

^2H NMR STUDIES OF METALLOCENES IN HOST LATTICES

Nigel J. Clayden, Christopher M. Dobson,
Stephen J. Heyes and Philip J. Wiseman
University of Oxford
Inorganic Chemistry Laboratory
South Parks Road Oxford OX1 3QR

We are using ^2H NMR spectroscopy in conjunction with lineshape simulations to investigate the structure and dynamics of organometallic compounds incorporated into a variety of host lattices. Here, the potential of this approach is illustrated with results from studies of perdeuterated Fecp_2 and Cocp_2^+ in different crystalline environments.

Figure 1 shows spectra of $\text{Cocp}_2^+\text{PF}_6^-$. At low temperature (160K) the spectrum exhibits a characteristic Pake doublet pattern with a splitting of 65 kHz. This splitting, half that expected for a rigid lattice, arises from rapid motional averaging about the principal axes of Cocp_2^+ , i.e. from rapid spinning of the cp rings, which is known to occur in metallocenes even at low temperatures [1]. At high temperature ($\geq 315\text{K}$) a single narrow line is observed, indicating that rapid, effectively isotropic motion is experienced by the Cocp_2^+ ions. This can be understood using a model proposed for $\text{Febzcp}^+\text{PF}_6^-$ from Mössbauer studies [2]. Between 308 and 314K a phase change occurs from a distorted (low temperature) to a regular (high temperature) cubic structure. In the former the Cocp_2^+ molecules are restricted to a defined orientation within the distorted cube of PF_6^- ions, whilst in the latter, fast hopping between different orientations, related by symmetry operations within the regular cubic structure, leads to effectively complete spherical averaging of the ^2H NMR spectrum. Another example where 'fast' motional averaging provides direct information about molecular orientation is the case of Cocp_2^+ in the intercalation compound $\text{TaS}_2-(\text{Cocp}_2)_{1/4}$, see figure 2. The spectrum at 296K shows two overlapping Pake doublets, one with a splitting of 65kHz, the other with a splitting of approximately half this value. This demonstrates that Cocp_2^+ is in two environments with different motional behaviour. A previous ^1H NMR study [3] concluded that the Cocp_2^+ ions were oriented with their principle axes parallel to the interlamellar plane, whereas an X-ray powder diffraction study of alkyl substituted metallocenes in TaS_2 and ZrS_2 [4] concluded that the axis was perpendicular to the plane. The ^2H NMR spectra are consistent with both orientations being present in the structure, providing that fast molecular motions are restricted in both cases to those about axes perpendicular to the layers. Then in the case of molecules with their

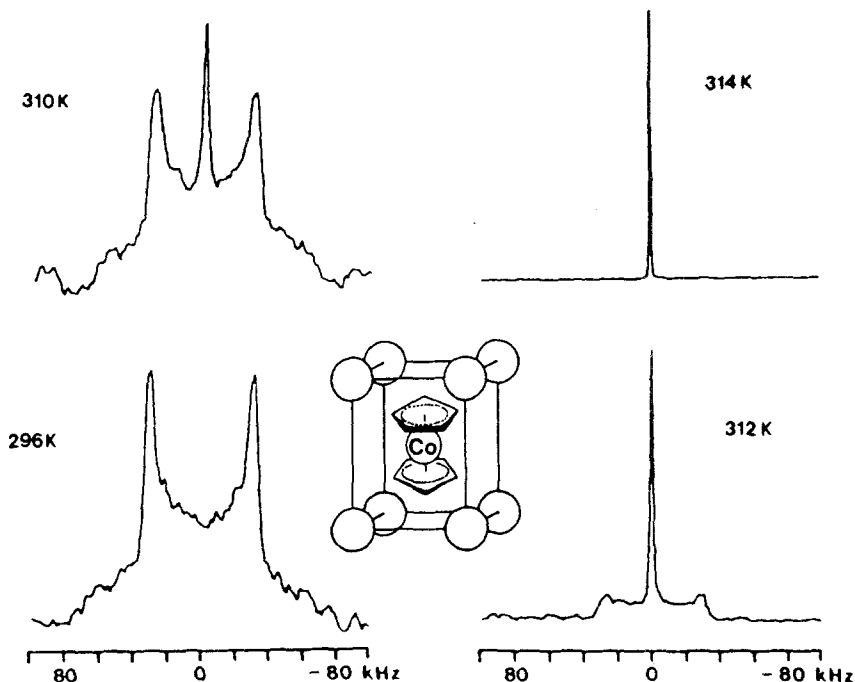


Figure 1: ^2H NMR spectra of $\text{Cosp}_2^+\text{PF}_6^-$. All spectra were recorded at 30.7MHz on a Bruker CXP200 spectrometer using a quadrupolar spin echo sequence with phase cycling.

