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Conformational Analysis of Diamagnetic Tris-Ethylenediamine Complexes by Proton Magnetic Resonance. Spectra of Rhodium(III) Tris(ethylenediamine)

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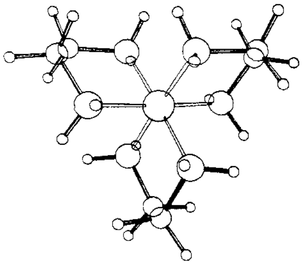
Received November 18, 1970

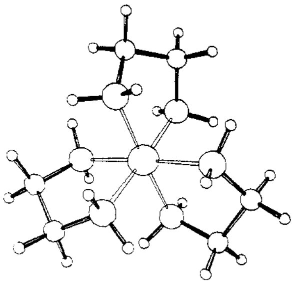
Proton magnetic resonance spectra of N-deuterated $Rh(en)_3^{3+}$ in D_2O at various temperatures and phosphate concentrations were obtained at 220 MHz. All spectra are of the AA′BB′X type and are interpreted in terms of a conformationally labile ethylenediamine ring system. The spectra were solved for chemical shifts and spin-coupling constants. From the spin-coupling constants, the fraction of time spent by any ring in each of two conformational states is determined. The conformer having one carbon–carbon bond perpendicular and two carbon–carbon bonds parallel to the C_3 axis (*e.g.*, Δ-δλλ) is found to be more stable than the conformer having all three carbon–carbon bonds parallel to the C_3 axis (*e.g.*, Δ-λλλ). The difference in free energy decreases at high phosphate concentrations. Reinterpretation of early equilibration–separation data and the most thorough calculations to date on cobalt(III) tris-diamine complexes all substantiate the claim that Δ-δλλ (or Λ-λδδ) is the most abundant conformer for tris-ethylenediamine complexes.

Introduction

Since Corey and Bailar's first results on the conformations of tris-ethylenediamine complexes,[1] a great deal of work has been carried out on this topic by equilibration–separation,[2-4] optical rotatory dispersion and circular dichroism (ORD and CD),[5-8] proton magnetic resonance (pmr),[9-19] and other methods.[20] Each five-membered chelate ring is puckered and can adopt one of two conformations: one with the carbon–carbon bond parallel to the threefold axis, I, and the other with the carbon–carbon bond perpendicular to the threefold axis, II. It has been widely accepted that the $Co(en)_3^{3+}$ species having all three carbon–carbon bonds parallel to the C_3 axis is the most abundant one and that it "costs" approximately 0.5 kcal/mol in free energy for each ring flipped with the carbon–carbon bond perpendicular to the C_3 axis. The fractions of species having zero, one, two, and three rings perpendicular to the C_3 axis have been widely quoted as 59, 29, 8, and 4%, respectively. In the present paper, both from new data and from a reexamination of previous data, we show that the above notions do not represent the true situation.



I



II

Although pmr has proven highly successful in conformational analysis of organic compounds, it has yielded little or no conformational information regarding diamagnetic tris-ethylenediamine complexes. This was due in the past largely to the absence of fine structure in the $-CH_2CH_2-$ resonances, which usually appeared as singlets (broad singlets for cobalt complexes) on low-frequency (*e.g.*, 60 MHz) pmr spectrometers. As higher frequency proton spectrometers (*e.g.*, 100 and 220 MHz) and heteronuclear decoupling of cobalt-59 have become available, fine structure has been revealed for the tris-ethylenediamine complexes of Ru(II),[15] Co(III),[19] and Rh(III).[16] In every case, the patterns of the N-deuterated complexes have proven to be of the AA′BB′ or AA′BB′X type, and it now appears that this is a general result whenever sufficient AB chemical shift difference is obtained through the use of high spectrometer frequencies, solvent shifts, etc.

The AA′BB′ patterns of $Ru(en)_3^{2+}$ at 60 and 100

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

[2] (a) F. P. Dwyer, T. E. MacDermott, and A. M. Sargeson, *ibid.*, **85**, 2913 (1963); (b) F. P. Dwyer, A. M. Sargeson, and L. B. James, *ibid.*, **86**, 590 (1964).

[3] A. M. Sargeson in "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor, Ed., Academic Press, New York, N. Y., 1964.

[4] (a) T. E. MacDermott, *Chem. Commun.*, 223 (1968); (b) *Inorg. Chim. Acta*, **2**, 81 (1968).

[5] T. S. Piper and A. G. Karipides, *J. Amer. Chem. Soc.*, **86**, 5039 (1964).

[6] (a) H. L. Smith and B. E. Douglas, *ibid.*, **86**, 3885 (1964); (b) *Inorg. Chem.*, **5**, 784 (1966).

[7] A. J. McCaffery, S. F. Mason, and B. J. Norman, *Chem. Commun.*, 49 (1965).

[8] A. J. McCaffery, S. F. Mason, B. J. Norman, and A. M. Sargeson, *J. Chem. Soc.*, 1304 (1968).

[9] D. B. Powell and N. Sheppard, *ibid.*, 791 (1959).

[10] P. Clifton and L. Pratt, *Proc. Chem. Soc., London*, 339 (1963).

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

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

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

[14] H. Yoneda, M. T. Emerson, and Y. Morimoto, *Inorg. Chem.*, **8**, 2214 (1969).

[15] (a) H. Elsbernd and J. K. Beattie, *J. Amer. Chem. Soc.*, **91**, 4573 (1969); (b) J. K. Beattie and H. Elsbernd, *ibid.*, **92**, 1946 (1970).

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

[17] L. R. Froebe and B. E. Douglas, *ibid.*, **9**, 1513 (1970).

[18] F. F. Ho and C. N. Reilley, *Anal. Chem.*, **42**, 600 (1970).

[19] J. L. Sudmeier and G. L. Blackmer, *J. Amer. Chem. Soc.*, **92**, 5238 (1970).

[20] (a) J. R. Gollogly and C. J. Hawkins, *Inorg. Chem.*, **8**, 1168 (1969); (b) *ibid.*, **9**, 576 (1970).

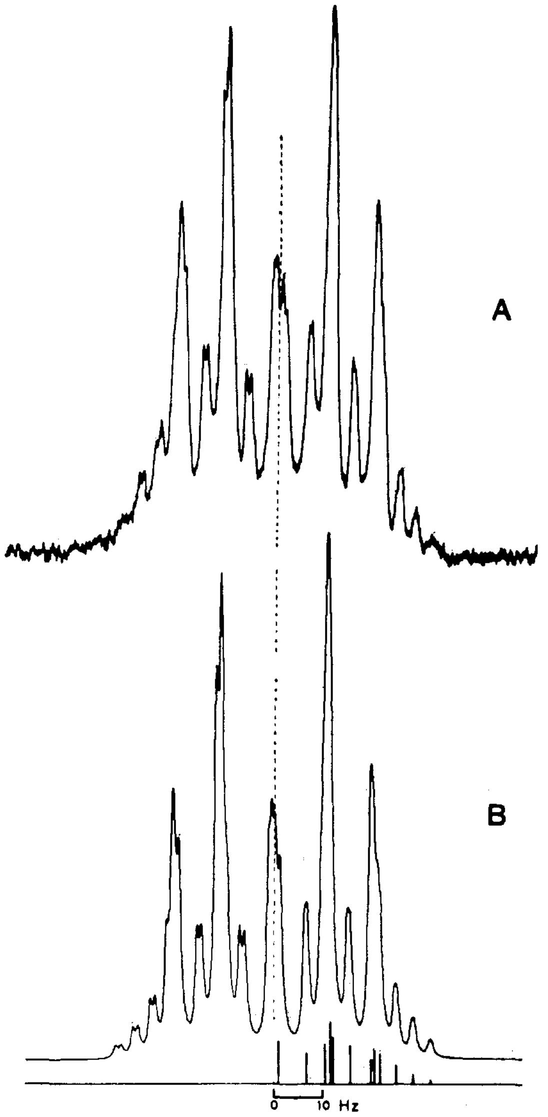

Figure 1.—(A) Observed 220-MHz pmr spectrum of 0.15 *M* N-deuterated $Rh(en)_3{}^{3+}$ in D_2O at 93°. (B) Calculated spectrum.

