Nuclear Magnetic Resonance Study of Ring Inversion and Nitrogen Inversion in Substituted Ethylenediamine Complexes of Praseodymium

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Summary At low temperatures, ring inversion is slow on a proton n.m.r. time-scale for the $Pr([^2H_9]fod)_3$-*NNN'N'*-tetramethylethylenediamine $\{[^2H_9]fod = (CD_3)_3CC(:O)\bar{C}HC(:O)CF_2CF_2CF_3\}$ complex (I), and the barrier to ring inversion, $\Delta G^\ddagger$, is 42·2 kJ mol^{-1} at -38 °C; in the corresponding *NNN'N'*-tetramethyl-1,2-propylenediamine complex (II), interchange of N–Me groups is observed above room temperature.

It is now clear[1] that in metal complexes of ethylenediamine and substituted ethylenediamines, the five-membered chelate ring is puckered (Figure 1). Although complexes of this type have been extensively studied by n.m.r. spectroscopy, conformational exchange between δ and λ forms has normally been fast on an n.m.r. time-scale.

Figure 2 (A and B) shows ^1H n.m.r. spectra for the $Pr([^2H_9]fod)_3$-*NNN'N'*-tetramethylethylenediamine $\{[^2H_9]fod = (CD_3)_3CC(:O)\bar{C}HC(:O)CF_2CF_2CF_3\}$ complex (I) in

$C_6D_5CD_3$ solution. As the temperature is lowered, the CH_2 and Me resonances broaden, and finally split into two. This splitting could arise from a slowing down of (a) ring inversion, (b) a process involving rupture of one Pr–N bond, or (c) intramolecular rearrangement in the 8-co-ordinate complex. It seems very likely that ring inversion is, in fact, responsible for the observed spectral changes. If mechanism (c) was involved, presumably the fod CH and Bu^t resonances would split, but this was not observed. However, this mechanism is probably responsible for the additional broadening of the split Me and CH_2 resonances, together with the fod resonances, which was found below −60 °C. In the corresponding *NNN'N'*-tetramethyl-1,2-propylenediamine complex (II) (see below), bond cleavage was observed only at high temperatures ($\geqslant$ 35 °C), and in the *NNN'N'*-tetraethylethylenediamine complex (III), where both ring inversion and bond cleavage could be studied, the former was considerably faster than the latter.

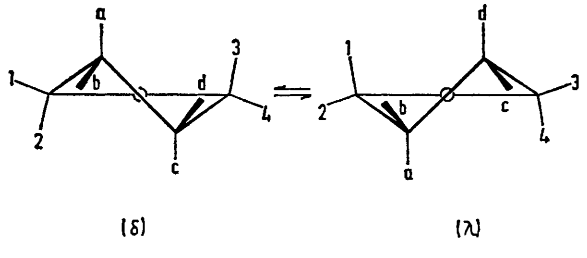

FIGURE 1

For complex (I) substrate exchange is much slower than ring inversion, even in the presence of an excess of amine,† since separate resonances from free and complexed substrate were observed at −30 °C in a solution containing 0·3M amine and 0·2M shift reagent. It is therefore possible to calculate the barrier to ring inversion from the coalescence temperatures of the CH_2 and Me resonances. The value of $\Delta G^{\ddagger}$ so obtained (42·2 kJ mol^{-1} at −38 °C) is much higher than those estimated for ethylenediamine complexes of transition metals such as Co^{III}, Ni^{II}, and Rh^{III} (*ca.* 20 kJ mol^{-1}).[2] This difference could arise both from the presence of the four bulky Me groups, and also the long Pr–N distance, which will tend to increase the extent of ring puckering.[2] That the first effect is important is indicated by the higher barrier to ring inversion in (III) (48·1 kJ mol^{-1} at −13 °C).

