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Solid state ^{2}H NMR study of the orientation and dynamics of cobaltocenium intercalated in the layered silicate LaponiteRD

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Ion-exchange intercalation of $[Co(\eta\text{-}C_5D_5)_2]^+$ ions in the smectite clay LaponiteRD $[Na_{0.46}Mg_{5.42}Li_{0.46}Si_8(OH)_4O_{20}]$ yields $[Mg_{5.42}Li_{0.46}Si_8(OH)_4O_{20}\{Co(\eta\text{-}C_5D_5)_2\}_{0.4}Na_{0.1}]$. Structural and dynamic information about the material was obtained with the benefit of ^{2}H NMR spectroscopic measurements, performed on powder and specially prepared oriented samples, combined with comparisons to ^{2}H NMR lineshape simulations. The cobaltocenium cations adopt an ordered arrangement in the host lattice with their principal molecular axes parallel to the silicate layers. In addition to rotation about the principal molecular axis, previously observed for similar cobaltocenium layered intercalates, the emergence of an inner component with a splitting of 22.3 kHz over the temperature range 220–300 K strongly suggests the molecule is undergoing n-fold reorientations about the C_2 axis of symmetry. Concurrent to this dynamic motion is an additional vibrational motion in and out of the plane parallel to the silicate layers. Coupled with rotation about the C_2 axis, this gives rise to a gyratory motion in the slow–intermediate regime which increases with temperature until the fast regime is reached at 330 K.

Introduction

Clay minerals that possess the 2 : 1 silicate structure can be used extensively as ion-exchange materials, hosts for intercalation reactions,[1,2] sorbents and host lattices in the synthesis of organic–inorganic hybrid composite materials. For example, the synthetic smectite clay, LaponiteRD $\{Na_{0.46}Mg_{5.42}Li_{0.46}Si_8(OH)_4O_{20}\}$[3] is typical of the 2 : 1 layered charged silicates, with an octahedral magnesium oxide layer sandwiched between two tetrahedral silicate layers. The material swells in water and the interlayer Na^+ ions can be exchanged for a range of other cations such as organic dyes. The swelling and ultimately the exfoliation ability of Laponite has been used to modify electrode surfaces for sensing applications. In recent years, we have been interested in intercalating organometallic guest ions or molecules, especially metallocenium ions, into layered materials giving compounds such as: $SnX_2\{Co(C_5D_5)_2\}_{0.3}$ (X = Sn,Se),[4,5] $CdPS_3\{Co(C_5D_5)_2\}_{0.4}$[6] and $V_5O_5\{Co(C_5D_5)_2\}_{0.2}(H_2O)_x$.[7] The properties of these intercalation compounds are remarkably different to the parent host, and the guest ions or molecules can act as probes for gaining considerable structural information about the system. For example, both the extent of order of the guest species within the layers[6] or the degree of stacking disorder in the host[7] can be examined. Here, we report the synthesis of a cobaltocenium intercalate of Laponite and a study of the orientation and dynamics of the metallocenium cation within the silicate structure using solid state ^{2}H NMR spectroscopy.

Experimental

Synthesis

$Co(\eta\text{-}C_5D_5)_2$ was prepared using literature procedures, and $[Co(\eta\text{-}C_5D_5)_2]^+PF_6^-$ prepared as described previously.[7] LaponiteRD, $Na_{0.46}Mg_{5.42}Li_{0.46}Si_8(OH)_4O_{20}$, was supplied by Laporte Absorbents Widnes, UK. Ion exchange intercalation samples of LaponiteRD were prepared using the following procedure: 200 mg of host was suspended in an acetone solution of guest, containing a 5 molar excess of $[Co(\eta\text{-}C_5D_5)_2]^+PF_6^-$. After stirring for 12 h, the solution was filtered over a glass frit and washed with three 50 ml portions of acetone, then dried under reduced pressure. Oriented platelet samples of LaponiteRD were prepared by applying wet samples of the clay to a series of glass substrates (thin slides) and then drying at 30–40 °C. Ion exchange could be achieved by immersing oriented host samples in acetone solutions of $[Co(\eta\text{-}C_5D_5)_2]^+PF_6^-$ at the same molar ratio. Elemental microanalysis; Found (calc.) for $Mg_{5.42}Li_{0.46}Si_8(OH)_4O_{20}\{Co(\eta\text{-}C_5D_5)_2\}_{0.4}Na_{0.1}$: D, 1.26 (0.98); C, 5.02 (5.82); Co, 2.71 (2.86)%.

