Proton Nuclear Magnetic Resonance Behaviour of Acetylacetonato(chloro)-2-chloromethylpyridineplatinum(II)

By **Flaviano Coletta, Renato Ettorre,*** and **Alessandro Gambaro,** Institute of Physical Chemistry and Institute of General Chemistry, University of Padua, Italy

The temperature dependence of the ^{1}H n.m.r. spectrum of the complex PtCl(acac)(2-chloromethylpyridine) indicates the presence at low temperature of a locked structure wherein the methylene protons occupy two non-equivalent positions. An averaging process of the proton sites is observed at higher temperatures. The following activation parameters for the exchange process have been calculated: $\Delta H^\ddagger = 57$ kJ mol^{-1}, $\Delta S^\ddagger = -15$ J K^{-1} mol^{-1}, $E_a = 60$ kJ mol^{-1}, log $A = 12{\cdot}5$. The results are interpreted in terms of the barrier to rotation about the Pt–N co-ordination bond.

STUDIES of hindered internal rotations of square planar d^8 complexes by means of n.m.r. spectroscopy have been reported.[1,2] Knowledge of rotational barriers in these systems is also of interest in the light of correlations between chemical behaviour and conformation. For example, the retardation of rates of planar substitution reactions in complexes of platinum(II) with *ortho*-substituted pyridine or aryl ligands is ascribed to steric shielding of the metal by the *ortho*-substituents, caused by restricted rotation about the platinum–ligand co-ordination bond.[3] Also, the marked stability of *ortho*-substituted aryl derivatives of nickel(II) is related to electronic and steric effects due to blocking of the ligands.[4]

Here we describe an investigation of the intramolecular dynamics of the platinum(II) complex PtCl(acac)(2-chloromethylpyridine) (see Figure 1) by variable-temperature ^{1}H n.m.r. measurements.

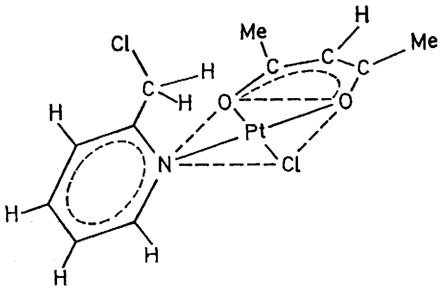

FIGURE 1 PtCl(acac)(2-chloromethylpyridine) in a possible conformation

EXPERIMENTAL

Preparation of Acetylacetonato(chloro)-2-chloromethylpyridineplatinum(II).—HPt(acac)$_2$Cl[5] was dissolved in the minimum volume of benzene and treated with an equimolar amount of 2-chloromethylpyridine, freshly prepared from the commercial hydrochloride. The mixture was set aside for two days, when yellow crystals of the product were collected. Further crystals were obtained from the solution by precipitation with n-pentane. The compound was dissolved in chloroform and recrystallized by addition of n-pentane (Found: C, 29·15; H, 2·9; N, 3·1. Calc. for $C_{11}H_{13}Cl_2NO_2Pt$: C, 28·9; H, 2·85; N, 3·05).

Spectroscopic Measurements.—N.m.r. spectra for dilute $CDCl_3$ solutions, with tetramethylsilane as internal reference, were recorded on Varian A 56/60 and 90 MHz HFX Bruker spectrometers equipped with variable-temperature probes. Temperatures at the probes were measured by chemical shifts of precalibrated methanol and ethylene glycol samples. Measurements were made under the appropriate conditions of low sweep and low r.f. power with the field homogeneity optimized for the internal tetramethylsilane.

