Conformational Analysis of Coordination Compounds. X. ^1H NMR Study of Paramagnetic Five-membered Diamine Chelate Rings

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Dedicated to Jannik Bjerrum on the occasion of his 70th birthday

Conformational populations of a number of mono and tris five-membered diamine chelates of nickel(II) have been determined from their proton magnetic resonance spectra by a chemical shift method. Intrinsic chemical shift differences between protons in axial and equatorial orientations were determined directly from the spectra of the nickel(II) complexes of 3,3-dimethyl-1,2-ethanediamine for the primary amine ligands and of N,N,N',N' -tetramethyl-1,2-propanediamine for the tertiary amine ligands. These ligands are stereospecific. The data for the secondary nitrogen ligands were determined by an indirect method based on N -methyl-1,2-ethanediamine. The influence of counter-ion and solvent on the conformational populations of $[\text{Ni}(\text{en})_3]^{2+}$ has also been studied. In addition activation parameters have been determined for the configurational inversion of $[\text{Ni}(\text{en})_3]^{2+}$ in dimethyl sulfoxide (DMSO) and 1.6 M aqueous NaCl and for the nitrogen inversion in mono complexes of secondary amine donors.

A technique based on proton-proton coupling constants has been utilized for the conformational analysis of diamagnetic diamine and aminoalcohol chelate rings.^{1,2} For paramagnetic complexes the proton resonances are usually too broad to observe any fine structure due to coupling. A chemical shift technique based on the chemical shift difference between axial and equatorial protons or other nuclei, which has been used extensively for organic systems,³ has been applied to tris(diamine) complexes of the diamagnetic metal ions, cobalt(III), rhodium(III), ruthenium(II), and platinum(IV).⁴ However, for diamagnetic systems, if the determina-

tion of the intrinsic chemical shift difference between the axial and equatorial protons in a frozen conformation requires the use of a model compound, such as an analogous compound with a substituent that stereospecifically imposes a particular conformation on the system, long-range anisotropic shielding within the model system can significantly affect the chemical shift difference and make it a crude approximation for the 'intrinsic' value. For paramagnetic systems, in which contact interactions yield large chemical shift differences between axial and equatorial protons, the long-range anisotropic diamagnetic shielding factors are too small to affect the application of model systems. Because of this, complexes of nickel(II) have proven to be ideal for the application of the chemical shift technique to the conformational analysis of chelate rings.^{5–10}

Milner and Pratt first reported the ^1H NMR spectra of the 1:1 nickel(II) 1,2-ethanediamine complex in aqueous solution in 1962.¹¹ A single CH resonance was observed. Zamaraev and co-workers varied the metal:ligand ratio and observed a single resonance for the 1:1 and 1:2 complexes and a two line spectrum for the 1:3 complex.¹² The observation of a single resonance for both the 1:1 and 1:2 complexes was attributed to fast conformational interconversion that averaged the CH resonances, whereas the interconversion was considered to be resisted in the 1:3 complex due to the close packing of the rings resulting in separate peaks for axial and equatorial protons.¹² Ho and Reilley later reinvestigated the 1:3 system and analysed the ^1H NMR spectrum in terms of incomplete averaging of the axial and equatorial protons due to

a difference in energy of the δ and λ conformations for a particular distribution of chelate rings.⁶ The conformational interconversion was considered to be fast on the NMR time scale, but the inversion of the tris(bidentate) complexes was slow on this time scale. Ho and Reilley applied the chemical shift method of conformational analysis to determine the energy difference between the δ and λ conformations.⁶ More recently, Cramer and Harris have reinvestigated $[\text{Ni}(\text{en})_3]^{2+}$ and also studied a limited solvent and anion dependence of the conformational interconversion equilibrium.^{9,10}

Reilley and his coworkers have extended their studies to tris(*meso*-2,3-butanediamine)nickel(II).⁷ As the methine proton resonances could not be observed, the calculations of the conformer populations were based on observed methyl frequencies. The analogous system with the racemic isomer of the diamine provided no stereochemical information as only one resonance was observed and this was assigned to overlapped methyl and methine peaks.⁷ An earlier report¹³ that the 1:3 nickel(II) complexes of *meso*- and *racemic*-2,3-butanediamine have identical optical and ¹H NMR spectra is incorrect.⁷

