of sterically restraining host layers and reduced dimensionality may considerably affect the transition. A layered system can also be viewed as a storage medium which could provide new pathways to act on the spin states by irradiation of the host lattice and subsequent host to guest energy transfer.[10] Spin crossover in two complexes synthesized *in situ* in Y-zeolite cages or layered silicates have been reported.[11–13] No evidence for intermolecular interactions was found, but the zeolite host lattice appears to stabilize configurations that differ from those in the usual solid state. We report here the thermally induced spin crossover of a cationic $[Fe^{III}(SalEen)_2]^+$ complex intercalated in the layered diamagnetic $CdPS_3$ thiophosphate.

The $[Fe^{III}(SalEen)_2]Cl$ compound **I**, where SalEen is the monoanion of the condensation product of salicylaldehyde and *N*-ethylethylenediamine, was synthesised according to the procedure used for the NO_3, BPh_4 and PF_6 analogues, using $FeCl_3{\cdot}6H_2O$.[7] The composition of **I** was verified by elemental analysis and IR spectroscopy.

The $CdPS_3$ layered compound[14] is known to react with solutions of certain ionic salts G^+X^- to give intercalation compounds of a general formula $Cd_{1-x}PS_3G_{2x}{\cdot}(\text{solvent})_y$.[15] In these compounds, charge balance is maintained by the loss of one Cd^{2+} ion from the intralayer region for every two G^+ ions that are inserted in the interlayer region. In the present case, no reaction occurred upon treating $CdPS_3$ with a methanolic solution of **I**. A two-step procedure was therefore employed. (i) A pre-intercalate $Cd_{1-x}PS_3(Me_4N)_{2x}$ was prepared by treating $CdPS_3$ (typically 200 mg) with Me_4NCl (1 g) in dry methanol (20 ml) at 20 °C for 1 day. As already seen for cobaltocenium intercalated into $CdPS_3$, the Cd^{2+} ions extracted from $CdPS_3$ form a sparingly soluble $(Me_4N)(CdCl_3)$ diamagnetic salt.[15] Extensive washing by methanol allowed dissolution of this impurity but caused partial decomposition of the pre-intercalate into $CdPS_3$. (ii) Two samples of the above pre-intercalate, one moderately washed with methanol, the other one thoroughly, were then treated with a methanolic solution of **I** at 110 °C for 20 h in a Pyrex ampoule sealed under vacuum. The dark red solids thus formed (**IIa** and **IIb**, respectively) were washed with methanol until the supernatant liquor became colourless.

The intercalates **IIa** and **IIb** were characterised by their powder X-ray diffractograms which showed quite sharp 00*l* reflections corresponding to an interlayer spacing of 14.8 Å (6.5 Å for $CdPS_3$ and 11.5 Å for the pre-intercalate). The diffractogram of **IIb** also exhibited the broadened 001 reflection of pure $CdPS_3$. The reflections given by **IIa** are somewhat sharper than those of **IIb**, hence **IIa** is better crystallized. Elemental analyses indicate that **IIa** retains 3% chloride while **IIb** only retains a negligible amount. On the other hand, the presence of re-formed $CdPS_3$ in **IIb** results in a lower complex content. The P, S and Fe contents in **IIa** suggest a formula close to $Cd_{0.86}PS_3[Fe^{III}(SalEen)_2]_{0.28}$ for the intercalate,† in agreement with the stoichiometry usually observed for guest species of that size. The IR spectra of **IIa** and **IIb** were almost identical. They showed numerous bands slightly broader and weaker than those of salt **I**, but at essentially the same wavenumbers, as well as a strong signal assignable to the $\upsilon(PS_3)$ stretching modes of $CdPS_3$, split into three components at 560, 580 and 605 cm^{-1}. This set of characterisation data is therefore consistent with the presence in **IIa** and **IIb** of nearly close-packed $[Fe^{III}(SalEen)_2]$ cations lying in the interlayer galleries.

