The Conformation of Chelated (—)-Propylenediamine and Related Compounds in their Diamagnetic Palladium(II), Platinum(II), and Cobalt(III) Complexes in Aqueous Solution

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THE propylenediamine (pn) chelate ring is thought to form a fixed nonplanar *gauche* structure in solution,[1,2] but no direct experimental evidence has been reported for such a structure. We have measured ^{1}H n.m.r. spectra of [Pd(—)-pn$_2$]Cl$_2$, [Pt(—)-pn$_2$]Cl$_2$, and K[Co(CN)$_4$(—)-pn] in D_2O using a Varian HA-100 spectrometer. Nuclear magnetic double resonance was used, in which the methyl signal was decoupled to give a simpler ABC pattern. For example, the spectrum of [Pd(—)-pn$_2$]Cl$_2$ exhibits a doublet due to the methyl groups (1·22 p.p.m.), two quartets (2·53 and 2·81 p.p.m.), and a complicated multiplet (3·18 p.p.m.). The multiplet is converted into a quartet when the methyl signal is irradiated. These results indicate that the new quartet corresponds to the methine proton and the original two quartets to the methylene protons. These quartets are denoted tentatively A, B, and C, from higher to lower magnetic field.

The coupling constants, the chemical shifts, and the intensities were calculated according to Waugh's exact analysis.[3]

Two possible conformers can be present when (—)-propylenediamine co-ordinates to a metal, the λ-*gauche* and δ-*gauche* forms, with the methyl group equatorial and axial to the chelate ring, respectively. The λ-*gauche* form can provide three kinds of coupling: *geminal, trans,* and *gauche*. On the other hand, the δ-*gauche* form gives two different kinds of coupling: one *geminal* and two *gauche*. The calculated coupling constants have been compared with the theoretical values[4,5] shown in the Table. The calculated coupling constant J_{AB} (—12·5 c./sec.) is for geminal coupling, because A and B are the methylene signals. The calculated constants J_{BC} (4·2 c./sec.) and J_{AC} (9·9 c./sec.)

Coupling constants of [Pd(—)-pn$_2$]Cl$_2$ *in* D_2O

	Experimental (c./sec.)	Theoretical (c./sec.)	
J_{trans} (J_{AC})	9·9	11·0	16·1 (ref. 4)
J_{gauche} (J_{BC})	4·2	2·0	4·0 (ref. 4)
J_{gem} (J_{AB})	—12·5	13·2	13·4 (ref. 5)

are in good agreement with the theoretical values for the *gauche* and the *trans* coupling, respectively. Consequently, A corresponds to the axial and B to the equatorial proton. This assignment leads to the conclusion that the (−)-propylenediamine chelate ring has λ-*gauche* form even in a solution at room temperature.

Little information is available about chelating ligands having energetically equal δ- and λ-conformers such as *meso*-butylenediamine (*meso*-bn), *meso*-stilbenediamine (*meso*-stbn) and isobutylenediamine (iso-bn). Woldbye *et al.*[5] measured the ^{1}H n.m.r. spectrum of $[Co(meso\text{-}bn)_3]^{3+}$ in aqueous solution at room temperature and suggested that the chelate had a fixed *gauche* structure. We have measured the 100 Mc./sec. ^{1}H n.m.r. spectra of $[Pd(iso\text{-}bn)_2]Cl_2$, $[Pt(iso\text{-}bn)_2]Cl_2$, $[Pt(NH_3)_2(meso\text{-}bn)]Cl_2$, $[Co(NH_3)_4(meso\text{-}bn)]Br_3$, and $[Pt(en)(meso\text{-}bn)]Cl_2$. The methylene and the methyl signals of $[Pd(iso\text{-}bn)_2]Cl_2$ and the methine signal of the methyl-decoupled spectrum of $[Co(NH_3)_4(meso\text{-}bn)]Br_3$ consist of sharp singlets. The methylene signal of $[Pt(iso\text{-}bn)_2]Cl_2$, the methine and the ethylene signals of $[Pt(en)(meso\text{-}bn)]Cl_2$ exhibit sharp singlets with satellites corresponding to ^{195}Pt (J_{Pt-H} 38 c./sec.). On the basis of these data, we can conclude that these chelates change their conformation from δ to λ and *vice versa* rapidly on the n.m.r. time scale in a solution at room temperature. An alternative interpretation involving a planar chelate ring seems less appropriate. In these chelates the energy corresponding to δ- and λ-*gauche* forms is equal and the energy barrier for the interconversion between them may be small even when bulky phenyl groups are attached to the chelate.

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