Intrinsic Axial–Equatorial Chemical Shift Difference in the Conformational Analysis of Trisethylenediamine and Trispropylenediamine Complexes of Ruthenium(II), Cobalt(III), and Platinum(IV)

James K. Beattie* and Lucille H. Novak

Contribution from the Noyes Chemical Laboratory,
University of Illinois, Urbana, Illinois 61801. *Received June 25, 1970*

Abstract: The proton magnetic resonance spectra of the N-deuterated trispropylenediamine complexes of Ru(II), Co(III), and Pt(IV) have been analyzed. The coupling constants indicate that the ligands are predominantly in one conformation with the methyl group equatorial. The chemical shift differences between the axial and equatorial methylene protons are 0.87, 0.33, and 0.13 ppm, respectively. These intrinsic chemical shift differences are considerably reduced by conformational averaging in the corresponding trisethylenediamine complexes, and the large differences among the metal ions account for the variety of spectra observed for the $M(en)_3$ complexes. Evidence of scalar coupling between ^{59}Co and the equatorial proton in the propylenediamine complex is observed.

A model to account for the nmr spectra of a series of N-deuterated $M(en)_3$ complexes which have spin-paired d^6 electron configurations has recently been proposed.[1] Spectra are available for the Pt(IV),[2] Co(III),[3] Rh(III),[4] Ir(III),[4] and Ru(II)[2] complexes. The appearance of these vary enormously from a single narrow line for Pt(IV) (with satellites due to coupling with ^{195}Pt) to a well-resolved AA′BB′ spectrum of 24 lines for Ru(II). It was suggested that in all of the complexes there is rapid inversion between the two possible conformations, δ and λ, of each chelate ring.[5] In a fixed conformation of the chelate ring there is an axial and an equatorial proton on each carbon atom.[6] These are in different chemical environments and consequently have different chemical shifts. The two axial protons and the two equatorial protons are related by a C_2 symmetry operation and all four protons are strongly coupled, resulting in an AA′BB′ nmr spectrum. On inversion from the δ to λ conformation the axial and equatorial protons are interconverted. In an $MenX_4$ complex there is no energy difference between the two conformations and each proton will spend an equal time in the axial and equatorial positions. Consequently, the average chemical shift of all of the protons will be the same and the nmr spectrum will consist of a single line.

In the $M(en)_3$ complexes there are free energy differences between the various possible configurations of chelate conformers about the metal ion. For Co(III) these were estimated to be $\Lambda(\delta\delta\delta) < \Lambda(\delta\delta\lambda) < (\Lambda\delta\lambda\lambda) < \Lambda(\lambda\lambda\lambda)$ for the Λ configuration of the three chelate rings around the metal ion.[6] Further calculations,[1] consideration of statistical effects,[1] and experimental results[7] obtained from separation of isomers of propylenediaminecobalt complexes indicate that the relative free energies are probably in the order $\Lambda(\delta\delta\delta) \sim \Lambda(\delta\delta\lambda) < \Lambda(\delta\lambda\lambda) \ll \Lambda(\lambda\lambda\lambda)$. The energy and nmr spectra of the $\Delta(\lambda\lambda\lambda)$ are of course identical with those of the enantiomeric $\Lambda(\delta\delta\delta)$ configuration; in the subsequent discussion only the Λ configuration will be described, although it should be understood that racemic mixtures were used. As a consequence of the free energy differences between the various configurations a chemical shift difference is maintained between pseudoaxial and pseudoequatorial protons since on the average each ligand is more often in the δ than in the λ conformation.[8] The spectra of $M(en)_3$ complexes thus reflect an effective chemical shift difference which is the result of conformational averaging of the intrinsic chemical shift difference between an axial and an equatorial proton in a fixed conformation.

