The Structure of *ac*-Dichloro-*b*-ethylene-*d*-pyridineplatinum(II) from Hydrogen-1 and -2 Nuclear Magnetic Resonance Spectra of Liquid-crystal Solutions

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A ^1H n.m.r. spectrum of the complex $[PtCl_2(C_2H_4)(NC_5D_5)]$ has been obtained by decoupling of the spin coupling to deuterium for samples dissolved in thermotropic liquid crystals. The dipolar couplings have been used to obtain the relative positions of the protons and platinum. The quadrupole splittings observed in the ^2H n.m.r. spectra are used in conjunction with the order parameters derived from the proton spectra to show that the equilibrium structures have the pyridine ring inclined at an angle to the $PtCl_2$ plane, with rapid reorientation between the symmetry-related forms.

THE shapes of organic ligands attached to metals may be investigated by studying the n.m.r. spectra of liquid-crystal solutions.[1] The method has the considerable advantages over diffraction experiments in that the derived structure refers to the liquid state, and can give information on internal rotations. The disadvantages are principally the difficulty of dissolving these compounds in liquid-crystal solvents, and the limitation to molecules containing no more than eight interacting spins. The platinum–ethylene complexes form a class of compounds which demonstrate these difficulties of the n.m.r. method; thus Zeise's salt, $K[PtCl_3(C_2H_4)]$, contains only four protons, but does not dissolve in thermotropic liquid crystals, and the spectrum obtained for lyotropic solution did not resolve coupling to platinum.[2] The complex $[PtCl_2(C_2H_4)(py)]$ (py = pyridine) does dissolve in thermotropic nematogens to a sufficient extent to give a proton spectrum by the Fourier-transform repeated-pulse technique, but the ten interacting spins do not yield a resolved spectrum. McMillin and Drago [3] attempted to overcome these problems by using a polypeptide solution in CD_2Cl_2 as the liquid-crystal phase, and a deuteriated pyridine ligand. The low solute ordering in this phase resulted in a spectrum showing only about 10 lines, which was interpreted as due to non-resolution of ^1H–^2H and ^1H–^{195}Pt spin–spin coupling. The spectrum was analysed to yield the interproton coupling and some useful structural information was obtained. We show here that a study of this same species by ^1H-{^2H}, and by ^2H n.m.r. of thermotropic liquid-crystal solutions, yields much more information, and that the method is capable of application to many other similar organometallic compounds.

EXPERIMENTAL

The complex *trans*-$[PtCl_2(C_2H_4)(py)]$ and its $[^2H_5]$pyridine derivative were prepared by adding an equivalent molar amount of pyridine or $[^2H_5]$pyridine to Zeise's dimer. Subsequent solvent removal, crystallisation, and vacuum drying yielded the yellow crystalline product. The rate of pyridine exchange is known to be dependent on the presence of free pyridine.[4] In the absence of free pyridine the ^1H n.m.r. spectrum in $CDCl_3$ exhibits ^{195}Pt satellite lines for the ethylene and pyridine resonances.[4] The sample prepared by the above method has a ^1H spectrum in $[^2H_8]$-toluene showing sharp satellite lines for pyridine resonances up to *ca.* 60 °C, and at >70 °C the ethylene satellite lines also begin to broaden. The spectra in liquid-crystal solutions were recorded at temperatures <60 °C. Two liquid-crystal solvents were found to give good spectra: 4,4′-di-n-heptylazoxybenzene (dhab) which exhibits nematic and smectic A phases, and a mixture of 4-alkyl-4′-cyanobiphenyls supplied by B.D.H. Ltd. as mixture E7. Both solvents must be thoroughly dried before adding the complex to avoid premature decomposition, and in both cases *ca.* 1 mg dissolved in 0.3 g of solute; thus time-averaging techniques are essential to obtain either ^1H or ^2H spectra. The spectra were recorded using a Varian XL100-12 spectrometer in the Fourier-transform mode at 50 °C for dhab and 31 °C for E7. The ^2H spectra were obtained by averaging 40 K transients using *ca.* 40° pulse angles, 0.1-s acquisition times, and no pulse delay. In the case of the solution in dhab the spectrum showed only four instead of six lines, possibly because the deuterium nucleus which is in the γ position relative to nitrogen exchanges with solvent. The ^1H-{^2H} spectra were obtained by irradiating at the centre of the ^2H spectrum with 100 W of radiofrequency (r.f.) power. The decoupler was gated for 0.2 s whilst acquiring the ^1H-free induction decay, and off for 2 s to allow for dissipation of heat. The averaging of 4 500 decays was necessary to obtain an adequate signal-to-noise ratio, as shown in the Figure.

