

mining steps. These factors include: (a) macroscopic diffusion control: when the rate is determined by the rate of mixing the reactant solutions; (b) microscopic diffusion control: when the rate is determined by the formation of encounter pairs in homogeneous solution; (c) limitation of rates of nitration by the rate of formation of nitronium ions; (d) contributions from other mechanisms of nitration, especially from nitration *via* nitrosation.

Factors a, b, and d can complicate competitive nitrations and factors b, c, and d can complicate kinetic

studies. Nitration *via* nitrosation is often very important with highly reactive substrates.<sup>15,21,25</sup> Another possible complication comes from the incursion of addition-elimination reactions,<sup>9</sup> for these may deflect some of the initial  $\sigma$  complex to products without nitro groups. Thus, although recent studies have helped to reestablish the importance of nitration through the nitronium ion, they have shown that the interpretation of the relative rates obtained requires considerable care.

(25) J. G. Hoggett, R. B. Moodie, and K. Schofield, *Chem. Commun.*, 605 (1969).

## Conformational Analysis of Tris(ethylenediamine) Complexes

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The principles of conformational analysis were first applied to the stereochemistry of coordination complexes in a seminal paper by Corey and Bailar<sup>1</sup> published in 1959. These authors recognized that coordination of a ligand such as ethylenediamine<sup>2</sup> with a metal ion forms a five-membered chelate ring with many of the stereochemical characteristics of cyclopentane or cyclohexane. The ring is twisted or puckered so that the hydrogen atoms on adjacent atoms are in a staggered or gauche conformation. This confers an approximately axial or equatorial character to each hydrogen atom with respect to the plane of the metal ion and two nitrogen atoms (Figure 1).

When the bidentate ligand is propylenediamine,<sup>2</sup> in which a methylene hydrogen atom is replaced by a methyl group, the conformer with the methyl group equatorial is preferred, just as in methylcyclohexane. The conformational preference is probably much greater in the metal complex than in cyclohexane since there are steric interactions in the complex with other ligands about the metal ion whereas in cyclohexane there are only 1,3 interactions with hydrogen atoms.

An additional feature of the stereochemistry of metal complexes is absent in cyclohexanes. Steric interactions *between* the ligands in a tris(ethylenediamine) complex lead to preferred conformations for the chelate rings. Octahedral complexes of three bidentate ligands exist as optical isomers differing in the configuration of the three rings about the metal ion, designated  $\Delta$  or  $\Lambda$  according to the relative helicity of any pair of chelate rings<sup>3</sup> (Figure 2). Moreover, each ligand can adopt a  $\delta$  or  $\lambda$  conformation defined by the helicity

of the carbon-carbon bond relative to the plane of the nitrogen atoms and metal ion (Figure 1).

Examination of interactions between the ligands indicated that the most stable configuration for the  $\Lambda$  configuration occurs with each ethylenediamine ligand in the  $\delta$  conformation, designated  $\Lambda(\delta\delta\delta)$ , while in the  $\Delta$  isomer each ring is in the  $\lambda$  conformation, designated  $\Delta(\lambda\lambda\lambda)$ . These *enantiomers* were designated as parallel or *lel* configurations since the carbon-carbon bond of each ligand is approximately parallel to the threefold axis of the complex. Since inversion of each ligand from its stable conformation results in an increase in interligand repulsions, estimated<sup>4</sup> at approximately 0.6 kcal mole<sup>-1</sup> ligand<sup>-1</sup>, the relative enthalpies of the complexes are  $\Lambda(\delta\delta\delta) < \Lambda(\delta\delta\lambda) < \Lambda(\delta\lambda\lambda) < \Lambda(\lambda\lambda\lambda)$ .<sup>4</sup> Statistical and other entropy effects were not explicitly considered. It was recognized that solvation effects might differ among the various configurations and lead to a modification of the relative energies estimated from intramolecular interactions alone.

These ideas are consistent with the crystal structure<sup>5</sup> of tris(ethylenediamine)cobalt(III) chloride, which contains the  $\Lambda(\delta\delta\delta)$  isomer predicted to be most stable, and with the contemporary studies of Dwyer and his associates<sup>6</sup> on the relative abundance of isomers of cobalt-amine complexes in solution. Assuming that the methyl group of a coordinated propylenediamine ligand is almost exclusively equatorial, the  $\lambda$  conformation is formed with (-)-propylenediamine, which

(4) Only the conformations of the ligands in the  $\Lambda$  configuration will be given. Since enantiomers have the same free energy and give identical nmr spectra in the absence of an optically active environment, only one configuration will be specified for  $M(en)_3$  complexes, although in the nmr studies both  $\Delta$  and  $\Lambda$  configurations were present in solution, *i.e.*,  $\Lambda(\delta\delta\lambda)$  implies that  $\Delta(\lambda\lambda\delta)$  was also present.

(5) K. Nakatsu, M. Shiro, Y. Saito, and H. Kuroya, *Bull. Chem. Soc. Jap.*, **30**, 158 (1957).

(6) F. P. Dwyer, F. L. Garvan, and A. Shulman, *J. Amer. Chem. Soc.*, **81**, 290 (1959); F. P. Dwyer, T. E. MacDermott, and A. M. Sargeson, *ibid.*, **85**, 2913 (1963).

