

Structure and Dynamics of Cobaltocene Intercalated in Tantalum Disulphide Investigated by ^2H N.M.R. Spectroscopy

Stephen J. Heyes, Nigel J. Clayden, Christopher M. Dobson,* Malcolm L. H. Green, and Philip J. Wiseman

Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, U.K.

^2H N.m.r. spectroscopy reveals the existence of two orientations of the cobaltocenium ion in the $[\text{Co}(\eta\text{-C}_5\text{H}_5)_2]_{1/4}\text{TaS}_2$ intercalate, with different dynamic properties in each orientation.

It is now well established that a rich variety of materials containing organometallic guest molecules intercalated into layered inorganic solids can be prepared.¹ Examples include metallocenes and bis-arene metal compounds intercalated into layered transition metal dichalcogenides,²⁻⁴ and more recently electron-rich metal cluster compounds intercalated into TaS_2 ⁵ and MoO_3 .⁶ These materials have interest with respect to their electrical, magnetic, and other bulk properties, and their use as model surface systems for study of heterogeneous catalysis.

An inherent difficulty in the structural characterisation of such materials lies in their generally microcrystalline nature. There has, in particular, been considerable discussion of the orientation of metallocenes in metal dichalcogenide layers. The lattice expansion resulting from metallocene intercalation, as measured by *X*-ray powder diffraction, does not definitively establish the orientation of the simple metallocene molecule in the interlayer space because of its almost spherical shape.⁴ A ^1H n.m.r. study of $[\text{Co}(\eta\text{-C}_5\text{H}_5)_2]_{1/4}\text{TaS}_2$,⁷ in which second moment data were studied as a function of temperature, and *X*-ray diffraction data from an oriented film of $\text{Na}_{0.19}[\text{Co}(\eta\text{-C}_5\text{H}_5)_2]_{0.13}\text{TaS}_2$ ⁵ were both interpreted in terms of a structure with the principal axis of the cobaltocene molecule lying parallel to the TaS_2 layers. On the other hand, *X*-ray powder diffraction studies and elemental analysis of alkyl-substituted metallocenes and bis-arene metal compounds intercalated in TaS_2 and ZrS_2 ^{3,4} indicated that the principal axes of these guests (although not necessarily the unsubstituted derivatives) lie perpendicular to the interlamellar plane. In this communication we describe a ^2H solid-state n.m.r. study of cobaltocene intercalated in TaS_2 and demonstrate the value of this technique in defining the structure of such compounds, and the dynamics of the intercalated species.

The ^2H n.m.r. studies of cobaltocene in TaS_2 were designed to explore the orientation of the metallocene guest by observation of its dynamic properties as revealed by the lineshape of the $I = 1$ nucleus. Figure 1 shows ^2H n.m.r. spectra of $[\text{Co}(\eta\text{-C}_5^2\text{H}_5)_2]_{1/4}(2\text{H}\text{-TaS}_2)$ at temperatures between 200 and 350 K. The spectra at low temperatures

(< 240 K) show the typical Pake doublet lineshape expected for a ^2H nucleus in an axially symmetric environment.⁸ They show a splitting of approximately 65 kHz, and resemble closely spectra obtained under similar conditions for $[\text{C}_5\text{H}_5]_2\text{ferrocene}$ and $[\text{C}_5\text{H}_5]_2\text{cobaltocenium hexafluorophosphate}$.^{9,10} The observed splitting is about half that expected for an aromatic C-H bond in a static molecule.¹¹ This result is consistent with the rapid reorientation of the cyclopentadienyl rings about their C_5 axes, known to occur in metallocenes even at temperatures below 100 K;¹² the averaging of the electric field gradient (e.f.g.) tensor about a single axis perpendicular to the C-H bond vector produces a reduction in the quadrupole splitting by a factor of exactly 2.0 provided that the rate of motion, either continuous or hopping, is $\gtrsim 10^7$ Hz. This motion results in a new effective e.f.g. tensor directed along the axis of rotation, the principal molecular axis.¹³

As the temperature is increased, however, the ^2H n.m.r. spectrum changes dramatically, Figure 1, indicating that the cobaltocenium ions in TaS_2 at temperatures above 230 K experience motion in addition to that arising from the cyclopentadienyl ring rotation. To investigate this we have simulated the effect on the ^2H n.m.r. lineshapes of constrained interlamellar motion for the two orientations suggested by previous studies (Figure 3). The reorientation is assumed to be restricted to that about an axis perpendicular to the interlamellar plane;⁷ there is likely to be no preferred orientation within this plane. For the orientation of the metallocene molecule with its principal axis perpendicular to the layers this motional axis coincides with the principal molecular axis and so there is no further averaging of the e.f.g. tensor. For the orientation with the principal axis of the metallocene parallel to the layers further averaging will, however, occur, and comparison of the simulations with the experimental spectra shows at once some striking similarities. In particular, an inner component is present in the simulated spectra with a splitting reduced, in the fast limit, by a factor of 2 from the splitting found in the absence of the motion. This correlates exactly with the experimental splitting found for the inner component.

