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Molecular dynamics in solid bis(η-arene)molybdenum complexes studied by solid-state deuterium nuclear magnetic resonance spectroscopy

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Variable-temperature solid-state ^2H NMR spectra have been recorded on microcrystalline samples of $[Mo(\eta\text{-}C_6D_6)_2]$, $[Mo\{\eta\text{-}C_6D_3(CD_3)_3\text{-}1,3,5\}_2]$ and $[ZrS_2\{Mo[\eta\text{-}C_6D_3(CD_3)_3\text{-}1,3,5]_2\}_{0.15}]$. In the case of $[Mo(\eta\text{-}C_6D_6)_2]$ the spectra are invariant in the range 160–360 K and are consistent with rapid ring rotation at all accessible temperatures.For both $[Mo\{\eta\text{-}C_6D_3(CD_3)_3\text{-}1,3,5\}_2]$ and $[ZrS_2\{Mo[\eta\text{-}C_6D_3(CD_3)_3\text{-}1,3,5]_2\}_{0.15}]$ the $\eta\text{-}C_6D_3(CD_3)_3$ ligands were found to be static at all temperatures up to 360 K.

Nuclear magnetic resonance spectroscopy is now a well established technique for the study of solids. In particular, solid-state ^2H NMR spectroscopy is an invaluable tool for investigations into molecular motions with a wide range of rates, and for studying molecular ordering in solids[1] such as crystal hydrates,[2] biological materials,[3] polymers,[4] liquid crystals,[5] inclusion complexes,[6] molecular organometallic solids[7] and metallocene intercalation compounds.[8] Deuterium nuclei in polycrystalline samples are randomly oriented in a static field, resulting in a solid-state ^2H NMR powder spectrum consisting of a superposition of the resonances from all the possible orientations of the ^2H nuclei. Theoretical powder lineshapes for second-rank tensor interactions can be calculated using expressions calculated by Bloembergen and Rowland.[9] The principal components of the tensor (eq_{zz}, eq_{xx}, eq_{yy}) can be obtained directly from the discontinuities in the powder spectrum. The ^2H NMR powder lineshape is the superposition of the powder patterns of two single-quantum transitions, related to one another by reflection through the Larmor frequency, ω_0.

The environment of a particular molecule in a solid can often result in anisotropic motional averaging, in contrast to the isotropic molecular tumbling generally observed for molecules in liquids. The electric field gradient (e.f.g.) tensor at the deuterium nucleus is averaged by motional processes the rates of which are comparable in magnitude to that of the quadrupolar interaction. This averaging is reflected in the lineshapes of the ^2H NMR spectra and facilitates the determination of information relating to molecular motion. The magnitude and intramolecular nature of the quadrupole interaction, the axial symmetry of most C–D bonds and the poor spin diffusion between ^2H nuclei make solid-state ^2H NMR spectroscopy an ideal technique to probe selectively the mechanisms and rates of molecular motions in solids. Molecular motions fall into three categories: those which are slow, those which are of intermediate rate and those which are fast on the ^2H NMR spectroscopic time-scale. This time-scale is determined by the magnitude of the quadrupole interaction, $e^2q_{zz}Q/h$, called the nuclear quadrupole coupling constant (n.q.c.c.).

Motions in the slow-exchange regime have rates of less than *ca.* 10^3 Hz ($\ll$n.q.c.c.) and do not average the e.f.g. tensor at the nucleus. Thus slow motions do not change the spectral profile observed using the quadrupole echo-pulse sequence for the rigid, non-exchanging system. Motions in the intermediate-exchange regime have rates in the range *ca.* 10^3–10^8 Hz, and a magnitude comparable to that of the quadrupole interaction. These motions partially average the e.f.g. tensor resulting in spectra with lineshapes that are highly dependent on the rate and extent of the motion. Motions in the fast-exchange regime have rates greater than 10^8 Hz ($\gg$n.q.c.c.) and exchanging components of the e.f.g. tensor are completely averaged. The spectral lineshape reflects the extent of the motional process but shows no further dependence on its absolute rate. The e.f.g. tensor for a static aromatic deuteron is expected to be axially symmetric with its principal direction along the C–D bond vector; the doublet separation between the inner discontinuities will have a value of $\frac{3}{4}$ n.q.c.c.

In ferrocene, for example, the cyclopentadienyl rings reorient rapidly about the principal molecular axis of the molecule at temperatures above 80 K.[10] This motion reduces the quadrupole interaction, and hence the observed quadrupolar splitting, by a factor of 2 as shown schematically in Fig. 1.