This intrinsic chemical shift difference cannot be obtained from the spectra of ethylenediamine complexes without an exact knowledge of the relative populations of the various configurations. An experimental estimate of this chemical shift difference can be obtained, however, by analysis of the spectra of propylenediamine complexes. The coordinated propylenediamine ligand is believed to exist primarily in a single conformation with the methyl group in the sterically favored equatorial position, fixing the methylene protons in axial and equatorial positions.[6] Evidence for this conformational preference for complexes in solution has been obtained from the analysis of the nmr spectra of $Pd(pn)_2{}^{2+}$, $Pt(pn)_2{}^{2+}$, and $Co(CN)_4pn^-$ in which the coupling constants are consistent with a ligand conformation with the methyl group predominantly equatorial.[9] We have now analyzed the spectra of $Ru(pn)_3{}^{2+}$, $Co(pn)_3{}^{3+}$, and $Pt(pn)_3{}^{4+}$ to determine the effect of changing the metal ion and its oxidation state on the intrinsic chemical shift

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[1] J. R. Gollogly, C. J. Hawkins, and J. K. Beattie, *Inorg. Chem.*, in press.

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

[3] S. T. Spees, L. J. Durham, and A. M. Sargeson, *Inorg. Chem.*, **5**, 2103 (1966); L. R. Froebe and B. E. Douglas, *ibid.*, **9**, 1513 (1970).

[4] T. G. Appleton, J. R. Hall, and C. J. Hawkins, *ibid.*, **9**, 1299 (1970).

[5] For a description of the recently proposed nomenclature for conformations and configurations, see *ibid.*, **9**, 1 (1970).

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

[7] F. P. Dwyer, A. M. Sargeson, and L. B. James, *ibid.*, **86**, 590 (1964).

[8] It has recently been pointed out[4] that in an $M(en)_3$ complex inversion of one chelate ring does not strictly interconvert the protons, since the axial position of the δ conformation is not equivalent to the axial position of the λ conformation, owing to the presence of the other chelate rings. There is presently no experimental evidence that this inherent nonequivalence contributes to the chemical shift difference, and we will assume that inversion does effectively interconvert the protons.

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

Table I[a]

	$Ru(pn)_3^{2+}$	$Co(pn)_3^{3+}$	$Pt(pn)_4^{4+}$ [b]	$Co(CN)_4pn^-$ [c,d]	$Pd(pn)_2^{2+}$ [c]	$Pt(pn)_2^{2+}$ [c]
ν_1	2.03	2.55	3.13		2.53	
ν_2	2.90	2.90	3.26		2.78	
ν_3	2.55	3.08	3.64		3.18	
ν_{CH_3}	1.29	1.40	1.60	1.25	1.22	
J_{12}	−12.2	−13.0	−12.5	−12.8	−12.5	−12.3
J_{13}	12.0	12.5	15.0	12.7	9.9	10.0
J_{23}	2.5	3.5	4.0	4.4	4.2	4.3
J_{34}	6.0	6.0	6.0	6.0		
δ_{12}	0.87	0.35	0.13	0.48	0.33	0.31
δ_{13}	0.52	0.53	0.51	0.63	0.62	0.61

[a] Chemical shifts reported in ppm downfield from DDS; coupling constants in Hz. [b] See text. [c] Reference 9; only relative chemical shifts were given. [d] Mixed pyridine–water solvent.

difference and to apply these data to the interpretation of the spectra of the $M(en)_3$ complexes.

Experimental Section

Preparation of Compounds. Tris(propylenediamine)cobalt(III) iodide was prepared from cobalt(II) sulfate and racemic propylenediamine and fractionally crystallized three times.[10] This method yields almost exclusively the $\Lambda(\delta\delta\delta)$ and $\Delta(\lambda\lambda\lambda)$ racemic mixture as was verified by column chromatography.[11] The iodide salt was converted to the more soluble chloride salt for the nmr experiments by stirring with freshly precipitated silver chloride, filtering to remove the silver halides, and evaporating to dryness.