Solid state ^{2}H NMR spectroscopy

Variable temperature solid state deuterium NMR spectra were recorded on a Bruker MSL400 pulse spectrometer with an Oxford Instruments 9.4 T wide bore superconducting solenoid magnet (400.13 MHz for ^{1}H NMR) and equipped with an Aspect 3000 data system. All ^{2}H NMR spectra were recorded at 61.42 MHz with a Bruker 232V high-power probe and a horizontal 7 mm solenoid coil. Temperatures were accurate to ± 1 K and stable to 0.1 K, maintained by a Bruker BVT 1000 temperature-control unit equipped with a constant thermocouple, interfaced with a heater element inside the probe body. Between 30 min and 1 h was allowed for the sample to obtain thermal equilibrium before acquisition commenced. It was found to be essential to re-tune the probe at each new temperature. The spectrometer was set up using multiple procedures on a Wilmad glass sphere of Cu^+ doped D_2O, placed in the centre of the coil, the pulse lengths, shimming and receiver phase balance were optimised on a bulk sample of D_2O. The pulse lengths and tuning frequency were finally refined using a sample of deuterated poly(methyl methacrylate) (DPMMA). The quadrupole spin–echo echo sequence $[\pi/2\text{–}\tau\text{–}\pi/2\text{–}\tau'\text{–acquire}]$[8] was used to acquire all spectra using the pulse program ECHOCYCL, with standard precautions[9–11] and phase-cycling (to remove off resonance effects). Spin echo-delay times of 20–40 µs and recycle delays of 4–5 s were employed. The quadrupole echo delay sequence values were also adjusted to ensure that the digitised points constituting the FID (free induction decay) were symmetrically situated about the point at the top of the quadrupole echo. The FID acquisition was started prior to the top of the echo, so that a software correction to remove the left most points from the echo could be implemented, to allow the processed FID to start at the top of the echo.

All samples were packed in 5 mm tubes under nitrogen. In order to be able to rotate thin film samples about the stacking axis through an angle with an accuracy of ±2° a Teflon® disk was attached to the top of the NMR tube after sealing under nitrogen. Across the centre of the disk a line was drawn which could be aligned with the angular graduations situated on an outer circle attached to the probe insert. A more detailed description of this setup has been described previously.[7] Spacers were added to the tube to prevent the films moving during the experiment. A schematic of the oriented sample and holder can be viewed in Fig. 4.

^{2}H NMR simulations

Simulations of the ^{2}H NMR quadrupole echo lineshapes of ordered and partially ordered cobaltocenium ion orientations were performed by the weighted summation of lineshapes calculated for discrete orientations. Full details of the simulations and the computer programs used have been described in full detail elsewhere.[5]

Results and discussion

Synthesis of metallocene–clay intercalate

In its fully dehydrated state LaponiteRD exhibits a basal-layer spacing of 10.2 Å. However, under normal conditions the observed interlayer spacing depends strongly upon the extent of hydration of the intercalated Na^+ ions, and is typically *ca.* 12.5 Å. LaponiteRD undergoes an ion-exchange intercalation reaction by suspending the host in a concentrated acetone solution of $[Co(\eta\text{-}C_5H_5)_2]^+PF_6^-$ for 3–4 h at room temperature. A yellow solid can be obtained by filtration of the reaction mixture. Elemental microanalysis shows that the intercalate has a Co loading of 2.7%, which is consistent with the formula $[Mg_{5.42}Li_{0.46}Si_8(OH)_4O_{20}\{Co(\eta\text{-}C_5H_5)_2\}_{0.4}\text{-}Na_{0.1}]$, for simplicity the formula is hereafter abbreviated to Laponite$\{Co(\eta\text{-}C_5H_5)_2\}_{0.4}$. The cobaltocenium cations are larger than the Na^+ ions they replace, causing an interlayer expansion of 4.5 Å which can be deduced from the X-ray powder diffraction patterns of preferred orientation samples. The X-ray powder diffraction pattern of the material showed a broadened diffraction profile of relatively low intensity. This is ascribable to turbostratic disorder and is in agreement with a model of stacked disordered layers. Cobaltocenium can be considered as an almost cylindrical molecule with van der Waals dimensions of *ca.* 6.4 Å × *ca.* 6.8 Å.[12] The intercalation of metallocenes in layered oxides and sulfides normally results in interlayer expansions of *ca.* 5.3 Å.[13,14] In this case an additional 4.5 Å lattice expansion is required to accommodate the $[Co(\eta\text{-}C_5H_5)_2]^+$ ion.