In the present work, solid-state ^2H NMR spectroscopy was used to investigate the dynamic properties of bis(perdeuteriobenzene)molybdenum and bis(perdeuteriomesitylene)molybdenum and the intercalation compound $[ZrS_2\{Mo[\eta\text{-}C_6D_3(CD_3)_3\text{-}1,3,5]_2\}_{0.15}]$.

Results and Discussion

Solid-state ^2H NMR studies of microcrystalline $[Mo(\eta\text{-}C_6D_6)_2]$

The compound $[Mo(\eta\text{-}C_6D_6)_2]$ was prepared by co-condensation of molybdenum vapour with perdeuteriobenzene at 77 K using the metal-vapour-synthesis technique.[11] Its quadrupole

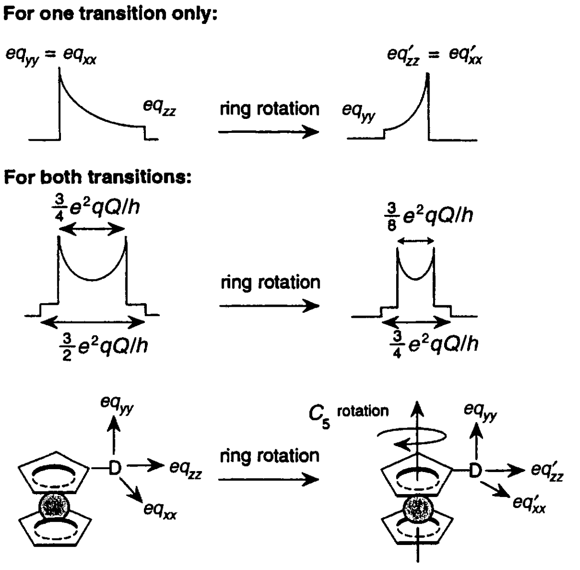


Fig. 1 Illustration of the spectral averaging due to the rapid ring rotation about the principal molecular axis for ferrocene. Note the change in the sign of the anisotropy between static and reorienting situations

echo solid-state ^2H NMR spectrum was recorded over the range 160–350 K (Fig. 2). The spectra have the classic 'Pake Doublet' lineshapes characteristic of a spin $I = 1$ nucleus in an axially symmetric environment. Since the n.q.c.c. for an aromatic C–D bond is typically 150–200 kHz for static deuterons,[12] the observed values for the doublet separation of around 70 kHz are about half those expected for a static molecule. The measured doublet separations change only slightly with temperature. This halved splitting is characteristic of averaging of the quadrupolar e.f.g. tensor by rapid ($> 10^8$ Hz) reorientation about a single axis perpendicular to the C–D bond vector (Fig. 1). The only axis which simultaneously fulfils this requirement for all the deuterons in the molecule is the C_6 axis of the molecule, and therefore we propose that it is undergoing rapid ring rotation about this axis. Although the spectra do not enable us to distinguish between continuous and jump-type processes, the latter mechanism is generally accepted for other ring-reorientation processes.[13] Experimental evidence is provided by single-crystal structure determinations such as that of decamethylferrocene[14] which undergoes rapid ring rotation at room temperature[15] and shows discrete atomic positions.

In Fig. 2 the growth of the central spike as the temperature is increased above room temperature is reversible. This spike could be due to isotropically averaged gas-phase $Mo(\eta\text{-}C_6D_6)_2$ molecules, or possibly to benzene molecules arising from a trace amount of sample decomposition. The rapid ring rotation observed in $[Mo(\eta\text{-}C_6D_6)_2]$ parallels that previously found in other unsubstituted sandwich compounds. For example, variable-temperature T_1 measurements have shown rapid rotation for $[Cr(\eta\text{-}C_6H_6)_2]$, and yield an activation barrier for ring rotation of 18.9 kJ mol^{-1}.[16] Inelastic neutron scattering experiments suggest values of 12.6 and 15.5 kJ mol^{-1} for solid $[Cr(\eta\text{-}C_6H_6)_2]$ and $[Cr(\eta\text{-}C_6H_6)_2]^+I^-$ respectively.[17]