(1) E. J. Corey and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **81**, 2620 (1959).

(2) Ethylenediamine = 1,2-diaminoethane = en; propylenediamine = 1,2-diaminopropane = pn.

(3) *Inorg. Chem.*, **9**, 1 (1970).

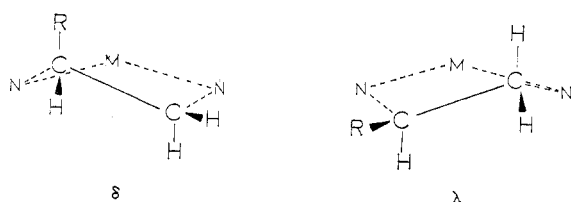


Figure 1. Gauche conformations of five-membered chelate rings. R = H: ethylenediamine; R = CH<sub>3</sub>: (*R*)-(-)-propylenediamine.

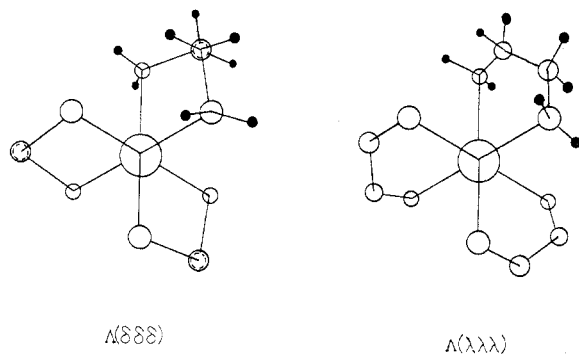


Figure 2. The  $\Lambda$  configuration of a tris(ethylenediamine) complex. With the ligands in the  $\delta$  conformation the C-C bonds are parallel to the C<sub>3</sub> axis of the complex.

has the absolute configuration shown in Figure 1. The  $\Delta$  isomer of Co(pn)<sub>3</sub><sup>3+</sup>, in which the  $\lambda$  conformation is more stable, consequently forms in preference to the  $\Lambda$  isomer, in which the  $\lambda$  conformation is less stable. The observed equilibrium constant of 14.6, equivalent to a free energy difference of 1.6 kcal mole<sup>-1</sup>, was considered a good approximation to the free-energy difference between the most stable  $\Lambda(\delta\delta\delta)$  and the least stable  $\Lambda(\lambda\lambda\lambda)$  configurations of Co(en)<sub>3</sub><sup>3+</sup>, since the interligand interactions are likely to be similar in the propylenediamine and ethylenediamine complexes. The close agreement with the estimate of 1.8 kcal mole<sup>-1</sup> proposed by Corey and Bailar helped lead to the general acceptance of their model.

A similar determination of conformational energy differences is not possible for ethylenediamine complexes. With propylenediamine the isomers are stable because of the large free-energy difference between conformers with axial and equatorial methyl groups and the very slow racemization of cobalt(III). Once an equilibrium mixture is formed, the isomers can be separated by fractional crystallization or chromatography. The ethylenediamine ligands are conformationally labile and conformational isomers cannot be separated.

Attempts to examine conformational preferences of ethylenediamine complexes by nmr spectroscopy were initially unsuccessful. The spectrum of Co(en)<sub>3</sub><sup>3+</sup> is a broad band, 21-Hz width, which narrows only slightly to 18 Hz when the amine protons are deuterated<sup>7,8</sup> (Figure 3). In contrast, the spectra of the M(en)<sub>3</sub>

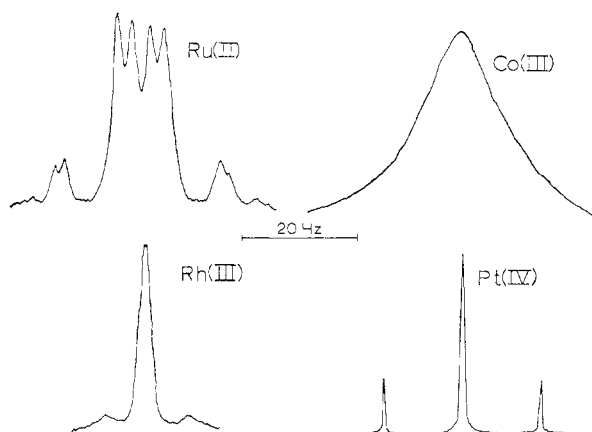


Figure 3. Nmr spectra (60 MHz) of N-deuterated M(en)<sub>3</sub> complexes in D<sub>2</sub>O at 42°.

complexes of Rh(III), Zn(II), and Cd(II) were reported<sup>8</sup> to be single, narrow bands. Various explanations were offered for the broad spectrum of the cobalt complex. The methylene protons of an ethylenediamine ligand in a single conformation are expected to exhibit an AA'BB' spectrum. The two axial protons (A) have a chemical shift different from that of the two equatorial protons (B) and the axial protons are magnetically nonequivalent due to unequal coupling with the two equatorial protons. Up to 24 lines may result, depending on the relative values of the four coupling constants and the chemical shift difference between the axial and equatorial protons. The broad spectrum might arise from overlapping AA'BB' patterns from both  $\delta$  and  $\lambda$  conformers in the complex.<sup>7</sup> Alternatively, an intermediate rate of inversion could lead to dynamic broadening of the nmr spectrum.<sup>7</sup> Finally, coupling between the ligand protons and the <sup>59</sup>Co nucleus with nuclear spin of 7/2 was suggested.<sup>8</sup> Attempts to observe a resolved spectrum at lower temperatures to -39° were unsuccessful.<sup>7</sup>

