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## Evidence of Ordering of Cobaltocenium Ions in $SnSe_2\{Co(\eta\text{-}C_5D_5)_2\}_{0.3}$ Using Single-Crystal Solid State $^2H$ NMR Spectroscopy

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Solid state $^2H$ NMR spectroscopy is well established as a powerful technique for exploring molecular dynamics in a variety of solid state environments. It is ideally suited for studying the dynamics and orientations of guest molecules intercalated into inorganic lattices.[1] In this paper we demonstrate the power of single-crystal solid state $^2H$ NMR experiments to derive precise molecular orientations by describing our experiments on single crystals of the organometallic intercalation compound $SnSe_2\{Co(\eta\text{-}C_5D_5)_2\}_{0.3}$.

We have studied extensively the solid state and electronic structure of cobaltocene intercalates of the $SnSe_xS_{2-x}$ solid solution $\{0 \leq x \leq 2\}$ using a variety of physical techniques including X-ray photoelectron spectroscopy (XPS),[2] X-ray and neutron diffraction,[3] and electrical conductivity measurements.[4] In particular, we have characterized $SnSe_2\{Co(\eta\text{-}C_5D_5)_2\}_{0.3}$ as a type II superconductor with a $T_c = 8.3$ K and temperature-dependent critical fields $d\mathrm{H}_{c\parallel}/dt$ and $d\mathrm{H}_{c\perp}/dt$ of 0.09 and 0.19 T $K^{-1}$, respectively.[5] We believe that this material has currently the highest superconducting critical temperature of any intercalation compound, with a remarkably low anisotropy in the derived Ginberg–Landau coherence lengths $\{\zeta(0)/\zeta_z(0)\}$ of *ca.* 2.[5] We have been interested in determining the arrangements of organometallic sandwich complexes intercalated into lamellar solids for some time.[6] In particular, most intriguing structural questions involve the determination of whether the metallocenes lie with their molecular axes parallel or perpendicular to the host layers and whether the molecules are ordered in terms of their packing within the interlamellar space. However, in general the crystal chemistry of intercalation compounds is complex and presents very difficult crystallographic problems due to the disorder inherent in such samples. The question of whether there is two-dimensional order of guests in the interlamellar space remains especially elusive. Therefore, we have been interested in developing additional physical techniques which might yield further structural information.

Treatment of crystals of $SnSe_2$ (*ca.* 1 × 1 × 0.1 mm, grown by iodine vapor phase transport) with a saturated solution of $Co(\eta\text{-}C_5D_5)_2$ in toluene at 120 °C for 1–2 weeks results in complete intercalation, giving crystals of a first-stage compound of chemical composition $SnSe_2\{Co(\eta\text{-}C_5D_5)_2\}_{0.3}$.[7] The lattice expansion ($\Delta c = 5.3$ Å) and the chemical composition are consistent with close packing of cobaltocene molecules between the chalcogenide layers of the host. The quadrupolar echo solid state $^2H$ NMR spectrum of a crystal of $SnSe_2\{Co(\eta\text{-}C_5D_5)_2\}_{0.3}$ orientated with the layer planes (crystallographic *ab*-plane) perpendicular to the static magnetic field is shown in Figure 1.

A single quadrupolar doublet is observed, indicating that one chemically unique deuteron environment is present within the chalcogenide layers. The doublet is centered about the isotropic chemical shift with a quadrupolar splitting of 67 kHz and can be assigned to the diamagnetic $[Co(\eta\text{-}C_5D_5)_2]^+$ cations. In contrast to a microcrystalline sample, in a single crystal only one orientation of the host lattice is presented to the static field. This means that any orientational preferences of the $[Co(\eta\text{-}C_5D_5)_2]^+$ molecules within the host layers will result in a correspondingly restricted distribution of orientations of the effective field gradient (EFG) tensors of $^2H$ nuclei in the spectrometer field and thus will be reflected in the solid state $^2H$ NMR spectral profile. The rapid $C_5$ rotation of the cyclopentadienyl rings in metallocenes at room temperature results in the principal (*zz*) component of the averaged axially symmetric effective electric field gradient (EFG) tensors of all of the $^2H$ nuclei being along the principal molecular axis. Therefore the $^2H$ NMR single doublet with a 67 kHz separation