Static solid state ^{2}H NMR studies on microcrystalline samples of Laponite$\{Co(\eta\text{-}C_5D_5)_2\}_{0.4}$

The variable temperature static solid state ^{2}H NMR spectra of powder samples of Laponite$\{Co(\eta\text{-}C_5D_5)_2\}_{0.4}$ measured in the temperature range 130–400 K are shown in Fig. 1. A significant transition in this range is apparent in the spectra, and can be attributed to reorientation dynamics. In the temperature range 130–220 K (and also <130 K) the spectra exhibit a Pake doublet lineshape, which is the characteristic lineshape exhibited by ^{2}H nuclei experiencing an axially symmetric environment. The separation ($\Delta\nu$) between the inner discontinuities decreases from 66.2 to 65.2 kHz, corresponding to an effective observed nuclear quadrupole coupling constant of 87–88 kHz (*cf.* 90.7 kHz observed in 2H-SnS$_2$$\{Co(\eta\text{-}C_5D_5)_2\}_{0.33}$).[4] This value is approximately half that expected for a static C–D bond in a rigid aromatic molecule[15] and is consistent with the rapid (>10^8 Hz) reorientation of both $\eta\text{-}(C_5D_5)_2$ rings about their C_5 axes.[4]

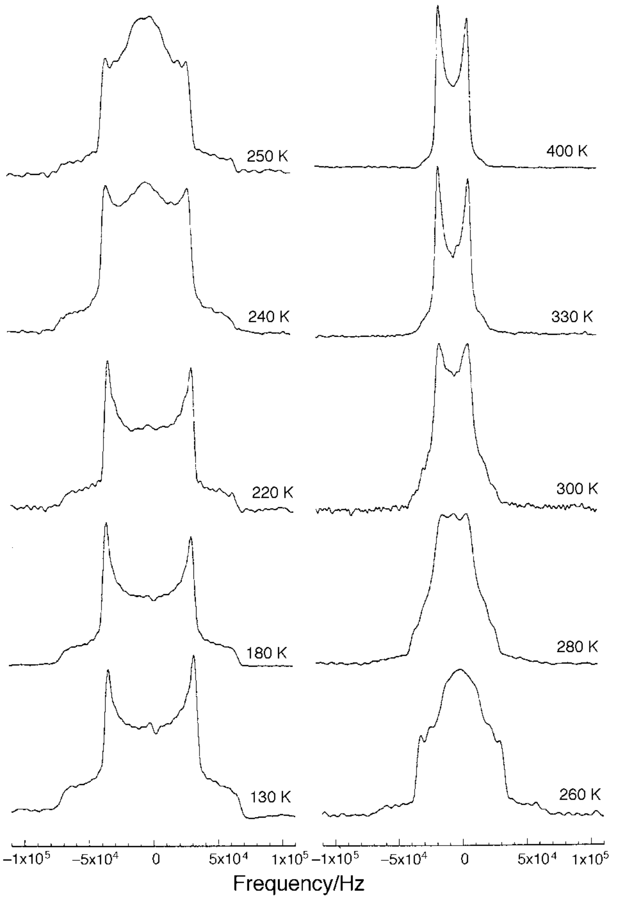

Fig. 1 Variable temperature static solid state ^{2}H NMR spectra of a polycrystalline sample of Laponite$\{Co(\eta\text{-}C_5D_5)_2\}_{0.4}$. Spin echo delay = 30 μs, recycle delay = 5 s. Number of transients varied from 512 to 1024.

As the temperature is increased above 230 K, an inner component emerges in the spectra (see Fig. 1) and the outer component diminishes. Above 330 K the inner discontinuities achieve a well defined splitting of 22.3 kHz, with no evidence for the original outer component. The decrease in the magnitude of the splitting is indicative of an increase in the motional degrees of freedom of the metallocene, *i.e.* the cobaltocenium molecules undergo motion in addition to that arising from the cyclopentadienyl ring rotation. In the temperature range 220–330 K there is a coexistence of cobaltocenium ions which are (a) undergoing reorientation about the C_5 axis only, which reduces the NQCC by a factor of half and (b) undergoing concurrent reorientation which further reduces the NQCC. After 330 K, the spectra remain unchanged, with a splitting of 22.3 kHz, up to 430 K. At 440 K an isotropic singlet was solely observed, which persisted on cooling to 400 K. This indicated decomposition of the sample, confirmed by its appearance when it was retrieved from the spectrometer.