The nmr spectra of these M(en)<sub>3</sub> complexes and their relation to the conformations of the ligands remained a puzzle until recently. As a result of intense activity in a number of different laboratories, a fairly complete and consistent account has emerged. The ligands are in rapid inversion between the  $\delta$  and  $\lambda$  conformations. Chemical shifts, coupling constants, and the temperature dependence of contact shifts in Ni(en)<sub>3</sub><sup>2+</sup> indicate that 60-75% of the ligands are in the  $\delta$  conformation predicted to be more stable in the Corey and Bailar model. Recognition of a statistical entropy effect suggests, however, that the relative free energies are  $\Lambda(\delta\delta\lambda) < \Lambda(\delta\delta\delta) \sim \Lambda(\delta\lambda\lambda) \ll \Lambda(\lambda\lambda\lambda)$ , with the  $\Lambda(\delta\delta\lambda)$  configuration most abundant.

The substantial differences among the nmr spectra do not reflect large differences in conformational preferences but rather variations among the complexes of the intrinsic chemical shift difference between axial and equatorial protons. Scalar coupling is observed between the ligand protons and most of the metal nuclei, accounting for the broad spectrum of Co(en)<sub>3</sub><sup>3+</sup>

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

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

in the absence of relaxation mechanisms. The configurations observed in crystals apparently result from lattice effects and do not reflect thermodynamic stability in solution. Finally, the interpretation of conformational effects on the optical activity of these complexes requires revision in view of the results obtained from the nmr spectra.

### Nmr Spectra of $M(en)_3$ and $M(pn)_3$ Complexes

**Ruthenium(II).** N-Deuterated  $Ru(en)_3^{2+}$  was the first example of a well-resolved spectrum of a tris(ethylenediamine) complex, exhibiting at least 20 of the possible 24 lines of the AA'BB' pattern at 100 MHz<sup>9</sup> (Figure 4). Analysis yielded the four coupling constants and a chemical shift difference of 0.23 ppm between the A and B protons. An interpretation in terms of the conformations of the  $M(en)_3$  complex is not immediately obvious. At least three different cases could lead to the observed AA'BB' spectrum.

(1) *Inversion between conformers is slow.* Each ligand in a fixed conformation would give an AA'BB' spectrum. The observation of a single AA'BB' spectrum requires that all three ligands be magnetically equivalent. This would occur if the complex were in the configuration  $\Lambda(\delta\delta\delta)$  predicted by Corey and Bailar to predominate in solution. Alternatively, mixed configurations such as  $\Lambda(\delta\delta\lambda)$  could occur if the nmr parameters are identical in each conformation.

(2) *Inversion between conformers is rapid; there is no conformational preference.* In an  $M(en)_3$  complex the ethylenediamine ligands do not lie on a plane of symmetry and, consequently, even with rapid inversion and no preference for either conformer, the two methylene protons are never completely equivalent.<sup>10</sup> The additional mechanism of racemization of the tris complex is necessary to produce complete equivalence, and this is known to occur very slowly.<sup>11</sup> This inherent magnetic nonequivalence leads inevitably to an AA'BB' pattern, but the magnitude of the chemical shift difference is not known. Evidence presented below suggests that it is very small and is not responsible for the observed spectra.

(3) *Inversion between conformers is rapid; there is a free-energy difference between the  $\delta$  and  $\lambda$  conformations.* If the magnetic nonequivalence mentioned above is negligible and there is rapid inversion between the  $\delta$  and  $\lambda$  conformers, an AA'BB' spectrum would still result if there is a preference for one of the conformers. If the  $\delta$  conformation is of lower free energy than the  $\lambda$  conformation, then the observed spectrum reflects an average chemical shift difference between the chemical shift of an equatorial proton in the  $\delta$  conformation, which spends part of its time in an axial position in the  $\lambda$  conformation, and that of an axial proton in the  $\delta$  conformation, which spends part of its time

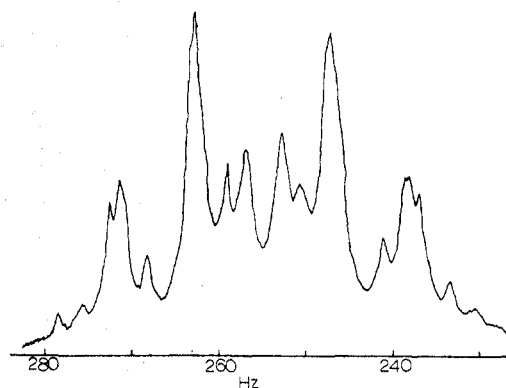


Figure 4. Nmr spectrum (100 MHz) of N-deuterated  $Ru(en)_3^{2+}$  in  $D_2O$ .

in an equatorial position in the  $\lambda$  conformation. The coupling constants between the protons are similarly averaged. Rapid inversion makes the three ligands equivalent.

