

Evidence for the Chemical Nature and Ordering of Cobaltocene Intercalated in CdPS₃ using Single Crystal Solid State ²H NMR Spectroscopy

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Solid state ²H NMR spectra of single crystal samples of CdPS₃{Co(η-C₅D₅)₂}_{0.4} indicate the co-existence of both Co(η-C₅D₅)₂ and [Co(η-C₅D₅)₂]⁺ between the CdPS₃ layers; all the metallocene guest molecules reside in ordered domains within the *ab*-plane of the host lattice at a 90° angle to each other, and with their principal C₅-symmetry axes parallel to the layers of the host lattice.

The layered transition metal hexathiohypodiphosphates, MPS₃, (M = Cd, Mn, and Fe) have been previously shown to undergo a wide variety of intercalation reactions.¹ For example, cobaltocene can be intercalated into these materials by either direct reaction or by ion-exchange routes.² Of particular interest is that intercalates of MPS₃ (M = Fe, Mn) have been shown to exhibit spontaneous magnetisation at 45–92 K (M = Fe, Mn).³ As part of our ongoing program of developing an understanding of the physical properties of these materials we have recently completed a detailed structural investigation of Mn_{0.83}PS₃{Co(η-C₅H₅)₂}_{0.33} using both photographic X-ray and powder neutron diffraction techniques.⁴ In general, the crystal chemistry of intercalation compounds is complex and presents very difficult crystallographic problems due to the disorder inherent in the samples. Therefore, we have been interested in developing other physical techniques which could give us comparable structural information relating to the structure of guest ions and molecules in intercalation compounds.

Here, we report how single crystal solid state ²H NMR can conveniently provide both chemical information and also detailed, precise orientational information about the guest molecules in intercalation compounds.

Treatment of crystals of CdPS₃ (*ca.* 1 × 1 × 0.1 mm) with a saturated solution of Co(η-C₅D₅)₂ in toluene at 120 °C for 2 weeks results in complete intercalation giving a first stage product of chemical composition CdPS₃{Co(η-C₅D₅)₂}_{0.4}. The lattice expansion (Δ*c* = 5.3 Å) and the chemical composition are consistent with close packing of the metallocene molecules between the chalcogenide layers of the host. The solid state ²H NMR spectrum of a crystal of CdPS₃{Co(η-C₅D₅)₂}_{0.4} orientated with the *ab*-plane perpendicular to the static magnetic field is shown in Fig. 1.

Two quadrupolar doublets are clearly resolved in Fig. 1 indicating that two chemically unique deuteron environments

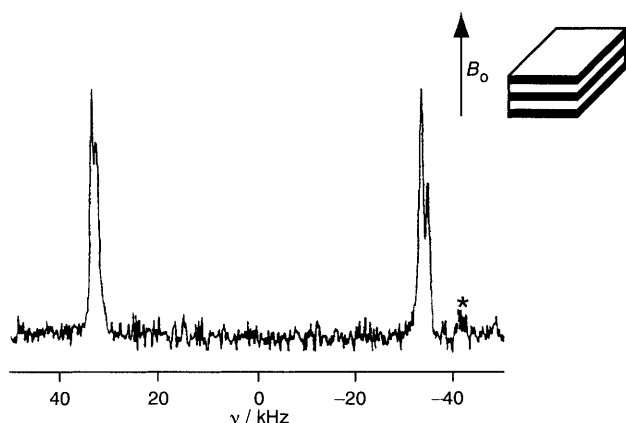


Fig. 1 Room temperature 61.4 MHz quadrupolar spin echo solid state ²H NMR spectra of a single crystal of CdPS₃{Co(η-C₅D₅)₂}_{0.4} oriented with its stacking axis parallel to the field. A quadrupolar spin echo sequence [(π/2)_x-30μs-(π/2)_y-30μs-observe] was used with π/2 pulses of 1.5 μs, and a recycle delay of 5 s.

are present within the layers. The most intense doublet is centred about the isotropic chemical shift of [Co(η-C₅D₅)₂]⁺ with a quadrupolar splitting of 67 kHz. The less intense doublet, also with a quadrupole splitting of 67 kHz is centred at 1.1 kHz (*ca.* δ 18) upfield of the [Co(η-C₅D₅)₂]⁺ isotropic chemical shift, and has been assigned to the paramagnetic Co(η-C₅D₅)₂ molecules by comparison with the solid state ²H NMR spectrum of a physical mixture of solid Co(η-C₅D₅)₂ and [Co(η-C₅D₅)₂]⁺[PF₆]⁻. The presence of unoxidised cobaltocene molecules intercalated in the host has been previously postulated by Kim *et al.*,⁵ using EPR. However, these NMR experiments give us direct evidence of the existence of both the neutral and oxidised species in the same crystal. The ²H NMR spectra also indicate that any electron-transfer processes between intercalated molecules must be slow (< 10⁴ s⁻¹).