Ho and Reilley have also applied the chemical shift technique to a number of 1:1 nickel(II) diamine complexes, in particular the complexes formed by *meso*- and *racemic*-*N,N'*-dimethyl-1,2-ethanediamine.⁵ For this application, as for the above applications of this technique, it was necessary to know the chemical shift difference between an axial and an equatorial proton for the 'frozen' conformation. Five-membered diamine chelate rings invert rapidly on the NMR time scale even at low temperatures,^{14,15} and therefore, this intrinsic chemical shift difference cannot be determined directly. A number of indirect methods have been used previously, but as discussed later in this paper, they have weaknesses associated with them. New approaches to this problem are employed in the current study which reinvestigates 1:1 and 1:3 nickel(II) diamine complexes in a number of solvents, and examines the influence of concentration and counter-ions on the conformer populations.

EXPERIMENTAL

Reagents. Anhydrous nickel chloride was prepared by adding freshly distilled thionyl chloride to nickel chloride hexahydrate, stirring for 1 h and removing the excess thionyl chloride under vacuum.

The compound was stored over potassium hydroxide *in vacuo*. 1,2-Ethanediamine (en, Ajax) was dried and purified by distillation from sodium metal. 1,2-Propanediamine (pn, Ajax), *N*-methyl-(men), *N,N*-dimethyl- (*N,N*-dmen), *N,N'*-dimethyl- (*N,N'*-dmen), and *N,N,N',N'*-tetramethyl-1,2-ethanediamine (tmen) (Koch-Light), 3,3-dimethyl-1,2-butanediamine (dmbn),¹ and *N,N,N',N'*-tetramethyl-1,2-propanediamine (tmpn)¹⁶ were distilled from barium oxide. The solvents used in the study, DMSO-*d*₆, methanol-*d*₄, acetone-*d*₆, acetonitrile-*d*₃, formamide, dimethylformamide and tetrahydrofuran, were purified and dried as has been described previously.¹⁷ The salts employed, sodium chloride, sodium nitrate, sodium nitrite, sodium fluoride, sodium phosphate, sodium perchlorate, and potassium fluoride, were all AnalaR grade.

The 1:1 complexes were prepared in solution by dissolving anhydrous nickel chloride in slight excess over that required for a 1:1 ratio in the solvent required, adding the calculated weight of diamine, and making the solution up to a pre-determined volume.

$[\text{Ni}(\text{en})_3]^{2+}$ was made in solution with a nickel:ligand ratio of 1:3.5. For the anion dependence investigations the calculated weight of salt was added before the solution was made up to volume. For the solvent dependence studies, solubility problems required the preparation of tris complexes with different counter-ions. The chloride, nitrate, and acetate salts were prepared by the published method¹⁸ using the different nickel(II) salts. The tetraphenylborate salt was prepared by adding an excess of a filtered aqueous solution of sodium tetraphenylborate to an aqueous solution of $[\text{Ni}(\text{en})_3]\text{Cl}_2$. The solid, which precipitated, was filtered off, washed well with water, and dried under vacuum. $[\text{Ni}(\text{R-pn})_3](\text{MeCO}_2)_2$ and $[\text{Ni}(\text{dmbn})_3](\text{MeCO}_2)_2$ were prepared by an analogous method to the corresponding 1,2-ethanediamine complex.

Spectroscopic studies. All ¹H NMR spectra were recorded on a JEOL-PS-100 with a JEOL JES-VT-3 variable temperature controller. The temperatures were measured with a Chromel-Alumel thermocouple under full operating conditions before and after the recording of the spectra.