MHz have been solved for chemical shifts and coupling constants but were interpreted as arising from the presence of a single conformer. In the present work, the spectra of $Rh(en)_3{}^{3+}$ are interpreted in terms of a conformationally labile model.[15,21] The effect of phosphate ion upon the conformation of $Rh(en)_3{}^{3+}$ is investigated because of its remarkable effects upon ORD, CD, and nmr spectra.[6-8,17] Using identical methods for treatment of data, a study of $Co(en)_3{}^{3+}$ at 250 MHz with cobalt-59 decoupling is currently under way.[22] The distributions of conformers found in these pmr studies should be useful in the assignment of oscillator strengths in ORD and CD.

Experimental Section

Tris(ethylenediamine)rhodium(III) iodide, $[Rh(en)_3]I_3$, was prepared by the method of Watt and Crum.[23] The analytically pure complex was dissolved in 250 ml of water and converted to the more soluble chloride form by allowing it to pass through 250 ml of a Dowex 1-X8 anion-exchange resin column (100–200 mesh, Cl^- form) at a drop rate of 10 drops/min. The pure chloride salt was obtained upon evaporation of the resultant solution to dryness.

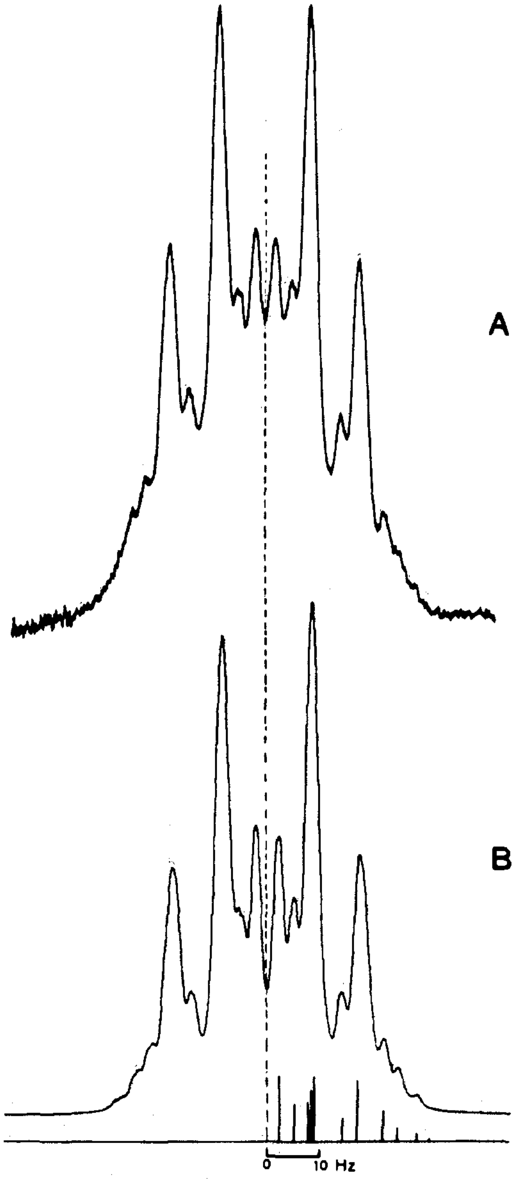

Figure 2.—(A) Observed 220-MHz pmr spectrum of 0.15 *M* N-deuterated $Rh(en)_3{}^{3+}$ in D_2O at 17°. (B) Calculated spectrum.

The concentration of N-deuterated $Rh(en)_3{}^{3+}$ samples in 1 ml of D_2O was 0.15 *M*. To investigate the influence of phosphate ions, drop quantities of a stock phosphate solution in D_2O were added and the pmr spectra were recorded. Base-catalyzed deuterations of the amine protons were accomplished by the addition of NaOD to achieve a final pD value of ~10.

The proton magnetic resonance spectra were recorded using a Varian HR-220 nmr spectrometer with a variable-temperature probe. All spectra were recorded at a sweep width of 250 Hz (5 Hz = 1 cm) and a scan rate of 0.5 Hz/sec.

Results

Spectral Analyses.—Figure 1A shows the 220-MHz pmr spectrum of 0.15 *M* N-deuterated $Rh(en)_3{}^{3+}$ at 93° in D_2O. The pattern is slightly unsymmetrical due to greater spin coupling of ^{103}Rh ($I = {}^1/_2$, 100% abundant) to the low-field proton than to the high-field proton, and thus the pattern is actually AA'BB'X.

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[21] After this article was submitted, the interpretation of the $Ru(en)_3{}^{2+}$ spectrum was revised to one in agreement with the conformationally labile model espoused here (see J. R. Gollogly, C. J. Hawkins, and J. K. Beattie, *Inorg. Chem.*, **10**, 317 (1971)). This paper also includes the $R \ln 3$ statistical factors favoring mixed tris-ethylenediamine ring conformers.

[22] J. L. Sudmeier, G. L. Blackmer, C. H. Bradley, and F. A. L. Anet, *Inorg. Chem.*, *J. Amer. Chem. Soc.*, in press.

[23] G. W. Watt and J. K. Crum, *ibid.*, **87**, 5366 (1965).

TABLE I

CALCULATED SPECTRAL[a] AND CONFORMATIONAL PARAMETERS FOR $Rh(en)_3^{3+}$

Case	$[PO_4^{3-}]$, M	Temp, °C	Line width, Hz	$\Delta\delta_{AB}$, ppm	J_{12}, Hz	J_{13}, Hz	J_{34}, Hz	J_{14}, Hz	ω, deg	J(trans), Hz	J(gauche), Hz	f_λ
I	0.0	93	1.2	0.1336	9.4[b]	4.4	5.3	−13.2	56	12.1	3.5	0.71 ± 0.02
II	0.0	17	2.0	0.1120	9.5[c]	3.9	6.2	−13.1	59	12.5	3.6	0.68 ± 0.05
III	0.1	93	1.2	0.1472	9.8[b]	4.2	5.2	−13.3	57	12.2	3.5	0.75 ± 0.03
IV	0.1	17	2.0	0.1400	9.4[c]	4.1	5.3	−13.5	57	12.0	3.4	0.72 ± 0.05
V	0.3	93	1.2	0.1762	10.4[b]	4.3	4.7	−13.0	57	12.3	3.5	0.80 ± 0.03
VI	0.3	17	~3.0	0.198	. . .	. . .	. . .	. . .	. . .	. . .	. . .	(0.84)[d]
$Ru(en)_3^{2+}$ [e]	0.0		~1.8	0.230	9.4	3.8	5.5	−12.5	58	11.9	3.4	0.72

[a] For $Rh(en)_3^{3+}$, J_{15} = 0.3 Hz and J_{25} = 1.0 Hz. [b] Random error estimated as ±0.1 Hz for all spin-coupling constants in this case. [c] Random error estimated as ±0.2 Hz for all spin-coupling constants in this case. [d] Derived from the $\Delta\delta_{AB}$ value by extrapolation of Figure 8. [e] Spectral parameters from ref 15b.

This is consistent with previous findings for Pt(II)[24] and Co(III)[19] complexes and supports the notion that axial protons are always upfield of equatorial protons in diamine chelates, with greater M–$\dot{N}$–C–H spin couplings existing for equatorial protons than for axial. Some of the lines on the left-hand portion of the spectrum are clearly split with a spacing of ~1.0 Hz. The benefits to be derived from higher frequency pmr are obvious from a comparison of the 60-MHz spectrum of $Rh(en)_3^{3+}$,[16] where only a hint of fine structure appears at higher temperatures.

