Detection of Diastereoisomers in the ^{1}H Nuclear Magnetic Resonance Spectra of Tetrahedral Nickel Complexes

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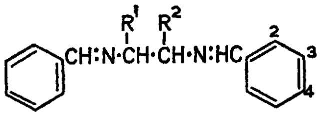
Summary Sizeable ^{1}H n.m.r. frequency differences are found to exist for corresponding resonances of fully tetrahedral diastereoisomeric nickel(II) complexes.

THE detection of diastereoisomers in the ^{1}H n.m.r. spectra of paramagnetic metal complexes containing two or more asymmetric centres has been reported for a number of cases, most of which involve four-co-ordinate nickel(II) complexes which undergo a dynamic planar(diamagnetic) $\rightleftharpoons$tetrahedral(paramagnetic) equilibrium in solution.[1] Complexes containing two asymmetric centres are capable of existing in active: (+,+), (−,−), or *meso* (+,−) forms which in principle have distinguishable ^{1}H n.m.r. spectra. Paramagnetic complexes show large isotropic shifts (resonance frequency displacements from the diamagnetic positions) owing to the presence of unpaired electrons. For systems for which the planar–tetrahedral interconversion is rapid on the n.m.r. time scale (a report of a system involving slow interchange has recently appeared[2]) the isotropic shifts $\Delta\nu_i$ are given by the following equation[3]

$$\frac{\Delta\nu_i}{\nu} = \frac{a_i\gamma_e g\beta S(S+1)}{2S\gamma_{\rm H}\,3kT}\,[\exp(\Delta G^0/\boldsymbol{R}T)+1]^{-1}$$

where a_i is the isotropic electron-nuclear hyperfine interaction constant (which may contain both Fermi contact and dipolar contributions[4]), ΔG^0 is the standard free energy change for the planar–tetrahedral equilibrium, and the other symbols have their usual significance.[3] It has been convincingly demonstrated[1] for β-keto-imine and salicylaldimine nickel(II) complexes that differences in isotropic shifts between diastereoisomers are due predominantly to a difference in the standard free energy changes $\Delta\Delta G^0$, the contribution of a difference in hyperfine constant Δa_i being either zero or small in comparison. We report our results on fully paramagnetic pseudotetrahedral complexes where the diastereoisomeric splitting is large and attributable solely to a Δa_i term.

Complexes of general formula $NiLX_2$, where L is a Schiff base formed from benzaldehyde derivatives and aliphatic diamines have been prepared.[5] The complexes



are fully paramagnetic and pseudotetrahedral both in the solid state and in solution as shown by solution susceptibility measurements[6] and electronic mull and solution spectra. The isotropic ^{1}H n.m.r. shifts exhibit a Curie law behaviour over the temperature range −40° to 40° in $CDCl_3$ solution.

The ^{1}H n.m.r. spectra of nickel bromide complexes of Schiff bases obtained from benzaldehyde or *p*-tolualdehyde and a mixture of *meso* and racemic 2,3-diaminobutane ($R^1 = R^2 = CH_3$, bn) shows a doubling of every peak observed, *i.e.*, the three aromatic proton resonances and the aliphatic methyl signal (see Figure). When *meso*-bn, obtained by fractional crystallization of the dihydrochloride,[7] is used to form the Schiff bases, the complexes derived show ^{1}H n.m.r. spectra with but a single peak for each position (see Figure). The peaks for the *meso*-isomers exhibit smaller isotropic shifts than those of the racemic complexes. In the absence of a planar–tetrahedral equilibrium these differences must be attributed to differences in the hyperfine interaction constants Δa_i.

It is significant that the shifts of the aliphatic methyl resonances are upfield and the methyl shift of the racemic complex is similar to that found for the complex derived from 2,3-diaminopropane ($R^1 = CH_3$, $R^2 = H$, pn). If attention is focused on the chelate ring, two *gauche* conformations are possible:[8] *k* and *k*′, with the aliphatic chain substituents occupying either pseudo-axial (*ax*) or -equatorial (*eq*) positions. Methyl substituents prefer

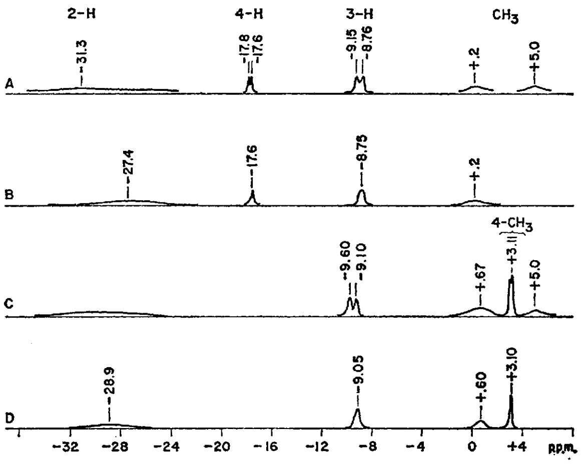


FIGURE. ^{1}H *n.m.r. spectra of complexes in* CDCl$_3$ *at* 39° *referred to tetramethylsilane as internal standard. A*: Ni[B$_2$bn]Br$_2$, B = PhCH-; *B*: Ni[B$_2$*meso*-bn]Br$_2$; *C*: Ni[(4-CH$_3$B)$_2$bn]Br$_2$, (4-CH$_3$B) = *p*-CH$_3$·C$_6$H$_4$CH-; *D*: Ni[(4-CH$_3$B)$_2$*meso*-bn]Br$_2$.

the *eq* positions[9] and this conformation is expected to predominate for complexes derived from pn; however, for bn complexes only in the racemic forms can both methyl groups be *eq*. In the *meso*-form one methyl *must* be *ax*. A rapid $k \rightleftharpoons k'$ interconversion will render the methyl groups equivalent so far as the ^{1}H n.m.r. experiment is concerned. An upfield shift for an aliphatic proton resonance is unusual and suggests that the dipolar interaction is the dominant cause of the isotropic shift. The *ax* and *eq* methyl groups will have different geometric factors,[4,10] the latter lying nearer the C_2 ligand field axis and the N–Ni–N plane. This may account for the large difference in aliphatic methyl resonance frequencies for the racemic and *meso*-complexes, the isotropic shift of the former being four times that of the latter. The present results demonstrate that diastereoisomeric ^{1}H n.m.r. splittings may be large even in the absence of a planar-tetrahedral equilibrium, particularly if a significant dipolar interaction is present.

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