RESULTS AND DISCUSSION

The ^{1}H n.m.r. data for the complex in deuteriochloroform at a probe temperature of 41 °C are given in the Table. Relative intensities in agreement with the assignments were measured. The three low-field resonances (pyridine protons) are complex and have not been examined in detail. All other resonances appear as triplets, due to coupling with ^{195}Pt (33·7%, $I = 1/2$); the high-field CH_2 satellite overlaps with the low-field CH satellite. ^{195}Pt–^{1}H Coupling constants (temperature invariant) and chemical shifts are in the range found for related platinum(II) complexes.[1,6]

N.m.r. data for PtCl(acac)(2-chloromethylpyridine)

Type of proton	Chemical shift (τ)	^{195}Pt-^{1}H coupling/Hz
Pyridine ring	*ca.* 1·0 *ca.* 2·1 *ca.* 2·6	Not analysed
CH_2Cl [a]	4·30	10·0
CH [b]	4·45	9·3
$CH_3(1)$ [b]	8·03	4·3
$CH_3(2)$ [b]	8·18	5·0

[a] $J_{H-H} = 14{\cdot}4$ Hz (see text). [b] Acetylacetone resonances; (1) and (2) correspond to two methyl environments.

A temperature dependence of the methylene protons is observed. Lowering the temperature causes broaden-

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[1] C. E. Holloway, G. Hulley, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc.* (*A*), 1969, 53; 1970, 1653 and references therein.

[2] J. W. Faller and M. J. Mattina, *Inorg. Chem.*, 1972, **11**, 1296.

[3] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' J. Wiley and Sons, New York, 1967, 2nd edn., p. 387.

[4] G. E. Coates, M. L. H. Green, and K. Wade, 'Organometallic Compounds,' Methuen, London, 1968, vol. 2, 3rd edn., p. 225.

[5] D. Gibson, J. Lewis, and C. Oldham, *J. Chem. Soc.* (*A*), 1967, 72.

[6] G. Hulley, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc.* (*A*), 1970, 1732; A. R. Brause, F. Kaplan, and M. Orchin, *J. Amer. Chem. Soc.*, 1967, **89**, 2661.

ing in the lines of the initial triplet, which is eventually split into a new complex pattern (see Figure 2). The limiting low-temperature spectrum [Figure 2(d)] is assigned as an AB pattern (66·3% due to Pt with $I = 0$), where $J_{AB} = 14{\cdot}4$ Hz and $\Delta\nu_{AB} = 0{\cdot}15$ p.p.m., superimposed upon an ABX pattern (33·7% due to Pt with $I = 1/2$).

The AB system is confirmed by comparison of the spectra recorded at 60 and 90 MHz. As far as the proposed ABX system is concerned, only the central peaks of the downfield pseudo-AB quartet are clearly observable, but the existence of up-field peaks, overlapping with major resonances in the spectrum, is also apparent. The outer lines of the two subspectra are possibly too weak to be detected.

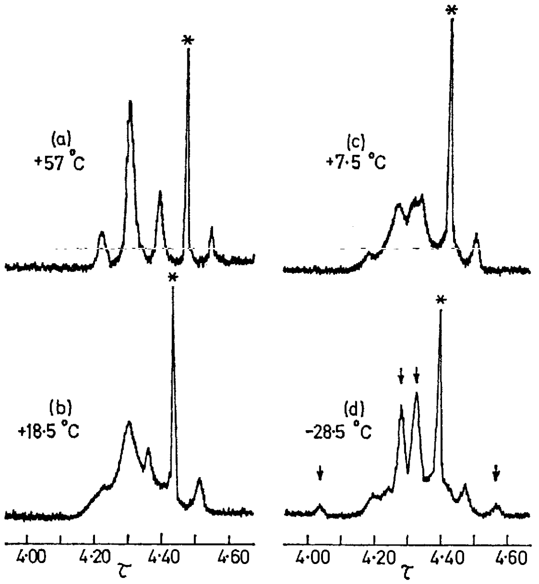

FIGURE 2 60 MHz spectra of PtCl(acac)(2-chloromethylpyridine) in the CH_2 and CH region. The asterisk denotes the central peak of the CH resonance. The methylene AB pattern in (d) is indicated by arrows

These observations can be explained by the presence at low temperature of a locked structure (on the n.m.r. time scale) wherein the methylene protons occupy two non-equivalent positions; the exchange of protons between the A and B sites through internal rotations, leads to an $A_2 + A_2X$ system at higher temperatures. Magnetic non-equivalence is expected to occur for any non-dynamic structure where the pyridine ring is not coplanar with the platinum–ligands square plane or the methylenic H–H line is not perpendicular to the plane of the pyridine ring. Averaging of non-equivalence of these protons can, in principle, occur by rotation about the Pt–N bond and/or the C–CH_2Cl bond, such that interchange of the chloromethyl group is produced between two positions symmetrical with respect to each other through a plane defined by the co-ordination square plane.