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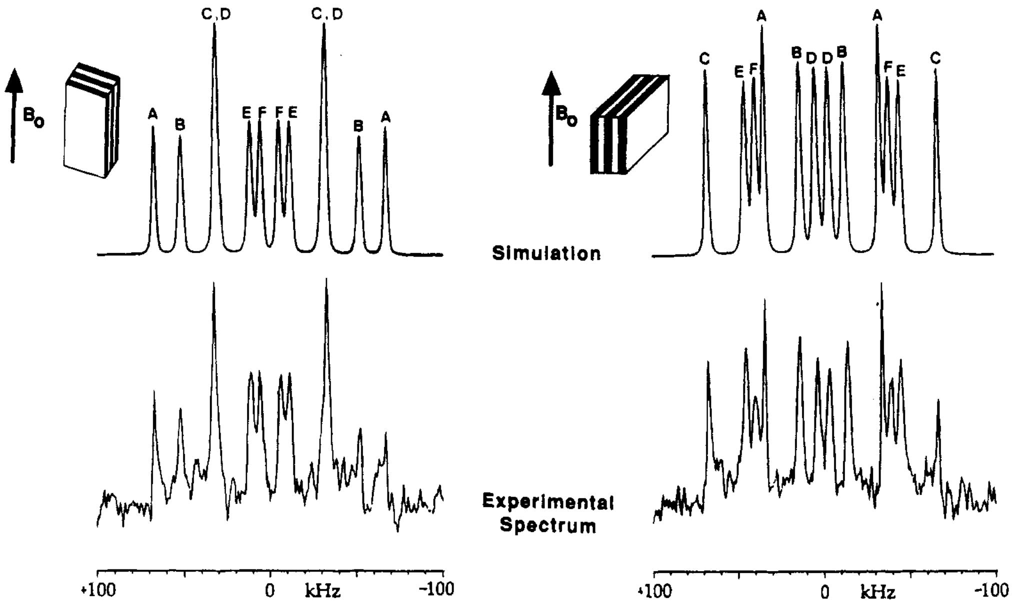

**Figure 1.** (Bottom) Room-temperature 61.4 MHz solid state $^2$H NMR spectra of a crystal of $SnSe_2\{Co(\eta\text{-}C_5D_5)_2\}_{0.3}$ in two different orientations, both with the stacking axes perpendicular to the field. The quadrupolar spin echo sequence $[(\pi/2)_x-30\ \mu s-(\pi/2)_y-30\ \mu s-\text{observe}]$ with full phase cycling was used with $\pi/2$ pulses of 1.5 $\mu$s and a recycle delay of 5 s. (Top) $^2$H NMR line shape simulation assuming equal populations of six different metallocenium orientations to the field (A–F), as described in the text, and a $e^2qQ/h$ of 90 kHz. The variation of peak height arises from a small distribution in the angular orientations; the best fit was observed with a Gaussian distribution about each mean orientation with $\sigma$ = 0.70°.

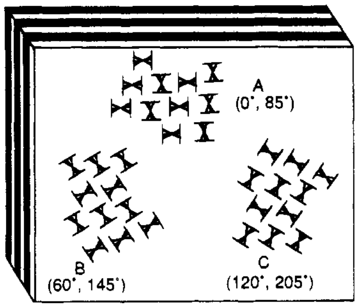

**Figure 2.** Schematic illustration of the three domains of differently oriented cobaltocene molecules present within the host lattice in the compound $SnSe_2\{Co(\eta\text{-}C_5D_5)_2\}_{0.3}$. The domains are probably larger than shown and are not necessarily in the same layer.

is consistent with rapid rotation of the cyclopentadienyl rings about the $C_5$ molecular axis and with all the molecules lying with their $C_5$ axes perpendicular to the stacking axis (*c*-axis), i.e. within the interlamellar plane. The observation of a single isotropic chemical shift is consistent with the existence of only cobaltocenium ions within the $SnSe_2$ layers.