In the complex (II) (Figure 2, C, D, and E), the Me group should predominantly occupy an equatorial position,[1] and the n.m.r. spectra are essentially unchanged from *ca.* −60 to *ca.* 30 °C. However, one pair of Me resonances starts to broaden at *ca.* 35 °C, and the other pair at *ca.* 55 °C. At 85 °C, both pairs of Me resonances have coalesced to a very broad band, but the rest of the spectrum remains sharp. A plausible mechanism is that initially one Pr–N bond is broken. Inversion at the nitrogen atom and rotation about the C–N bond, followed by ring closure, will interchange Me(1) and Me(2), or Me(3) and Me(4).

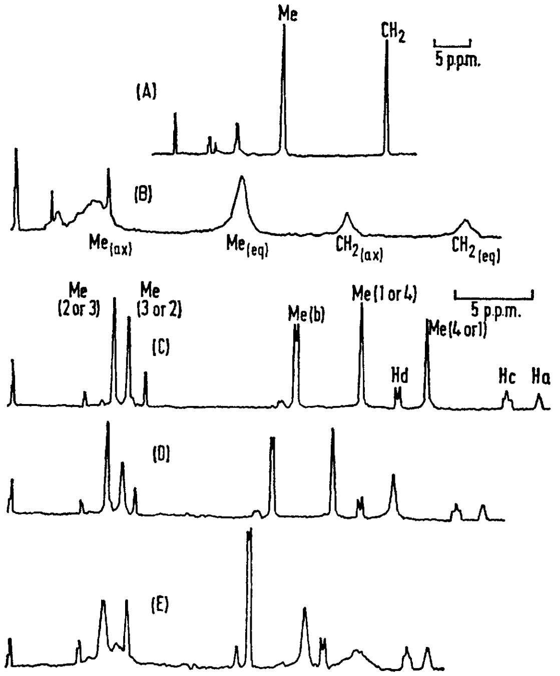

FIGURE 2. ^1H N.m.r. spectra (60 MHz) of 0·20 M solution of $Pr([^2H_9]fod)_3$ and 0·20 M *NNN'N'*-tetramethylethylenediamine in $C_6D_5CD_3$ at 35 °C (A) and −60 °C (B). The probable assignment given for the low temperature spectrum is based on the results for (II) and also the *NN'*-dimethylethylenediamine complex. ^1H N.m.r. spectra of 0·20 M solution of $Pr([^2H_9]fod)_3$ and 0·15 M *NNN'N'*-tetramethyl-1,2-propylenediamine in C_6D_5-CD_3 at 20 °C (C), 35 °C (D), and 55 °C (E). The assignments are based on the observed spin–spin splittings[3] and refer to the δ conformation. The additional resonances arise from the solvent and the $[^2H_9]$fod.

In metal complexes of 1,3-propylenediamine, the six-membered ring normally adopts a chair conformation.[1] ^1H N.m.r. spectra of the $Pr([^2H_9]fod)_3$-*NNN'N'*-tetramethyl-1,3-propylenediamine complex in $C_6D_5CD_3$ were studied over a range of temperatures. Ring inversion was faster than in (I) but from the coalescence temperature of the two Me resonances, $\Delta G^{\ddagger}$ was found to be *ca.* 37 kJ mol^{-1} at −60 °C.

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† For the $Pr([^2H_9]fod)_3$-*NNN'N'*-tetramethyl-1,4-butylenediamine system, where formation of a chelate ring is very unlikely, substrate exchange could not be slowed down even at −80 °C.

[1] C. J. Hawkins, 'Absolute Configuration of Metal Complexes,' Wiley–Interscience, New York, 1971.

[2] J. R. Gollogly, C. J. Hawkins, and J. K. Beattie, *Inorg. Chem.*, 1971, **10**, 317.

[3] J. L. Sudmeier, G. L. Blackmer ,C. H. Bradley, and F. A. L. Anet, *J. Amer. Chem. Soc.*, 1972, **94**, 757.