In the basic operating mode of Wide Sweep with a sweep width of 10.8 G, serious problems were encountered from the overlap of peaks emanating from the centre-band and the first lower side-band (8 kHz). This problem was overcome by employing Wide Offset, which allows a variable side-band of between 30 Hz and 30 kHz to be selected. In the Wide Sweep mode, both the superstabilizer and the lock cannot be used to minimize field drift. For each spectrum, therefore, four scans (two upfield and two downfield) were recorded to compensate for any small amount of drift. Also the conditions of

measurement, that is, high RF and AF levels, required the sample to be non-spinning and the pre-amplifier gain to be on low to maximize probe balance. The spectra were calibrated using the separation between the first and second lower sidebands which was equal to the preselected frequency of the variable oscillator. Sodium 3-trimethylsilylpropane-1-sulfonate was used as internal reference for the aqueous and DMSO solutions. The contact shifts were calculated from the peak for uncoordinated 1,2-ethanediamine.

RESULTS

Spectral analyses

Octahedral complexes of nickel(II) ($S=1$) possess an orbital singlet ground state (${}^3A_{2g}$ in O_h symmetry) and hence their isotropic shifts are essentially contact in origin¹⁹ and are described for protons by equation (1),*

$$\delta_i^{\text{iso}} = A_i \left(\frac{\gamma_e}{\gamma_H} \right) \frac{g\beta S(S+1)}{6SkT} \quad (1)$$

where the symbols have their usual meaning. The isotropic shift is proportional to T^{-1} (Curie behaviour) and a plot of δ_i^{iso} against T^{-1} should be a straight line with a slope proportional to A_i , the hyperfine coupling constant. Deviations from this linear relationship are indicative of the presence of equilibria between different structures or different spin states. If all equilibria are absent, a plot of $\delta_i^{\text{iso}} \times T$ against T should be independent of T . For a chelate ring undergoing rapid ring inversion, the

* Resonances which are less shielded than the diamagnetic reference are assigned here a positive isotropic shift according to the normal convention for chemical shifts.

observed isotropic shift for a particular nucleus will be a time-averaged shift over all species present in the conformational equilibrium and the plots of $\delta \times T$ against T generally will not be independent of T except where one conformation markedly predominates, or the equilibrium is between two conformations of equal energy.

Mono complexes

1,2-Ethanediamine. For the 1:1 complex in water a single peak was observed at δ 93.8 at 300 K. A plot of δ against T^{-1} was a straight line over the range 300–365 K and the plot of $\delta \times T$ against T (Fig. 1) was independent of temperature consistent with the rapid chelate ring inversion between the enantiomeric δ and λ conformations. In fact, if wet methanol was used below ambient, the δ against T plot was linear over the range 183–365 K. In methanol and DMSO, a single peak was again observed. The plots of δ against T^{-1} were linear over the temperature ranges 189.7–301.5 K (methanol) and 301.75–455.5 K (DMSO) but the $\delta \times T$ against T plots showed positive deviations from Curie behaviour as the temperature increased (Fig. 1).

3,3-Dimethyl-1,2-butanediamine. At 301.75 K three peaks were observed in water at δ 3.2 (9 H), 11.7 (2 H) and 170.8 (1 H). For $[\text{Ni}(R\text{-dmbn})_4]^{2+}$, where S is the solvent and the (R) configuration is assumed to simplify the discussion although the racemate was used, the λ conformation with the *tert*-butyl group equatorial should be stereospecifically favoured because of the severe non-bonded interactions between the axial *tert*-butyl group and an apical ligand in the alternative δ conformation. This stereospecificity was confirmed by the strict observance of Curie behaviour in the δ against T^{-1} and $\delta \times T$ against T plots (Fig. 2) for the

Fig. 1. $\delta \times T$ against T for $[\text{Ni}(\text{en})\text{S}_4]^{2+}$: $\circ$, $S = \text{MeOH}$; $\bullet$, $S = \text{H}_2\text{O}$; ∇ , $S = \text{Me}_2\text{SO}$.

