Fluxional Motion in Bis(ethane-1,2-dithiolato)nickel(IV) from Nematic-phase Proton Magnetic Resonance

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We have recorded the nematic-phase ^{1}H n.m.r. spectrum of bis(ethane-1,2-dithiolato)nickel(IV) (I) at several temperatures. These spectra are consistent only with a fluxional geometry in which the two organic ligands rotate rapidly with respect to one another on the time-scale of the n.m.r. experiment. More than one orientation parameter is required to describe the molecular orientation, implying that this rotation is slow compared to the molecular reorientation time of the liquid crystal.

NUCLEAR magnetic resonance studies of molecules partially oriented in a liquid crystal have yielded structural information on a wide range of molecules.[1,2] In the present study, however, we have obtained unambiguous evidence for rapid intramolecular rotation in the symmetrical pseudo-square-planar diamagnetic nickel complex (I). Such evidence would be difficult to obtain by other methods. In addition we have been able to determine that this intramolecular motion occurs more slowly than the reorientation rate of the liquid crystal.

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[1] P. Diehl and C. L. Khetrapal, 'NMR Basic Principles and Progress,' Springer-Verlag, Berlin, Heidelberg, New York, 1969, **1**, 1.

[2] A. D. Buckingham and K. A. McLauchlan, *Progr. N.M.R. Spectroscopy*, 1967, **2**, 63.

EXPERIMENTAL

Compound (I) was prepared from nickel(II) chloride and disodium ethane-1,2-dithiolate.[3] The purple solid was recrystallised from carbon disulphide to remove all traces of the paramagnetic $[Ni(S_2C_2H_2)_2]^-$ ion (II) from the sample. We found that (I) dissolves in the Vari-Light liquid crystal VL-3268-N (which is primarily EBBA), but we were unable to record any n.m.r. signal of the solute from the solution. We attribute this result to the formation of traces of the paramagnetic ion (II) by reduction. We therefore dissolved (I) in the inert liquid crystal 4-cyano-4′-n-pentylbiphenyl and were then able to observe the n.m.r. signal of the partially oriented solute.

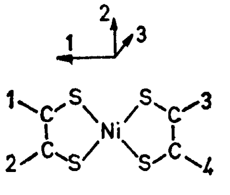

FIGURE 1 Numbering of the protons in (I)

^1H N.m.r. spectra were recorded at several temperatures on a Varian XL-100-15 spectrometer operating in Fourier-transform mode. An eight-line spectrum was observed at all temperatures, although marked changes in the ratios of splittings occurred.

DISCUSSION

The single ^1H n.m.r. peak of (I) in the isotropic phase will split up into many lines when the solute is ordered by a nematic liquid crystal because the dipolar couplings between protons will then not average to zero. For sufficiently symmetrical molecules (*e.g.* D_{2d}) the dipolar couplings between nuclei i and j are given by

$$T_{ij} = -\frac{\hbar\gamma_i\gamma_j}{2\pi r^3_{ij}}(3\cos^2\beta_3 - 1)S_{33} \qquad (1)$$

where r_{ij} is the distance between nuclei i and j, β_3 is the angle between the internuclear vector and the 3-axis (the symmetry axis), and S_{33} is the single orientation parameter required. For the less-symmetrical molecules of D_{2h} symmetry the dipolar couplings are determined by two orientation parameters

$$T_{ij} = -\frac{\hbar\gamma_i\gamma_j}{2\pi r^3_{ij}}[S_{33}(3\cos^2\beta_3 - 1) + (2S_{11} + S_{33})(\cos^2\beta_1 - \cos^2\beta_2)] \qquad (2)$$

where β_k is the angle between the internuclear vector and the k-th molecule-fixed axis.

Dipolar couplings for $[Ni(S_2C_2H_2)_2]$ in the liquid crystal 4-cyano-4′-n-pentylbiphenyl

Approximate [a] temperature (t/°C)	T_{12}/Hz [b]	T_{13}/Hz [b]	$-T_{12}/T_{13}$	S_{33}	S_{11}	R.m.s. error in line-fit (in Hz)
6	2994·7 (2·4)	−253·9 (1·6)	11·79	−0·413	0·592	1·8
12	2884·0 (2·0)	−248·4 (2·0)	11·61	−0·406	0·579	2·9
12	2878·0 (4·2)	−247·3 (2·1)	11·64	−0·404	0·576	2·8
15	2707·2 (2·4)	−239·1 (1·7)	11·32	−0·395	0·557	2·3
20	2379·8 (5·6)	−216·2 (4·0)	11·01	−0·361	0·503	2·4
37	1556·2 (2·7)	−161·4 (2·0)	9·64	−0·282	0·375	1·9
37	1524·7 (4·0)	−158·7 (2·1)	9·61	−0·278	0·369	5·1
37	1493·5 (2·4)	−157·9 (1·6)	9·46	−0·278	0·367	0·8
37	1487·2 (2·4)	−156·8 (1·6)	9·48	−0·276	0·364	0·6

[a] The temperature variation between several of the experiments was too small (<1 °C) to be detected. [b] Standard errors (based on the estimated errors in line positions) are given in parentheses.