Tris(propylenediamine)platinum(IV) chloride was prepared from racemic propylenediamine and alcoholic hydrogen hexachloroplatinate(IV).[12] A portion of the crude chloride salt was recrystallized from water. A second portion was partially fractionated to increase the proportion of the $\Lambda(\delta\delta\delta)$ and $\Delta(\lambda\lambda\lambda)$ isomers by formation of the oxalate salt following the procedure given by Dwyer and Garvan for purification of the L-*ddd* isomer prepared from pure *d*-propylenediamine.[13] This procedure effectively separates the L-*ddd* isomer, but it is uncertain whether any separation of isomers containing both *d*- and *l*-propenylenediamine is achieved. A perchlorate salt was obtained by metathesis with silver perchlorate.

Tris(propylenediamine)ruthenium(II) chloride was prepared from $[Ru(pn)_3]ZnCl_4$ obtained by the same procedure[2] as $[Ru(en)_3]ZnCl_4$. Dry amalgamated zinc, 1.70 g of $[Ru(pn)_3]ZnCl_4$, 1.40 g of the disodium salt of ethylenediaminetetraacetic acid, and 1.02 g of sodium acetate were deoxygenated in a flask with an Ar atmosphere. About 7 ml of hot deoxygenated water was added by syringe and the resulting solution was filtered in an Ar atmosphere while hot. The solution was cooled and 1–2 ml of concentrated deoxygenated sodium chloride solution was added. The resulting bright yellow precipitate was filtered in air and washed with absolute ethanol and ether. The product could be recrystallized in an Ar atmosphere by dissolving it in a minimum volume of hot deoxygenated 0.01 *M* trifluoroacetic acid and cooling. The yield was about 90 mg (7%).

Anal. Calcd for $C_9N_6H_{32}ORu$: C, 26.2; H, 7.8; N, 20.4; Cl, 17.2. Found: C, 26.0; H, 7.7; N, 20.5; Cl, 17.0.

Nmr Spectra. Solutions for the nmr spectra were prepared by dissolving $[Pt(pn)_3]Cl_4$ in D_2O and $[Co(pn)_3]Cl_3$ in D_2O to which a drop of NaOD had been added to ensure deuteration of the amine protons. Solutions of N-deuterated $[Ru(pn)_3]Cl_2$ were prepared in the same manner as described previously[2] for $Ru(en)_3^{2+}$. The spectra were measured using Varian A60-A, HA-100, and HR-220 spectrometers at the ambient probe temperatures (42, 28, and 23°, respectively), using the sodium salt of 3-(trimethylsilyl)propanesulfonic acid (DSS) as an internal reference.

The spectra were analyzed using the computer program NMRIT.[14] Owing to the large number of overlapping lines (at least 150) of the six-spin system, the iterative feature of the program was not used, but a trial and error technique was employed to find the appropriate coupling constants and chemical shifts. The lines shown in calculated spectra are sums of intensities of a number of closely spaced transitions in a narrow frequency range. Some of the coupling constants are consequently accurate only to within ±1–2 Hz and the chemical shifts to within ±0.02–0.05 ppm.

Results

The nmr spectra of the methylene and methine proton region of N-deuterated $Ru(pn)_3^{2+}$, $Co(pn)_3^{3+}$, and $Pt(pn)_3^{4+}$ at 60, 100, and 220 MHz, together with the calculated spectra, are presented in Figures 1–3. The coupling constants and chemical shifts for these complexes and for others available in the literature are collected in Table I. Our numbering convention for the