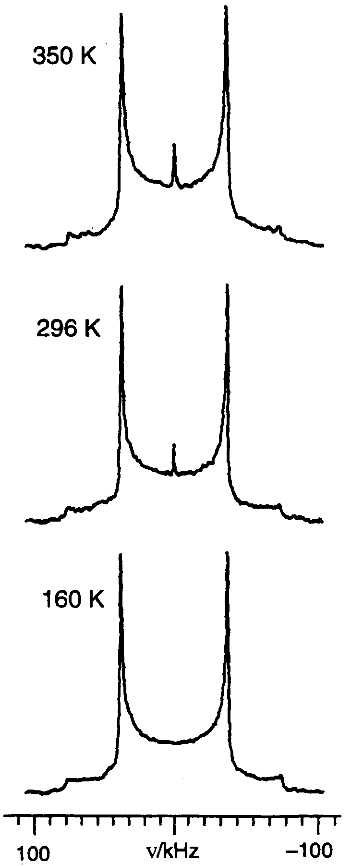


Fig. 2 Solid-state ^2H NMR spectra of a microcrystalline sample of $[Mo(\eta\text{-}C_6D_6)_2]$ between 160 and 350 K using the quadrupole echo sequence with an interpulse delay of 20 s. The narrow centre line is attributable to the molecule in the vapour phase. It represents about 1% of the sample at 296 K

Solid-state ^2H NMR studies of microcrystalline $[Mo\{\eta\text{-}C_6D_3(CD_3)_3\text{-}1,3,5\}_2]$

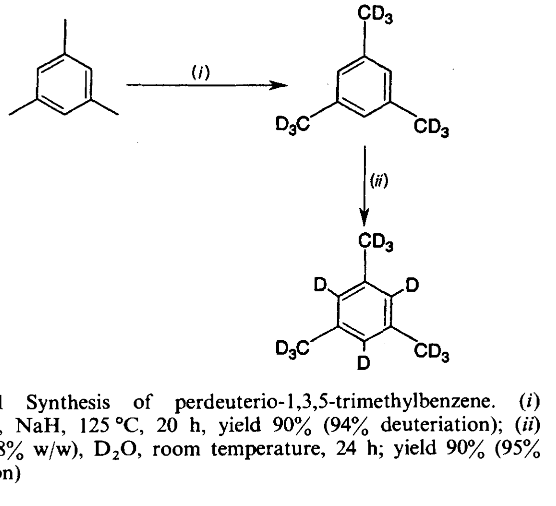
The compound $[Mo\{\eta\text{-}C_6D_3(CD_3)_3\text{-}1,3,5\}_2]$ was prepared by co-condensation of molybdenum vapour with perdeuteriomesitylene at 77 K using the metal-vapour-synthesis technique.[11] The deuteriated ligand was prepared by a two-step H/D exchange reaction as shown in Scheme 1.[18,19] The isotopic purity was found to be > 94% by mass spectrometry.

The room-temperature and 380 K solid-state ^2H NMR spectra of a microcrystalline sample of $[Mo\{\eta\text{-}C_6D_3(CD_3)_3\text{-}1,3,5\}_2]$ are shown in Fig. 3. This powder lineshape can be deconvoluted into two 'Pake Doublets', one arising from the aromatic deuterons and the other from the methyl deuterons of the mesitylene ring. For the aromatic deuterons, the n.q.c.c. will be close to that found for $[Mo(\eta\text{-}C_6D_6)_2]$, *i.e. ca.* 190 kHz. In the absence of any averaging motions, the splitting of the 'Pake Doublet' would therefore be 143 kHz. If the rings were rotating about the principal molecular axis, the splitting would be expected to be to 71 kHz.

For the methyl deuterons the n.q.c.c. will be approximately 165 kHz, by analogy with $C_6H_5CD_3$.[20] In the absence of any motion, a splitting of 124 kHz should therefore be observed. Rotation of the methyl group will reduce the splitting to a third of its static value, *i.e.* 41 kHz. If the mesitylene ring is also rotating about the principal molecular axis the splitting will be further reduced by a factor of two.

For bis(perdeuteriomesitylene)molybdenum the observed splittings of 147 kHz for the aromatic deuterons (one quarter of the ^2H nuclei in the sample) and 37 kHz for the methyl deuterons (three quarters of the ^2H nuclei) are consistent with fast methyl rotation only; *i.e.* there is no ring rotation in the sample (Fig. 4). Little change in the spectrum is seen when the compound is heated to 380 K. This behaviour contrasts to that of $[Mo(\eta\text{-}C_6D_6)_2]$ and $[Fe(\eta\text{-}C_5D_5)_2]$ where rotation is observed about the C_6 and C_5 axes respectively, even at 160 K. The compound $[Fe(\eta\text{-}C_5Me_5)_2]$ is also found to undergo rapid C_5 rotation at room temperature.[15] Solid-state ^{13}C NMR studies have also found that partially substituted rings in $[Cr(CO)_3(\eta\text{-arene})]$ complexes tend not to rotate as easily as fully substituted or unsubstituted rings.[21] The inability of the mesitylene rings to rotate is probably due to crystal-packing effects; it is possible that the 1,3,5 substitution of the benzene rings results in adjacent rings interlocking. Similar interlocking effects have been noted by Braga[13] in the single-crystal structure of $[Mo(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)(CO)_3]$.[22]