The variation of $\Delta\nu$ of the outer component with temperature, shown in Fig. 2 appears to be linear, decreasing with a gentle gradient until the onset of the inner component at *ca.* 230 K, at which point the decrease in separation of the outer discontinuities is more appreciable. The gradual decrease is consistent with the notion that the principal molecular axis of the cobaltocenium molecules is slightly non-axially symmetric, owing to an additional vibrational-type averaging of the deuteron EFG tensor over a restricted angular range. Such motion might also be expected to increase in magnitude with the additional onset of further motional degrees of freedom.

Based on previous solid state ^{2}H NMR spectra and simulations of cobaltocenium intercalates of this kind, the powder samples of Laponite$\{Co(\eta\text{-}C_5D_5)_2\}_{0.4}$ indicate that

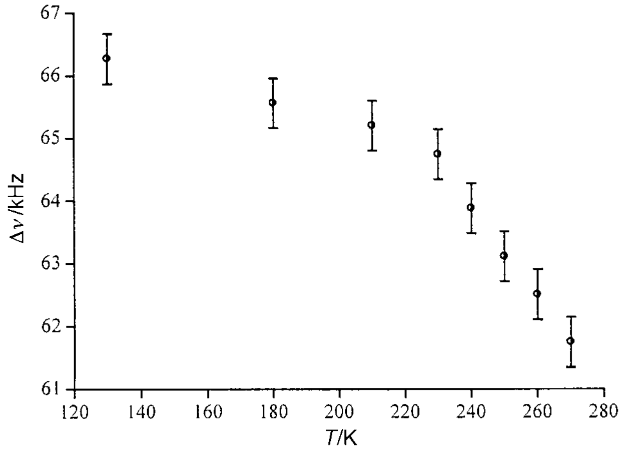

Fig. 2 Plot of the separation of the discontinuities, Δν, in the static solid state ^{2}H NMR spectra of a powder sample of Laponite{$Co(\eta\text{-}C_5D_5)_2$}$_{0.4}$ over the temperature range 130–270 K.

the cobaltocenium ions are probably locked tightly between the layers at low temperatures ($T < 230$ K) by the guest–guest and host–guest interactions and adopt a single orientation parallel to the layers. In order to determine the extent of preferred orientation adopted within the layers and further elucidate the orientation dynamics of the inter-layer cobaltocenium cations, it was necessary to perform ^{2}H NMR experiments on oriented thin film samples of Laponite{$Co(\eta\text{-}C_5D_5)_2$}$_{0.4}$.

Static solid state ^{2}H NMR studies on oriented films of Laponite{$Co(\eta\text{-}C_5D_5)_2$}$_{0.4}$

^{2}H NMR of oriented films of the material allow us to unambiguously ascertain whether the cobaltocenium ions intercalated into LaponiteRD lie with their principal axes parallel or perpendicular to the layers. Fig. 3 shows two postulated orientations and motions for the $[Co(C_5D_5)_2]^+$ molecule in layered materials. In the absence of a powder averaged distribution all molecules would be aligned either (a) perpendicular or (b) parallel, when the static magnetic field is aligned perpendicular to the basal plane. Based on a nuclear quadrupole coupling constant of 177 kHz extracted from the powder data, the expected splittings of the discontinuities would be: (a) 133 kHz for the perpendicular orientation, and (b) 66.4 kHz for the parallel orientation. When single crystals of 2H-SnS_2 were intercalated with $Co(C_5D_5)_2$, the value of the splitting was predicted to be 68 kHz (based on a NQCC of 181 kHz) for the parallel orientation, in agreement with the experimentally observed values.[4]

Since it was not possible to obtain large single crystals of Laponite{$Co(\eta\text{-}C_5D_5)_2$}$_{0.4}$, a sample comprising of a stack of oriented platelets was prepared. First oriented platelets of pristine Laponite were prepared on microscope cover slides. Once dry, these were then treated with saturated acetone solutions of $[Co(\eta\text{-}C_5D_5)_2]^+PF_6^-$ to produce oriented films of Laponite{$Co(\eta\text{-}C_5D_5)_2$}$_{0.4}$. After washing and drying the supported films were inserted into the 5 mm NMR tubes, as shown in Fig. 4.

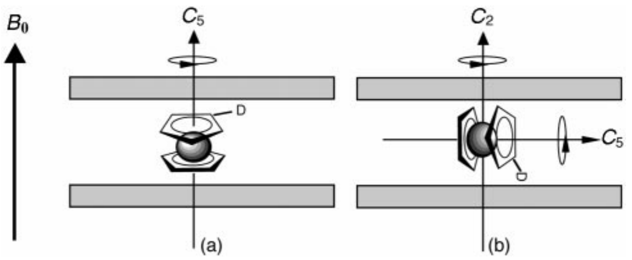

Fig. 3 Two postulated orientations and motions for the $[Co(C_5D_5)_2]^+$ molecule in layered materials.