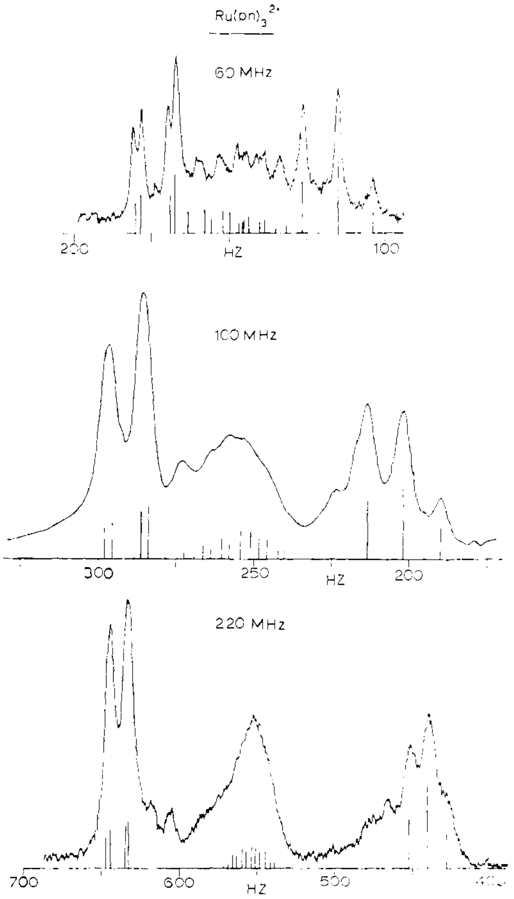

Figure 1. The 60-, 100-, and 220-MHz spectra of N-deuterated $Ru(pn)_3^{2+}$, together with calculated spectra.

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(10) F. P. Dwyer, F. L. Garvan, and A. Shulman, *J. Amer. Chem. Soc.*, **81**, 290 (1959).

(11) F. P. Dwyer, T. E. MacDermott, and A. M. Sargeson, *ibid.*, **85**, 2913 (1963).

(12) A. P. Smirnoff, *Helv. Chim. Acta*, **3**, 177 (1920).

(13) F. P. Dwyer and F. L. Garvan, *J. Amer. Chem. Soc.*, **81**, 1043 (1959).

(14) J. D. Swalen and C. A. Reilley, *J. Chem. Phys.*, **37**, 21 (1962); for a description of this program see D. F. DeTar, Ed., "Computer Programs for Chemistry," Vol. I, W. A. Benjamin, New York, N. Y., 1968, p 54.

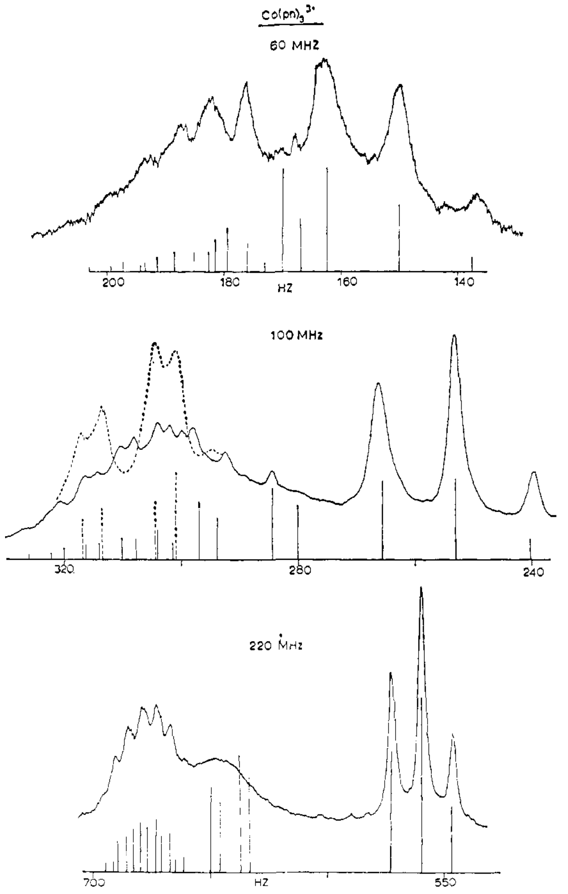

Figure 2. The 60-, 100-, and 220-MHz spectra of the Λ(δδδ) and Δ(λλλ) isomers of N-deuterated Co(pn)$_3$$^{3+}$. The 100-MHz spectrum with the methyl group decoupled is shown as a dotted line.