A number of features of the experimental spectra are,

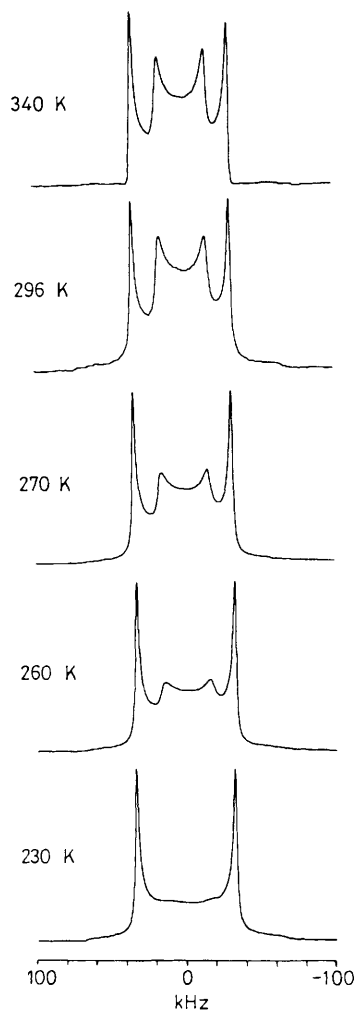


Figure 1. Variable-temperature ^2H n.m.r. spectra of $[\text{Co}(\eta\text{-C}_5\text{H}_5)_2]_{1/4}\text{-(2H-TaS}_2\text{)}$ recorded at 30.7 MHz with a Bruker CXP200 spectrometer using a quadrupolar spin-echo sequence with phase cycling.¹⁴ A $4.2\ \mu\text{s}$ 90° pulse was used with a spin-echo delay time of $20\ \mu\text{s}$. 1T-TaS_2 was prepared by the reaction of TaCl_5 with H_2S ,¹⁵ and 2H-TaS_2 was prepared by annealing 1T-TaS_2 .¹⁶ The intercalation compounds were prepared by reaction of TaS_2 powder with a toluene solution of $[\text{C}_5\text{H}_5]_2\text{Co}$ in sealed ampoules at 400 K for 3 days.⁴ The materials were all characterised by X-ray powder diffraction and elemental analyses. The relative intensities of the components in the ^2H n.m.r. spectra varied slightly with sample history and environment.

however, inconsistent with the simulations. In particular, on the assumption of a steadily increasing rate of reorientation with increasing temperature, the spectra should change progressively towards the fast motion limit where only the inner doublet is observed. In fact the experimental spectral changes cease at about 300 K; above this temperature the inner and outer components of the spectrum remain at approximately equal intensities. The simulations show further that the outer component of the spectrum should broaden progressively as the inner component increases in intensity. In fact, the outer component is narrow in comparison with the inner component at all temperatures.

The lineshape changes show, therefore, that neither of the orientations of cobaltocene in the TaS_2 layers by itself provides a complete explanation on this motional model of the experimental spectra. An excellent correlation between the experimental spectra and the simulations can, however, be made if *both* orientations are assumed to be present. The

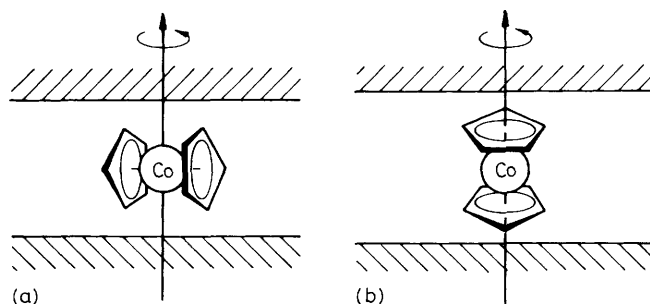


Figure 2. Proposed models for the TaS_2 -metallocene intercalation compounds, with the metallocene principal axis (a) parallel to and (b) perpendicular to the interlamellar plane. In each case the axis about which rapid molecular motion is assumed to take place is indicated. Note that in (b) this axis is coincident with the principal molecular axis.