The 210 and 298 K solid state ^{2}H NMR spectra of oriented films of Laponite{$Co(\eta\text{-}C_5D_5)_2$}$_{0.4}$ are shown in Fig. 5, with the stacking axis of the films oriented parallel to the field. The spectra consist of a broad doublet with separations of 64.5 and 56.4 kHz, respectively (the small peak at 0 Hz in the 210 K spectrum is an artefact). The doublet in the spectrum is similar to, yet broader than that reported previously for single crystals of SnS_2{$Co(\eta\text{-}C_5D_5)_2$}$_{0.3}$,[4] and more reminiscent of the spectrum reported for V_2O_5{$Co(\eta\text{-}C_5D_5)_2$}$_{0.2}(H_2O)_{0.5}$.[7]

At 210 K, the splitting between the discontinuities of 64.5 kHz is indicative of the cobaltocenium ions lying with their principal molecular axes perpendicular to the magnetic

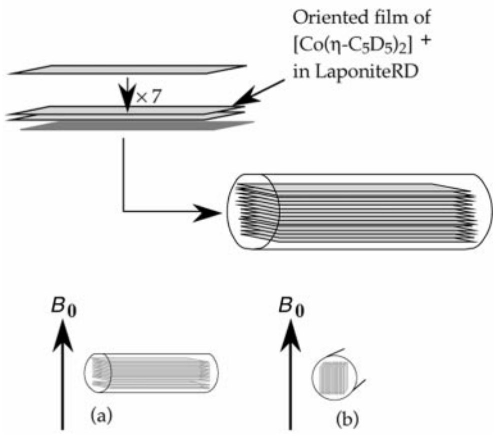

Fig. 4 Preparation of platelets in an NMR tube and alignment of the stacking axis (a) parallel and (b) perpendicular to the magnetic field.

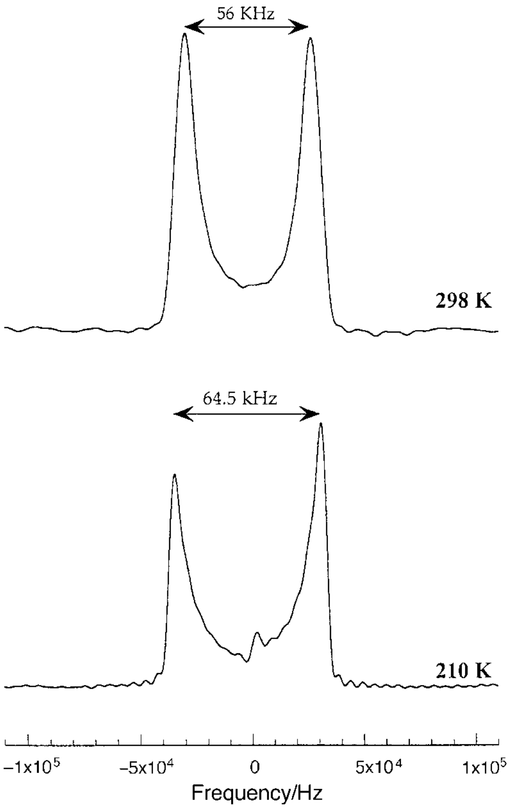

Fig. 5 Static solid state ^{2}H NMR spectra of an oriented sample of Laponite{$Co(\eta\text{-}C_5D_5)_2$}$_{0.4}$ at 210 and 298 K. Spin echo delay = 30 μs, recycle delay = 5 s. Number of transients = 3300.

field, and hence parallel to the silicate layers. There is no evidence in the spectrum of peak intensity beyond this feature, and so we can conclude that no guest ions are held perpendicular to the field, which would give rise to a splitting of 133 kHz. The tailing of the intensity towards the centre of the doublet suggests a distribution of orientations of the intercalated molecules relative to the static field $\boldsymbol{B}_0$ (z-axis). Such a phenomenon can now readily be explained through simulations of the ^{2}H NMR lineshape described in ref. 7. The solid state ^{2}H NMR lineshape simulations were performed with the intention of determining the extent of disorder of the orientations of cobaltocenium ions within layered materials such as Laponite$\{Co(\eta\text{-}C_5H_5)_2\}_{0.4}$, and can be modified in order to allow a weighted distribution of orientations of the guest principal axes.