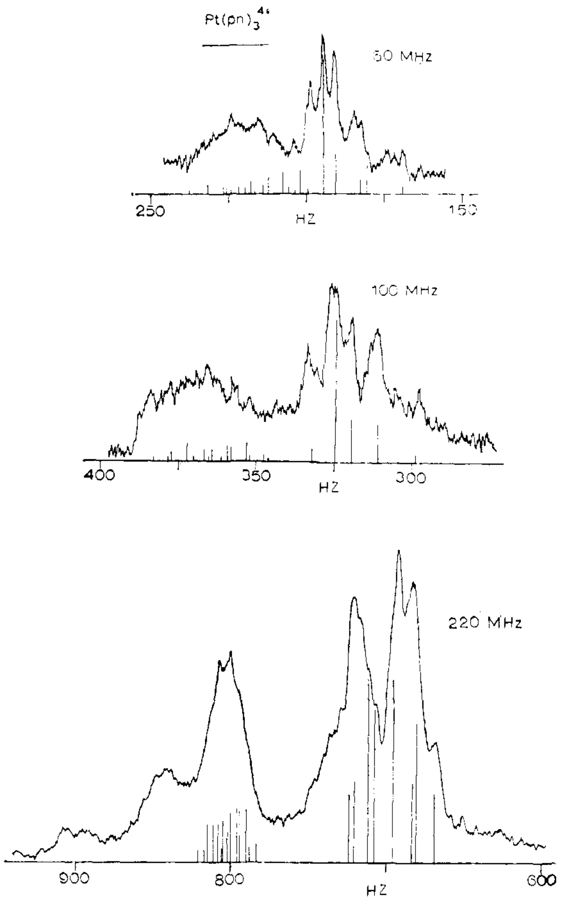

Figure 3. The 60-, 100-, and 220-MHz spectra of N-deuterated Pt(pn)$_3$$^{4+}$, together with calculated spectra.

propylenediamine ligand is given in Figure 4a, where H^1 and H^2 denote the axial and equatorial protons of the methylene group, respectively, H^3 the methine proton, and H^4, H^5, and H^6 the three equivalent methyl protons.

The λ conformation of *R*-(−)-pn is illustrated in Figure 4a; the corresponding δ conformation of *S*-(+)-pn is shown in Figure 4b. In both of these conformations the methyl group is in the sterically favored equatorial position which is thought to be the predominant conformation for coordinated propylenediamine. This conformation has been found in the crystal structures examined,[15] and analysis of nmr coupling constants indicates that it is maintained in solution as well.[9] Our results support this conclusion. A second type of stereospecificity occurs in the trisdiamine complexes in addition to the strong preference of the methyl group for the equatorial position. Nonbonded interactions between the ligands favor the λ conformation for the Δ configuration of the three ligands about the metal ion, while in the Λ configuration the δ are favored.[6] If sufficiently large this effect would lead to exclusive formation of Δ-[M(*R*-pn)$_3$] and Λ-[M(*S*-pn)$_3$]. The free energy differences are not large enough, however, between these preferred configurations and less stable configurations such as Δ-[M(*R*-pn)$_2$(*S*-pn)], in which the conformation of the ligands is λλδ, and a mixture of configurations forms when racemic propylenediamine is used. Even if resolved propylenediamine is employed some of the less stable Λ-[M(*R*-pn)$_3$] configuration is found together with a preponderance of the favored Δ-[M(*R*-pn)$_3$] isomer.[10] These various isomers have been separated for the cobalt(III) complexes and we were able to use a racemic mixture of Δ-[Co(*R*-pn)$_3$$^{3+}$] and Λ-[Co(*S*-pn)$_3$$^{3+}$] for the Co(III) spectra.