The temperature dependence of the methylene resonance cannot be accounted for by processes such as dissociation of 2-chloromethylpyridine from the metal or bimolecular exchange of the ligand between two platinum atoms, since ^{195}Pt–^{1}H coupling for the CH_2Cl group persists over the entire range of temperature. Also, changes of conformer populations about the Pt–N and C–CH_2Cl bonds are ruled out on the basis of the negligible effect of temperature upon the mean chemical shift of the CH_2 protons and the chemical shift of the $CH_3(1)$ and $CH_3(2)$ protons. Shift of the midpoint of these resonances in the 60 MHz spectrum is less than 2 Hz over a range of 90 °C; the frequency separation between the methyl resonances is not affected at all. Some appreciable drift with temperature is observed only for the acetylacetone CH resonance (see Figure 2) and this may be ascribed to local solvent interactions.

Kinetic analysis of the n.m.r. data was performed by matching of observed and calculated spectra for the AB part of the AB + ABX system in the intermediate exchange conditions. Computer simulation of the spectra was carried out using the method of Binsch.[7] The following rate constants (s^{-1}) at different temperatures (°C, values in parentheses) and activation parameters have been obtained for the averaging process: 290 (41), 100 (23·5), 45 (18·5), 30 (12·5), 20 (7·5); $\Delta H^{\ddagger} = 57 \pm 3$ kJ mol^{-1}, $\Delta S^{\ddagger} = -15 \pm 11$ J K^{-1} mol^{-1}, $E_a = 60 \pm 3$ kJ mol^{-1}, $\log A = 12{\cdot}5 \pm 0{\cdot}5$. The uncertainty intervals, based on the least-square fit of the Eyring and Arrhenius plots, are on the optimistic side. The activation parameters probably carry even greater errors, due to difficulties in spectral resolution, to the small value of the AB chemical shift, and to the fact that the latter was assumed to be temperature invariant. The change of $\Delta\nu_{AB}$, however, should not exceed 0·04 Hz K^{-1} at 60 MHz.

It can be postulated that the relative stability of conformations in PtCl(acac)(2-chloromethylpyridine) is chiefly dependent on non-bonded interactions between the chloromethylpyridine ligand and the rest of the square planar complex, although electronic contributions caused by double-bond character of the Pt–N bond might also be involved. Thus, the most likely ground-state structure of the complex is one in which non-bonded repulsions are minimized, that is, the pyridine ring lies approximately perpendicular to the co-ordination square plane. On the basis of this proposed orientation, averaging of the methylene proton sites requires rotation of nearly 180° of the ligand about the Pt–N axis, possibly accompanied by rotation about the C–CH_2Cl bond.* The energy threshold for the latter rotation should be relatively small, judging from examination of molecular models and comparison with the steric hindrance in polyhalogeno-*ortho*-bis(monohalogenomethyl)benzenes. For

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* The lowest barrier pathway for the process would probably involve an activated complex where the α-hydrogen of the pyridine is adjacent to the chloride ligand and the hydrogens of the chloromethyl group are adjacent to an acetylacetone oxygen atom.

[7] G. Binsch, *J. Amer. Chem. Soc.*, 1969, **91**, 1304.

these systems free internal rotation at room temperature has been detected.[8] On these grounds the calculated activation energy of the averaging process can be regarded primarily as the result of the barrier to rotation of the ligand about the Pt–N co-ordination bond.

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[8] V. Mark and V. A. Pattison, *Chem. Comm.*, 1971, 553.