Three different investigations were undertaken to determine which interpretation applies to  $Ru(en)_3^{2+}$ . Analysis of the spectra of the related tris(propylenediamine)ruthenium(II) ion indicates that the ligands are predominantly in a single conformation with the methyl groups equatorial.<sup>12</sup> The chemical shift difference between the axial and equatorial methylene protons is 0.87 ppm, considerably larger than the value of 0.23 ppm in  $Ru(en)_3^{2+}$ . This suggests that considerable conformational averaging occurs in the ethylenediamine complex. Were the chemical shift difference between the axial and equatorial protons in the propylenediamine complex identical with that in the ethylenediamine complex in a single conformation, the observed chemical shift difference in  $Ru(en)_3^{2+}$  would indicate that 63% of the ligands were in the stable  $\delta$  conformation and 37% in the unstable  $\lambda$  form. Although the chemical shift differences are probably not identical due to the effect of the methyl group and possibly different geometries of the ligands, evidence given below suggests that this estimate of conformational averaging is approximately correct.

The intraligand coupling constants obtained from the spectrum of  $Ru(en)_3^{2+}$  were also analyzed to obtain another estimate of conformational averaging.<sup>13</sup> Using a ratio of trans and gauche vicinal coupling constants assumed to be appropriate for a single conformation, Sudmeier and Blackmer calculated from the observed coupling constants that 72% of the ligands were in the favored  $\delta$  conformation and 28% in the  $\lambda$  conformer. Incomplete averaging of the coupling constants strongly suggests a conformational preference and appears to eliminate inherent magnetic nonequivalence as the principal origin of the observed chemical shift difference.

Finally, calculations<sup>14</sup> estimate that the potential-

(9) J. K. Beattie and H. Elsbernd, *J. Amer. Chem. Soc.*, **92**, 1946 (1970).

(10) T. G. Appleton, J. R. Hall, and C. J. Hawkins, *Inorg. Chem.*, **9**, 1299 (1970).

(11) H. Elsbernd and J. K. Beattie, *ibid.*, **8**, 893 (1969).

(12) J. K. Beattie and L. H. Novak, *J. Amer. Chem. Soc.*, **93**, 620 (1971).

(13) J. L. Sudmeier and G. L. Blackmer, personal communication.

(14) J. R. Golligly, C. J. Hawkins, and J. K. Beattie, *Inorg. Chem.*, **10**, 317 (1971).

energy barrier to ring inversion is 5–7 kcal mole<sup>-1</sup>, too low to prevent rapid ring inversion on the nmr time scale. Further evidence that the ligands undergo rapid inversion is the very small temperature dependence of the spectra,<sup>9</sup> indicating a low barrier to exchange between states of nearly the same free energy.

These results indicate that the ligands in Ru(en)<sub>3</sub><sup>2+</sup> undergo rapid inversion between conformations of unequal free energy with substantial fractions of the ligands in both conformations. Estimates obtained from both the chemical shifts and the coupling constants indicate that the difference in free energy between the two conformers is in the range 0.3–0.6 kcal mole<sup>-1</sup>.

**Platinum(IV).** The spectra of N-deuterated Pt(en)<sub>3</sub><sup>4+</sup> at 60 MHz and 100 MHz are in sharp contrast with those of Ru(en)<sub>3</sub><sup>2+</sup>. Whereas the ruthenium complex gives well-resolved spectra with detailed fine structure, each spectrum of the platinum complex consists of a single narrow line together with satellites due to coupling with the 33.8% <sup>195</sup>Pt of nuclear spin 1/2.<sup>10,11</sup> (Figure 3). The stereochemistry of the tris(ethylenediamine)platinum(IV) ion is probably not substantially different from that of the cobalt(III) or ruthenium(II) complexes since it is intermediate in size between these two ions, both of which apparently exhibit conformational preference. Spectra with some AA'BB' character would be likely. An explanation for the narrow line is evident from the spectrum of tris(propylenediamine)platinum(IV), however, since the intrinsic chemical shift difference between the axial and equatorial methylene protons is only about 0.15 ppm, compared with 0.87 ppm found for ruthenium(II).<sup>12</sup> Partial conformational averaging in the ethylenediamine complex results in a very small effective chemical shift difference between the axial and equatorial protons and, consequently, a very narrow line.