principle axes parallel to the layers, calculations show that motional averaging results in a reduction by a factor of 2 in the splitting of the Pake doublet from the value of 65kHz anticipated for Cosp_2^+

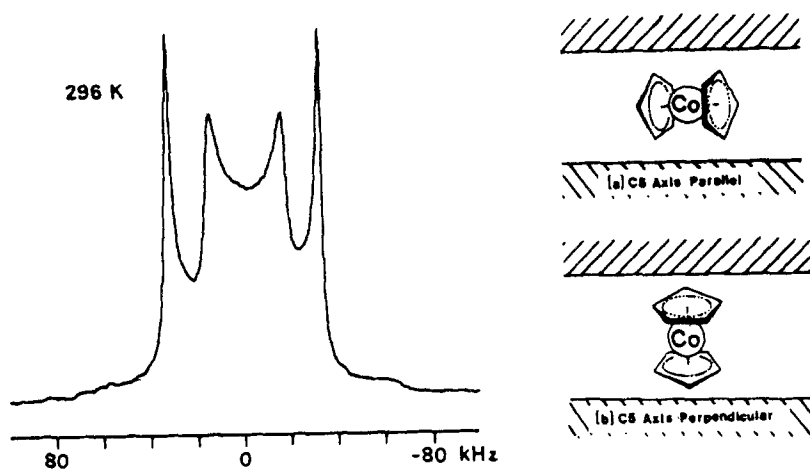


Figure 2: ^2H NMR spectrum of $2\text{H-TaS}_2\text{-(d}_{10}\text{Cosp}_2)_{1/4}$

experiencing motion only about the molecular axis [5].

Both these examples illustrate situations where the axes about which motion is possible are well defined by the lattice structures and the motion is always in the 'fast' limit compared to the ^2H nuclear quadrupole coupling constant (180kHz). ^2H NMR can, however, provide detailed evidence about the nature of more complex motions. Figure 3 shows an example of Fecp_2 in its thiourea clathrate. Here, as for $\text{Cocp}_2^+\text{PF}_6^-$, the ^2H NMR lineshape shows dramatic changes with temperature, but this time the changes are more gradual. At 160K the spectra show that the only fast motions involve the spinning of the cp rings about the molecular axis. At higher temperatures the changing lineshapes indicate the onset of more extensive motional averaging, although the motion is of limited amplitude until temperatures above 200K. The changes in the ^2H NMR spectra correlate well with the results of Mössbauer studies of this compound [6]. The existence of residual splitting in the ^2H NMR spectrum shows, however, that the motion is not entirely isotropic even at 300K, indicating that there are still preferred orientations of the rapidly reorienting ferrocene molecules.