The orientation parameters will in general vary with the temperature of the sample.

A pseudo-square-planar geometry for (I) has been proposed previously[4] and confirmed in the solid state.[5,6] If this rigid D_{2h} geometry is maintained in solution, we should have observed a ten-line spectrum (twelve-line if the indirect couplings were not negligible).[7] In order to analyse the spectra in this way it was therefore necessary to assume that two pairs of lines were overlapping. This interpretation fails on two counts. An accidental overlap at all temperatures would be improbable, in view of the two-fold change in the width of the spectrum at the extremes of the temperature range (this consideration also rules out any structure of lower symmetry). Furthermore, the dipolar couplings which result are incompatible with any reasonable geometry.

We therefore considered the possibility of a pseudo-tetrahedral symmetry (D_{2h}). The effect of varying the single orientation parameter in equation (1) would then be to produce an overall scaling of the predicted eight-line spectrum[7] (*i.e.* the ratios of splittings would remain the same); this was not observed, as may be seen from the Table, which displays the calculated dipolar couplings for each spectrum.

Since no rigid structure is consistent with the spectra, we considered the possibility of intramolecular motion. The condition for an overlap of two pairs of lines in the ten-line spectrum is that the dipolar couplings T_{14} or T_{12} should equal T_{13} (Figure 1).[7] There is clearly no reasonable intramolecular motion which would make T_{12} equal T_{13}; we therefore conclude that the dipolar couplings T_{14} and T_{13} are equal due to an intramolecular rotation of one dithiolate ligand with respect to the other, or some other equivalent motion.

Such a motion must occur more rapidly than the change in long-range dipolar couplings produced by one rotation. Assuming that the molecule is planar except when quickly flipping we used X-ray diffraction distances for the planar molecule[5] to compute the orientation parameters, and hence the individual dipolar couplings

[3] E. Hoyer and W. Schroth, *Chem. and Ind.*, 1965, 652.

[4] G. N. Schrauzer and V. P. Mayweg, *J. Amer. Chem. Soc.*, 1965, **87**, 3585.

[5] E. Hohne, P. Prokop, and E. Hoyer, *Z. Chem.*, 1966, **6**, 71; J. Sieler, personal communication.

[6] K. W. Browall, L. V. Interrante, and J. S. Kasper, *J. Amer. Chem. Soc.*, 1971, **93**, 6289.

[7] J. Bulthuis, J. Gerritsen, C. W. Hilbers, and C. MacLean, *Rec. Trav. chim.*, 1968, **87**, 417.

T_{13} (rigid) and T_{14} (rigid) which average to the $T_{14}(= T_{13})$ observed. The difference between these couplings (see Table) represents a lower limit to the rate of rotation. The upper limit is set by the time needed for the molecule to reorient in the liquid crystal (otherwise a single orientation parameter would suffice to describe the molecular orientation). These experimental results also rule out any intermolecular exchange mechanism, as this would effectively remove dipolar couplings between protons in different ligands and give rise to a single doublet. In Figure 2 we show a typical spectrum and a computer simulation generated by a modified version of the n.m.r. program LAOCOON2.

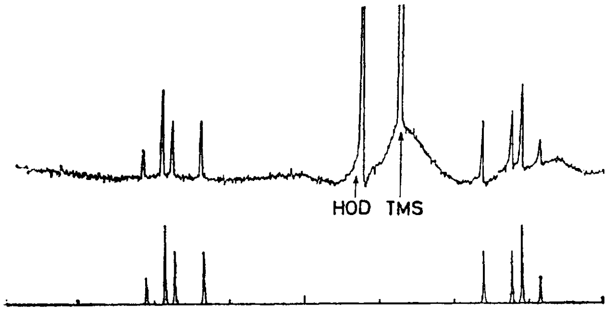

FIGURE 2 Observed and calculated nematic-phase proton n.m.r. spectra of (I). Scale divisions are at 1000 Hz intervals

It is interesting to note the unusually large degree of alignment of (I). For some of the spectra the orientation parameter S_{11} exceeds 0·5 in magnitude, and must therefore be positive. The smallest orientation parameter is S_{22}, indicating that the molecule is fairly free to rotate in such a way that the plane of the dithiolate ring system remains parallel with the optic axis of the liquid crystal. This suggests that the large orientation parameters result from interactions between the aromatic rings of the solvent molecules and the dithiolate ring system.

Equilibria between diamagnetic planar and paramagnetic tetrahedral forms of certain nickel complexes have been observed[8] by variable-temperature ^1H n.m.r. in the isotropic phase, since the observed proton signal occurs at the weighted mean frequency of the planar and tetrahedral forms. These studies have placed the rate of rotation between 10^3 and 10^9 Hz. We have measured the isotropic shift of (I) in $[^2H_8]$toluene from −56 to 100 °C, and noted a shift of the resonance frequency to low field of only 0·22 p.p.m. This may reflect an insignificant amount of the paramagnetic tetrahedral form in equilibrium with the planar ground state (or a small contact shift), or it may mean that the intermediate state during rotation does not involve a paramagnetic species.

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[8] R. H. Holm and M. J. O'Connor, *Progr. Inorg. Chem.*, 1971, **14**, 241.