Fig. 2. Plot of $\delta \times T$ against T for $[\text{Ni}(\text{dmbn})\text{S}_4]^{2+}$: $\circ$, $\text{S} = \text{MeOH}$; $\bullet$, $\text{S} = \text{H}_2\text{O}$; ∇ , $\text{S} = \text{Me}_2\text{SO}$ for 1. H_{eq} , 2. mean of H_{eq} and H_{ax} , 3. H_{ax} .

individual protons. The 1-proton peak has therefore been assigned to the equatorial methylene proton H_2 and the 2-proton peak to the two axial protons H_1 and H_3 (Fig. 3). This assignment is consistent with the Karplus-like relationship between the isotropic shift and the dihedral angle between the NiNC and NCH planes (Fig. 4).¹² The dihedral

Fig. 3. Conformational interconversion for a C-substituted five-membered diamine chelate ring.

Fig. 4. Dihedral angles for $\text{Ni}-\text{N}-\text{C}-\text{H}$.

angle for the equatorial proton approaches 180° whereas it is in the vicinity of 60° for the axial protons, and hence the equatorial proton should experience a larger isotropic shift.

Considering the mean of the $\delta \times T$ against T lines for the axial and equatorial peaks, a straight line independent of temperature was obtained for the aqueous solution but, for the methanol and DMSO solutions, the line showed a positive deviation with increasing temperature (Fig. 2) as was found for the 1,2-ethanediamine complex.

1,2-Propanediamine. At 329.2 K three peaks were observed in water, at δ 18.0, 21.0, and 148.3 with intensity ratios 3:2:1. For $[\text{Ni}(\text{R-pn})\text{S}_4]^{2+}$, the λ conformation with the methyl equatorial is preferred but not to the exclusion of the δ conformation with the methyl axial.^{20,21} Hence the time-averaged signals for each nucleus will reflect the frozen λ conformation more than the δ . The one-proton peak at δ 148.3 corresponds to the methylene proton that is equatorial in the λ conformation (H_2 in Fig. 3). The two-proton peak at δ 21.0 corresponds to the two protons that are axial in the λ conformation (H_1 and H_3). The remaining signal at δ 18.0 has been assigned to the methyl group.

In the plot of $\delta \times T$ against T (Fig. 5) the lines corresponding to the equatorial and axial protons showed deviations from normal Curie behaviour. For the 'equatorial' proton a negative deviation was noted: as the temperature increased, the chemical shift was less than that for normal Curie behaviour. This arose because, as the temperature increased, the less favoured conformer became more

Fig. 5. Plot of $\delta \times T$ against T for $[\text{Ni}(\text{pn})\text{S}_4]^{2+}$: $\circ$, $\text{S} = \text{MeOH}$; $\bullet$, $\text{S} = \text{H}_2\text{O}$; ∇ , $\text{S} = \text{Me}_2\text{SO}$ for 1. H_{eq} , 2. mean of H_{eq} and H_{ax} , 3. H_{ax} , 4. CH_3 .

populated and the 'equatorial' proton became more weighted towards the axial isotropic shift. The axial proton correspondingly showed a positive deviation.

The pattern of peaks found in methanol and DMSO was similar to that found in water, and hence the same assignments apply. In methanol, the methyl resonance was superimposed on the axial proton resonance at all temperatures, and hence the same chemical shift has been assumed for the protons under the peak. The mean of the $\delta \times T$ against T lines for the axial and equatorial protons again was found to be independent of temperature for the aqueous solution, but showed a positive deviation from Curie behaviour for the methanol and DMSO solutions (Fig. 5).

N-Methyl-1,2-ethanediamine. The spectrum of the complex in water had four peaks, which at 300 K were positioned at δ 59.2, 125.4, 133.9 and 140.6. The peak at δ 133.9 was the largest and has been assigned to the methyl protons. The remaining three had intensity ratios 2:1:1 for the above order.