The simulation shown in Fig. 6 is a weighted summation of the solid state ^{2}H NMR simulated lineshapes calculated for discrete orientations about an angle of 90° to the field $\boldsymbol{B}_0$. The angular distribution function that best reproduced the experimental spectrum of Laponite$\{Co(\eta\text{-}C_5D_5)_2\}_{0.4}$ at 210 K was a Gaussian function with a standard deviation, $\sigma = 15.8°$, also shown in Fig. 6. The tailing of intensity in the room temperature (298 K) spectrum, which appeared closer to a Gaussian function with a standard deviation of 31°, indicates a greater extent of disorder. Two descriptions of the system can be put forward to rationalise this disorder: the first possibility is that the silicate layers are stacked in perfect registry and the range of orientations observed in the ^{2}H NMR spectra reflect a variety of guest orientations within the layers. The alternative explanation is that the $[Co(Cp)_2]^+$ ions are aligned with their principal axes at 90° to the silicate layers, and the distribution is a consequence of stacking faults in the LaponiteRD film. If stacking faults existed, *i.e.* the layers of the Laponite clay did not lie perfectly parallel, there would obviously be angular deviations from layers that were perpendicular to the stacking axis (c axis). This phenomenon (turbostatic disorder) would be in addition to disorder in the ab plane (turbostratic disorder). Imperfect stacking of the Laponite layers would give rise to a range of orientations of the principal molecular axes of the intercalated cobaltocenium ions relative to the spectrometer field. This is illustrated in Fig. 7. We presume that since the spectra were easily simulated using a series of layers with some stacking faults, that most of the molecules were in fact residing within the layers rather than at edge sites or exposed basel surfaces where they might be expected to have much more motional freedom.

In the case of $V_2O_5\{Co(\eta\text{-}C_5D_5)_2\}_{0.2}(H_2O)_{0.5}$, it was proposed that a range of orientations of the cobaltocenium ions within the layers could not be tolerated, owing to the expectation of dynamic ordering of guest orientations, which would be observed as dynamic ordering of the spectrum at higher temperatures.[7] Since the ^{2}H NMR spectrum of a powdered sample of the material was virtually independent of temperature, even up to 450 K, a turbostatic model seemed highly favourable. For the clay intercalate, this assumption is less reasonable to make, given that the lineshapes of the powder sample show significant dynamic averaging at temperatures exceeding 230 K. Furthermore, an increased amount of disorder is evident in the oriented samples of Laponite$\{Co(\eta\text{-}C_5D_5)_2\}_{0.4}$ at room temperature, since $\Delta\nu$ decreases from 64.5 to 56.4 kHz in the ^{2}H NMR spectrum. This can be attributed to additional rapid vibrational-type averaging of the deuteron EFG tensor over a restricted angular range. Turbostatic disorder is therefore a significant contributor, but not the only factor to account for the observed lineshapes in this case. It can be concluded that the cobaltocenium ions are not rigidly held within the layers of Laponite$\{Co(\eta\text{-}C_5D_5)_2\}_{0.4}$, as a result of relatively weak guest–host interactions.

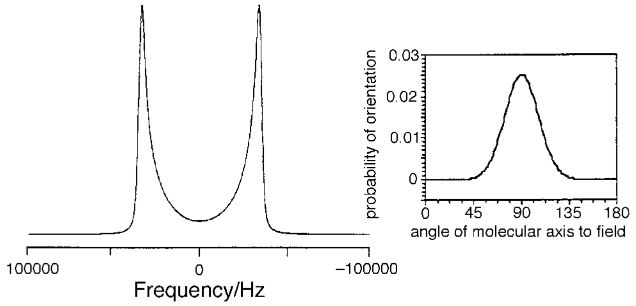

Fig. 6 Simulation of the static solid state ^{2}H NMR spectrum for an axial EFG tensor (NQCC = 92 kHz) distributed in a plane about an angle of 90° to the field, together with the distribution of disorder in the Euler angle, θ. The function is a Gaussian with standard deviation, $\sigma = 15.8°$, and describes the orientation of the principal molecular axes of the intercalated cobaltocenium ions relative to the spectrometer field.

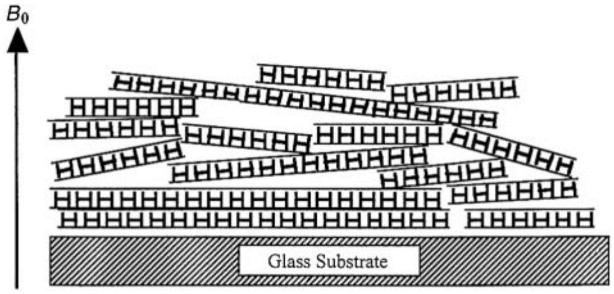

Fig. 7 Schematic to illustrate the stacking faults relative to the c axis in oriented films of Laponite$\{Co(\eta\text{-}C_5D_5)_2\}_{0.4}$ (turbostatic disorder) which might give rise to a range of orientations observed in the ^{2}H NMR spectrum. Disorder is also expected in the ab plane (not shown).