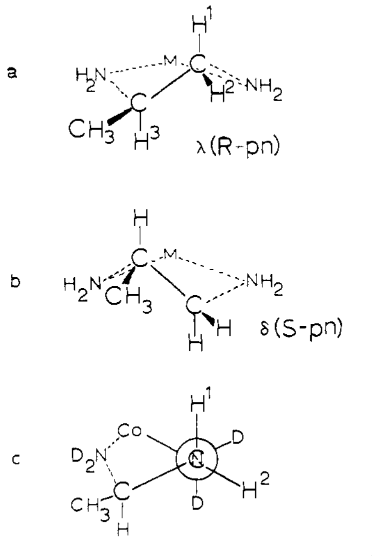

Figure 4. The conformations and proton numbering used for coordinated propylenediamine. The conformations with the methyl group equatorial are shown for absolute configuration *R* in a and *S* in b. The dihedral angles between the cobalt nucleus and the methylene protons are illustrated in c.

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(15) Y. Saito and H. Iwasaki, *Bull. Chem. Soc. Jap.*, **35**, 1131 (1962); H. Iwasaki and Y. Saito, *ibid.*, **39**, 92 (1966).

For the platinum(IV) complexes a separation between the Δ and Λ configurations has been reported for the products obtained using resolved propylenediamine but not for the mixed complexes obtained from racemic propylenediamine. We applied this procedure to the mixed complexes nonetheless and obtained some fractionation as indicated by the nmr spectra. The peaks in the regions around 3.3 and 3.9 ppm which are unaccounted for in Figure 3 are attributed to the remaining mixed isomers. These peaks are considerably more intense in the spectrum of the $[Pt(pn)_3]Cl_4$ product obtained from the reaction mixture and recrystallized once but not fractionated as the oxalate salt. In addition the spectra of the platinum(IV) complex were influenced by ion-pairing effects, as evidenced by differences in the chemical shifts observed between solutions of $[Pt(pn)_3]Cl_4$ and $[Pt(pn)_3](ClO_4)_4$ and by changes in the spectra of $[Pt(pn)_3]Cl_4$ on addition of DCl or NaCl. The spectra reported are those of a nearly saturated solution of $[Pt(pn)_3]Cl_4$ in D_2O at room temperature. A further complication in the analysis is the possibility of coupling between the protons and ^{195}Pt. Some evidence for coupling with ^{195}Pt was observed for the equatorial proton with an approximate coupling constant of 52 Hz. In view of these difficulties we believe that the assignment for the Pt complex is incomplete. It is adequate for the present purposes, however, since the chemical shifts of the ligand protons have been determined with reasonable certainty.

The $[Ru(pn)_3]Cl_2$ product was not fractionated at all. The unassigned peaks in Figure 1 at 2.17 and 2.23 ppm are attributed to mixed isomers. Their low intensity suggests that formation of $Ru(pn)_3^{2+}$ is rather stereospecific, although the procedure used to obtain the chloride salt from the product mixture may serve to fractionally crystallize one isomer.

The assignments of the protons require some further comments. The resonance of the axial proton H^1 invariably occurs at the highest field strength in the previously assigned spectra[9] and this is observed in each of the three complexes studied here. The methine proton H^3 usually occurs at the lowest field strength, as is observed in the Pt(IV) complex. This proton is coupled to the methyl group as well as to the methylene protons H^1 and H^2, resulting in a broad band of overlapping lines. Decoupling of the methyl group in a double-resonance experiment at 100 MHz confirmed this assignment for the $Pt(pn)_3^{4+}$ complex.