Closer inspection of the outer 'Pake Doublet' from the aromatic deuterons shows that two discontinuities are present,



Scheme 1 Synthesis of perdeuterio-1,3,5-trimethylbenzene. (*i*) $(CD_3)_2SO$, NaH, 125 °C, 20 h, yield 90% (94% deuteriation); (*ii*) D_2SO_4 (98% w/w), D_2O, room temperature, 24 h; yield 90% (95% deuteriation)

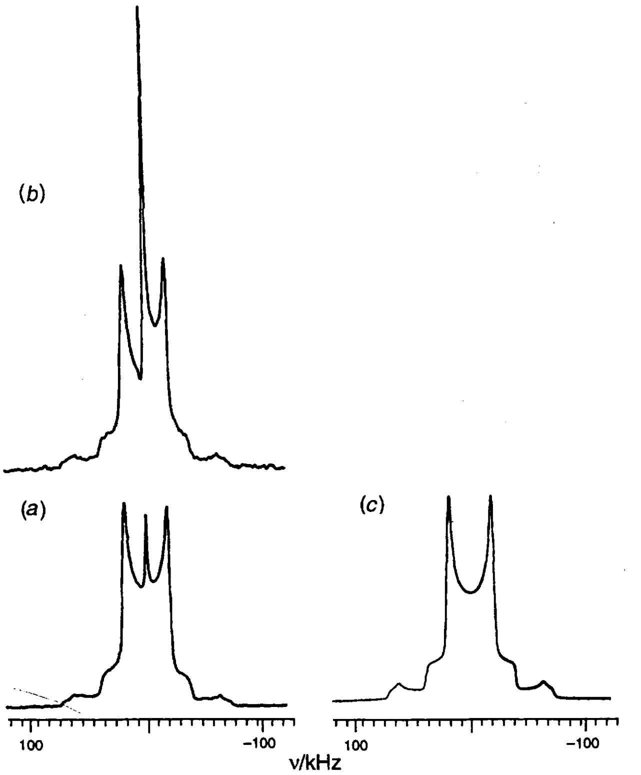


Fig. 3 Quadrupole echo, solid-state ^2H NMR spectra of a microcrystalline sample of $[Mo\{\eta\text{-}C_6D_3(CD_3)_3\text{-}1,3,5\}_2]$ at (*a*) 298 and (*b*) 380 K; (*c*) is a ^2H lineshape simulation of the $\eta\text{-}C_6D_3(CD_3)_3$ ring containing a rapidly rotating CD_3 group undergoing an additional ± 15° libration about the principal C_3 molecular axis

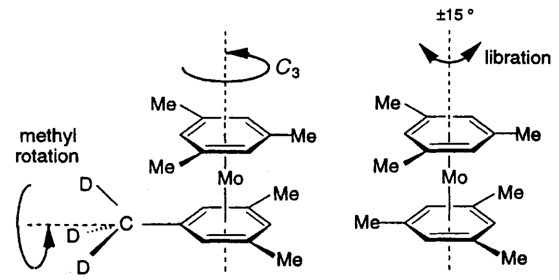


Fig. 4 Possible motional averaging process for $[Mo\{\eta\text{-}C_6D_3(CD_3)_3\text{-}1,3,5\}_2]$