This striking difference in chemical shifts between metal ions presumably arises from the effect of the oxidation state on the chemical shielding of the ligand protons. The equatorial protons are in an environment determined largely by the solvent and are little affected by changes in the metal ion. The axial protons, in contrast, are directed toward the d-electron density of the filled t<sub>2g</sub> orbitals of the metal which have much greater radial extension in the lower oxidation state ruthenium(II) ion than in the platinum(IV) ion. Additional studies of the propylenediamine complexes of cobalt(III) and rhodium(III) reveal the expected order of chemical shift differences Ru ≫ Rh ~ Co ≫ Pt.<sup>12,15</sup>

Evidence for incomplete conformational averaging in the platinum(IV) complex is found in the satellite peaks and in the 220-MHz spectrum. The central peak at 220 MHz is a narrow doublet with an effective chemical shift difference of about 0.04 ppm.<sup>16</sup> The satellite peaks in both the 100- and the 200-MHz spectra are of unequal width, with the low-field peak

considerably wider than the high-field peak. In other complexes of known stereochemistry equatorial protons have much larger coupling constants with platinum than do axial protons, a consequence of larger dihedral angles with the platinum–nitrogen bond.<sup>17</sup> Furthermore, equatorial protons invariably resonate at a lower magnetic field than axial protons. Consequently, if conformational averaging is incomplete, the equatorial protons will have a slightly larger average coupling constant with <sup>195</sup>Pt and will occur at a slightly lower magnetic field than will the axial protons. This leads to the asymmetry of the satellite peaks illustrated in Figure 5. Approximately 65% of the ligands are in the lower energy conformation and 35% in the higher energy form. The difference in the platinum–proton coupling constants is further evidence that incomplete conformational averaging is responsible for most of the chemical shift difference. The alternative hypothesis, that a significant chemical shift difference results from the inherent magnetic nonequivalence required by the symmetry of the complex, does not account for the observed differences in the platinum–proton coupling constants.

**Nickel(II).** The large contact shifts of the protons in ligands coordinated to paramagnetic nickel(II) provide a more sensitive probe into the conformations of these ligands than do the nmr spectra of the diamagnetic complexes described above. Ho and Reilly<sup>18</sup> have determined the energy difference between the δ and λ conformations in Ni(en)<sub>3</sub><sup>2+</sup> without introducing assumptions regarding the intrinsic chemical shift difference or the coupling constants. The spectrum of Ni(en)<sub>3</sub><sup>2+</sup> at 100 MHz and 32° consists of two broad bands separated by 37 ppm, corresponding to the axial and equatorial methylene protons of the ligands. The chemical shifts are strongly temperature dependent due both to the Curie dependence of the contact shifts and to the temperature dependence of the equilibrium between the δ and λ conformers. These two effects can be separated and the conformational equilibrium evaluated with the results: ΔG = 0.30 ± 0.03 kcal mole<sup>-1</sup>, ΔH = 0.36 ± 0.03 kcal mole<sup>-1</sup>, and ΔS = 0.20 ± 0.02 eu at 305°K.

This appears to be the first direct determination of the energy difference for the conformational inversion (δ ⇌ λ) in solution. The experimental parameters are for the inversion of a single ligand, however, and are a weighted average for the three reactions (δδδ) ⇌ (δδλ), (δδλ) ⇌ (δλλ), and (δλλ) ⇌ (λλλ). Because of rapid conformational averaging, the relative energies of the Λ(δδδ), Λ(δδλ), Λ(δλλ), and Λ(λλλ) configurations cannot be determined directly by nmr spectroscopy. An additional assumption is necessary: that the increment of enthalpy is constant for each configuration with an additional ligand in the λ conformation. The mixed configurations (δδλ) and (δλλ) are additionally favored by a statistical factor of

(15) H. Elsbernd, J. Peiper, and J. K. Beattie, unpublished observations.

(16) L. H. Novak and J. K. Beattie, *Inorg. Chem.*, in press.

(17) L. E. Erickson, J. K. Howie, J. W. McDonald, and R. P. Clow, *J. Amer. Chem. Soc.*, **90**, 6371 (1968); see also ref 18.

(18) F. F.-L. Ho and C. N. Reilly, *Anal. Chem.*, **42**, 600 (1970).

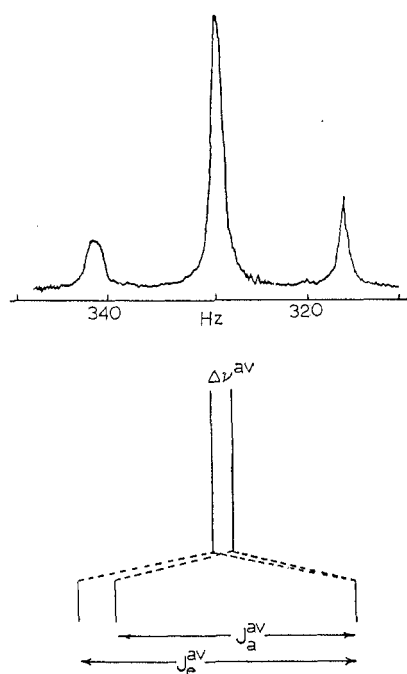


Figure 5. Nmr spectrum (100 MHz) of N-deuterated  $\text{Pt}(\text{en})_3^{4+}$  and a schematic illustration of the origin of unequal satellite peak widths for the condition  $\Delta J^{av} = 2\Delta J^{av}$ .

three over the configurations  $(\delta\delta\delta)$  and  $(\lambda\lambda\lambda)$ , since in the  $(\delta\delta\lambda)$  configuration, for example, any one of the three ligands may occur in the  $\lambda$  conformation. At the temperature of these studies this results in a free-energy stabilization of the mixed configurations by 0.66 kcal mole<sup>-1</sup>. As a consequence, the relative free energies of the four configurations are in the order  $\Lambda(\delta\delta\lambda) < \Lambda(\delta\delta\delta) \sim \Lambda(\delta\lambda\lambda) \ll \Lambda(\lambda\lambda\lambda)$  and *not* in the order originally suggested. This statistical entropy effect was not explicitly mentioned by Corey and Bailar and has been overlooked by many workers in this field, although it has been recognized several times.<sup>19,20</sup>