Figure 2A shows the spectrum of the same $Rh(en)_3^{3+}$ sample at 17°. The decreased resolution and chemical shift difference are readily observed, the former presumably due to decreased spin relaxation times T_1 and T_2 with greater viscosity. Figure 3A shows the spectrum of $Rh(en)_3^{3+}$ containing 0.3 M K_3PO_4 at 93°. The increased chemical shift difference is readily apparent. For reasons which are obscure, phosphate causes appreciable line broadening of $Rh(en)_3^{3+}$ at 17° but causes little or no line broadening at 93°.

In addition to the cases shown in Figures 1A, 2A, and 3A, spectra were obtained for the cases shown in Table I. As shown in the table, no line width less than 1.2 Hz was observed, and some line widths are great enough to make spectral analysis extremely imprecise. Although spin decoupling of ^{103}Rh, ^{2}H, and/or ^{14}N would be highly desirable for resolution enhancement, they were not available with the present instrumentation.

All spectra were analyzed with the aid of LAOCOON III[25] by well-known procedures. Initially, the presence of the ^{103}Rh spin coupling was ignored, and each case was treated as a four-spin problem, using line positions measured from the right-hand side of the spectrum only. Each of the two most intense peaks in the right half is composed of three unresolved peaks, and in certain cases, *e.g.*, Figure 1A, the central peak is composed of overlapping peaks. Because of the greater uncertainty associated with the line positions where overlap occurs, we eliminated as many overlapping lines as possible from our input data. Five or six lines from each half-spectrum are required for a solution.

The calculated spectral parameters are given in Table I. While it is difficult to estimate the random errors in the coupling constants, we judge the precision of 93 and 17° parameters to be ±0.1 and ±0.2 Hz, respectively.

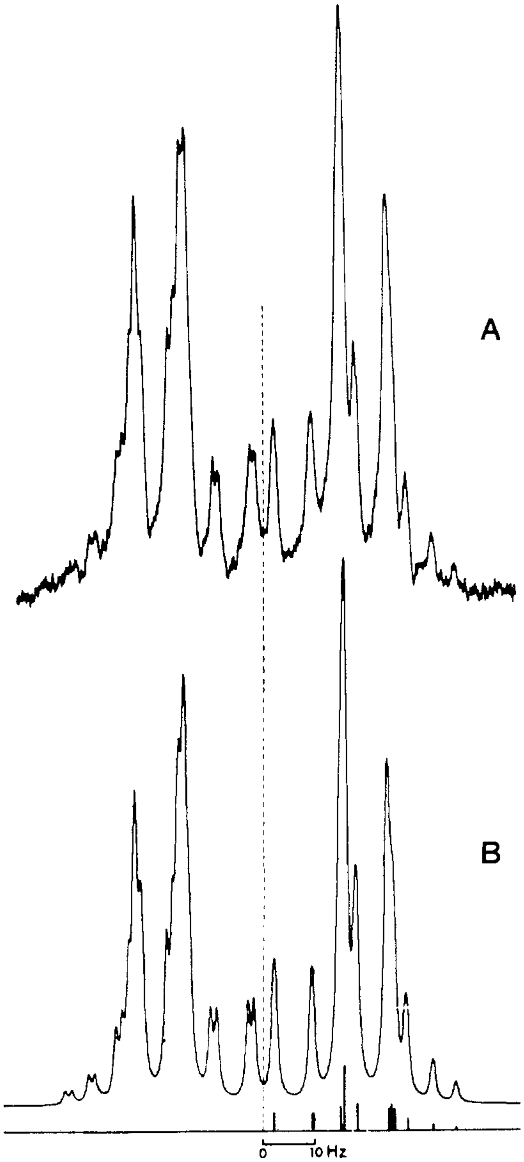

Figure 3.—(A) Observed 220-MHz pmr spectrum of 0.15 M N-deuterated $Rh(en)_3^{3+}$ in D_2O containing 0.3 M K_3PO_4 at 93°. (B) Calculated spectrum.

Figures 1B, 2B, and 3B are computed spectra produced by a Cal-Comp plotter using the output of LAOCOON III. These computed spectra include a Lorentzian line shape function and empirically determined values of the ^{103}Rh–H spin-coupling constants J_{15} = 0.3 Hz and J_{35} = 1.0 Hz (Figure 4). In every case, the agreement between calculated and observed

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(24) L. E. Erickson, J. W. McDonald, J. K. Howie, and R. P. Clow, *J. Amer. Chem. Soc.*, **90**, 6371 (1968).

(25) LAOCOON III is an improved version of the least-squares nmr spectral-fitting computer program described by S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3363 (1964).

spectra was excellent, both in line positions and intensities.

Ring Conformer Populations.—How do we interpret the fact that only a single AA′BB′X or AA′BB′ pattern is obtained for $Rh(en)_3^{3+}$ and for other tris-ethylenediamine complexes? The fact that only two proton chemical shifts are found indicates the presence of a C_2 axis passing from the metal ion through the midpoint of the carbon–carbon bond of each ligand. This can be either a static symmetry, such as would exist if the sample consisted exclusively of $\lambda\lambda\lambda$ or $\delta\delta\delta$ conformers, or a time-averaged symmetry, such as would exist for any distribution of rapidly interconverting conformers.

The former interpretation[15] has the following objectionable features, which will be clarified below.

(1) The J(trans) (*i.e.*, for the H–C–C–H dihedral angle, $\phi = 180°$) and J(gauche) (*i.e.*, $\phi = 60°$) spin-coupling constants are too small and too large, respectively, compared to other diamines (see Figure 4).

(2) Distortions of ω (Figure 4), the N–C–C–N dihedral angle, to values larger than 60° are required in order to explain the magnitudes of the coupling constants, in opposition to X-ray data which show ω to be smaller than 60° (*i.e.*, 43–53°[26]).

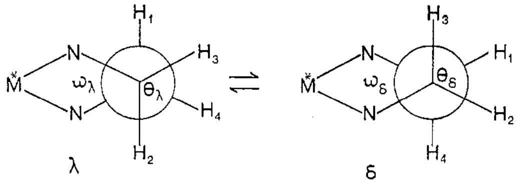

Figure 4.—Conformational equilibrium for each ring of a metal–tris(ethylenediamine) complex.

(3) Because there are no extraneous lines present in the AA′BB′ patterns, it is unlikely that any conformer other than $\delta\delta\delta$ or $\lambda\lambda\lambda$ is present (*i.e.*, in this view) to greater than ~2% abundance. This contradicts all previous studies on tris-ethylenediamine complexes, which indicate that rather small energies normally separate the various conformers. Alternatively, the postulation of slow kinetics of conformational exchange contradicts all evidence for aliphatic five-membered rings, which interconvert rapidly down to extremely low temperatures.

In contrast, a model involving conformational lability, where significant amounts of various conformers are in rapid equilibrium, explains all the features of the nmr spectra and provides valuable new insight into the conformational equilibria of tris-diamine complexes. Figure 4 shows the conformational equilibrium of a given ring of a tris-ethylenediamine complex. The designations λ and δ refer by international convention to the absolute conformations of the rings as shown. Mirror-image compounds yield identical pmr spectra and the present $Rh(en)_3^{3+}$ sample was actually a racemic mixture of the Δ and Λ configurations. The compound might have been resolved, however, and for purposes of simplifying the ensuing discussion, we shall assume that only the Δ configuration is present. By inspection of the vicinal coupling constants J_{12} and J_{34} in Table I, it is clear that unequal amounts of λ and δ are present. From previous data[2–4] it is known that the λ conformation is preferred in the Δ complex, and on that basis we shall assume in this work that the equilibrium favors λ in the Δ complex and δ in the Λ complex (rather than δ in the Δ complex and λ in the Λ complex).