Analysis of Spectra.—The ^2H spectrum comprises a doublet from each non-equivalent ^2H nucleus, broadened by unresolved dipolar coupling. The quadrupole splittings [1] $\Delta\nu$ are given in Table 1. The ^1H-{^2H} spectra show the expected ten lines from an oriented AA′A″A‴ system arising from the four protons in molecules not containing ^{195}Pt, together with satellite lines arising from molecules containing the spin-$\frac{1}{2}$ isotope. The two separate spin systems were analysed using a version of LAOCN 3 modified to include dipolar coupling. The isotropic spin–spin coupling constants between protons were given the magnitude and signs appropriate to isotropic solution; [2] the magnitude of $J(^{195}Pt–^1H)$ was taken from an isotropic

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[1] J. W. Emsley and J. C. Lindon, ' NMR Spectroscopy using Liquid Crystal Solvents,' Pergamon, Oxford, 1975.

[2] P. Diehl and A. S. Tracey, quoted in ' NMR, Basic Principles and Progress,' eds. P. Diehl, E. Fluck, and R. Kosfeld, Springer-Verlag, Berlin, vol. 9, p. 73.

[3] D. R. McMillin and R. S. Drago, *Inorg. Chem.*, 1974, **13**, 546.

[4] F. Pesa and M. Orchin, *J. Organometallic Chem.*, 1974, **78**, C26.

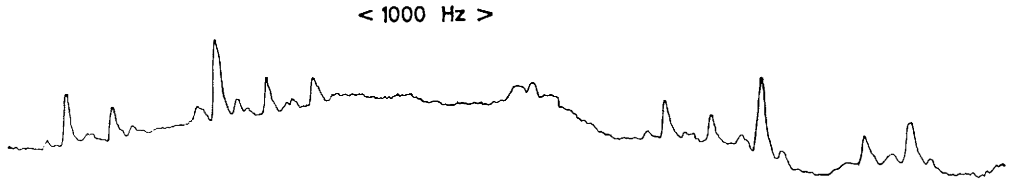
solution spectrum, but both positive and negative signs were used in deriving the dipolar coupling constant. Only the negative sign is consistent with a reasonable geometry. The dipolar couplings, D_{ij}, derived from both spectra are given in Table 1.

Vibrational corrections. Dipolar couplings are averages over vibrational motion, and are related to the equilibrium nuclear positions for a molecule with z as a C_2 axis by[5] equation (1) where D_{ij}^0 is given by (2). The terms $f_{ij\alpha\beta}$ in equation (1) may be computed from a knowledge of the normal co-ordinates of the molecule. There has not been a full analysis of the vibrational spectrum of this molecule, but it suffices to calculate the normal co-ordinates only for

$$D_{ij} = D_{ij}^{0} - \frac{h\gamma_i\gamma_i}{8\pi^2}[S_{zz}(2f_{ijzz} - f_{ijxx} - f_{ijyy}) + (S_{xx} - S_{yy})(f_{ijxx} - f_{ijyz}) + 4S_{xy}f_{ijxy}] \quad (1)$$

$$D_{ij}^{\circ} = -\frac{h\gamma_i\gamma_i}{8\pi^2 r_{ij}^3}[S_{zz}(3\cos^2\theta_{ijz} - 1) + (S_{xx} - S_{yy})(\cos^2\theta_{ijx} - \cos^2\theta_{ijy}) + 4S_{xy}\cos\theta_{ijx}\cos\theta_{ijy}] \quad (2)$$

