Structure of Cobaltocene in SnS_2: a Single Crystal Solid State ^2H NMR Study

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Solid state ^2H NMR spectra of single crystals of 2H-SnS_2 intercalated with cobaltocene $[Co(\eta\text{-}C_5D_5)_2]$ indicate that the guest molecules are ordered within the host layers with their principal axes parallel to the host layers.

The orientation of metallocenes such as $[Co(\eta\text{-}C_5H_5)_2]$ and $[Cr(\eta\text{-}C_5H_5)_2]$ intercalated into lamellar host lattices has been the subject of a long-running discussion.[1–3] Owing to the almost spherical shape of an unsubstituted metallocene, the lattice expansion resulting from intercalation, as measured by X-ray powder diffraction, does not definitively establish the orientation of this guest molecule in the interlayer space.[4] Recently, the ^2H NMR powder lineshapes, obtained in a study of $[Co(\eta\text{-}C_5D_5)_2]$ intercalated into microcrystalline 2H-TaS_2, were interpreted by the coexistence of $[Co(\eta\text{-}C_5D_5)_2]$ molecules with their principal axes both parallel and perpendicular to the lattice layers (see Fig. 2), with different dynamic behaviour in each orientation.[5] In this communication we describe a ^2H solid state NMR study of $[Co(\eta\text{-}C_5D_5)_2]$ intercalated into both microcrystalline and single crystals of the related material 2H-SnS_2 and demonstrate that by suitable orientation of the single crystals in the magnetic field we can obtain unambiguously the orientation of the cobaltocene molecules in this host lattice.

Rapid full (1st stage) intercalation of the microcrystalline 2H-SnS_2 was achieved in 3–4 h by treatment, at room temperature, with a concentrated solution of $[Co(\eta\text{-}C_5D_5)_2]$ in 1,2-dimethoxyethane (DME). Fig. 1 shows representative ^2H NMR spectra obtained from these samples in the temperature range 240–350 K. The spectra at low temperatures ($\leqslant$240 K) show the characteristic 'Pake doublet' expected for a ^2H ($I = 1$) nucleus in an axially symmetric environment. The effective observed quadrupole coupling constant, of 90.7 kHz is about half that expected for an aromatic C–^2H bond in a rigid molecule.[6] This is consistent with the rapid ($>10^8$ s^{-1}) reorientation of the η-C_5D_5 rings about their C_5 axis which is known to occur in metallocenes at temperatures as low as 100 K.[7,8]

As the temperature is raised an inner component emerges for which the separation of the inner discontinuities is exactly half of the outer component, and by 350 K dominates the spectra; this behaviour is not dissimilar to that observed in the ^2H powder spectra of 2H-$TaS_2[Co(\eta\text{-}C_5D_5)_2]_{0.25}$[5] and 1T-$TaS_2[Co(\eta\text{-}C_5D_5)_2]_{0.25}$.[9] Fig. 2(*a*) shows the two orientations and low energy motional processes that have been postulated[9] for the cobaltocene molecule in these classes of materials. These powder ^2H NMR lineshapes and those obtained with varying spin echo delay times cannot be completely simulated[10] by assuming a single cobaltocene orientation parallel to the layers with the cyclopentadienyl rings undergoing rapid rotation about the metallocene C_5 axis, and the molecule as a whole undergoing *n*-fold reorientations around the C_2 axis of symmetry that is in the slow regime at 240 K but approaches the fast limit at 350 K. Improved simulations can be obtained, however, by assuming either (*a*) the coexistence of both the parallel and perpendicular orientations or (*b*) that all the molecules are parallel to the layers but with some of molecules being able to undergo reorientation around the C_2 axis and some not being able to (or do so with much slower rates), perhaps owing to packing restrictions. The ^2H powder spectra were, therefore, inconclusive in ruling out the existence of the perpendicular orientation.

If single crystals of 2H-SnS_2 (typically of dimensions 3 × 3 × 0.1 mm) are refluxed in a concentrated soution of $[Co(\eta\text{-}C_5D_5)_2]$ in DME for 2–3 weeks then complete intercalation can again be achieved. Fig. 2 demonstrates that by orienting a single crystal basal plane (crystallographic *a*–*b* plane) perpendicular to the static magnetic field we can obtain ^2H NMR spectra that could indicate the orientation(s) of the cobaltocene molecules. In the case of all interlamellar motion being rapid on the ^2H NMR timescale, we should observe only one sharp doublet per orientation, the expected splitting for each