The temperature dependence of the magnetic susceptibility χ (per mole of Fe) of both intercalates, measured with a Quantum Design SQUID magnetometer over the range 4–400 K, is shown in Fig. 1 as a plot of χT *versus* T. These results clearly demonstrate that the Fe^{III} centres undergo a spin crossover between low-spin (LS) $S=1/2$ and high-spin (HS) $S=5/2$, centered at a half-conversion temperature $T_{1/2}=255$ K. The transition is relatively smooth. No hysteresis was observed when a full temperature cycle was followed. Focussing on **IIa**, the experimental χT value on the low temperature plateau (1.23–1.40 $cm^3\ mol^{-1}$ K) is significantly higher than that expected for the LS state of Fe^{III} ($\chi T \approx 0.50\ cm^3\ mol^{-1}$ K, taken from **I** in the LS state; see below; this is ascribed to residual HS molecules (28%). In contrast, the crossover is complete on the high temperature side. Comparing the two intercalates, the crossover is very slightly more abrupt in **IIa** ($\Delta T^{80}=180$ K)‡ than in **IIb** ($\Delta T^{80}=200$ K), the completeness of the crossover is larger in **IIa** (HS residue at low T for **IIb** ≈ 36%), but the crossover temperatures are very similar. These features are consistent with the better crystallinity of **IIa**, and hence the presence of fewer defects.[16] The incom-

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† Analytical data for the intercalates. **IIa**: C, 21.12; H, 2.68; N, 4.60; Fe, 3.96; Cd, 24.96; P, 7.79; S, 23.03; Cl, 3.38. Calc. for $Cd_{0.86}PS_3[Fe(salEen)_2]_{0.28}[(Me_4N)(CdCl_3)]_{0.10}$: C, 20.89; H, 2.57; N, 4.53; Fe, 4.16; Cd, 28.98; P, 8.22; S, 25.45; Cl, 2.78%. **IIb**: C, 12.09; H, 1.53; N, 2.52; Fe, 2.50; Cd, 37.40; P, 10.11; S, 30.46; Cl, 0.22. Calc. for $Cd_{0.94}PS_3[Fe(salEen)_2]_{0.12}[(Me_4N)(CdCl_3)]_{0.01}$: C, 11.11; H, 1.3; N, 2.37; Fe, 2.32; Cd, 37.38; P, 10.7; S, 33.14; Cl, 0.36%.

‡ ΔT^{80} represents the temperature interval over which the spin conversion varies from 10 to 90%.

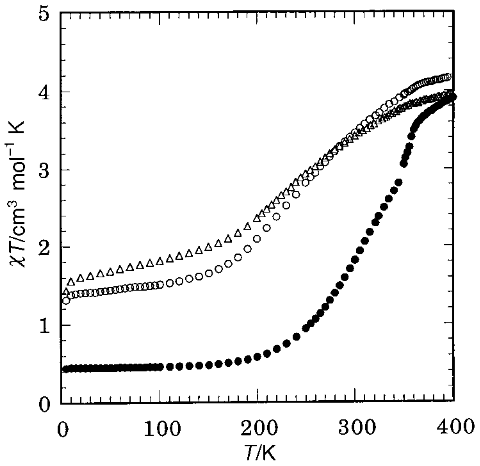

Fig. 1 χT *vs.* T plot of $[\mathrm{Fe^{III}(SalEen)_2}]\mathrm{Cl}$ (●) and of the $\mathrm{CdPS_3}$ intercalates **IIa** (○) and **IIb** (△). χ is expressed per mole of Fe in all cases.

pleteness of the crossover at low temperature might also be ascribed to $\mathrm{Fe^{3+}}$ impurities resulting from a slight decomposition of the complex, but the analytical data for Fe, C and N show good agreement with the expected composition $\mathrm{Fe(SalEen)_2}^+$.

The magnetic behaviour of the intercalated $\mathrm{Fe^{III}}$ complex should of course be compared to that of the starting chloride **I**. The temperature dependence of χT measured for **I** is also shown in Fig. 1. This compound undergoes a smooth but complete spin crossover centered at $T_{1/2} = 320$ K, more abrupt than the intercalates ($\Delta T^{80} = 148$ K).

From these results, one might conclude that intercalation of the $\mathrm{Fe^{III}}$ complex does not suppress its spin crossover, but exerts a damping effect. However the effect of intercalation appears more positive if the intercalated complex is compared to other salts. Thus, $[\mathrm{Fe^{III}(SalEen)_2}]\mathrm{PF_6}$ has been reported to show a gradual spin crossover centered at $T_{1/2} = 140$ K only and the nitrate salt exhibits a very incomplete transition.[7] Although other complexes and intercalates should be studied in order to draw a general conclusion, the present result tells us that intercalation could be used as worthwhile strategy to pack active species, especially because it brings additional degrees of freedom.

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