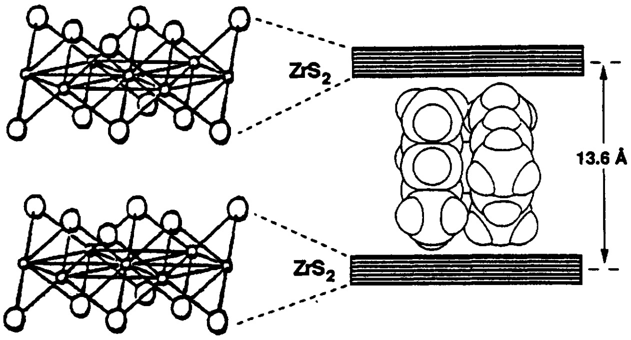


Fig. 5 Schematic illustration of the orientation of $[Mo\{\eta\text{-}C_6D_3(CD_3)_3\text{-}1,3,5\}_2]$ intercalated in ZrS_2

i.e. one at ± 73.7 kHz (the 'edge' of the spectrum) and one at ± 62.0 kHz (the point of maximum intensity for this doublet), revealing that the deuterium electric field gradient tensor is no longer axially symmetric. This asymmetry of the electric field gradient about the ^2H nuclei can be attributed to an asymmetric motion, one possible origin for which is a libration about the principal axis of the molecule. Lineshape simulations for such a motion using axially symmetric n.q.c.c. of 190 and 165 kHz for the aromatic C–D and methyl C–D groups respectively indicated that the angular extent of this libration would be about ± 15° (Fig. 4). A simulation for a mesitylene ring, with fast methyl rotations, librating at ± 15° (simulation used 30 equispaced, equipopulated sites in a single plane) about its principal axis is shown in Fig. 3(*c*). The growth of the central spike as the temperature is increased is reversible, and we attribute the spike to isotropically averaged gas-phase molecules or possibly to free mesitylene molecules arising from a trace amount of sample decomposition.

Solid-state ^2H NMR studies of $[Mo\{\eta\text{-}C_6D_3(CD_3)_3\text{-}1,3,5\}_2]$ intercalated in ZrS_2

We were interested in comparing the dynamics of deuteriated sandwich compounds in a different environment with that of the pure solid. It has previously been shown that $[Mo(\eta\text{-}C_6H_6)_2]$ and $[Mo\{\eta\text{-}C_6H_3Me_3\text{-}1,3,5\}_2]$ can be intercalated into ZrS_2.[23] We have found that the phase and guest orientation observed is dependent on a variety of factors including reaction time, temperature and solvent and/or the crystallinity of the chalcogenide host lattice.[24]

Unfortunately we were unable to acquire satisfactory spectra on the ZrS_2 intercalate of $[Mo(\eta\text{-}C_6D_6)_2]$. We attribute this to our inability to tune the spectrometer due to the metallic nature of the sample. However, we were able to obtain spectra for the $[Mo\{\eta\text{-}C_6D_3(CD_3)_3\text{-}1,3,5\}_2]$ intercalate. The sample investigated here was obtained by reaction of microcrystalline ZrS_2 with $[Mo\{\eta\text{-}C_6D_3(CD_3)_3\text{-}1,3,5\}_2]$ in refluxing toluene for 3 d giving $[ZrS_2\{Mo[\eta\text{-}C_6D_3(CD_3)_3\text{-}1,3,5]_2\}_{0.15}]$. The X-ray powder diffraction pattern of this particular sample exhibited a set of 001 reflections corresponding to a *c* axis of 13.6 Å. This interlayer separation is consistent with the $[Mo\{\eta\text{-}C_6D_3(CD_3)_3\text{-}1,3,5\}_2]$ molecules having their C_3 axes parallel to the ZrS_2 layers (Fig. 5). The solid-state ^2H NMR spectrum of $[ZrS_2\{Mo[\eta\text{-}C_6D_3(CD_3)_3\text{-}1,3,5]_2\}_{0.15}]$ exhibited a Pake doublet lineshape with the same separation between the inner discontinuities as for the pure guest molecular crystals. Therefore, it appears that the $[Mo\{\eta\text{-}C_6D_3(CD_3)_3\text{-}1,3,5\}_2]$ molecules are packed in the interlayer region of the ZrS_2 in a manner which prevents ring rotation. This may involve interlocking with neighbouring guest molecules or with the sulfur atoms in the chalcogenide layer.

Conclusion

Rapid ring rotation is observed for bis(benzene)molybdenum, as has previously been observed for half-sandwich-arene metal derivatives. It is also found for $[Mo(\eta\text{-}C_6D_6)_2]$, whilst replacement of the $\eta\text{-}C_6D_6$ ligand by $\eta\text{-}C_6D_3(CD_3)\text{-}1,3,5$ results in interlocking of the rings to give a much greater barrier to ligand rotation. These results parallel the differences previously observed between unsubstituted and partially substituted $[Cr(CO)_3(\eta\text{-arene})]$ (M = Cr or Mo) complexes.