Because of rapid interconversion, each vicinal coupling constant is a weighted average of its values in the λ and δ conformers, and we can write

$$J_{12} = f_\lambda J_{12(\lambda)} + f_\delta J_{12(\delta)} \tag{1}$$

$$J_{13} = f_\lambda J_{13(\lambda)} + f_\delta J_{13(\delta)} \tag{2}$$

$$J_{34} = f_\lambda J_{34(\lambda)} + f_\delta J_{34(\delta)} \tag{3}$$

where f_λ and f_δ are the fractions of time spent by each ring in the λ and δ conformations, respectively. Using the relationship

$$f_\lambda + f_\delta = 1 \tag{4}$$

we can eliminate f_δ in eq 1–3. Assuming that the vicinal coupling constants can be described by simple Karplus equations[27] of the form

$$J = A_1 \cos^2 \phi \qquad 0° \leq \phi \leq 90° \tag{5}$$

$$J = A_2 \cos^2 \phi \qquad 90° \leq \phi \leq 180° \tag{6}$$

where ϕ is the H–C–C–H dihedral angle and A_1 and A_2 are constants, we can write

$$J_{12(\lambda)} = A_2 \cos^2 (\theta_\lambda + \omega_\lambda) \tag{7}$$

$$J_{12(\delta)} = A_1 \cos^2 (\theta_\delta - \omega_\delta) \tag{8}$$

$$J_{13(\lambda)} = A_1 \cos^2 \omega_\lambda \tag{9}$$

$$J_{13(\delta)} = A_1 \cos^2 \omega_\delta \tag{10}$$

$$J_{34(\lambda)} = A_1 \cos^2 (\theta_\lambda - \omega_\lambda) \tag{11}$$

$$J_{34(\delta)} = A_2 \cos^2 (\theta_\delta + \omega_\delta) \tag{12}$$

where the projected H–C–H geminal angles θ_λ and θ_δ are symmetric with respect to the adjacent C–N bond axes.

Substituting eq 7–12 into eq 1–4, we obtain three equations in seven unknowns

$$J_{12} = f_\lambda A_2 \cos^2 (\theta_\lambda + \omega_\lambda) + A_1 \cos^2 (\theta_\delta - \omega_\delta) - f_\lambda A_1 \cos^2 (\theta_\delta - \omega_\delta) \tag{13}$$

$$J_{13} = f_\lambda A_1 \cos^2 \omega_\lambda + A_1 \cos^2 \omega_\delta - f_\lambda A_1 \cos^2 \omega_\delta \tag{14}$$

$$J_{34} = f_\lambda A_1 \cos^2 (\theta_\lambda - \omega_\lambda) + A_2 \cos^2 (\theta_\delta + \omega_\delta) - f_\lambda A_2 \cos^2 (\theta_\delta + \omega_\delta) \tag{15}$$

A computer program was written for iterative solution of eq 13–15, so that for a set of input values J_{12}, J_{13}, J_{34}, θ_λ, θ_δ, ω_{diff} (*i.e.*, $\omega_\delta - \omega_\lambda$), and ratio of J(trans)/J(gauche) [J(trans)/J(gauche) $= 4A_2/A_1$], one obtains ω_λ, ω_δ, J(trans), J(gauche), and, most importantly, f_λ. An analysis of random error in f_λ, based on random errors in J_{12}, J_{13}, and J_{34}, is included. Equations 13–15 are rearranged so as to eliminate A_1 and A_2, and a quadratic equation in f_λ is obtained (or a linear equation when $\omega_\lambda = \omega_\delta$). A value of ω_λ is guessed and the corresponding f_λ is calculated. Putting f_λ back into eq 13 and 14, the J(trans)/J(gauche) ratio is checked. Based on the magnitude and sign of any error, a new

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(26) See Table II in ref 20a.

(27) W. A. Thomas, *Annu. Rev. NMR Spectros.*, **1**, 72 (1968).

TABLE II

SPIN-COUPLING CONSTANTS FOR DIAMINE COMPOUNDS FROM CHEMICAL LITERATURE

Entry	Compd	J(trans)	J(gauche)	J(gem)	J(trans)/ J(gauche)	Ref
1	Theory				4.0–5.5	*a*
2	*trans*-2,5-Dimethylpiperazine (P)	10.8	2.9	−12.5	3.7	*b*
3	*trans*-2,5-Dimethylpiperazine (HP^+)	11.5	3.0	−13.5	3.7	*b*
4	*trans*-2,5-Dimethylpiperazine (H_2P^{2+})	12.2	3.4	−14.2	3.6	*b*
5	1,2-Propanediaminetetraacetic acid ($PDTA^{4-}$)–alkali metal salts	10.2	3.0	−13.5	3.4	*c*
6	$CaPDTA^{2-}$	11.0	3.2	−14.0	3.4	*c*
7	"Proton chelate" ($HPDTA^{3-}$)	11.8	3.8	−14.5	3.1	*c*
8	$Co^{III}PDTA^-$	. . .	3.4	−13.2	. . .	*d*
9	$Co^{III}(CN)_4((R)\text{-pn})$	12.4	4.4	−12.4	2.8	*e*
10	$Pd^{II}((R)\text{-pn})_2{}^{2+}$	9.9	4.2	−12.5	2.4	*e*
11	$Pt^{II}((R)\text{-pn})_2{}^{2+}$	10.0	4.3	−12.3	2.3	*e*

[a] M. Karplus, *J. Chem. Phys.*, **30,** 11 (1959); R. V. Lemieux and J. W. Lown, *Can. J. Chem.*, **42,** 893 (1964); R. J. Abraham and K. A. McLauchlan, *Mol. Phys.*, **5,** 513 (1962). [b] J. L. Sudmeier, *J. Phys. Chem.*, **72,** 2344 (1968). [c] J. L. Sudmeier and A. J. Senzel, *J. Amer. Chem. Soc.*, **90,** 6860 (1968); *Anal. Chem.*, **40,** 1693 (1968). [d] J. L. Sudmeier, A. J. Senzel, and G. L. Blackmer, *Inorg. Chem.*, **10,** 90 (1971). [e] S. Yano, H. Ito, Y. Koike, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jap.*, **42,** 3184 (1969).

ω_λ is guessed and the process is repeated until convergence is obtained.

The following simplifications are made: (1) assume $\theta_\lambda = \theta_\delta = 120°$; (2) assume $\omega_\lambda = \omega_\delta$; (3) assume a fixed ratio of A_1 to A_2. The first assumption is justified on the basis of X-ray crystallographic data[28] which show little or no deviation from tetrahedral in the N–C–C angles, which implies tetrahedral angles for the H–C–H angles. Although Hawkins' calculations[20b] indicate that ω_λ and ω_δ may differ, the direction and magnitude of any difference is impossible to predict at present, and we have little choice but to assume that $\omega_\lambda = \omega_\delta$ (but not necessarily equal to 60°). To fix the ratio of A_1 to A_2, which is equivalent to setting the J(trans)/J(gauche) ratio, is felt to be more reasonable than trying to fix the actual values of A_1 and A_2, because allowance is made for changes in substituent electronegativity, which affects A_1 and A_2 more than it affects their ratios.

Table II is a compilation of J(trans) and J(gauche) values from the chemical literature. Entries 2, 3, and 4 or 5, 6, and 7 exemplify electronegativity effects of this kind. True values of J(trans) and J(gauche) could only be obtained from compounds having dihedral angles of 180 and 60°, respectively. Entries 2–7 represent either free diamine compounds or labile metal chelates and should be less prone to bond angle distortions than the inert chelates in entries 8–11. Therefore an average value of 3.5 was obtained from entries 2–7 and applied to the $Rh(en)_3{}^{3+}$ problem as representative of a reasonable J(trans)/J(gauche) ratio.