**Rhodium(III) and Iridium(III).** The 60-MHz spectra of both  $\text{Rh}(\text{en})_3^{3+}$  and  $\text{Ir}(\text{en})_3^{3+}$  are narrow bands of 3–4-Hz width with barely discernible fine structure.<sup>10</sup> At 220 MHz, however, a well-resolved AA'BB' spectrum is observed for  $\text{Rh}(\text{en})_3^{3+}$ .<sup>13</sup> The chemical shift difference of 0.12 ppm for  $\text{Rh}(\text{en})_3^{3+}$  is intermediate between that of  $\text{Ru}(\text{en})_3^{2+}$  (0.23 ppm) and that of  $\text{Pt}(\text{en})_3^{4+}$  (0.04 ppm), a result consistent with the trends in chemical shift differences observed in  $\text{M}(\text{pn})_3$  complexes ( $\text{Ru}(\text{II})$ , 0.87 ppm;  $\text{Rh}(\text{III})$ , 0.33 ppm; and  $\text{Pt}(\text{IV})$ , 0.13 ppm). Approximately 67–70% of the ligands are estimated from the chemical shifts to be in the  $\delta$  conformation. Nearly identical results are obtained independently from analysis of the partially averaged intraligand proton–proton coupling constants, which suggests that both methods of estimating conformational averaging are approximately correct although neither is very accurate. An estimate of 0.4 to 0.7 kcal ligand<sup>-1</sup> is obtained for the free-energy difference between  $\delta$  and  $\lambda$  conformers with the as-

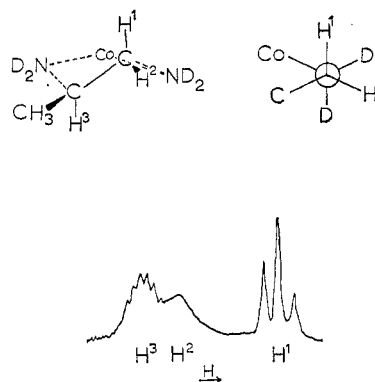


Figure 6. The  $\lambda$  conformation of (*R*)-(-)-propylenediamine illustrating the dihedral angles of 180° between the Co–N and C–H<sup>2</sup> bond and 60° between the Co–N and C–H<sup>1</sup> bond. Strong coupling with <sup>59</sup>Co produces a broad band for proton H<sup>2</sup> in the 220-MHz spectrum.

sumption that the difference is identical between the configurations except for statistical effects.

**Cobalt(III).** The broad featureless spectrum of  $\text{Co}(\text{en})_3^{3+}$  is anomalous. The spectra of the other diamagnetic  $\text{M}(\text{en})_3$  complexes are consistent with rapid inversion between  $\delta$  and  $\lambda$  conformations resulting in identical spectra for all three ligands. Interligand steric interactions result in conformational preferences, but interligand magnetic interactions are negligible. It seems unlikely in cobalt(III) that the rate of inversion is sufficiently slow to result in dynamic line broadening or that the broad spectrum is due to overlapping AA'BB' patterns of the three different ligands. Furthermore, the intrinsic chemical shift difference between the axial and equatorial methylene protons in  $\text{Co}(\text{pn})_3^{3+}$  is only 0.33 ppm, comparable with that of  $\text{Rh}(\text{pn})_3^{3+}$  but much less than the 0.87 ppm observed in  $\text{Ru}(\text{pn})_3^{2+}$ . This suggests that with some conformational averaging the AA'BB' spectrum of  $\text{Co}(\text{en})_3^{3+}$  should be relatively narrow.

That the cobalt nucleus is responsible for the unusual broadness of the  $\text{Co}(\text{en})_3^{3+}$  spectrum was evident in our laboratory<sup>21</sup> from the spectrum of  $\text{Co}(\text{pn})_3^{3+}$  (Figure 6). A single broad band was observed instead of a four-line multiplet for the equatorial methylene proton, H<sup>2</sup>. This proton should be most strongly coupled with the cobalt nucleus due to the favorable dihedral angle between the two nuclei. Scalar coupling with the cobalt nuclear spin of 7/2 would broaden the four-line multiplet into a band of 32 lines. In contrast, four-line multiplets are observed<sup>22,23</sup> in the spectra of  $\text{Co}(\text{CN})_4\text{pn}^-$  and  $\text{Co}(\text{ox})_2\text{pn}^-$ . The asymmetry of the ligand field in the latter complexes results in an electric field gradient at the nucleus. Molecular motion in solution causes quadrupolar relaxation of the cobalt nucleus, effectively decoupling its nuclear spin from the proton.

(21) J. K. Beattie, *Inorg. Chem.*, **10**, 426 (1971).

(22) S. Yano, H. Ito, Y. Koike, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jap.*, **42**, 3184 (1969).