When the coordinated nitrogen has the (S) configuration, the λ conformation has the methyl group equatorial, which is preferred to the alternative δ conformation with the methyl axial. As for the 1,2-propanediamine complex, the protons that are predominantly equatorial will resonate at lowest field because of their angular relationship with respect to the paramagnetic nickel. The resonances at δ 140.6 and 125.4 have therefore been assigned to the two protons that are equatorial in the λ conformation. They have different chemical

shifts because they experience different contact interactions as one is on a carbon adjacent to a secondary nitrogen and the other is on a carbon adjacent to a primary nitrogen. Ho and Reilley assigned the more downfield peak to the methylene proton adjacent to the primary nitrogen arguing that *N*-alkyl substitution would weaken the Ni–N bond and reduce the coupling with the adjacent methylene protons.⁵ From an extended Hückel molecular orbital calculation, Cramer came to the opposite conclusion that the protons adjacent to the substituted nitrogen would resonate at lowest field.²² This latter conclusion is supported by the observation that the average chemical shift of the methylene protons of the *N,N'*-dimethyl-1,2-ethanediamine complex is greater than that for the 1,2-ethanediamine complex implying that a greater degree of delocalization of unpaired electrons takes place through the secondary nitrogen donor. Therefore the latter assignment will be used in this paper. The remaining peak at δ 59.2 (2 H) has been assigned to the two protons that are axial in the λ conformation. It is interesting to note that the two axial protons showed no observable chemical shift difference arising from the different degrees of substitution at the two nitrogens.

For the aqueous solution, the plot of $\delta \times T$ against T was what was expected for a ring undergoing rapid exchange between conformers of differing populations: the 'equatorial' and 'axial' proton lines showed negative and positive deviations, respectively, while the lines for the methyl protons and the mean of the 'equatorial' and 'axial' protons showed

Fig. 6. Plot of $\delta \times T$ against T for $[\text{Ni}(\text{men})\text{S}_4]^{2+}$: $\bullet$, $\text{S} = \text{H}_2\text{O}$; ∇ , $\text{S} = \text{Me}_2\text{SO}$ for 1. $^s\text{NCH}_{\text{eq}}$; 2. NCH_3 ; 3. $^p\text{NCH}_{\text{eq}}$; 4. mean of $^s\text{NCH}_{\text{eq}}$ and $^s\text{NCH}_{\text{ax}}$; 5. mean of $^p\text{NCH}_{\text{eq}}$ and $^p\text{NCH}_{\text{ax}}$; 6. H_{ax} ; 7. NCH_3 ; 8. NCH_2 ; 9. $^p\text{NCH}_2$.

no dependence on T (Fig. 6).

In methanol solution, the pattern of peaks was as for water, and therefore the same assignments were made for the various peaks. However, no variable temperature data were obtained because as the temperature was decreased, the peaks broadened to such an extent that the chemical shifts measured were extremely inaccurate.

In DMSO, the pattern was different to that found for water. At 301.5 K the methyl group was at δ 129.3, approximately the same position as in water, but both equatorial protons were further downfield than in water with the proton adjacent to the primary nitrogen resonating downfield of the methyl group. The plot of $\delta \times T$ against T for the region 300–340 K showed the characteristic deviations for the equatorial and axial protons, but the mean of the axial and equatorial lines did not show any temperature dependence. Above 340 K the axial and equatorial $\delta \times T$ against T lines converged at a greater rate than expected from the conformational equilibrium until at 380 K the protons had been completely averaged. Above this temperature, averaged peaks were observed in the spectrum for the two sets of protons. These peaks and the methyl peak all showed positive deviations from Curie behaviour. The averaging of the peaks is due to the inversion of the coordinated secondary nitrogen and an approximate value for the rate of inversion was calculated to be $6.4 \times 10^3 \text{ s}^{-1}$ from the expres-

$$k = \frac{\pi \Delta v_{\text{ax,eq}}}{\sqrt{2}} \quad (2)$$

where $\Delta v_{\text{ax,eq}}$, the separation of the axial and equatorial resonances without inversion, was estimated to be 2870 Hz at 380 K by extrapolating the $\delta \times T$ against T curves from where no inversion effects were observed.

N,N-Dimethyl-1,2-ethanediamine. As the ligand does not have an asymmetric centre, the δ and λ conformations will be of equal energy. In water, the spectrum consisted of two peaks at δ 99.9 and 65.2 with an intensity ratio of 8:2. Obviously the peaks due to methyl protons and one set of methylene protons overlap under the δ 99.9 peak. As the methylene protons in the 1,2-ethanediamine complex resonated at δ 94.0, the methylene protons adjacent to the primary nitrogen have been assigned to the resonance at δ 99.9 and the methylene protons adjacent to the tertiary nitrogen to the resonance at δ 65.2. The $\delta \times T$ against T plots showed a slight dependence on temperature (Fig. 7).