Table I shows the calculated values of ω, J(trans), J(gauche), and f_λ for $Rh(en)_3{}^{3+}$. In addition to the random errors in f_λ, these values are subject to systematic errors in the assumed values of θ_λ, θ_δ, ω_{diff}, and J(trans)/J(gauche) ratio. Figure 5 shows the effect of the J(trans)/J(gauche) ratio upon the results for cases I and II. At $f_\lambda = 1.0$, the results are the same as would be obtained in the single-conformer interpretation.[15] This interpretation would be accompanied by the following values for $Rh(en)_3{}^{3+}$: case I, J(trans)/J(gauche) = 1.9 and $\omega_\lambda = \omega_\delta = 62°$; case II, J(trans)/J(gauche) = 1.9 and $\omega_\lambda = \omega_\delta = 64°$. Clearly these values are in less satisfactory agreement with literature values than those given in Table I. Figures 6 and 7 show the sensitivity of f_λ to changes in θ (where it is assumed that $\theta_\lambda = \theta_\delta$) and ω_{diff}, respectively.

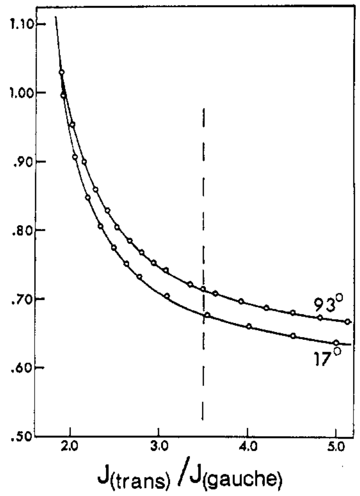

Figure 5.—Calculated values of f_λ, the fraction of time spent by a ring of a Δ-$Rh(en)_3{}^{3+}$ molecule in the λ conformation, *vs.* the assumed ratio of J(trans) to J(gauche), which are the vicinal spin-coupling constants for dihedral angles of 180 and 60°, respectively. It is assumed that $\theta_\delta = \theta_\lambda = 120°$ and $\omega_\delta - \omega_\lambda = 0$.

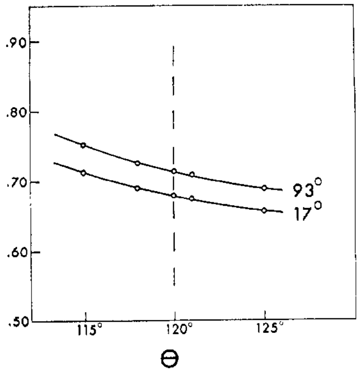

Figure 6.—Calculated values of f_λ *vs.* the assumed value of θ, the projection of the H–C–H geminal angle. It is assumed that $\theta_\delta = \theta_\lambda$, $\omega_\delta - \omega_\lambda = 0$, and J(trans)/J(gauche) = 3.5.

Although it had not been anticipated, there is a linear correlation between $\Delta\delta_{AB}$ and f_λ, and a least-squares fit of exceptional quality was obtained In a plot of $\Delta\nu_{AB}/2$ *vs.* f_λ (Figure 8) the slope and intercept

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(28) S. Ooi, Y. Komijana, Y. Saito, and H. Kuroya, *Bull. Chem. Soc. Jap.*, **32,** 263 (1959); L. N. Swink and M. Atoji, *Acta Crystallogr.*, **13,** 639 (1960); K. Nakatsu, *Bull. Chem. Soc. Jap.*, **35,** 832 (1962); other references cited in ref 20a.

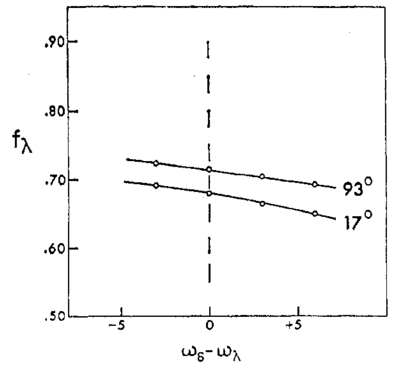

Figure 7.—Calculated values of f_λ *vs.* the assumed value of $\omega_\delta - \omega_\lambda$. It is assumed that $\theta_\delta = \theta_\lambda = 120°$ and J(trans)/J(gauche) = 3.5.

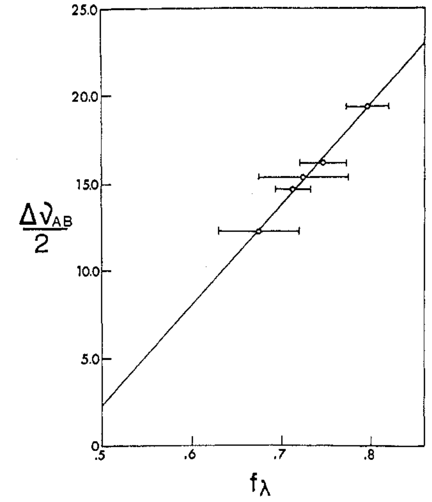

Figure 8.—Chemical shift difference of $Rh(en)_3^{3+}$ *vs.* f_λ.

are 58 ± 2 and 2.24 ± 0.07, respectively, where the standard deviations refer only to the quality of the fit. Considering the uncertainties in the f_λ values, we conclude that the quality of the fit is fortuitous, although this depends somewhat on the difficult-to-estimate precision of J_{12}, J_{13}, and J_{34}. To the extent that the plot is significant, it would indicate the surprising absence of appreciable temperature or salt effects upon $\Delta\nu_{AB}$ and it would indicate by its finite intercept the truth of the claim that $\Delta\nu_{AB}$ need not collapse to zero in the case of complete conformational averaging (*i.e.*, $f_\lambda = 0.50$).[16,19,29] Figure 8 would also allow the estimation of f_λ for case VI in Table I, where excessive line width prevented precise determination of the coupling constants, although $\Delta\delta_{AB}$ could be determined by second-moment analysis.[30]

Discussion

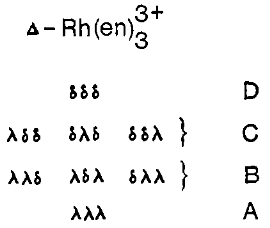

Figure 9.—Conformational isomers of Δ-$Rh(en)_3^{3+}$.

Molecular Conformer Populations.—Having determined f_λ, we know the λ–δ equilibrium constant for each ethylenediamine ring at various temperatures and phosphate concentrations. However, what is of greatest concern to most investigators is the equilibrium between the molecular species represented in Figure 9. Each symbol lists the conformations of the first, second, and third rings of a tris-ethylenediamine complex as if they could be distinguished. The vertical axis is meant to suggest the energy scale for a complex of the Δ configuration. However, it must be kept in mind that various crossovers may exist. If we designate as A, B, C, and D the total concentrations (in mole fraction) of the conformers as shown in Figure 9, we can write

$$A + B + C + D = 1 \qquad (16)$$

A sample containing pure A would yield $f_\lambda = 1.00$. Samples containing pure B, C, or D would yield f_λ values of $^2/_3$, $^1/_3$, or 0, respectively. Thus we can write

$$f_\lambda = A + {}^2/_3B + {}^1/_3C \qquad (17)$$

Combining eq 16 and 17, we obtain

$$f_\lambda K_{DA} + (f_\lambda - {}^1/_3)K_{CA} + (f_\lambda - {}^2/_3)K_{BA} + (f_\lambda - 1) = 0 \qquad (18)$$

where the equilibrium constants are defined as

$$K_{BA} = B/A, \quad K_{CA} = C/A, \quad K_{DA} = D/A \qquad (19)$$

Equation 18 has three unknowns and cannot be solved.