In contrast to microcrystalline samples, for oriented single crystal samples only certain orientations of the host lattice are presented to the static field. This means that any orientational preferences of the metallocene guest molecules within the host layers will result in a corresponding distribution of orientations of the EFG tensors of ²H nuclei in the spectrometer field and thus will be reflected in the solid state ²H NMR spectral profile. The rapid C₅-rotation of the cyclopentadienyl rings in metallocenes at room temperature results in the principal components of the averaged axially symmetric EFG tensors of all of the ²H nuclei lying along the principal molecular axis. Therefore, the ²H NMR doublet separation observed in the single crystal experiment is a direct indicator of the orientation of the guest molecules. Thus, a simulated spectrum for a 35:65 ratio of Co(η-C₅D₅)₂ and [Co(η-C₅D₅)₂]⁺ molecules oriented with their

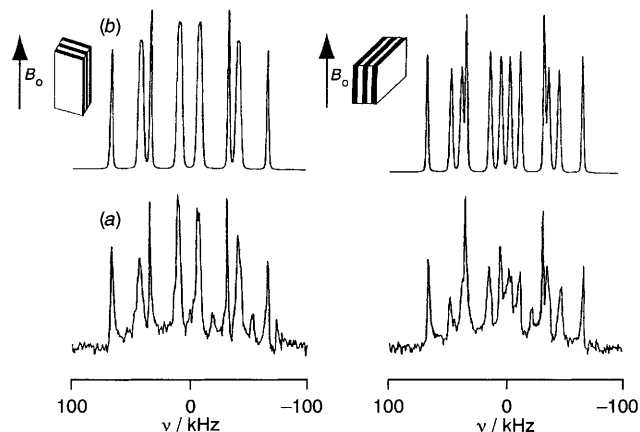


Fig. 2 (a) Room temperature quadrupolar spin echo solid state ²H NMR spectrum of a crystal of CdPS₃{Co(η-C₅D₅)₂}_{0.4} oriented with its stacking axis perpendicular to the field. A quadrupolar spin echo sequence [(π/2)_x-30μs-(π/2)_y-30μs-observe] was used with π/2 pulses of 1.5 μs, and a recycle delay of 5 s. (b) ²H NMR lineshape simulation assuming equal populations of six different metallocene orientations to the field, as described in the text, and assuming (e²qQ/h) of 88 kHz. The variation of peak height arises from a small distribution in the angular distributions; the best fit was observed with Gaussian distribution of s.d. (σ) = 0.70°.

C_5 -axes parallel to the $CdPS_3$ layers is in excellent agreement with the experimental spectrum.

In order to study the dynamics and orientational preferences of the guest molecules within the layers the 2H NMR of the $CdPS_3\{Co(\eta-C_5D_5)_2\}_{0.4}$ crystal was measured in two other orientations. The two other orientations chosen were the remaining orthogonal directions perpendicular to the stacking axis of the crystal (Fig. 2). The solid state 2H NMR spectra for the crystals recorded with the crystal stacking axes oriented perpendicular to the magnetic field are shown in Fig. 2. The 2H NMR spectra for each crystal orientation consists of a number of sharp doublets, superimposed on a broad resonance. We believe the broad resonance arises from the paramagnetic Co ($\eta-C_5D_5$)₂ guests. Since $Co(\eta-C_5D_5)_2$ has an axially symmetric g -tensor, when the principal axis of the g -tensor lies perpendicular to the magnetic field as in Fig. 1, no broadening of the 2H NMR resonances is observed but when the crystal is rotated through 90° (as in Fig. 2) then it couples strongly with the static field in all the molecular orientations producing a broad signal envelope.