For the three solvents, water, methanol, and DMSO, there were changes in the relative positions of the resonances for the three types of nuclei. The resonance for the methylene protons adjacent to the primary nitrogen, which was under the methyl peak in water, moved downfield for methanol and DMSO, whereas the resonances for the methyl and the other methylene protons moved upfield. For methanol and DMSO, the $\delta \times T$ against T plots

Fig. 7. Plot of $\delta \times T$ against T for $[\text{Ni}(\text{N},\text{N}'\text{-dmen})\text{S}_4]^{2+}$: $\circ$, $\text{S} = \text{MeOH}$; $\bullet$, $\text{S} = \text{H}_2\text{O}$; ∇ , $\text{S} = \text{Me}_2\text{SO}$ for 1. $^p\text{NCH}_2$, 2. NCH_3 , 3. $^i\text{NCH}_2$.

Fig. 8. Chelate rings for N,N' -dimethyl-1,2-ethanediamine.

were all straight lines, but as observed for the other complexes showed a dependence on T .

N,N'-Dimethyl-1,2-ethanediamine. In $[\text{Ni}(\text{N},\text{N}'\text{-dmen})\text{S}_4]^{2+}$ the two nitrogens are asymmetric and give rise to a racemic and a *meso* form as shown in Fig. 8. In the racemic form, the two methyl groups are either both axial or both equatorial, whereas in the *meso* form both conformations have one equatorial and one axial methyl group.

In water, five peaks were observed at 301.5 K at δ 40.0, 86.7, 129.1, 133.8 and 156.3 with the broad peak with δ 86.7 consisting of two poorly resolved peaks. The same assignments were deduced here as

Fig. 9. Plot of $\delta \times T$ against T for $[\text{Ni}(\text{N},\text{N}'\text{-dmen})\text{S}_4]^{2+}$: $\circ$, $\text{S} = \text{MeOH}$; $\bullet$, $\text{S} = \text{H}_2\text{O}$; ∇ , $\text{S} = \text{Me}_2\text{SO}$ for 1. $\text{H}_{\text{eq}}, \text{rac}$; 2. NCH_3, rac ; 3. $\text{NCH}_3, \text{meso}$; 4. mean of H_{eq} and $\text{H}_{\text{ax}}, \text{rac}$; 5. $\text{H}_{\text{ax,eq}}, \text{meso}$; 6. $\text{H}_{\text{eq}}, \text{rac}$; 7. NCH_3 ; 8. CH_2 .

has been published by Ho and Reilly.⁵ The peaks at 129.1 and δ 133.8 arise from the methyl protons of the *meso* and racemic forms. The peaks at δ 40.0 and 156.3 were assigned to the 'axial' and 'equatorial' methylene protons, respectively, in the racemic form. The $\delta \times T$ against T plots for these two resonances showed positive and negative deviations from Curie behaviour, whereas their mean was independent of temperature (Fig. 9). For the *meso* isomer, both conformations are of equal energy and the broad peak corresponding to the four methylene protons had a $\delta \times T$ against T line independent of T . At 301.5 K the ratio of the total areas of the methylene peaks for the racemic and *meso* isomers was 1.3.

The data for methanol were similar to that in water. The $\delta \times T$ against T plots are given in Fig. 9. The racemic:*meso* ratio was calculated to be 2.2 at 300 K. The data for DMSO were also similar until 360 K. Above 360 K all the methyl protons and all the methylene protons were averaged, again due to inversion of the coordinated nitrogen. The two averaged lines had $\delta \times T$ against T plots with a positive deviation from Curie behaviour. At 301.5 K the racemic:*meso* ratio was calculated to be 1.7. The rate of inversion of the asymmetric nitrogens was calculated at the coalescence temperature of 370 K to be $9.0 \times 10^3 \text{ s}^{-1}$ based on an estimated $\Delta\nu_{\text{ax,eq}}$ value of 4054 Hz.