The orientation of the cobaltocenium ions, and the provisionally established turbostatic disorder in the sample can also be verified by examining the spectra of oriented thin films of Laponite$\{Co(\eta\text{-}C_5D_5)_2\}_{0.4}$ with the stacking axis perpendicular to the field $\boldsymbol{B}_0$. Static disorder in the stacking of the layers of thin films, and motional freedom additional to rotation about the C_2 and C_5 axes will be evident if the principal molecular axes of the cobaltocenium ions are not confined to a two dimensional plane. A room temperature ^{2}H NMR spectrum of thin films of Laponite$\{Co(\eta\text{-}C_5D_5)_2\}_{0.4}$ with the stacking axis perpendicular to the magnetic field is shown in Fig. 8, together with lineshape simulations for randomly distributed orientations of a C–D bond within a 2-D plane. One distribution is modelled with the host layers well aligned, and the other distributed about angles of 45 and 135° to the field in the 2-D plane, a Gaussian function with a standard deviation of 31° was used.

In the room temperature static solid state ^{2}H NMR spectrum of the oriented film perpendicular to the field shown in Fig. 8, the presence of a prominent inner component with poorly defined discontinuities ($\Delta\nu = ca.$ 18 kHz) can be observed. The spectrum can be considered to be a superposition of two Pake doublets, and it must be noted that for the range of orientations and dilute nature of the intercalate (thin clay layers on a glass substrate), a relatively high signal to noise ratio can be anticipated. The outer doublet, with a $\Delta\nu$ of *ca.* 62 kHz is similar to the pattern observed in the ^{2}H NMR spectrum for the powder sample at $T < 230$ K. The continuous profile of the outer component suggests that the cobaltocenium ions exist in all possible parallel orientations with respect to the magnetic field. This data alone cannot provide evidence that the thin films of Laponite$\{Co(\eta\text{-}C_5D_5)_2\}_{0.4}$ are ordered with respect to each other in the lateral plane (ab plane) owing to the additional rapid reorientation of the cobaltocenium molecules about the C_2 axis in this plane [depicted in Fig. 3(b)], and it is therefore conceivable that the spectrum is representa-

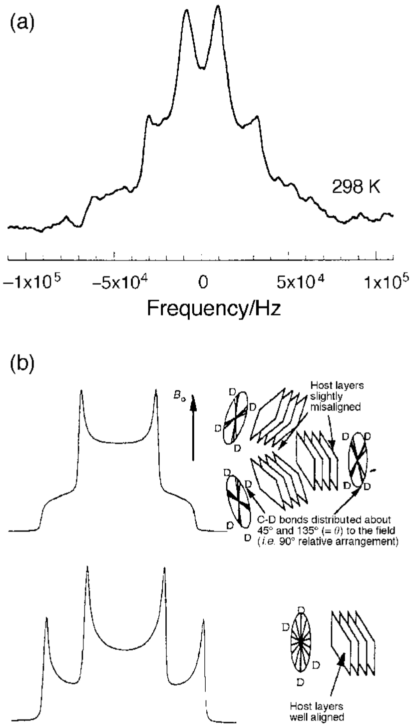

Fig. 8 (a) Room temperature ^{2}H NMR spectrum of an oriented film of Laponite{Co(η-C_5D_5)$_2$}$_{0.4}$ with the stacking axis perpendicular to the field. Spin echo delay 36 μs, recycle delay 2 s, number of transients = 9300. (b) Simulations of the solid state ^{2}H NMR spectrum for an axial EFG tensor (NQCC = 92 kHz) distributed in a 2-D plane about an angle of 45 and 135° to the field (top). A well aligned series of layers is shown for comparison (bottom).

tive of random orientations of the $Co(C_5D_5)_2^+$ ions with their principal axes parallel to the planes but with a range of orientations with respect to each other.

Comparison of the solid state ^{2}H NMR spectrum with the simulations shown in Fig. 8 suggest that there is considerable disorder in the stacking of the Laponite{Co(η-C_5D_5)$_2$}$_{0.4}$ layers. The 'feet' of the outer Pake doublet appear to decline in intensity with increasing frequency, and there is no evidence for an outer discontinuity of significant intensity, which is present in the simulation for well aligned host layers. The extent of disorder ($\sigma = 31°$) is in good agreement with that observed previously for oriented films of Laponite{Co(η-C_5D_5)$_2$}$_{0.4}$ with the stacking axis parallel to the field.