(23) L. G. Stadtherr and J. G. Brushmiller, *Inorg. Nucl. Chem. Lett.*, **6**, 907 (1970).

(19) F. P. Dwyer, A. M. Sargeson, and L. B. James, *J. Amer. Chem. Soc.*, **86**, 590 (1964).

(20) T. S. Piper and A. G. Karipides, *ibid.*, **86**, 5039 (1964).

Other evidence consistent with the hypothesis of significant scalar coupling between the cobalt nucleus and the ligand protons in  $\text{Co}(\text{en})_3^{3+}$  includes the temperature dependence of the 60-MHz spectrum,<sup>24</sup> the identical line widths of both the 60- and the 100-MHz spectra, and the asymmetry observed in both the 60-MHz spectrum<sup>24</sup> at 82° and the 220-MHz spectrum<sup>21</sup> at room temperature. This hypothesis was confirmed independently by Sudmeier and Blackmer,<sup>25</sup> who performed the definitive experiment of decoupling the cobalt nucleus from the protons. The spectrum of  $\text{Co}(\text{en})_3^{3+}$  sharpened to one similar to  $\text{Rh}(\text{en})_3^{3+}$ , and the broad band appearing in the spectrum of  $\text{Co}(\text{pn})_3^{3+}$  sharpened to the expected four-line multiplet. Scalar coupling with the quadrupolar cobalt nucleus thus accounts for the anomalous spectrum of  $\text{Co}(\text{en})_3^{3+}$ , and the conformational properties of  $\text{Co}(\text{en})_3^{3+}$  seem to be consistent with those of the other  $\text{M}(\text{en})_3$  complexes.

**Summary of Nmr Observations.** With a satisfactory explanation for the anomalous spectrum of  $\text{Co}(\text{en})_3^{3+}$ , the nmr spectra of the methylene protons in the various  $\text{M}(\text{en})_3$  complexes can be interpreted with a single model.

(1) The ligands undergo rapid inversion between  $\delta$  and  $\lambda$  conformations. There is no evidence for dynamic line broadening or slow inversion in aqueous solution.

(2) There is extensive conformational averaging, with 30–40% of the ligands in the conformation of higher free energy in all of the complexes. The relative free energies of the four possible configurations have not been determined, but the differences among them are probably smaller than originally proposed by Corey and Bailar. Together with the statistical entropy effect, this suggests that the most abundant configuration in solution may be  $\Lambda(\delta\delta\lambda)$  and not  $\Lambda(\delta\delta\delta)$ .

(3) The dramatically different spectra of the various complexes are the consequence of large variations in the intrinsic chemical shift difference between axial and equatorial protons, probably the result of differences in chemical shielding in the various oxidation states. Coupling between the ligand protons and the metal nucleus accounts for the unusual spectrum of the cobalt(III) complex.

### Comparisons with Other Observations

**Crystal Structures.** All of crystal structures of  $\text{M}(\text{en})_3$  complexes examined before 1968 contained the configuration  $\Lambda(\delta\delta\delta)$  or its enantiomer,  $\Delta(\lambda\lambda\lambda)$ , the preferred configurations in the Corey and Bailar model. Examples have been found recently of each of the other three possible configurations,  $\Lambda(\delta\delta\lambda)$ ,  $\Lambda(\delta\lambda\lambda)$ ,  $\Lambda(\lambda\lambda\lambda)$ .<sup>26</sup> In these structures the complex is strongly hydrogen bonded to anions or water molecules in the lattice through the amine protons of the ethylenediamine ligands. This led to the suggestion<sup>26</sup> that hydrogen

bonding specifically stabilizes these configurations since their structure permits more hydrogen bonding than the  $\Lambda(\delta\delta\delta)$  configuration. The preference for the  $\Lambda(\delta\delta\delta)$  configuration in nonhydrogen-bonded structures is apparently a lattice effect. This configuration is the most compact and probably leads to better packing in the lattice, but it is not thermodynamically the most stable in solution.

**Solvent and Anion Effects.** Whether hydrogen bonding markedly alters conformational energies in solution has not been determined. Most of the experiments reported were performed with cobalt(III) complexes before it was realized that quadrupolar relaxation effects could dominate the spectra. From the circular dichroism spectrum of  $\text{Co}(\text{en})_3^{3+}$ , the phosphate ion is believed to ion-pair stereospecifically by hydrogen bonding with the three amine protons directed along the  $C_3$  axis. Such a structure has been found in the solid state.<sup>27</sup> This stereospecific ion-pair formation apparently stabilizes the  $\Lambda(\delta\delta\delta)$  configuration in solution. Contrary to earlier reports, addition of phosphate results in a narrowing of the broad nmr spectrum of  $\text{Co}(\text{en})_3^{3+}$ ,<sup>24</sup> probably due to more effective quadrupolar relaxation. Higher concentrations of phosphate result in nearly identical 60-MHz spectra for  $\text{Co}(\text{en})_3^{3+}$  and  $\text{Rh}(\text{en})_3^{3+}$ . Quantitative analysis of the 220-MHz rhodium spectrum indicates a substantial increase in the fraction of ligands in the  $\delta$  conformation.<sup>13</sup> These observations indicate a strong conformational preference for the  $\Lambda(\delta\delta\delta)$  configuration due to stereospecific hydrogen bonding with phosphate ion.