In the spectrum of $Co(pn)_3^{3+}$ both H^2 and H^3 are observed as broad bands as shown in the 220-MHz spectrum in Figure 2. This is in contrast to the appearance of the expected four-line multiplet for H^2 observed[9] in the spectrum of $Co(CN)_4pn^-$. The initial assignment of these protons was consequently uncertain. A decoupling experiment at 100 MHz led to the spectrum shown as a dotted line in Figure 2 indicating that proton H^3 occurs at the lowest field. With this tentative assignment reasonable coupling constants were obtained and found to reproduce the spectrum at 220 MHz quite well except for the unusual broadness of the H^2 proton resonance. Various attempts to account for this by calculations simulating the expected effects of ligand vibrations or inversion to the unstable conformation with the methyl group in an axial position did not lead to any preferential broadening of this resonance. A consistent explanation can be found, however, if there is additional scalar coupling with the cobalt nucleus (^{59}Co: $I = 7/2$). Proton H^2 is the proton expected to be most strongly coupled with the metal nucleus due to its trans position with respect to the metal–nitrogen bond when viewed along the N–C bond axis, as illustrated in Figure 4c. This dihedral angle dependence of the coupling constant, which is well established for scalar coupling between protons, has been observed for metal–ligand coupling[16] and for contact shifts in a number of metal complexes.[17] Further evidence for coupling with the metal nucleus in cobalt–amine complexes has been presented elsewhere.[18] With this assumption the proton assignments for $Co(pn)_3^{3+}$ lead to reasonable values of the coupling constants and are consistent with the spectra of other propylenediamine cobalt complexes. An uncertainty in the chemical shift of proton H^2 results from the broadness of the peak.

For the spectra of $Ru(pn)_3^{2+}$ a consistent assignment with reasonable coupling constant could be achieved only if the positions of protons H^2 and H^3 were reversed, *i.e.*, with H^2 occurring at lowest field. In this complex the methyl resonance occurs too close to the other protons for a successful decoupling experiment.

With these assignments reasonable values of the coupling constants and chemical shifts were obtained which reproduce most of the features of the spectra. There is experimental evidence that the peaks unaccounted for arise from the presence of other isomers in the preparations and that the differences in relative intensities observed in the cobalt spectrum are due to coupling with the metal nucleus. The spectra were slightly temperature dependent over a wide temperature range, but consistent values of the spectral parameters were obtained over the 19° temperature range of the ambient probe temperatures of the three spectrometers employed.

Discussion

The most striking result of this study is the strong influence of the metal ion on both the absolute and the relative chemical shifts of the ligand protons. The axial protons H^1 and H^3 occur at progressively higher fields in the series Pt(IV) < Co(III) < Ru(II) over a range of 1.1 ppm. The methyl resonance also shifts slightly to higher field by 0.3 ppm from Pt(IV) to Ru(II). The equatorial proton H^2 shifts by 0.4 ppm from Pt(IV) to Co(III) and occurs with essentially the same chemical shift in the Co(III) and Ru(II) complexes. A similar trend occurs in the positions of the methylene proton resonances in the trisethylenediamine complexes of these metals: Pt(IV), 3.26; Co(III), 2.83; and Ru(II), 2.55 ppm. This has been attributed[1] to the increased shielding from the metal ion d electrons which probably have a much greater radial extension in the lower oxidation state Ru(II) complex than in Pt(IV). The *differences* between the chemical shifts of the two *axial* protons (δ_{13} in Table I) which are similarly directed toward the metal-ion electron density are constant from Ru(II) to Pt(IV), while the *differences* between the chemical shifts of the *axial* and *equatorial* methylene protons (δ_{12}) decrease enormously from 0.87 ppm for Ru(II) to 0.35

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

(17) L. Pratt and B. B. Smith, *Trans. Faraday Soc.*, **65**, 915 (1969); F. F.-L. Ho and C. N. Reilley, *Anal. Chem.*, 41, 1835 (1969).

(18) J. K. Beattie, *Inorg. Chem.*, in press.

for Co(III) to 0.13 for Pt(IV). This suggests that the axial protons are shielded much more strongly by the metal ion than is the equatorial proton. The chemical shifts of the equatorial proton (ν_2) which is directed toward the solvent are identical in the Ru(II) and Co(III) complexes, whereas the axial proton is shifted considerably further upfield in the lower valent Ru(II) complex than in the Co(III) complex. In the Pt(IV) complex both axial and equatorial protons occur at lower fields but the difference between them is much less than in the Co(III) and Ru(II) complexes. We again attribute these trends to the greater radial extension of the metal ion d electrons in the lower oxidation states which results in preferential shielding of the axial protons relative to the equatorial proton.