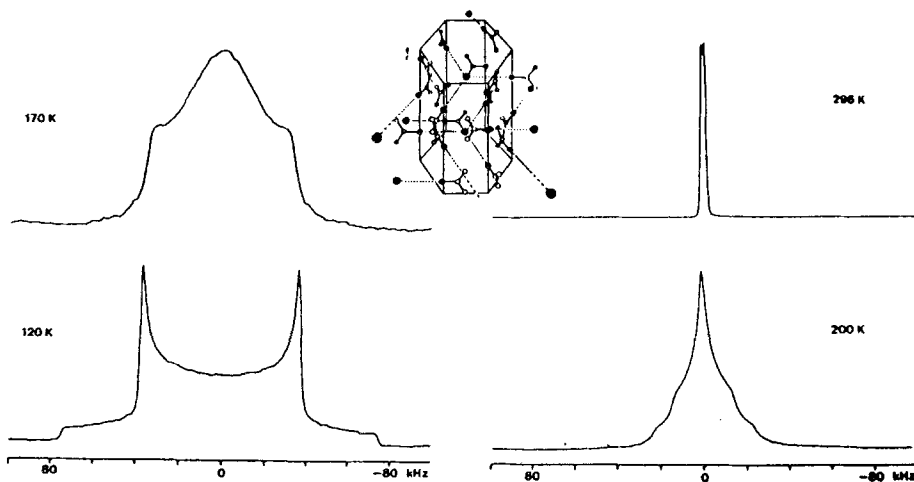


Figure 3: ^2H NMR spectra of thiourea:ferrocene (3:1) clathrate.

Similar spectral changes have been observed for Fecp_2 in its inclusion complexes with cyclodextrins. Of particular interest is a comparison of the motional behaviour of ferrocene included in α -, β - and γ -cyclodextrins, which have 6, 7, and 8 rings respectively in the cyclic structures. The spectra of the Fecp_2 inclusion complexes of α - and β -cyclodextrins are closely similar, but marked differences are observed for the complex with γ -cyclodextrin. These differences are broadly consistent with proposals from CD studies of the inclusion complexes in solution which indicate that in both α - and β -cyclodextrins the Fecp_2 molecular axis is parallel to the cavity axis, but in γ -cyclodextrin it is perpendicular to it [7]. The different motional averaging experienced in the different complexes therefore relates closely to the

different behaviour of Cocp_2^+ in its different orientations in TaS_2 . In the case of the cyclodextrins, however, it is apparent from the NMR lineshapes that the included Fcpcp_2 molecules experience a considerably wider range of motions within the cavities.

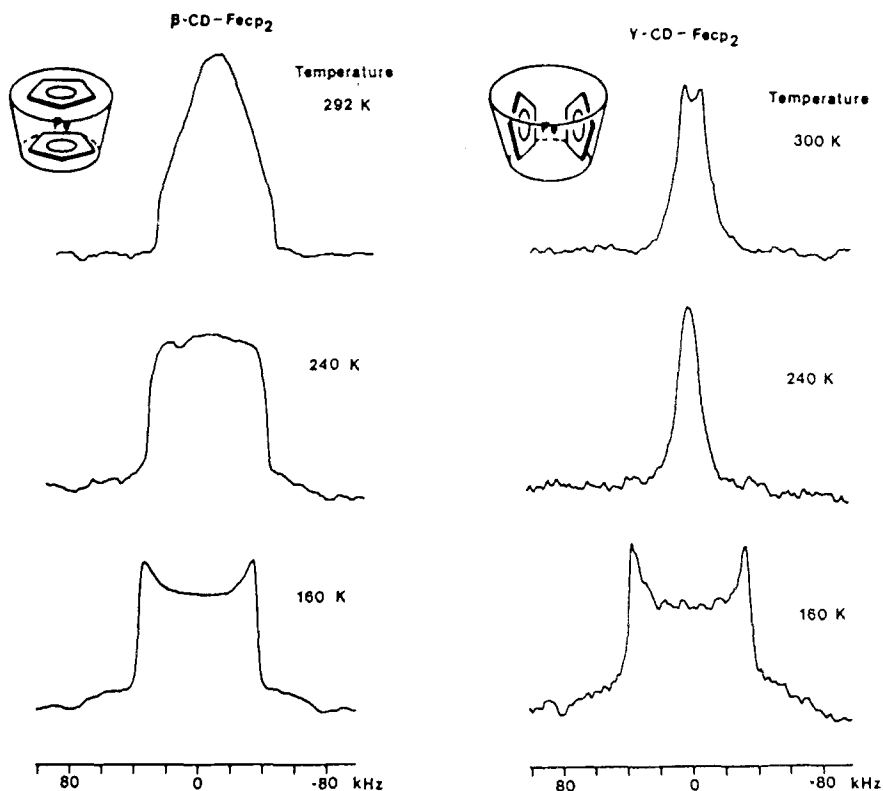


Figure 4: ^2H NMR spectra of the ferrocene inclusion complexes of β -cyclodextrin and γ -cyclodextrin

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