**Optical Activity.** The conformations of coordinated ligands influence the optical activity of these metal complexes. The effects on the circular dichroism spectra of tris(diamine)cobalt(III) complexes are large in the charge-transfer region and relatively small in the visible region of the d–d transitions. By examining the circular dichroism spectra of various propylenediamine complexes with known conformations, a linear relationship was observed between the ligand conformations and the circular dichroism at the maximum of the charge-transfer absorption band.<sup>28</sup> Application of this relationship to  $\text{Co}(\text{en})_3^{3+}$  led to the conclusion that the complex exists exclusively in the  $\Lambda(\delta\delta\delta)$  configuration in solution. This result contradicts the conclusion obtained from the nmr spectra. Although a quantitative estimate of conformation averaging is not yet available for  $\text{Co}(\text{en})_3^{3+}$ , it appears certain that the complex is *not exclusively* in the  $\Lambda(\delta\delta\delta)$  configuration.

In platinum(IV) complexes charge-transfer effects dominate the optical activity, and the influence of conformation is observed even at the sodium D line in the visible region of the spectrum. A similar linear relationship was obtained between ligand conformation and the molecular rotation of tris(diamine)platinum(IV) complexes.<sup>29</sup> Application to  $\text{Pt}(\text{en})_3^{4+}$  led to the

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conclusion, however, that no conformational preference exists in solution. This is more in accord with the nmr results which indicate substantial but incomplete conformational averaging in  $\text{Pt}(\text{en})_3^{4+}$ .

Phosphate and similar anions cause substantial changes in the visible circular dichroism spectrum of  $\text{Co}(\text{en})_3^{3+}$ . It has been suggested that these are the consequence of changes in the conformations of the ligands,<sup>30</sup> an interpretation which is consistent with the effects of phosphate on the nmr spectra.<sup>13,24</sup>

**Calculations.** Attempts have been made to obtain more reliable estimates of the relative energies of the various conformational configurations by more sophisticated calculations of the type initiated by Corey and Bailar. Although the results are highly dependent on the force field adopted, a number of interesting conclusions emerge.<sup>14,31</sup> The enthalpy differences among the configurations decrease as the size of the metal ion increases since the interligand interactions are reduced, although there is some increase in strain energy in each ligand. Since the statistical entropy contribution to the free energy remains constant, the net result is that the  $\Lambda(\delta\delta\lambda)$  configuration is decidedly of lowest free energy in the larger complexes of nickel(II)

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and ruthenium(II) but probably of nearly the same free energy as the  $\Lambda(\delta\delta\delta)$  configuration in the smallest complex of cobalt(III). In every case the energy barrier to ring inversion is only 5-7 kcal mole<sup>-1</sup>, which accounts for the absence of dynamic effects in the nmr spectra.

## Conclusions

The model advanced by Corey and Bailar for the conformational analysis of tris(ethylenediamine)-metal complexes is generally verified by the nmr spectra of the complexes. The ligands are in rapid conformational equilibrium, with the  $\delta$  conformer more stable than the  $\lambda$  conformer in the  $\Lambda$  configuration by 0.3-0.6 kcal, depending on the size of the metal ion. A statistical entropy effect results in the  $\Lambda(\delta\delta\lambda)$  configuration being most abundant in solution, at least for the larger complexes. The very different nmr spectra of the various complexes result from large variations in chemical shielding and do not reflect substantially different stereochemical properties.

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# Atomic Fluorescence Flame Spectrometry<sup>†</sup>

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In atomic fluorescence flame spectrometry, the liquid sample to be analyzed is introduced through a "nebulizer" into a flame as a mist. The heat of the flame evaporates the solvent and vaporizes the analyte. The combustion flame acts as a convenient and relatively efficient atom-producing plasma. The atoms are then optically excited by some source and their fluorescence is observed.

The first reference to fluorescence of atomic vapors in flames was in 1924, when Nichols and Howes<sup>1</sup> observed the fluorescence of Ca, Sr, Ba, Li, and Na in a Bunsen burner flame. In 1927, Badger<sup>2</sup> published a classic paper on the atomic fluorescence of Tl, Hg, Mg, Cu, Ag, Cd, and Na in flames; in 1962, Alkemade<sup>3</sup>

mentioned the possible analytical use of atomic flame fluorescence spectrometry; and in 1964, Winefordner and Vickers<sup>4</sup> published the first paper on this phenomenon as an analytical method.

In Figure 1, several fluorescence processes of possible analytical use are indicated. The fluorescence of greatest analytical interest is the first resonance transition ( $1 \rightarrow 0$ ). In *resonance fluorescence*, the absorbed and emitted photons are of the same frequency.

*Stepwise line fluorescence* (Figure 1, process b) results when excitation is to a higher energy state which is deactivated to a lower excited state before emission. To date, this has been of little analytical use since the radiant flux of most commonly used sources at wavelengths corresponding to second and higher absorptions is low and the efficiency of populating the first excited state from higher states is small. *Direct line fluorescence*

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