In order to study the dynamics or orientational preferences of the guest molecules within the *ab*-plane, the $^2$H NMR spectra of the $SnSe_2\{Co(\eta\text{-}C_5D_5)_2\}_{0.3}$ crystals were measured for two additional orientations. We choose two orthogonal directions perpendicular to the stacking axis (crystallographic *c*-axis) of the crystal (Figure 1). The solid state $^2$H NMR spectra for the crystals recorded with the crystal stacking axes oriented perpendicular to the magnetic field are shown in Figure 1. It can be seen that each spectrum consists of a number of doublets, indicative of a discrete number of orientations for the $[Co(\eta\text{-}C_5D_5)_2]^+$ molecules within the host lattice.

From the doublet separations in the two spectra of each crystal, the experimentally determined orientations [assuming a quasistatic nuclear quadrupole coupling constant $e^2qQ/h$ = 90.0 kHz] of the principal molecular axes of the intercalated cobaltocenium ions were calculated to be as follows relative to the first orientation (labels A–F refer to the assignment of doublets in Figure 1): A, 0° (±2); B, 25° (±0.6); C, 85° (±2); D, 145° (±0.6); E, 120° (±1); F, 60° (±0.6). Simulations of the $^2$H NMR spectra based on equal population of metallocenium ions arranged in the *ab*-plane relative to each other at each of these angles reproduce the experimental spectra as shown in Figure 1.[8] The accuracy of the angular assignments for the principal molecular axes of the $[Co(\eta\text{-}C_5D_5)_2]^+$ ions depends on two factors: the accuracy to which the $^2$H NMR doublet separations can be determined and the sensitivity of the doublet separation to the molecular orientation relative to the field. Despite very conservative error estimates, this experiment leads to an extremely precise determination of the cobaltocenium orientations within the interlamellar plane.

In Figure 2 we present a proposed structural model which accounts for the six molecular orientations. The six guest ion orientations can be divided into three domains, with molecules oriented at (0°, 85°), (60°, 145°), and (120°, 205° ≡ 45°) in each domain, respectively. This model involves two independent molecules oriented at 85° to each other in each domain, and each domain is related by a rotation of ±60°. We believe the 60° relationship between domains arises from the 3-fold

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(8) The program NEWXTAL[9] was used to simulate the quadrupole spin-echo solid state $^2$H NMR spectral line shapes for a single crystal. Simulations of the $^2$H NMR quadrupole echo line shapes were performed by the weighted summation of line shapes calculated for discrete cobaltocenium orientations. For a given orientation (Euler angle $\theta$, $\phi$, $\psi$) of the axial $^2$H EFG tensor to the laboratory frame ($B_0$ along *z*-axis), the quadrupole frequency is given by $\nu_Q = \nu_0 \pm (3/8)(e^2qQ/h)(3\cos^2\theta - 1)$. Spectra simulations were performed by calculation and summation of the $^2$H NMR quadrupole FID's (calculated from $\nu_Q$ with the Bloch equations) at given orientations of the cobaltocenium ion principal $C_5$ axis to the applied field (denoted by the Euler angle, $\theta$); subsequent convolution of the total FID with Gaussian and Lorentzian line-broadening functions where necessary; Fourier transformation; and finally application of a Bloom correction factor[13] to account for power roll-off effects in the experimental spectra.

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symmetry of the close-packed selenium layers. 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; it is possible the different domains at 60° to each other correspond to separate interlayer regions. Similar orientations for phthalocyanine molecules deposited upon surfaces of $SnS_2$ and $MoS_2$ have been reported using electron diffraction techniques.[10] In this study, three domains oriented at 60° were observed; however, the two molecules within each domain were thought to subtend an angle of 90° with respect to each other.

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