On the Proton Magnetic Resonance of Tris-Ethylenediamine Complexes

Sir:

In view of inferences drawn from pmr spectra of tris-ethylenediamine complexes in recent publications,[1–3] it seems appropriate to correct a widely held misconception that any nonequivalence of protons in such complexes must be conformational in origin. In fact, neither the methylene group protons nor the $-NH_2$ protons can be equivalent, even if there is rapid conformational equilibrium, with no conformational preference. Consider, for example, an ethylenediamine chelate ring in a tris-bidentate complex with absolute configuration D (Figure 1). On ring inversion, proton H_B is transformed from an axial proton in a Dδ conformation to an equatorial proton in a Dλ conformation, in contrast to H_A, which is equatorial for δ and axial for λ. H_A when axial, say, is in a different environment from H_B when axial, as it is positioned above one of the other chelate rings and H_B is not. H_A and H_B are thus inherently nonequivalent in a tris-bidentate complex and the methylene groups might be expected to give an AA′BB′ pattern, even with rapid inversion of the ring, with no conformational preference. This argument is independent of the nature of the other chelate rings (*e.g.*, they could be oxalate or ethylenediamine in δδ, δλ, or λλ configurations). Similarly, the $-NH_2$ protons are inherently nonequivalent.

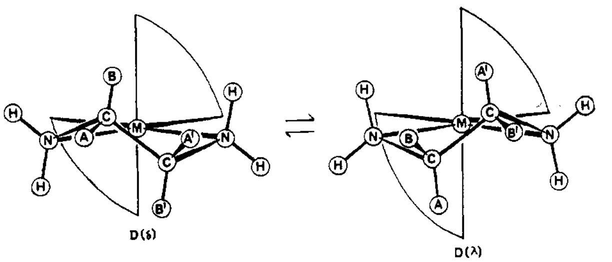

Figure 1.—The ethylenediamine chelate ring in a tris-bidentate complex.

It should also be noted that the two methyl groups of *meso*-butane-2,3-diamine (bn) must be inherently nonequivalent in a tris complex (*e.g.*, replacing H_A and H_B by methyl groups in Figure 1), so that the reported observation of two methyl resonances in $Co(bn)_3^{3+}$ [4] in itself does not allow any inference to be drawn about rates of conformational interconversion in this complex. With complexes of the type *trans*-M(diamine)$_2$A$_2$ and M(diamine)A$_2$B$_2$ and square-planar complexes, where there is no inherent nonequivalence, available nmr evidence strongly suggests that rapid conformational interconversion occurs (*e.g.*, sharp singlets obtained for methylene groups in N-deuterated ethylenediamine complexes; only one methyl resonance observed in *meso*-butanediamine complexes).[2,5–8]

Secondary effects, such as conformational and solvation, may enhance or mask the inherent nonequivalence. That these effects do influence the spectra is suggested first by the wide variation in the spectra of the methylene groups in N-deuterated tris-ethylenediamine complexes in D_2O. $Ru(en)_3^{2+}$ gives a well-resolved AA′BB′ pattern.[3] $Co(en)_3^{3+}$ gives a very broad band (width at half-height 18 Hz)[1] which could well arise from the overlapping lines of an AA′BB′ pattern. We have studied the pmr spectra at 60 MHz of tris-ethylenediamine complexes of Rh(III), Ir(III), and Pt(IV). The methylene peak of N-deuterated $[Rh(en)_3]Cl_3$ (τ′ 7.07[9] is not, as reported by Powell and Sheppard,[10] a sharp singlet but a narrow band (width 3.5 Hz at 30°) in which definite structure can be seen (Figure 2). N-Deuterated $[Ir(en)_3]Cl_3$ gives a similar band (τ′ 7.23, width 3.3 Hz). $[Pt(en)_3]Cl_4$ is exceptional in giving a very sharp peak (width 1.3 Hz, τ′ 6.74) with "satellites" due to coupling with ^{195}Pt ($I = {}^1/_2$, 34% abundance, $J_{Pt-N-C-H} = 27$ Hz).