The inner doublet has a $\Delta\nu$ approximately equal to 1/3 NQCC, and is reminiscent of the motional averaging observed at temperatures exceeding 330 K. This doublet is due to cobaltocenium ions undergoing motional averaging additional to rapid reorientation about the C_5 axis. Dynamic averaging of the cobaltocenium ions due to reorientation about the C_2 axis would not be reflected in this spectral profile if the layers were in perfect registry and parallel to the field (stacking axis perpendicular to $\boldsymbol{B}_0$). However the contribution of this motion explains the inner doublet present in the spectrum, and provides evidence for the model of turbostatic disorder. Overall, the spectrum appears to describe a series of randomly distributed cobaltocenium ions with their principal axes parallel to the layers of the clay, approximately half of which are undergoing rapid reorientation about the C_5 axis only, whereas the rest have additional motional freedom.

Conclusions

The intercalation of the Co(η-C_5D_5)$_2^+$ ions into the clay LaponiteRD ($Na_{0.46}Mg_{5.42}Li_{0.46}Si_8(OH)_4O_{20}$) gives an ordered arrangement of the cobaltocenium cations with their principal molecular axes parallel to the silicate layers. The compound exhibited some similar characteristics to Co(η-C_5D_5)$_2$/layered host systems we have studied previously by solid state ^{2}H NMR spectroscopy, in terms of the guest dynamics, and also demonstrated its own unique behaviour. The solid state ^{2}H NMR spectra of oriented thin films of the intercalate gave clear evidence for the extent of ordering of the host layers, and of the orientation of the cobaltocenium ions. The emergence of an inner component with a splitting of 22.3 kHz over the temperature range 220–300 K, strongly suggests the molecule is undergoing *n*-fold reorientations about the C_2 axis of symmetry. This motion alone would effectively halve the observed splitting, from 66.4 to 33.2 kHz. Concurrent to this dynamic motion is an additional vibrational motion, a 'wobble' in the slow–intermediate regime which slightly reduces the splitting of the outer discontinuities. The vibrational motion increases with temperature until the fast regime is reached, causing the splitting to be reduced to 22.3 kHz. The motion can be thought of as a rapid vibration of the cobaltocenium ion to a small angular extent about a mean orientation that averages the EFG tensor to reduce the splitting by 2/3. A rotation about a second C_2 axis would be expected to reduce the splitting by 1/2 and can therefore be ruled out. This vibration, combined with the rotation about the C_2 axis, causes an overall gyratory motion of the molecule between the silicate layers, as depicted in Fig. 9.

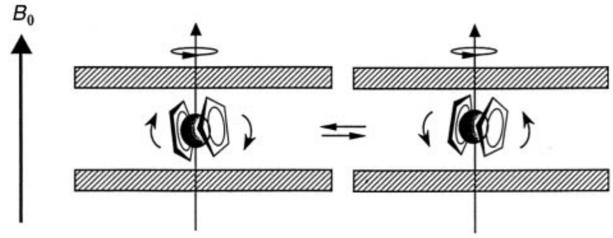

Fig. 9 Schematic to describe the additional motion to *n*-fold reorientations about the C_5 and C_2 axes: rapid vibrational-type averaging of the deuteron EFG tensor over a restricted angular range.

The overall spectral profile observed in the temperature range 220–330 K effectively represents a range of dynamic processes of the molecule in the interlamellar space, due to a Boltzmann distribution of cobaltocenium ions that gain orientational freedom with increasing temperature. The reason for this increased gain in motional freedom could be due to the presence of water molecules in the system. At lower temperatures much of the water will move out of the interlayer space and form small ice crystals in the interparticulate void space. As the temperature is increased this ice will melt and re-enter the clay galleries and may act as a molecular grease for organometallic motion. For example, reorientation about the C_2 axis may not be possible for the molecules at $T < 230$ K owing to packing restrictions, which are relaxed with the introduction of more water molecules at $T > 230$ K. Rapid ring reorientation about the principal molecular axis is already in the fast regime at 220 K (> 10^8 Hz). Increasing the temperature above 220 K provokes the onset of reorientation about the C_2 axis and increases vibrational motion, causing a distribution of metallocene molecules to undergo motional averaging in the regime 10^3–10^7 Hz. Above 330 K the additional motional averaging is in the fast regime for the majority of cobaltocenium ions.

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