However, if we are willing to assume that equal enthalpy differences exist between successive species (*i.e.*, $\Delta H_{BA} = {}^1/_2\Delta H_{CA} = {}^1/_3\Delta H_{DA}$) and that the entropy differences are due entirely to changes in symmetry number[31] (*i.e.*, $\Delta S_{BA} = \Delta S_{CA} = R \ln 3$ and $\Delta S_{DA} = 0$), we can write the equation

$$K = K_{BA}/3 = (K_{CA}/3)^{1/2} = (K_{DA})^{1/3} \qquad (20)$$

where K is the microscopic equilibrium constant between any two subspecies differing only in the conformation of a particular ring. The symmetry numbers, σ, of species A, B, C, and D are 6, 2, 2, and 6, respectively. Combining eq 18 and 20, we obtain the equation

$$f_\lambda K^3 + 3(f_\lambda - {}^1/_3)K^2 + 3(f_\lambda - {}^2/_3)K + (f_\lambda - 1) = 0 \qquad (21)$$

A value of K was determined for each f_λ value, and the K values were translated into the following concentrations of A, B, C, and D (and ΔH values in kcal/mol): case I, 0.36, 0.44, 0.18, 0.02 ($\Delta H = 0.65$); case II, 0.32, 0.44, 0.20, 0.03 ($\Delta H = 0.43$); case III, 0.41, 0.42, 0.14, 0.02 ($\Delta H = 0.78$); case IV, 0.37, 0.43, 0.17, 0.02 ($\Delta H = 0.54$); case V, 0.51, 0.38, 0.10, 0.01 ($\Delta H = 1.01$); case VI, 0.59, 0.34, 0.06, 0.01 ($\Delta H = 0.95$).

Although there is no justification for the assumption of equal ΔH for each ring inversion as we shall show, these results illustrate several trends. First of all, little of species D is present in any case. This agrees

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[29] H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2196 (1962).

[30] W. A. Anderson and H. M. McConnell, *ibid.*, **26**, 1496 (1957).

[31] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, N. Y., 1965, pp 11, 56; E. L. King, *J. Chem. Educ.*, **43**, 478 (1966).

with most previous studies of tris ethylenediamines.[1-4,20b] In cases I–IV, the concentration of species B is comparable to that of A and in some cases is greater than A. The large concentrations of B are largely the result of accounting for the entropy of mixing terms, which have never been properly considered in any previous literature. Increasing the phosphate concentration generally tends to populate A and to depopulate B, C, and D. In principle, ΔH should agree for case I with II, case III with IV, and case V with VI.

However, to impose the condition of equal energy gaps between successive species A, B, C, and D is not only too restrictive but is also contradicted by recent calculations[20b] and by previous experimental results.[2-4]

Discarding eq 20 and 21, we shall attempt alternative approaches to the solution of eq 18. If we assume that $D = 0$, the accuracy of our calculations should not be affected by more than a few per cent. Equation 18 then reduces to

$$(f_\lambda - {}^2/_3)K_{BA} + (f_\lambda - {}^1/_3)K_{CA} = 1 - f_\lambda \quad (22)$$

As before, we assume that the entropy of mixing terms are more important than any other contributions (although vibrational contributions may be important[21]), and we express the equilibrium constants in the form

$$K_{BA} = e^{-\Delta G_{BA}/RT} = e^{-\Delta H_{BA}/RT}e^{\Delta S/R} = 3e^{-\Delta H_{BA}/RT} \quad (23)$$

Substituting for K_{BA} and K_{CA} and dividing by 3, we obtain

$$(f_\lambda - {}^2/_3)e^{-\Delta H_{BA}/RT} + (f_\lambda - {}^1/_3)e^{-\Delta H_{CA}/RT} = (1 - f_\lambda)/3 \quad (24)$$

Using the temperature variations of f_λ at 93 and 17°, we can write two equations (one for each temperature) in two unknowns, x and y, of the form

$$a_1e^{b_1x} + c_1e^{b_1y} = g_1 \quad (25)$$

$$a_2e^{b_2x} + c_2e^{b_2y} = g_2 \quad (26)$$

where $x = \Delta H_{BA}$, $y = \Delta H_{CA}$, and all other terms are defined as in eq 24. Computer programs were written for solution of these equations by iterative least squares, by the Newton–Raphson method,[32] and by topological analysis. Convergence was obtained for the case III–IV combined data and for the case V–VI data. However, whether convergence could be obtained or not was very sensitive to the formulation of the equilibrium constants. For example, the case V–VI convergence could only be obtained for the eq 24 formulation, whereas the case III–IV convergence could only be obtained when equilibrium constants defined as $K_{AB} = A/B$ and $K_{CB} = C/B$ were employed. Although for the case I–II data no unique solution was found, the least-squares deviations were reduced to negligible levels (2×10^{-5}) for a range of x and y values. The results are as follows: case I–II, $\Delta H_{BA} \approx -2$ kcal/mol and $\Delta H_{CA} \approx 8$ kcal/mol (at 25°, $A \approx 0.03$, $B \approx 0.97$, $C \approx 0.00$); case III–IV, $\Delta H_{BA} = -1.5$ kcal/mol and $\Delta H_{CA} = 1.6$ kcal/mol (at 25°, $A = 0.03$, $B = 0.92$, $C = 0.05$); case V–VI, $\Delta H_{BA} = 0.8$ kcal/mol and $\Delta H_{CA} = 2.2$ kcal/mol (at 25°, $A = 0.54$, $B = 0.42$, $C = 0.04$). The precision of these results is difficult to calculate but is estimated to be very low. The difficulty is that we are attempting to fit many parameters, A, B, and C, from a few f_λ parameters. When f_λ approaches $^2/_3$, the constants A_1 and A_2 in eq 25 and 26 become very low in relative precision.

If we assume both $C = 0$ and $D = 0$, we have two equations, *i.e.*, (25) and (26), in one unknown, ΔH_{BA}, and we can calculate a weighted average, taking into account the differing precisions of the high- and low-temperature results. Giving cases I, III, and V approximately twice the weight of cases II, IV, and VI, the following results are obtained: case I–II, $\Delta H_{BA} = -0.8 \pm 0.5$ kcal/mol (at 25°, $A = 0.08$, $B = 0.92$); case III–IV, $\Delta H_{BA} = -0.1 \pm 0.2$ kcal/mol (at 25°, $A = 0.22$, $B = 0.78$); case V–VI, $\Delta H_{BA} = 0.5 \pm 0.1$ kcal/mol (at 25°, $A = 0.45$, $B = 0.55$). The free energy changes, ΔG_{BA}, at 25° are -1.4 ± 0.5, -0.7 ± 0.2, and -0.1 ± 0.1 kcal/mol, respectively. These results should be lower in random error, although they are subject to serious systematic error arising particularly from the rejection of species C.

Regardless of the method of treatment of the $Rh(en)_3{}^{3+}$ data, B tends to lie below A in free energy. The first suggestion in the chemical literature of a tris-ethylenediamine complex where this might be the case was Hawkins' calculation[20b] for $Co(en)_3{}^{3+}$, where the following energy differences were obtained: $\Delta H_{BA} = -0.1$ kcal/mol, $\Delta H_{CA} = 0.35$ kcal/mol, $\Delta H_{DA} = 0.85$ kcal/mol. These were obtained by using the author's empirical van der Waals formula, tailored to fit equilibration–separation data on Co(III) complexes.[2-4] However, if a higher energy van der Waals expression, such as Bartell's equation, is used, values of $\Delta H_{BA} = -0.7$ kcal/mol, $\Delta H_{CA} = 0.4$ kcal/mol, and $\Delta H_{DA} = 0.8$ kcal/mol were obtained,[20b] in better agreement with our results for $Rh(en)_3{}^{3+}$.

Another trend which is clear from our data is that increased phosphate concentration results in increased population of A, in agreement with earlier speculation regarding preferential stabilization of A through a hydrogen-bonded phosphate complex.[6-8]

Previous Results.—There are no previous quantitative results on the conformations of $Rh(en)_3{}^{3+}$. For comparison, we shall examine previous data obtained for tris-diamine complexes of Co(III). Several widely quoted studies[1-3] have created the impression that the free energy levels of species A, B, C, and D in $Co(en)_3{}^{3+}$ are evenly spaced, with a separation of 0.5–0.6 kcal/mol between adjacent levels, and have the following populations: 59% A, 29% B, 8% C, and 4% D. These results originated from experiments in which equilibrium mixtures of cobalt(III) tris-diamine compounds were separated by paper chromatography and determined spectrophotometrically. There were three main experiments, shown schematically in Figure 10. This diagram is identical with that of Figure 9, except for the addition of the Λ configuration. While again there may be crossovers in various energy levels, Λ and Δ levels on the same line (*e.g.*, Δ-λλλ and Λ-δδδ) are equal in energy.