Experimental

General

The bis(η-arene)molybdenum complexes are air sensitive, hence all manipulations were carried out under a nitrogen atmosphere, or *in vacuo*, using standard Schlenk techniques on a dual nitrogen/vacuum line or in an inert-atmosphere glovebox. Solvents, pre-dried over molecular sieves, were dried by refluxing, under a nitrogen atmosphere, over potassium metal (for tetrahydrofuran, thf), or sodium–potassium alloy (for light petroleum, b.p. 40–60 °C, and diethyl ether). All were subsequently stored over activated type 4 Å molecular sieves, and were deoxygenated by repeated evacuation and admission of nitrogen.

Syntheses

[Mo(η-C_6D_6)$_2$]. The metal-vapour technique which incorporates an electron-beam furnace and a ligand-inlet system was used as described previously.[4] Typically molybdenum metal vapour (3–4 g) was co-condensed with C_6D_6 (55 cm^3) onto the wall of a glass bell jar at 77 K. After the co-condensation was finished the reaction product was extracted with diethyl ether (*ca.* 1 l), passed through a bed of Celite and the solvent and excess of ligand removed under reduced pressure giving a deep green solid. The green solid was purified by extraction into thf followed by vacuum sublimation (yield 1.0 g, *ca.* 10% based on Mo evaporated).

$C_6D_3(CD_3)_3$-1,3,5. The methyl positions of mesitylene were deuteriated by three exchanges with $(CD_3)_2SO$ following the method of Chen *et al.*[18] Mesitylene (> 99%, 80 cm^3, 0.575 mol) was added to a flask containing NaH (60% suspension in mineral oil, 10 g, 0.250 mol) followed by $(CD_3)_2SO$ (> 99.5% D, 98 cm^3, 1.386 mol) *via* a cannula. The flask was then fitted with a condenser, put under a purge of nitrogen, and **cautiously** heated, with magnetic stirring, to 125 °C. Vigorous evolution of HD gas occurred at 80–100 °C and the contents of the flask became black. The reaction was held at 125 °C for *ca.* 20 h to allow exchange between $(CD_3)_2SO$ and mesitylene *via* a catalytic amount of $NaCD_2SOCD_3$. When the exchange was complete, volatile materials [exchanged mesitylene and $(CD_3)_2SO$] were distilled off at 100 °C in a vacuum line into a trap cooled in liquid nitrogen. The contents of the trap were transferred to a separating funnel and water (320 cm^3) added to extract the $(CD_3)_2SO$. The upper mesitylene layer was then exchanged twice more with fresh $(CD_3)_2SO$ and NaH.

The aromatic positions of mesitylene were deuteriated by three exchanges with a *ca.* 50% solution of deuterium sulfate in deuterium oxide.[19] Deuterium sulfate (98% w/w in D_2O, >99.5% D; 100 g, 0.971 mol D_2SO_4; 99.9 mmol D_2O) was added to D_2O (>99.9% D, 16 cm^3, 0.884 mol). The $C_6H_3(CD_3)_3$ layer from the third $(CD_3)_2SO$ exchange above was then added under a purge of nitrogen and the mixture magnetically stirred at room temperature for *ca.* 24 h. During the exchange a solid white by-product, assumed to be a sulfonated species, was obtained. The layers were then allowed to separate and the upper (organic) layer transferred *via* a cannula onto fresh D_2SO_4–D_2O. The white solid was then reconverted into mesitylene by brief heating to *ca.* 140 °C with the D_2SO_4–D_2O which was then added to that already separated off. After a total of three exchanges, 55 cm^3 of [$^2H_{12}$]mesitylene were obtained, degassed and stored under nitrogen over activated 4 Å molecular sieves. Mass spectrometry was used to show an overall deuteriation of >94%.

[Mo{η-$C_6D_3(CD_3)_3$-1,3,5}$_2$]. The compound $C_6D_3(CD_3)_3$-1,3,5 was prepared as described above. Using the metal-vapour technique, molybdenum metal vapour (3–4 g) was co-condensed with an excess of C_9D_{12} (55 cm^3) onto the walls of a glass bell jar at 77 K. After the co-condensation was finished the reaction product was extracted with light petroleum (b.p. 40–60 °C, *ca.* 1 l), and filtered through a bed of Celite. The solvents were removed *in vacuo* and the [$^2H_{12}$]mesitylene recovered from the light petroleum by distillation. The [Mo{η-$C_6D_3(CD_3)_3$-1,3,5}$_2$] was purified by extraction into light petroleum, followed by vacuum sublimation, yield (> 3.28 g). The deuteriation was confirmed by solution ^2H NMR (in C_6H_6, δ 1.72, 4.41)[25] and mass spectroscopy. Microcrystalline [Mo{η-$C_6D_3(CD_3)_3$-1,3,5}$_2$] used for the solid-state ^2H NMR measurements was prepared by recrystallisation from light petroleum.