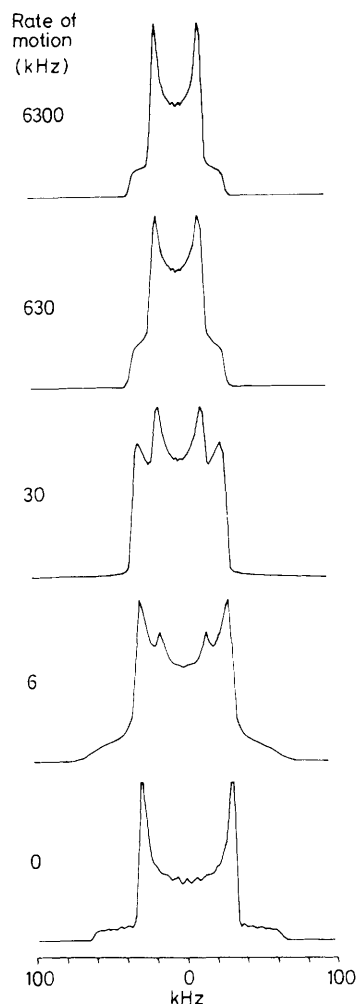


Figure 3. Simulations of the effect on the ^2H n.m.r. spectrum of motion about a single axis perpendicular to the principal axis of the metallocene; rapid cyclopentadienyl ring rotation was assumed in all cases.¹⁷ Continuous motion was simulated in the fast limit by calculation of the order parameters, and at low and intermediate rates by calculating the effect of all-site four-fold hops about C_4 axes by solving $G_{\text{thq}}(t) = G(0)\exp(i\omega_{\text{thq}} + \pi)t$ where ω is a diagonal matrix containing the frequencies of individual deuteron sites and π is a symmetric matrix containing the exchange rates between the different deuteron sites, and then performing a powder average. The computer programs, which take into account the spin-echo experiment and the finite pulse width, will be described elsewhere.¹⁸

spectra at 300 K and above are, on this model, a superposition of the spectra of the perpendicular orientation (the outer component) and of the parallel orientation in the fast limit (the inner component); the populations of the two being approximately equal. This explanation is supported by the observation that the inner and outer doublets in the experimental spectra are not centred at exactly the same frequency, implying that they arise from species with slightly different magnetic environments rather than from an intermediate exchange lineshape. The fact that the spectra of the two orientations are superimposed shows that the exchange of cobaltocenium ions between the different orientations is slow in comparison with the timescale of the motional properties within the layers. As the temperature is reduced the inner component broadens and declines in intensity. This could result simply from a slowing of interlamellar motion as indicated by the simulations in Figure 3; at low rates of reorientation the ^2H n.m.r. spectra have identical lineshapes for the two orientations. Although the broadening implies that the decrease in reorientation rate could be at least a small contribution to the temperature dependence, the intensity changes suggest that an increase in the population of the perpendicular orientation at the expense of the parallel orientation occurs at lower temperatures. Below 230 K the spectra are consistent with all the cobaltocenium ions being aligned perpendicular to the interlamellar plane.

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References

- 1 R. Schöllhorn in 'Inclusion Compounds,' eds. J. L. Atwood, J. E. D. Davies, and D. D. MacNicol, vol. 1, Academic Press, 1984, p. 249; M. S. Whittingham and A. J. Jacobson, 'Intercalation Chemistry,' Academic Press, 1982.
- 2 M. B. Dines, *Science*, 1975, **188**, 1210.
- 3 W. B. Davies, M. L. H. Green, and A. J. Jacobson, *J. Chem. Soc., Chem. Commun.*, 1976, 781.
- 4 R. P. Clement, W. B. Davies, K. A. Ford, M. L. H. Green, and A. J. Jacobson, *Inorg. Chem.*, 1978, **17**, 2754.
- 5 L. F. Nazar and A. J. Jacobson, *J. Chem. Soc., Chem. Commun.*, 1986, 570.
- 6 M. L. H. Green and M. E. Thompson, unpublished results.
- 7 B. G. Silbernagel, *Chem. Phys. Lett.*, 1975, **34**, 298.
- 8 G. E. Pake, *J. Chem. Phys.*, 1948, **16**, 327.
- 9 N. J. Clayden, C. M. Dobson, S. J. Heyes, and P. J. Wiseman, *J. Incl. Phenom.*, 1987, **5**, 65.
- 10 S. J. Heyes, Part II Thesis, Oxford University, 1985.
- 11 R. G. Barnes, *Adv. Quadrupole Reson.*, 1974, **1**, 335.
- 12 C. H. Holm and J. A. Ibers, *J. Chem. Phys.*, 1959, **30**, 885; S. E. Anderson, *J. Organomet. Chem.*, 1974, **71**, 263.
- 13 A. Abragam, 'Principles of Nuclear Magnetism,' Oxford University Press, 1961.
- 14 J. H. Davis, K. R. Jeffrey, M. Bloom, M. I. Valic, and T. P. Higgs, *Chem. Phys. Lett.*, 1976, **42**, 390; H. W. Spiess, *J. Chem. Phys.*, 1980, **72**, 6755.
- 15 W. B. Davies, Part II Thesis, Oxford University, 1976.
- 16 J. F. Revelli, *Inorg. Synth.*, 1979, **19**, 35.
- 17 H. W. Spiess in 'NMR: Basic Principles and Progress,' eds. P. Diehl, E. Fluck, and R. Kosfield, vol. 15, Springer Verlag, 1978; R. J. Wittebort, E. T. Olejniczak, and R. G. Griffin, *J. Chem. Phys.*, 1987, **86**, 5411.
- 18 N. J. Clayden, C. M. Dobson, S. J. Heyes, F. C. Rodgers, and P. J. Wiseman, in preparation.