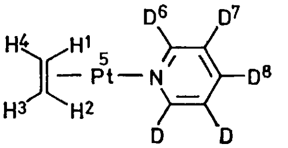
the $Pt(C_2H_4)$ fragment of the molecule. We have done this by computing normal co-ordinates for a moiety C_2H_4–$PtCl_2$–X, where X was a pseudo-atom of mass 30. The force field for the $PtCl_2(C_2H_4)$ group was taken to be one appropriate for Zeise's salt. There have been several i.r. and Raman studies on Zeise's salt, and there is some disagreement over the band assignments. We have used the assignments of Hiraishi,[6] who also derived a force field; however, symmetrical internal co-ordinates were used, which are not suitable for our purpose, hence we have derived a valence force field for Zeise's salt using the internal co-ordinates in Table 2. The force field has not been refined since the averaging of the D_{ij} values is not sensitive to small changes in the force field. Table 3 compares calculated frequencies for $[PtCl_2(C_2H_4)X]$ with those observed for Zeise's salt (X = Cl).



^1H-$\{^2H\}$ N.m.r. spectrum of $[PtCl_2(C_2H_4)(NC_5D_5)]$ as a solute in the nematic mixture E7

TABLE 1

Quadrupole splittings $\Delta\nu_i$/Hz derived from ^2H n.m.r. spectra, and dipolar couplings, D_{ij}/Hz, from ^1H-$\{^2H\}$ spectra of $[PtCl_2(C_2H_4)(NC_5D_5)]$ dissolved in 4,4′-di-n-heptylazoxybenzene (dhab) and nematic mixture E7



	dhab	E7
$\Delta\nu_6$ or $\Delta\nu_7$	±11 134 ± 20 or ±3 718 ± 20	±15 957 ± 20 or ±9 425 ± 20
$\Delta\nu_8$	Not observed	±65 525 ± 20
J_{12} *	9.0	9.0
J_{13} *	14.4	14.4
J_{14} *	0.0	0.0
J_{15} *	−60.8	−60.8
$D_{12} = D_{34}$	1 531.3 ± 0.5	1 695.1 ± 0.4
$D_{13} = D_{24}$	574.2 ± 0.6	565.5 ± 0.5
$D_{14} = D_{23}$	935.9 ± 0.6	129.6 ± 0.5
$D_{15} = D_{25} = D_{35} = D_{45}$	−153.7 ± 1.7	−137.3 ± 1.2

* Fixed at an isotropic value.

TABLE 2

Internal co-ordinates and valence force field for the complex $[PtCl_2(C_2H_4)X]$ (X = pseudo-atom)

Co-ordinate	Force constant *	Co-ordinate	Force constant *
R_{CH}	5.14	α_{ClPtX}	0.7
R_{CC}	6.55	α_{CPtX}	0.75
R_{PtCl}	2.00	α_{ClPtCl}	0.3
R_{PtX}	2.20	$R_{CH}R_{CH}$ (*gem*)	−0.199
R_{PtC}	1.67	$R_{CH}R_{CH}$ (*vic*)	−0.220
α_{HCH}	0.355	$R_{CH}R_{CC}$	−0.5
α_{HCC}	0.416	α_{CPtCl} (*cis*)	0.625
α_{CPtC}	0.242	$R_{PtC}R_{PtC}$	−0.355
α_{PtCH}	0.881	$R_{PtCl}R_{PtCl}$	0.387

* Units are mdyn $Å^{-1}$ for stretch and stretch–stretch force constants, and mdyn $Å^2$ rad^{-2} for angle bends (1 dyn = 10^{-5} N).

TABLE 3

Calculated vibrational wavenumbers with the force field of Table 2 compared to vibrational wavenumbers (cm^{-1}) of Zeise's salt

Wavenumber (cm^{-1})			
calc.	obs.	Symmetry	Dominant contribution to potential energy
2 839	3 013	a_1	R_{CH}
1 519	1 515		α_{CHH}
1 258	1 243		α_{PtCH}
914	975		α_{HCC} and α_{HCH}
414	405		R_{PtC}
360	309		R_{PtX}
338	338		R_{PtCl}
146	104		α_{CPtCl} and α_{ClPtX}
3 092	3 094	a_2	R_{CH}
1 222	Not observed		α_{PtCH} and α_{HCC}
845	841		α_{HCC}
145	158		α_{CPtCl}
2 989	2 988	b_1	R_{CH}
1 443	1 426		α_{HCH}
1 030	1 010		α_{HCC}
491	493		R_{PtC}
223	219		α_{CPtX}
91	88		α_{CPtCl}
3 083	3 079	b_2	R_{CH}
1 156	1 180		α_{PtCH}
721	720		α_{HCC}
329	327		R_{PtCl}
214	207		α_{CPtCl}
164	181		α_{ClPtX}

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[5] N. J. D. Lucas, *Mol. Phys.*, 1971, **22**, 233.