In the first equilibration–separation experiment, a 1:3 mole ratio of Co(III) and (*R*)-propylenediamine was equilibrated over a charcoal catalyst, and the Δ and Λ complexes (Ib and Ia, respectively) were separated and determined. Because (*R*)-pn forms vir-

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[32] H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," 2nd ed, Van Nostrand, Princeton, N. J., 1956, p 492.

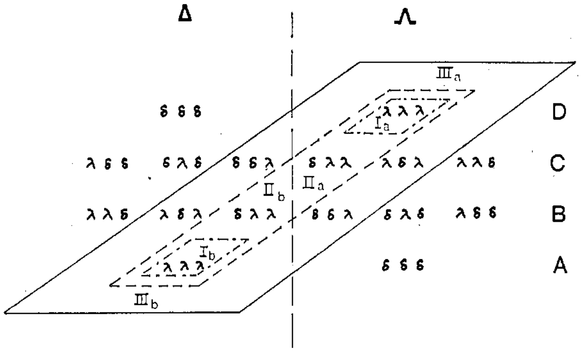

Figure 10.—Conformational isomers of $Co(en)_3^{3+}$ and mixed ethylenediamine–(*R*)-propylenediamine complexes of cobalt(III).

tually completely the λ conformation, the observed 14.6:1 ratio was translated into a value of $\Delta G = 1.6$ kcal/mol for conversion of the Δ-λλλ species into the Λ-λλλ species. In the second experiment, a mixture of Co(III), ethylenediamine, and (*R*)-propylenediamine was equilibrated over charcoal, and the $\Delta\text{-(en)(pn)}_2$ and $\Lambda\text{-(en)(pn)}_2$ complexes were separated and determined (ratio 7.5:1). The ethylenediamine ring is not restricted to the λ conformation but can adopt the conformation or mixture of conformations of greatest stability. Assuming the ethylenediamine ring to adopt the λ conformation in the Δ complex and the δ conformation in the Λ complex, the authors treated the resulting ΔG value (1.2 kcal/mol) as if it pertained to the conversion of the Δ-λλλ species into the Λ-δλλ species. In the third experiment, a mixture of Co(III), ethylenediamine, and (*R*)-propylenediamine was equilibrated over charcoal, and the $\Delta\text{-(en)}_2\text{(pn)}$ and $\Lambda\text{-(en)}_2\text{(pn)}$ complexes were separated and determined (ratio 2.1:1). The same assumptions were made in regard to the ethylenediamine ring conformations, and the ΔG value of 0.45 kcal/mol was treated as if it pertained to the conversion of the Δ-λλλ species into the Λ-δδλ species.

MacDermott[4a] subsequently corrected several assignments in the paper chromatographic bands, which changes the original results slightly. Hawkins[20b] recently pointed out the need to correct for the presence of equilibrium amounts of higher energy ethylenediamine ring conformers in the mixed en–pn complexes. For example, in the $\Delta\text{-(en)(pn)}_2$ complex, both Δ-λλλ and Δ-δλλ species are present in appreciable amounts, and the observed equilibrium constant actually includes all species enclosed in IIa and IIb in Figure 10. One reason this may not have been considered earlier is that when ΔH values between adjacent levels are equal, as was believed, this correction goes to zero. In his recalculation of the $\Delta\text{-(en)}_2\text{(pn)}$ experiment, Hawkins failed to include one of the species Δ-δλλ or Δ-λδλ enclosed in IIIb and the analogous species in IIIa, and he did not make full use of the available data.

Table III gives the corrected relative intensities and assignments of the paper chromatography bands in ref 2–4. In cases where multiple data points were reported, standard deviations have been estimated. Table III includes data from experiments where 2:1 ratios of en:pn were employed, as well as those employing 1:2 ratios of en:pn.

What is desired in these experiments is to find the concentration ratios of species at the A and D levels, the A and C levels, and the A and B levels. These ratios are microscopic equilibrium constants (designated K') between particular species and can be expressed as

TABLE III

EQUILIBRIUM CONCENTRATIONS OF Co(III) COMPLEXES OF ETHYLENEDIAMINE AND (*R*)-PROPYLENEDIAMINE

Fraction[a]	en:pn = 1:2		en:pn = 2:1		Av
a	4.2 ± 0.2		33.0		
b	7.1 ± 0.8		13.0		
c	5.7 ± 0.4		2.5		
d	2.0 ± 0.1		0.5		
e	14.7 ± 0.5	2.1	27.6 ± 0.1	0.33	
e†		12.6		27.3	
f	35.7 ± 1.5	~24	18.7 ± 0.1	~12	
g		~12		~6	
h, i	30.6 ± 0.7		4.9 ± 0.2		
X	30.6/2.1 = 14.6		4.9/0.33 = 14.6		14.6
Y	35.7/7.7 = 4.6 ± 0.4		18.7/3.0 = 6.2		5.4 ± 1.1
Z	12.6/7.1 = 1.8 ± 0.2		27.3/13.0 = 2.1		1.9 ± 0.2

[a] Fractions labeled using same letters as in ref 4: (a) Δ- and $\Lambda\text{-Co(en)}_3^{3+}$, (b) $\Lambda\text{-Co(en)}_2((R)\text{-pn})^{3+}$, (c) *trans*-$\Lambda\text{-Co(en)}((R)\text{-pn})^*((R)\text{-pn})^{3+}$ and *trans*-$\Lambda\text{-Co(en)}((R)\text{-pn})((R)\text{-pn})^{*3+}$, (d) *cis*-$\Lambda\text{-Co(en)}((R)\text{-pn})_2^{3+}$, (e) *cis*- and *trans*-$\Lambda\text{-Co}((R)\text{-pn})_3^{3+}$, (e†) $\Delta\text{-Co(en)}_2((R)\text{-pn})^{3+}$, (f) *trans*-$\Delta\text{-Co(en)}((R)\text{-pn})_2^{3+}$, (g) *cis*-$\Delta\text{-Co(en)}((R)\text{-pn})_2^{3+}$, (h) *cis*-$\Delta\text{-Co}((R)\text{-pn})_3^{3+}$, and (i) *trans*-$\Delta\text{-Co}((R)\text{-pn})_3^{3+}$.

$$K'_{DA} = [\Lambda\text{-}\lambda\lambda\lambda]/[\Delta\text{-}\lambda\lambda\lambda] = [\Delta\text{-}\delta\delta\delta]/[\Delta\text{-}\lambda\lambda\lambda] \quad (27)$$

$$K'_{CA} = [\Lambda\text{-}\delta\lambda\lambda]/[\Delta\text{-}\lambda\lambda\lambda] = [\Delta\text{-}\lambda\delta\delta]/[\Delta\text{-}\lambda\lambda\lambda] \quad (28)$$

$$K'_{BA} = [\Lambda\text{-}\delta\delta\lambda]/[\Delta\text{-}\lambda\lambda\lambda] = [\Delta\text{-}\lambda\lambda\delta]/[\Delta\text{-}\lambda\lambda\lambda] \quad (29)$$