[ZrS_2\{Mo[η-$C_6D_3(CD_3)_3$-1,3,5]$_2$\}$_{0.15}$]. Addition of an excess of [Mo{η-$C_6D_3(CD_3)_3$-1,3,5}$_2$] (150 mg, 2.38 mmol) in toluene (20 cm^3) to a suspension of microcrystalline ZrS_2 (200 mg, 2.39 mmol) gave, on refluxing at 120 °C for 3 d, [ZrS_2\{Mo[η-$C_6D_3(CD_3)_3$-1,3,5]$_2$\}$_{0.15}$].[23] The purity of the sample was checked by elemental microanalysis and by X-ray powder diffraction.

Solid-state ^2H NMR experiments

Solid-state ^2H NMR experiments were carried out using a Bruker CXP200 spectrometer, with a Bruker 232V high-power probe and a horizontal solenoid insert. Temperatures were accurate to ± 1 K and stable to 0.1 K, and maintained by a Bruker BVT 1000 temperature-control unit equipped with a copper–constantan thermocouple, interfaced with a heater element inside the probe body. Between 30 min and 1 h were allowed for the sample to attain thermal equilibrium before spectral acquisition was commenced. The samples were sealed in 5 mm NMR tubes under nitrogen. The spectrometer was set up using standard multiple-pulse procedures on a Wilmad sphere of D_2O, which was situated at the centre of the coil. The pulse lengths, shimming and receiver phase balance were optimised on a sample of bulk D_2O, and the quadrupole echo distortions were reduced to 0.5% on this sample by adjustment of the amplitude and phase gains of the receiver channels. The pulse lengths and tuning frequency were finally refined using a sample of deuteriated poly(methyl methacrylate). The quadrupole spin-echo technique ($\frac{\pi}{2}$–τ/μs–$\frac{\pi}{2}$–τ/μs–observe), with standard precautions and phase cycling, was used to acquire the spectra.[26] The quadrupole echo delay (τ) was adjusted to ensure that the digitised points constituting the free induction decay were symmetrically situated about the point at the top of the quadrupole echo. The free induction decay acquisition was started prior to the top of the echo, and the left most points before the echo maximum were removed with a software correction. Spin-echo delays in the range 30–200 μs and recycle delays in the range 0.5–10 s were used.

^2H NMR simulations

Averaged ^2H NMR spectral lineshapes in the fast motional limit (rate $\approx 10^8$ s^{-1}) were calculated from order parameter theory,[27] assuming averaging by discrete jump processes between distinct molecular orientations. A Bloom-type frequency-domain correction was applied to take account of power roll-off due to the finite radio frequency pulses used experimentally.[28] Molecular librations are rather insensitive to the potential for the vibration and were modelled with *ca.* 30–40 equispaced, equipopulated sites in a single plane. A more detailed description of the computer programs used to calculate the ^2H NMR lineshapes can be found elsewhere.[29]

References

1 M. Mehring, *Principles of High Resolution NMR in Solids*, Springer, Berlin, 1983; R. J. Wittebort and L. W. Jelinski, *Annu. Rev. Mater. Sci.*, 1985, **15**, 359; E. T. Olejniczak and R. G. Griffin, *J. Chem. Phys.*, 1987, **86**, 5411; N. Boden, L. D. Clark, S. M. Hanlon and M. Mortimer, *Faraday Symp. Chem. Soc.*, 1978, 109.

2 B. Berglun and J. Tagenfeldt, *J. Magn. Reson.*, 1976, **27**, 315.

3 I. C. P. Smith and H. H. Mantsch, in *NMR Spectroscopy: New Methods and Applications*, American Chemical Society, Washington, DC, 1982.

4 H. M. Spiess, *J. Mol. Struct.*, 1983, **111**, 119; H. Spiess, *Adv. Polym. Sci.*, 1985, **66**, 23.

5 J. W. Emsley, S. K. Koo and G. R. Luckhurst, *Mol. Phys.*, 1979, **37**, 959.

6 S. J. Heyes, N. J. Clayden and C. M. Dobson, *J. Phys. Chem.*, 1991, **95**, 1547; M. D. Lowery, R. J. Wittebort, M. Sorai and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1990, **112**, 4214.