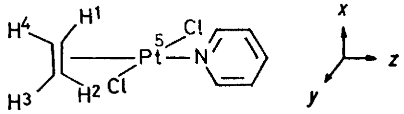
[6] J. Hiraishi, *Spectrochim. Acta*, 1969, **A25**, 749.

RESULTS AND DISCUSSION

The proton spectrum analyses as an AA′A″A‴ system, which means that the whole molecule must have a fixed structure with at least C_{2v} symmetry, or internal motion must generate this effective symmetry. Fixed structures with C_{2v} symmetry have S_{xy} zero in equation (1), whereas this off-diagonal matrix element is of equal magnitude but changes in sign for symmetry-related rotational isomers, hence averaging gives zero for the term $4S_{xy} \cos \theta_{ijx} \cos \theta_{ijy}$, provided that the bond lengths and angles are identical in each configuration. The proton spectrum alone, therefore, reveals the presence of internal rotation only if there are appreciable changes in structure in different rotational forms, in which case the relative nuclear positions derived from the dipolar couplings using equation (1) would be expected to differ appreciably from those derived for the crystalline form of Zeise's salt by neutron diffraction.[7] To derive nuclear positions and S values from equation (1), using proton data only, it is necessary to assume the value of one interproton distance, and we have chosen this to be $r_{12} = 1.833$ Å, giving the data in Table 4 for the two sets of dipolar couplings. It is seen that the neutron-diffraction and n.m.r. results agree within experimental error; thus the proton data are insensitive to any internal rotations.

TABLE 4

Nuclear co-ordinates (Å) of protons and platinum in $[PtCl_2(C_2H_4)(NC_5D_5)]$ and order parameters derived from dipolar couplings



Co-ordinate	Solution		Neutron diffraction
	dhab	E7	
$x_1 = x_4 = -x_2 = -x_3$	1.235 ±0.001	1.236 ±0.001	1.248 ±0.005
$y_1 = y_2 = -y_4 = -y_3$ *	0.916 3	0.916 3	0.916 3
$z_1 = z_2 = z_3 = z_4$	2.179 ±0.006	2.174 ±0.006	2.185 ±0.009
z_5 *	0.0		0.0
$x_5 = y_5$ *	0.0		0.0
S_{zz}	0.248 ±0.001	0.225 ±0.001	
$S_{xx} - S_{yy}$	−0.150 ±0.001	−0.217 ±0.001	

* Fixed.

The deuterium quadrupole splittings can also provide limited but useful structural information. The splittings $\Delta\nu$ are related to S values and γ_i, the angles made by the C–D bonds and the z axis, as in (3) where θ is the angle that the plane of the pyridine ring makes with the $PtCl_2$ plane. We have assumed that z is an axis of local C_{2v} symmetry for the pyridine ring The values of q_{CD}, the deuterium quadrupole coupling constant for the C–D bonds, and η, the asymmetry parameter, have been determined for pyridine to be[8] 181.9 ± 1.0 kHz and −0.039 respectively. With these values of q_{CD} and η it is possible to calculate the value for S_{zz} from the

$$\Delta\nu_i = \tfrac{3}{2}q_{CD}[S_{zz}(\cos^2\gamma_i - \tfrac{1}{3}\eta\sin^2\gamma_i) + S_{xx}(\sin^2\gamma_i\cos^2\theta + \tfrac{1}{3}\eta\sin^2\theta - \tfrac{1}{3}\eta\cos^2\gamma_i\cos^2\theta) + S_{yy}(\sin^2\gamma_i\sin^2\theta + \tfrac{1}{3}\eta\cos^2\theta - \tfrac{1}{3}\eta\cos^2\gamma_i\sin^2\theta) + 2S_{xy}\sin\theta\cos\theta(\sin^2\gamma_i - \tfrac{1}{3}\eta\cos^2\gamma_i)] \quad (3)$$