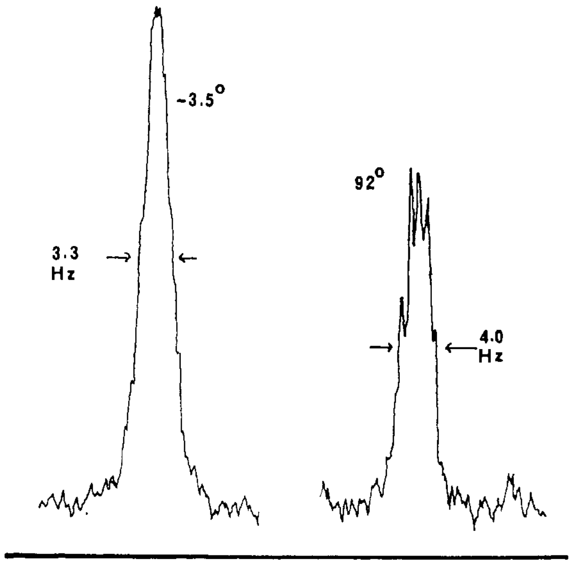

Figure 2.—The pmr spectrum at 60 MHz of $[Rh(en)_3]Cl_3$ in dilute NaOD solution.

Another complex where the inherent nonequivalence of methylene protons is not apparent is $Na[Co(en)(ox)_2]$, reported to give a sharp peak (width 3 Hz) in this region,[5] in contrast to the broad band of $Co(en)_3^{3+}$.

Secondary effects (*e.g.*, solvation or conformational) would be expected to be temperature dependent. The spectra of the tris-ethylenediamine complexes do vary slightly with temperature. Figure 2 illustrates the changes for $[Rh(en)_3]Cl_3$. These are similar for solu-

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[1] S. T. Spees, L. J. Durham, and A. M. Sargeson, *Inorg. Chem.*, **5**, 2103 (1966).

[2] B. M. Fung, *J. Am. Chem. Soc.*, **89**, 5788 (1967).

[3] H. Elsbernd and J. K. Beattie, *ibid.*, **91**, 4573 (1969).

[4] F. Woldbye, quoted by D. A. Buckingham, L. Durham, and A. M. Sargeson, *Australian J. Chem.*, **20**, 257 (1967).

[5] See reference cited in ref 4.

[6] S. Yano, H. Ito, J. Fujita, and K. Saito, *Chem. Commun.*, 460 (1969).

[7] T. G. Appleton and J. R. Hall, to be submitted for publication.

[8] C. J. Hawkins and J. R. Gollogly, to be submitted for publication.

[9] Spectra were run with *t*-butyl alcohol as internal reference. Chemical shift values are given in the τ′ scale, relative to DSS, using τ′ 8.77 for *t*-C_4H_9OH in D_2O.

[10] D. B. Powell and N. Sheppard, *J. Chem. Soc.*, 791 (1959).

tions acidified with DCl or made alkaline with NaOD. The behavior of $[Ir(en)_3]Cl_3$ parallels that of the rhodium complex. The peak of $[Pt(en)_3]Cl_4$ sharpens slightly on heating (band width 2.0 Hz at $-3.5°$, 0.9 Hz at 82°).

The splitting of the $-NH_2$ signal of tris-diamine complexes into an AB pattern in various solvents has been reported by several workers.[1-3,11] In neutral D_2O solution N deuteration of $[Rh(en)_3]Cl_3$ and $[Ir(en)_3]Cl_3$ is extremely slow (little observable change occurring in 1 week) and the $-NH_2$ signals are easily detected (centered at τ' 4.77 and 4.36 for the Rh and Ir complexes, respectively). In both cases the signal is clearly split into an AB pattern. Broadness of the peaks prevents accurate measurement, but in $[Rh(en)_3]Cl_3$ the chemical shift difference is of the order of 30 Hz and J_{AB} is approximately 10 Hz. In the iridium complex the separation is greater, approximately 35 Hz. The methylene group signals in these undeuterated complexes are broader (width 8.5 Hz for $[Rh(en)_3]Cl_3$) than in the deuterated complexes. After addition of a small amount of NaOD solution, N deuteration occurs within a few mintues. With $[Pt(en)_3]Cl_4$ N deuteration was too rapid, even in concentrated DCl solution, to allow a spectrum of the undeuterated complex to be obtained.

Analytically pure $[Ir(en)_3]I_3$ was prepared by the method of Watt, *et al.*[12] As its solubility in water was limited, it was converted to the chloride salt by ion exchange. Pure samples of the other complexes were available in this department.

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[11] H. Yoneda and Y. Morimoto, *Bull. Chem. Soc. Japan*, **39**, 2180 (1966).

[12] G. W. Watt, L. E. Sharif, and E. P. Helvenston, *Inorg. Chem.*, **1**, 6 (1962).

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