7 S. E. Woehler, R. J. Wittebort, S. M. Oh, D. N. Hendrickson, D. Inniss and C. E. Strouse, *J. Am. Chem. Soc.*, 1986, **108**, 2938;

M. I. Altbach, Y. Hiyama, R. J. Wittebort and L. G. Butler, *Inorg. Chem.*, 1990, **29**, 741.

8 D. O'Hare, J. S. O. Evans, P. A. Turner, S. Mason, S. J. Heyes and J. Greenwood, *J. Mater. Chem.*, 1995, **9**, 1383; C. P. Grey, J. S. O. Evans, D. O'Hare and S. J. Heyes, *J. Chem. Soc., Chem. Commun.*, 1991, 1382; S. Mason, D. O'Hare and S. J. Heyes, *J. Chem. Soc., Chem. Commun.*, 1995, 1657; *Inorg. Chem.*, 1995, **34**, 4287.

9 N. Bloembergen and J. A. Rowland, *Acta Metall.*, 1953, **1**, 731.

10 C. H. Holm and J. A. Ibers, *J. Chem. Phys.*, 1959, **30**, 885.

11 M. L. H. Green and D. O'Hare, *ACS Symp. Ser.*, 1987, **333**, 260.

12 R. G. Barnes, in *Adv. Nucl. Quadrupole Reson.*, 1974, **1**, 335.

13 D. Braga, *Chem. Rev.*, 1992, **92**, 633 and refs. therein.

14 D. P. Freyberg, J. L. Robbins, K. N. Raymond and J. C. Smart, *J. Am. Chem. Soc.*, 1979, 101, 892.

15 D. E. Weimmer, D. J. Ruben and A. Pines, *J. Am. Chem. Soc.*, 1981, **103**, 28.

16 A. J. Campbell, C. A. Fyfe, D. Harold-Smith and K. R. Jeffrey, *Mol. Cryst. Liq. Cryst.*, 1976, **36**, 1.

17 J. Howard, K. Robson and T. C. Waddington, *J. Chem. Soc., Dalton Trans.*, 1982, 977.

18 T. S. Chen, J. Wolinska-Mocydlarz and L. C. Leitch, *J. Labelled Compd.*, 1970, **VI**, 285.

19 J. A. Dixon and R. W. Schiessler, *J. Am. Chem. Soc.*, 1953, **76**, 2197; C. K. Ingold, C. G. Raisin and C. L. Wilson, *J. Chem. Soc.*, 1936, 915; E. L. Mackor, P. J. Smit and J. H. van der Waals, *Faraday Trans.*, 1957, **53**, 1309.

20 P. L. Olympia, I. Y. Wei and B. M. Fung, *J. Chem. Phys.*, 1969, **51**, 1610.

21 G. W. Wagner and B. E. Hanson, *Inorg. Chem.*, 1987, **26**, 2019.

22 D. E. Korshland, S. E. Myers and J. P. Chesick, *Acta Crystallogr., Sect. B*, 1977, **33**, 2013.

23 R. P. Clement, W. B. Davies, K. A. Ford, M. L. H. Green and A. J. Jacobsen, *Inorg. Chem.*, 1978, **17**, 2754.

24 J. S. O. Evans, S. Barlow, H.-V. Wong and D. O'Hare, *Adv. Mater.*, 1995, **7**, 163.

25 M. L. H. Green and W. E. Silverthorn, *J. Chem. Soc., Dalton Trans.*, 1973, 301.

26 J. H. Davis, K. R. Jeffrey, M. Bloom, M. I. Valic and T. P. Higgs, *Chem. Phys. Lett.*, 1976, **42**, 390; R. Hentschel and H. W. Spiess, *J. Magn. Reson.*, 1979, **35**, 157; A. D. Ronemus, R. L. Vold and R. R. Vold, *J. Magn. Reson.*, 1986, **70**, 416; J. Seelig, *Q. Rev. Biophys.*, 1977, **10**, 353; R. J. Wittebort, E. T. Olejniczak and R. G. Griffin, *J. Chem. Phys.*, 1987, **86**, 5411.

27 M. Bloom, J. H. Davis and M. I. Valic, *Can. J. Phys.*, 1980, **58**, 1510.

28 P. Meier, E. Ohmes, G. Kothe, A. Blume, J. Weidner and H. J. Eibl, *J. Phys. Chem.*, 1983, **87**, 4904.

29 S. J. Heyes, D.Phil. Thesis, Oxford University, 1989.

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