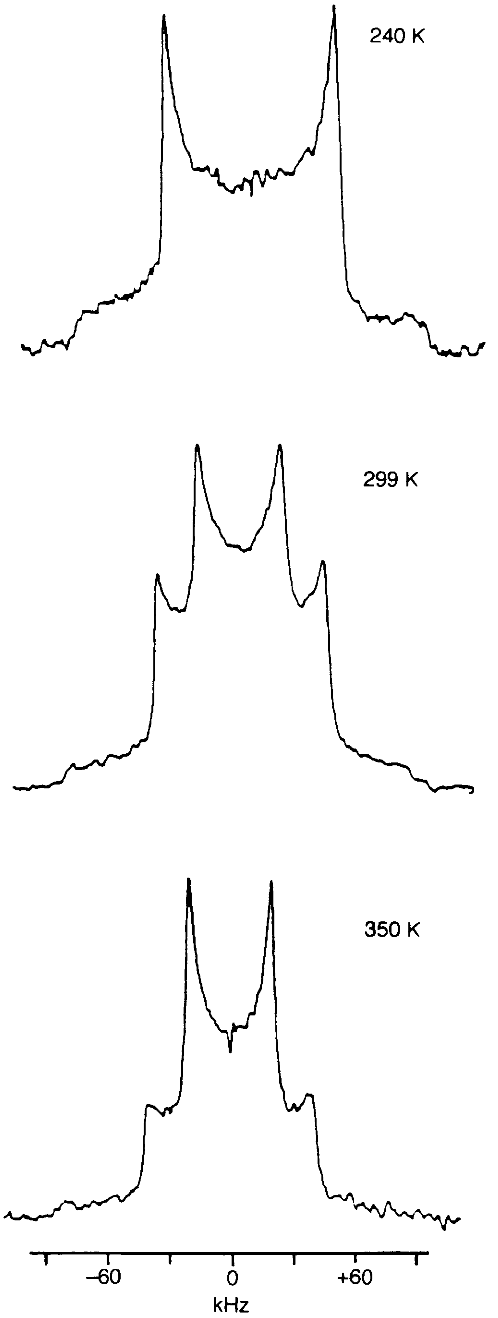

Fig. 1 Variable-temperature ^2H NMR spectra of $SnS_2[Co(\eta\text{-}C_5D_5)_2]_{0.33}$, recorded on a Bruker MSL200 spectrometer operating at 30.7 MHz. A quadrupolar spin echo sequence [$\pi_{/2}$–20 μs–$\pi_{/2}$–20 μs–observed] was used with $\pi_{/2}$ pulses of 1.5 μs. The temperature was maintained using a copper-constantan thermometer attached to a Bruker B-VT1000 temperature control unit.