We can, however, use the angular dependence of the sharp quadrupolar doublet separations to assign uniquely the orientations of the diamagnetic $[Co(\eta-C_5D_5)_2]^+$ guests. Using the doublet separation and intensity information from both spectra the orientations of the principal molecular axes of the intercalated diamagnetic $[Co(\eta-C_5D_5)_2]^+$ molecules have been calculated to be $1.1 (\pm 4.5)$, $25.3 (\pm 1.8)$, $146.7 (\pm 1)$, $88.7 (\pm 3.5)$, $116.6 (\pm 1)$ and $56.9^\circ (\pm 1)$ [assuming a quasistatic (e^2qQ/h) = 88 kHz].⁶ $[Co(\eta-C_5D_5)_2]^+$ molecules with equal populations at each of these angles produce the composite simulated spectra shown in Fig. 2(b).

The variation in the linewidths of the quadrupolar doublets is caused by slight deviations in the molecular orientations of the metallocene molecules from the nominal angle, which is dependent on $d(\Delta\nu)/d\theta$ ($\Delta\nu$ = quadrupolar doublet separation, θ = angle between the static field (B_0) and the molecular C_5 -axis). $d(\Delta\nu)/d\theta$ is minimal near the parallel and perpendicular orientations of the molecular axes of the guest molecules to the magnetic field and maximal when the molecular orientations are approximately 45° to the magnetic field. Hence, molecules with their C_5 -molecular axes oriented closely parallel or perpendicular to the field give rise to narrow lines and the doublet separation may be determined to within ± 1 kHz, whereas for the broader lines due to molecules at intermediate angles (e.g. 45° to the field) the doublet separation can only be determined to within ± 3 kHz. The dependence of the doublet separation on the orientation of the molecule to the field does mean however, that for orientations around 45° , the 2H NMR doublet splitting is very sensitive to and therefore a most accurate indicator of the orientation.

A close examination of the experimentally determined angular orientations of the cobaltocenium ions within the host lattice suggests there is a relationship between the observed molecular orientations [Fig. 3(a)]. The cobaltocenium ion orientations can be divided into three groups or domains, with molecules oriented at relative angles of $(0, 90)$, $(30, 120)$ and $(60^\circ, 150^\circ)$ in each domain respectively [Fig. 3(a)]. This model produces two independent molecules oriented at 90° to each other in each domain, and each domain is related by a rotation

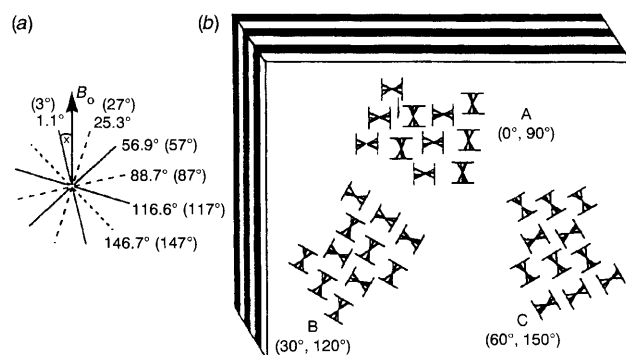


Fig. 3 (a) Schematic diagram showing the observed orientations of the cobaltocenium ions relative to the magnetic field (B_0). The values in parentheses are the orientations generated by a rotation of the six sites shown in Fig. 3(b) about the crystal stacking axis by an angle ($\alpha = 3^\circ$). (b) A schematic illustration of the three domains of differently oriented cobaltocene molecules present within the host lattice in the compound $CdPS_3\{Co(\eta-C_5D_5)_2\}_{0.4}$. The domains are probably larger than shown and are not necessarily in the same layer.

of $\pm 60^\circ$. This structural model is shown schematically in Fig. 3(b). We believe, the 60° relationship between domains is linked to the three-fold symmetry of the close packed sulfur layers in the host lattice. We have no way of estimating the sizes of these domains but since we see no evidence of edge effects we believe that the domains are large and that perhaps the 60° relationship comes about by random $\pm 60^\circ$ shifts in adjacent $CdPS_3$ layers.

In summary, these experiments indicate the power of solid state 2H NMR of single crystals for determining the structure and dynamics of molecules in solid matrices. These experiments also dramatically demonstrate the highly ordered nature of cobaltocene molecules intercalated within layered lattices. Finally, we would like to thank the Royal Society and the EPSRC for support. S. J. H. thanks the Glasstone benefaction for a fellowship.

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