The experimentally determined concentration ratios in the three experiments described above are called *X*, *Y*, and *Z* and are defined as

$$X = \frac{[\text{Ib}]}{[\text{Ia}]} = \frac{[\Delta\text{-Co}((R)\text{-pn})_3{}^{3+}]}{[\Lambda\text{-Co}((R)\text{-pn})_3{}^{3+}]} = \frac{[\Delta\text{-}\lambda\lambda\lambda]}{[\Lambda\text{-}\lambda\lambda\lambda]} = \frac{1}{K'_{DA}} \quad (30)$$

$$Y = \frac{[\text{IIb}]}{[\text{IIa}]} = \frac{[\Delta\text{-Co(en)}((R)\text{-pn})_2{}^{3+}]}{[\Lambda\text{-Co(en)}((R)\text{-pn})_2{}^{3+}]} = \frac{[\Delta\text{-}\lambda\lambda\lambda] + [\Delta\text{-}\delta\lambda\lambda]}{[\Lambda\text{-}\lambda\lambda\lambda] + [\Lambda\text{-}\delta\lambda\lambda]} = \frac{1 + K'_{BA}}{K'_{DA} + K'_{CA}} \quad (31)$$

$$Z = \frac{[\text{IIIb}]}{[\text{IIIa}]} = \frac{[\Delta\text{-Co(en)}_2((R)\text{-pn})^{3+}]}{[\Lambda\text{-Co(en)}_2((R)\text{-pn})^{3+}]} = \frac{[\Delta\text{-}\lambda\lambda\lambda] + 2[\Delta\text{-}\delta\lambda\lambda] + [\Delta\text{-}\delta\delta\lambda]}{[\Lambda\text{-}\lambda\lambda\lambda] + 2[\Lambda\text{-}\delta\lambda\lambda] + [\Lambda\text{-}\delta\delta\lambda]} = \frac{1 + 2K'_{BA} + K'_{CA}}{K'_{DA} + 2K'_{CA} + K'_{BA}} \quad (32)$$

Table III gives the values of *X*, *Y*, and *Z* obtained for the 1:2 and 2:1 ratios of en:pn and the average values of *X*, *Y*, and *Z*. The values of the microscopic equilibrium constants are determined from *X*, *Y*, and *Z* as

$$K'_{BA} = \frac{[(1 - Z)/X] - 1 + [(2Z - 1)/Y]}{2 - Z - [(2Z - 1)/Y]} = 1.29 \pm 0.80 \quad (33)$$

$$K'_{CA} = [(K'_{BA} + 1)/Y] - 1/X = 0.35 \pm 0.17 \quad (34)$$

$$K'_{DA} = 1/X = 6.9 \times 10^{-2} \quad (35)$$

Even after all errors in concentration of various species in the mixed en–pn experiment have been removed, the most serious error remains, which has not been pointed out previously. This is the error of direct application of ΔG values obtained from mixed en–pn systems to the $Co(en)_3^{3+}$ system. In mixed en–pn systems, all equilibria involve discrete species of corresponding symmetry numbers.

When applying the en–pn ΔG values to the $Co(en)_3^{3+}$ system, where different symmetry numbers ($\sigma = 2$ or 6)

TABLE IV

FREE ENERGIES AND CONFORMER POPULATIONS OF TRIS-ETHYLENEDIAMINE AND RELATED COMPLEXES AT 25°

Method	Ref	ΔG_{BA}, kcal/mol	ΔG_{CA}, kcal/mol	ΔG_{DA}, kcal/mol	% A	% B	% C	% D
Co(en)–Co(pn), equilibration–separation	3, 4a, 22	-0.8 ± 0.4	0.0 ± 0.4	1.60	17	65	17	1
$Co((S)\text{-pn})_x((R)\text{-pn})_y{}^{3+}$, equilibration–separation	2b	0.0	0.52	1.62	40	40	17	3
$M(en)_3$, M–N = 2.0 Å, calcd	21	0.15	0.75	1.5	47	36	13	4
$M(en)_3$, M–N = 2.3 Å, calcd	21	−0.55	−0.45	0.2	16	40	33	11
$Rh(en)^{3+}$, 0.15 *M*, nmr	This work	-1.4 ± 0.5	>0.5[a]	>0.5[a]	8	92	0[a]	0[a]
$Rh(en)_3{}^{3+}$, 0.15 *M* in 0.3 *M* $PO_4{}^{3+}$, nmr	This work	-0.1 ± 0.1	>1.0[a]	>1.0[a]	45	55	0[a]	0[a]

[a] Assumed.

apply to different species, the en–pn ΔG values may be set equal to the ΔH values for $Co(en)_3{}^{3+}$ and appropriate ΔS terms may be added. In one of the few prior works[5] recognizing the importance of the symmetry contributions to ΔS, the ΔS terms were needlessly subtracted from the en–pn ΔG values in order to find ΔH values for $Co(en)_3{}^{3+}$. Taking account of the entropy terms, from the original data in Table III we calculate the free energy values shown in Table IV.

In a study of mixed ((*R*)-pn)- and ((*S*)-pn)Co^{III} complexes Dwyer, *et al.*,[26] prepared equilibrium mixtures which included all conformers shown in Figure 10. Analysis of the various chromatographic fractions yielded the results listed in Table IV. Note that the free energy values in the mixed (*R*)-pn and (*S*)-pn system were directly applicable to $Co(en)_3{}^{3+}$ by virtue of the correspondence in symmetry numbers.

These free energy values[2] are applicable to $Co(en)_3{}^{3+}$ only insofar as one is willing to accept propylenediamine as a suitable model for ethylenediamine.

Note that the chromatographic data in Table III contain appreciable random error. There are also several sources of possible systematic error. One which deserves special examination is the basic assumption of the entire experiment—namely, that any ethylenediamine ring of the λ conformer can be substituted by an (*R*)-propylenediamine ring with negligible energy transfer. One way of assessing the merit of this assumption is by studying the distribution of geometrical isomers of $Co(pn)_3{}^{3+}$ and $Co(en)(pn)_2{}^{3+}$, *i.e.*, isomers formed by breaking metal–nitrogen bonds of propylenediamine rings and switching the rings end-for-end. The presence of geometrical isomers was largely ignored in the original papers,[2,3] although MacDermott later showed[4a] that *cis*- and *trans*-$Co(en)(pn)_2{}^{3+}$ were actually separated in the paper chromatography work. If propylenediamine is indeed an adequate model of ethylenediamine, there should be no energy differences between cis and trans isomers, and these isomers should always appear in correct statistical ratios in any equilibrium mixture. *cis*- and *trans*-$Co(pn)_3{}^{3+}$ have allegedly been separated[4b] in the correct statistical ratio of 1:3. The statistical ratio of *cis*- and *trans*-$Co(en)(pn)_2{}^{3+}$ is 1:1. However, the ratios of d:c and g:f in Table III show cis:trans ratios for $Co(en)(pn)_2{}^{3+}$ ranging from 1:2 to 1:5, casting doubt upon propylenediamine as an adequate ethylenediamine model.

The results of Hawkins' calculations[21] are also included in Table IV. We make no implication that the results for $Rh(en)_3{}^{3+}$ and $Co(en)_3{}^{3+}$ should agree. In fact, preliminary results[22] on $Co(en)_3{}^{3+}$ contain significant differences from the $Rh(en)_3{}^{3+}$ results. The important point, however, is that all results for tris-ethylenediamine complexes agree that species B is comparable to or below species A in free energy. The precision with which the conformational energies of $Rh(en)_3{}^{3+}$ can be calculated from nmr data is limited by the spectral line widths and might be greatly improved through spin-decoupling and other resolution-enhancement techniques.

It seems clear that nmr data alone cannot provide complete conformational analysis of tris-ethylenediamine complexes at the present time. However, these nmr data provide valuable new evidence that can be used in conjunction with other techniques.

Acknowledgments.—This research was supported in part by USPHS Grant No. RO1 ES00477-04. The Varian HR-220 nmr spectrometer facility at the California Institute of Technology was provided by an NSF regional instrument grant (No. GP-8540). We are grateful to the Campus Computing Network of the University of California at Los Angeles for their generous support of the computational work and to Mr. Terryl Farrell for programming advice. We also thank Professors J. K. Beattie and B. E. Douglas for sending preprints of ref 15 and 17. Professor R. M. Wing provided the drawings used in structures I and II.