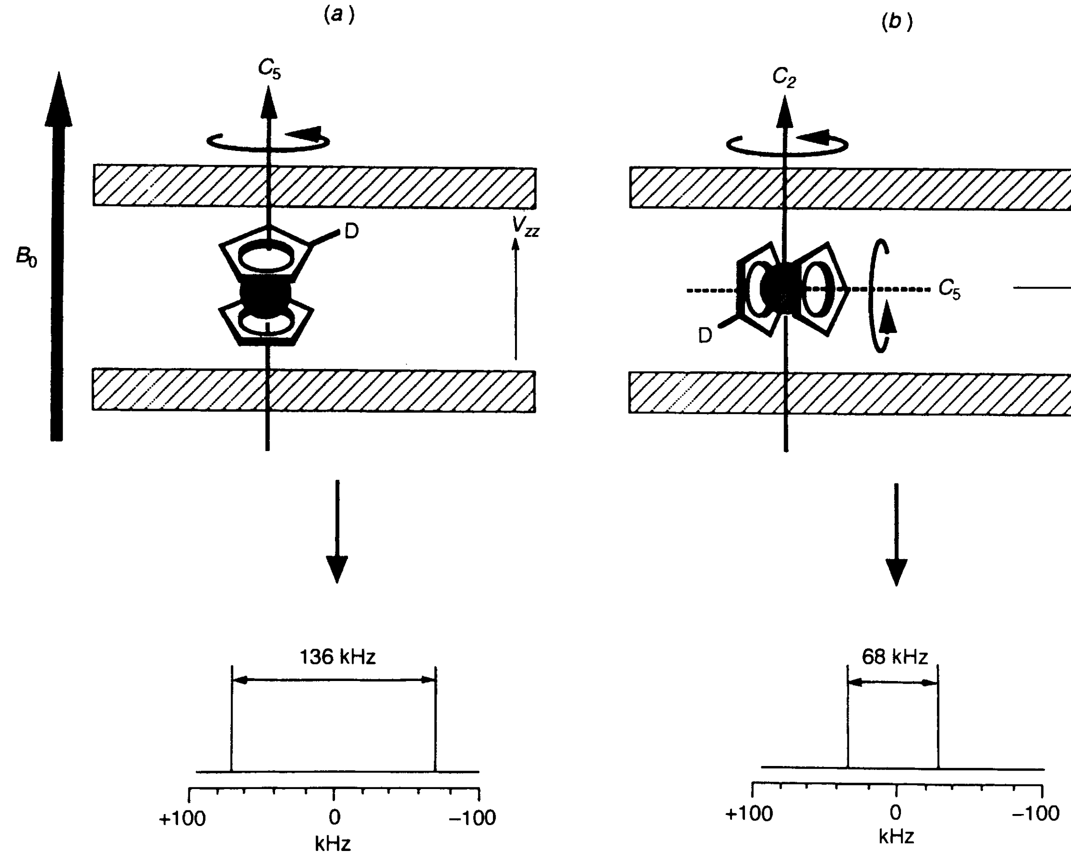

Fig. 2 The postulated motions for [Co(η-C_5D_5)$_2$] in the 2H-SnS_2 lattice in the (*a*) perpendicular and (*b*) parallel orientations and its predicted ^2H NMR spectra when the static magnetic field is aligned perpendicular to the basal plane. The doublet splitting is expected to be 136 kHz for the perpendicular and 68 kHz for the parallel orientation, based on a value for the nuclear quadrupole coupling constant of 181 kHz extracted from the ^2H NMR powder spectrum obtained at 240 K (Fig. 1). V_{zz} shows the direction of the principal component of the axial electric field gradient tensor.

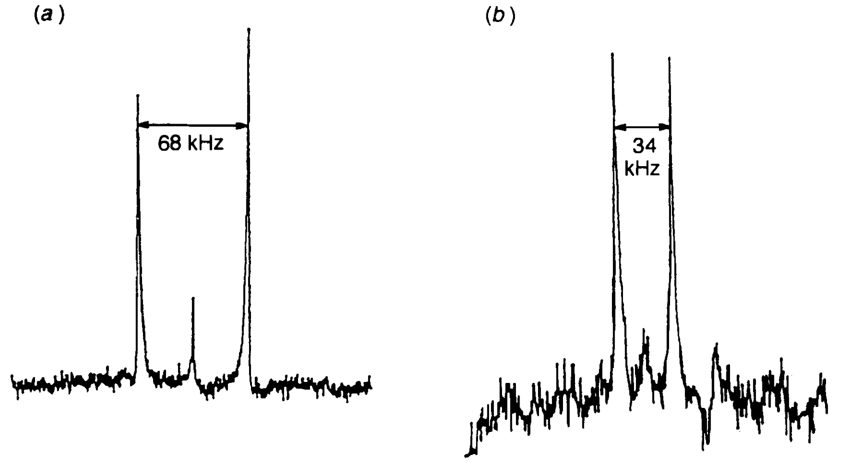

Fig. 3 ^2H NMR room temperature spectra of a single crystal of SnS_2[Co(η-C_5D_5)$_2$]$_{0.33}$ oriented with the single crystal basal plane (*a*) perpendicular and (*b*) parallel to the static magnetic field. Crystal alignment was accurate to within ±3°, which leads to an error in the measured splitting of ±2 kHz for (*a*) and 1 kHz for (*b*). Slight misalignments and crystal defects are most likely to be the cause of the broadening of the resonances. The spike at 0 ppm is an artifact. Each spectrum required approximately 30000 scans.

orientation being different. This is shown schematically in Fig. 2.

A single crystal of the intercalate was mounted on a flat glass plate within a sealed tube and mounted in the probe in such a way that its angle relative to the field could be measured to within ±3°. Fig. 3(*a*) shows the experimentally observed solid state ^2H NMR spectrum. Only one doublet is observed with a splitting of 68 kHz and is consistent, within the limits of the spectral signal to noise ratio, with the guest molecules adopting a single orientation with respect to the SnS_2 layers: the parallel orientation.

By orienting the crystal so that the magnetic field is parallel to the host lattice layers, we can then probe the rate of reorientation around the C_2 axis. In the fast exchange limit this motion, in addition to the rotation of the cyclopentadienyl ring will lead to a doublet splitting of approximately 34 kHz. This was observed experimentally for the spectrum of the single crystal shown in Fig. 3(*b*). Preliminary studies of other single crystals picked from the same initial sample gave spectra that were not all as simple as that shown in Fig. 3(*b*); broader components were observed at room temperature, the 34 kHz doublet only dominating the spectra at higher temperatures. These lineshapes result from cobaltocene molecules that are undergoing rotations about the C_2 axis at slower rates, and not in the fast limit. This appears to be indicative of a distribution of rates for rotation about this axis in these crystals.

^{2}H spectra from further single crystals all gave only one doublet with a splitting of 68 kHz when oriented perpendicular to the field and no evidence of the 136 kHz doublet was seen in any of the spectra. We can, therefore, conclude that in all the crystals we examined, the cobaltocene molecules are oriented parallel to the layers at room temperature.

This paper has demonstrated the advantages of performing solid state ^{2}H NMR studies on single crystals as opposed to polycrystalline samples of intercalation compounds in that the results can be interpreted straightforwardly to yield valuable information on the dynamics and orientation of the guest species; it is hoped, with the development of improved methods for the synthesis of large single crystals of these types of materials, that this will become a widespread method to yield information on the dynamics and orientations of cobaltocene and other intercalates in these types of host materials.

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