Short Communications

A Carbon-13 NMR Study of Platinum(II) Diamine Complexes

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Platinum(II) chelates with isomeric methyl-substituted 1,2-ethanediamines as ligands have been studied by carbon-13 NMR spectroscopy in an effort to elucidate their conformational behaviour in aqueous solution.

The compounds investigated are the square planar complexes $[Pt(NH_3)_2(mbn)]Cl_2$, $[Pt(NH_3)_2(lbn)]Cl_2$, and $[Pt(NH_3)_2(ibn)]Cl_2$ where mbn and lbn are the *meso-* and the $(-)_D$-form of 1,2-dimethyl-1,2-ethanediamine, and ibn is 1,1-dimethyl-1,2-ethanediamine.

The three *cis*-diammine salts were prepared from the pertinent *cis*-dichloro(diamine)platinum(II) compounds in accordance with the procedures for the corresponding ethylenediamine complexes.[1,2] The yellow *cis*-dichloro compounds were treated with conc. NH_3-water at 100 °C in a stoppered test tube till they dissolved; the solution was filtered and after evaporation *in vacuo* over conc. H_2SO_4 in a desiccator the colourless crystals of $[Pt(NH_3)_2(diamine)]Cl_2$ were collected.

The five-membered, chelate rings may adopt either δ or λ form,[3] the two conformations being interconvertible on ring inversion. From Fig. 1 it appears that the substituted methyl groups may be either equatorially or axially orientated relative to the ring.
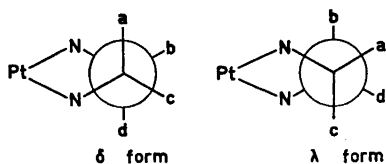

Fig. 1. The 1,2-ethanediamine-platinum moiety of the three complexes as wieved along the C–C bond of the five-membered ring (Newman projection). The conformations of the methyl-substituted 1,2-ethanediamines are obtained by adding methyl groups at two of the sites a, b, c, and d as specified in Table 1.

Table 1. Specification of the two methyl group positions in $[Pt(NH_3)_2(mbn)]^{2+}$, $[Pt(NH_3)_2(lbn)]^{2+}$, and $[Pt(NH_3)_2(ibn)]^{2+}$.

Methyl position (See Fig. 1)		Orientation in δ-ring	Orientation in λ-ring
mbn	b	equatorial	axial
	a	axial	equatorial
lbn	a	axial	equatorial
	d	axial	equatorial
ibn	a	axial	equatorial
	c	equatorial	axial

The δ and λ forms of each of the complexes $[Pt(NH_3)_2(mbn)]^{2+}$ and $[Pt(NH_3)_2(ibn)]^{2+}$ are mirror images of each other and must therefore have the same potential energy.

But as it is seen from Table 1 the two forms of $[Pt(NH_3)_2(lbn)]^{2+}$ are different; the δ conformation contains two axial and the λ conformation two equatorial methyl groups. In the conformationally related *trans*-1,2-dimethylcyclohexane the energy difference between the diaxial and the diequatorial conformations has been calculated to 2.7 kcal/mol.[4] By analogy it is estimated that the λ ring with lbn is favoured relative to the δ ring by 2–3 kcal/mol. This would mean that less than 4 % of the complex has the δ conformation in a solution at room temperature.

The proton-decoupled 22.63 MHz carbon-13 NMR spectra of the three complexes in D_2O solution were measured in the manner that has been described previously,[5] and the data are shown in Table 2.

The methyl resonances in all three spectra have two well-resolved satellite peaks due to coupling with ^{195}Pt ($I = \frac{1}{2}$, 34 % abundance). The coupling constants, $^3J_{Pt-N-C-C}$, are given in Table 2. It is seen that the value for the lbn complex is about twice that for the other two.

^{195}Pt sidebands were resolved and distinct for the methyl peaks only, so values for $^2J_{Pt-N-C}$ could not be obtained, but they must all be less than 10 Hz.

