Rigid Conformers of an Isoquinoline–Platinum(II) Complex

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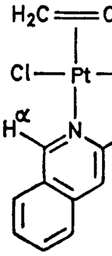
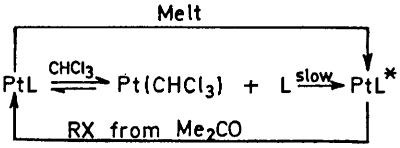
Summary The unusual n.m.r. spectral behaviour of dichloro(ethylene)isoquinolinylplatinum(II) suggests that the isoquinoline fragment exists in two different and mutually perpendicular rigid conformations leading to separately isolable but interconvertible isomers.

IN connection with our studies[1] of $(C_2H_4)PtCl_2(L)$ complexes we prepared complex (**1**). The n.m.r. spectrum of this complex in $CDCl_3$ at room temperature showed no coupling of the isoquinoline proton with ^{195}Pt. On gradual cooling, however, coupling with H^{α} (J 41 Hz) was clearly noted (at *ca.* 0°) and on further cooling, to a final temperature of −40 °C, coupling with $H^{\alpha'}$ (J 30 Hz) was observed. On warming to room temperature, the original spectrum was reproduced. We attribute this behaviour to the fact that in order for spin–spin coupling to be observed,[2] the average lifetime of the PtL complex must be larger than $1/J$ and apparently the rate of exchange of L with solvent at the intermediate temperature is such that coupling with the proton having the higher coupling constant is clearly discernible. At the lower temperature the rate of exchange is sufficiently slow on the n.m.r. time scale to discern coupling also with the proton having the smaller J value.



(1)

However, after 3 days at room temperature in $CDCl_3$ solution, coupling of both H^{α} and $H^{\alpha'}$ was clearly apparent. The chemical shifts and coupling constants of H^{α} and $H^{\alpha'}$ at room temperature were virtually the same as that observed in the spectrum previously determined at −40 °C. We propose that after being left for a long time in solution, the original complex PtL is slowly converted into a conformer PtL*. The original species may have a configuration in which the molecular plane of the isoquinoline coincides with square plane defined by the Pt, Cl_2, and N atoms. In this conformation access to the empty Pt 6*p* orbital permits rapid exchange with solvent. When left, this species is slowly converted into a more stable conformer, PtL*, in which the isoquinoline plane is now perpendicular to the $NPtCl_2$ plane. The resulting shielding of the empty *p* orbital makes solvent attack difficult. In this conformation there is minimal steric overlap between the chlorine atoms and the α protons. If this postulate is valid, the barrier to rotation from the rigid planar PtL form to the rigid perpendicular PtL* form must still be accounted for. This barrier may arise from weak hydrogen bonding between the chlorine atoms and the α protons in the planar conformation. When the perpendicular form, PtL*, is precipitated from $CHCl_3$ and recrystallized from acetone (a relatively good co-ordinating solvent) the original PtL species is regenerated (n.m.r. in $CDCl_3$). Heating of PtL to its m.p. causes conversion into PtL*. The interconversions may be represented as in the Scheme.



SCHEME

The isoquinoline complex (**1**) was prepared by extension of known procedures.[1] Elemental analyses for PtL and PtL* were similar and in good agreement with calculated values. The i.r. ($CHCl_3$ solution) and the n.m.r. spectra of PtL and PtL* were also essentially identical, as were physical properties and appearance. *X*-ray work is in progress.

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[1] M. Orchin and P. Schmidt, (a) *Inorg. Chim. Acta Rev.*, 1968, **2**, 123; (b) *Co-ordination Chem. Rev.*, 1968, **3**, 345.

[2] J. Emsley, J. Feeney, and L. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon New York, 1965, vol. 1.