magnitude of $\Delta\nu_8$ for the E7 solution. For position 8 the splitting is independent of θ and γ_8 is zero. The value of S_{zz} determined in this way is 0.233 7 ± 0.000 2 compared with 0.255 ± 0.001 found from the proton dipolar couplings and assuming $r_{12} = 1.833$ Å. The close agreement confirms our assumption that z is collinear with the C_{2v} axis of local symmetry for the pyridine ring. We can also use the value of S_{zz} found from $\Delta\nu_8$, together with dipolar couplings for the E7 solution given in Table 1, to determine an absolute size for the $Pt(C_2H_4)$ moiety. This gives the nuclear co-ordinates of proton 1, relative to Pt as origin, of $x_1 = 1.252 \pm 0.001$, $y_1 = 0.929 \pm 0.001$, and $z_1 = 2.085 \pm 0.006$ Å.

The splittings $\Delta\nu_6$ and $\Delta\nu_7$, and the order parameter S_{zz} and $S_{xx} - S_{yy}$, can be used to test whether the molecule is rigid or has internal motion. The conclusion drawn from the proton data for the ethylene group is that three models are possible: (*a*) a rigid structure with C_{2v} symmetry; (*b*) hindered rotation between the symmetry-related forms, each having only C_2 symmetry; and (*c*) effectively free rotation. For case (*a*) S_{xy} in equation (3) is zero, and θ is either 0 or 90°, and it is possible to determine the angles γ_6 and γ_7 from the $\Delta\nu$ values. Taking into account the uncertainties in sign and assignment of the $\Delta\nu_6$ and $\Delta\nu_7$ splittings means that there are several possible sets of values of γ_6 and γ_7 which can be derived from the data from the dhab and E7 solutions. However, not one assignment gives the same pair of angles for both sets of results, hence model (*a*) can be rejected. Case (*c*) contains three kinds of situation. True free rotation would imply a constant potential energy as θ is varied, and would also imply a rotational frequency approaching the limit imposed by the amount of inertia. In this case it is probable that internal rotation is much faster than the reorientational period for the molecule in the liquid crystal, and $\Delta\nu_i$ is dependent only on γ_i, S_{zz}, and η. However, the same conclusion is arrived at for the situation where the molecule moves between the two forms having C_{2v} symmetry, irrespective of the rate of motion. Both these cases may be tested again by calculating sets of values for γ_6 and γ_7, and again not one assignment gives the same values of γ_6 and γ_7, hence model (*c*) is rejected. There is a third kind of free rotation, one in which all the values of θ are sampled with near equal probability but the rate of rotation is slower than the rate of reorientation in the liquid crystal. Such a case is not solvable, and is, fortunately, most improbable.

[7] R. A. Love, T. F. Koetzle, G. J. B. Williams, L. C. Andrews, and R. Bau, *Inorg. Chem.*, 1975, **14**, 2653.

[8] J. W. Emsley, J. C. Lindon, and J. Tabony, *J.C.S. Faraday II*, 1975, 579.

For case (*b*) the unknowns in equation (3) are γ_6, γ_7, and a separate value of S_{xy} for each of the two sets of data. Calculations made with $\gamma_6 = 58.4°$ and $\gamma_7 = 62.2°$, the values appropriate for free pyridine,[9] show that values of S_{xy} can be chosen which bring observed and calculated splittings into close agreement when θ lies anywhere between *ca.* 30 and 70°, and when the assignments are made of the $\Delta\nu$ values (in Hz) as follows:

Solution	$\Delta\nu_6$	$\Delta\nu_7$
dhab	−3 718	−11 134
E7	−9 425	−15 957

Small changes in γ_6 and γ_7 will widen the range of acceptable solutions, hence θ cannot be determined with any greater precision than to state that it must be between about 10 and 80°. Values of θ have been determined by Meesler and Olie[10] for crystalline dichloro(ethylene)platinum(II) complexes of substituted pyridines as 50 (for *p*-methyl substituted) and 46° (*p*-cyano); thus our results are in broad agreement, with the additional information that the pyridine ring and ethylene groups move relative to one another so that the four positions with constant θ are equally probable.

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[9] G. O. Sorensen, L. Mahler, and N. Rastrup-Andersen, *J. Mol. Structure*, 1974, **20**, 119.

[10] M. A. M. Meesler and K. Olie, *Crystal. Struct. Comm.*, 1975, **4**, 725.