Platinum-proton three-bond coupling constants in $Pt-N-C-H$ fragments have been rationalized by assuming a Karplus type angular dependence.[6,7] It turns out that the variation of the platinum-carbon coupling constants

Table 2. ^{13}C NMR data.

	$\delta(-CH_3)$	$^3J_{Pt-N-C-C}$ in Hz	$\delta(>CH_2)$	$\delta(-\overset{\mid}{\underset{\mid}{C}}H-)$	$\delta(-\overset{\mid}{\underset{\mid}{C}}-)$
$[Pt(NH_3)_2(mbn)]^{2+}$	13.8	27.3	—	57.7	—
$[Pt(NH_3)_2(lbn)]^{2+}$	18.0	49.8	—	59.9	—
$[Pt(NH_3)_2(ibn)]^{2+}$	24.3	22.4	56.7	—	61.3

found here would similarly be explained if the relationship

$$^3J_{Pt-N-C-C} \approx a \cos^2 \phi$$

is valid, ϕ being the dihedral angle between the planes PtNC and NCC, and a being a constant.

Molecular models reveal that ϕ for equatorial and axial methylcarbons are $\sim 180°$ and $\sim 90°$, respectively, *i.e.* according to the equation above

$$^3J_{Pt-N-C-C_{eq}} \approx a \text{ and } ^3J_{Pt-N-C-C_{ax}} \approx 0$$

In $[Pt(NH_3)_2(mbn)]^{2+}$ and $[Pt(NH_3)_2(ibn)]^{2+}$ the methyl groups spend equal time in equatorial and axial orientations and averaged coupling due to rapid ring inversion would give $^3J \approx \frac{1}{2}a$. As discussed above the methyl groups in $[Pt(NH_3)_2(lbn)]^{2+}$ are predominantly equatorial, giving $^3J \approx a$.

Thus the experimental coupling constants are accounted for by the Karplus-like relationship with $a = 50$ Hz.

From the presence of only one methyl doublet in the proton NMR spectrum of $[Pt(NH_3)_2(mbn)]^{2+}$ it has been concluded [8] that in this complex the conformational inversion is rapid on the NMR time scale.

Considering that the ^{13}C chemical shift differences between equatorial and axial methyl groups in methylcyclohexanes are of the order of $5-9$ ppm,[9] the observed singularity of the methyl pattern in the ^{13}C spectra of $[Pt(NH_3)_2(mbn)]^{2+}$ and $[Pt(NH_3)_2(ibn)]^{2+}$ is a confirmation of the expected rapid ring inversion in these two complexes.

But in the case of $[Pt(NH_3)_2(lbn)]^{2+}$ the presence of only one methyl resonance does not necessarily imply rapid inversion; slow inversion would also result in a single methyl peak, as the energetically unfavourable δ conformation would scarcely be observable.

Internal molecular motion is one of the factors controlling the ^{13}C spin-lattice relaxation;[10] so any differences in the ring inversion rates of the three isomeric platinum complexes will to some degree influence the spin-lattice relaxation times, T_1. In order to explore this a relaxation study of the methyl carbon atoms was undertaken.

T_1 was determined from proton-decoupled, partially-relaxed Fourier transform spectra obtained by use of the pulse sequence $(T-180° - \tau - 90°)_n$,[10] where $T = 10$ s, $n = 100$, and $\tau = 3$, 2, 1, and 0.1 s. The concentration of the three complexes was 0.66 g per ml D_2O, the temperature was 30.0 °C, and the solutions were deoxygenated. The T_1 values obtained are estimated to be accurate and reproducible within ± 15 %.

T_1 for $[Pt(NH_3)_2(mbn)]^{2+}$, $[Pt(NH_3)_2(lbn)]^{2+}$, and $[Pt(NH_3)_2(ibn)]^{2+}$ was found to be 1.5, 1.4, and 1.3 s, respectively. So, considering the experimental uncertainty, these measurements do not demonstrate any significant differences between the spin-lattice relaxation times of the methyl carbon atoms.

The Bruker WH 90 spectrometer is placed at our disposal by Statens Naturvidenskabelige Forskningsråd.

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