The chemical shift difference between protons H^1 and H^2 may be considered the intrinsic chemical shift difference between an axial and an equatorial proton in a fixed conformation of the chelate ring if it is assumed that the propylenediamine ligand is always coordinated with the methyl group equatorial. Alternatively, if some small fraction of the ligands is in conformations with the methyl group axial the observed chemical shift difference δ_{12} is a lower limit to the intrinsic chemical shift difference. The observed coupling constants are consistent with the assumption that virtually all of the ligands have the methyl group equatorial. The large value of J_{13} of 12–15 Hz is indicative of trans-vicinal coupling with a dihedral angle close to 180° while the small value of J_{23} between the equatorial methylene proton and the axial methine proton indicates a gauche-vicinal coupling. We conclude that the ligands in the trispropylenediamine complexes exist primarily in one conformation, with the methyl group equatorial, and that the observed chemical shift difference δ_{12} can be taken as a good approximation to the intrinsic chemical shift difference between the axial and equatorial protons of the methylene group.

The application of these results to the interpretation of the spectra of the trisethylenediamine complexes requires an estimate of the intrinsic chemical shift difference between an axial and an equatorial proton in a fixed conformation of the ethylenediamine ligand. We suggest that the results obtained for the propylenediamine complexes are qualitatively correct for the ethylenediamine complexes as well. Replacement of the methyl group by a proton undoubtedly affects the chemical shifts of the adjacent methylene protons. The effect is probably similar for each of the three complexes, however, and owing to the staggered conformations of the ligands, the effect is likely to be comparable for both the axial and equatorial protons.[19] This assumes that the conformations of the ligands are similar in each of three propylenediamine complexes.

These estimates of the intrinsic chemical shift differences for the trisethylenediamine complexes substantiate our earlier interpretation[1] of the spectra of the trisethylenediamine complexes of these metal ions. The observation of a well-resolved AA'BB' spectrum for $Ru(en)_3^{2+}$ in contrast to a narrow line for $Pt(en)_3^{4+}$ is primarily the consequence of a much larger intrinsic chemical shift difference for Ru(II) than for Pt(IV). The effective chemical shift difference observed between the axial and equatorial protons of $Ru(en)_3^{2+}$ is 0.23 ppm, considerably smaller than the intrinsic chemical shift difference of 0.87 ppm observed in $Ru(pn)_3^{2+}$. This implies that the ethylenediamine ligands are not fixed in one conformation either by kinetic or thermodynamic factors but are in rapid equilibrium between δ and λ conformations with a substantial population of the less stable configurations. The observed effective chemical shift difference is only about one-fourth of the estimated intrinsic chemical shift difference. This requires that approximately three of every eight ligands are in the less stable λ conformation for the Λ configuration about the metal ion. This is consistent with recent calculations which indicate that the $\Lambda(\delta\delta\lambda)$ and $\Lambda(\delta\lambda\lambda)$ configurations may be of comparable or lower energies than the $\Lambda(\delta\delta\delta)$ configuration for complexes with larger metal–ligand distances such as $Ru(en)_3^{2+}$.

In the $Pt(en)_3^{4+}$ complex the intrinsic chemical shift difference is sufficiently small that conformation averaging leads to a very small effective chemical shift difference. An AA'BB' pattern is still expected, but the chemical shift difference between A and B is so small that they are nearly equivalent and a narrow resonance line results. On the basis of the intrinsic chemical shift difference a rather narrow line is predicted for $Co(en)_2^{3+}$ as well, but coupling with the cobalt nucleus leads to a broadened resonance, as described elsewhere.[18] A very rough estimate of a chemical shift difference of 0.08–0.15 ppm obtained from the 220-MHz spectrum of $Co(en)_3^{3+}$ indicates that the effective chemical shift difference is likewise reduced by conformational averaging to substantially less than the intrinsic chemical shift difference of 0.33 ppm.

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(19) We are indebted to a reviewer for this latter observation.