N,N,N',N'-Tetramethyl-1,2-ethanediamine. As the coordinated ligand has no asymmetric centres, the δ and λ conformations are of equal energy, and one peak would be expected for the four methyl groups and one for the four methylene protons. In all three solvents these two resonances were observed with the methyl protons to lower field of the methylene protons. The resonances in water are to lower field

of the corresponding resonances in methanol and these in turn are to lower field of the resonances in DMSO.

In water, as the temperature was increased above ambient, a precipitate formed, and therefore, only the probe temperature spectrum was recorded. This did not happen in methanol and DMSO. The $\delta \times T$ against T plots for the methanol solution showed positive deviations from Curie behaviour (Fig. 10). For the DMSO solution, the methylene protons showed a positive deviation but the methyl protons showed a curved line.

N,N,N',N'-Tetramethyl-1,2-propanediamine. The complex with this ligand was not sufficiently soluble in water to give a spectrum from which accurate chemical shifts could be obtained. The methanol and DMSO solutions were measured at 300 K. In methanol, the equatorial methylene proton resonated at δ 126.5, the NCH_3 groups at δ 106.7 and 91.2, and the CCH_3 at δ 7.4. The peak for the two axial protons was under the CCH_3 peak. In DMSO the observed chemical shifts were δ 127.7, 100.8, 88.0, and 5.5.

Tris complexes

As has been found previously,^{6,9,10,12} the ^1H NMR spectrum of $[\text{Ni}(\text{en})_3]^{2+}$ had two CH resonances. These result from the fact that for one distribution of the chelate rings, say Δ , the δ and λ conformations are not equally populated, and therefore the CH resonances are not averaged to one line. Implicit in this is that the $\Delta \rightarrow \Lambda$ inversion is slow on the NMR time scale. In line with the previous work, the downfield peak has been assigned to the protons that are largely equatorial and the upfield resonance to the 'axial' protons.

Fig. 10. Plot of $\delta \times T$ against T for $[\text{Ni}(\text{tmen})\text{S}_4]^{2+}$: $\circ$, $\text{S} = \text{MeOH}$; ∇ , $\text{S} = \text{Me}_2\text{SO}$ for 1. NCH_3 , 2. $^1\text{NCH}_2$.

Fig. 11. Plot of $\delta \times T$ against T for aqueous solutions of A. $[\text{Ni}(\text{en})_3]\text{Cl}_2$; B. $[\text{Ni}(\text{en})_3]\text{Cl}_2 + 1.6 \text{ M NaCl}$ for 1. H_{eq} , 2. mean of H_{eq} and H_{ax} , 3. H_{ax} .

The plots of $\delta \times T$ against T for these two peaks for $[\text{Ni}(\text{en})_3]\text{Cl}_2$ in water exhibited deviations from Curie behaviour with the 'equatorial' peak showing a negative deviation and the 'axial' a positive deviation (Fig. 11). The expected horizontal straight-line was observed for the mean of the two lines. As for the mono complexes, the deviations indicate a shift in the equilibrium between the λ and δ con-

formations. At temperatures above 340 K, the lines deviated at an increased rate and finally coalesced at approximately 373 K. This is due to the rapid configurational inversion of the complex.⁶

The variable temperature ^1H NMR spectra of $[\text{Ni}(\text{en})_3]\text{Cl}_2$ (0.4 M) in the presence of added sodium chloride (1.6 M) showed similar gross features to the above spectra but the chemical shift differences between the exchanging axial and equatorial protons, $\Delta\delta^{\text{obs}}$, were significantly larger (Fig. 11). The variable temperature spectra of $[\text{Ni}(\text{en})_3](\text{MeCO}_2)_2$ in methanol were attempted but, as the temperature was lowered, the peaks broadened to such an extent that all accuracy in chemical shift position was lost.

The effects of counter-ion and solvent were examined at 301.5 K and the results are presented in Table 1. The effects of added salts were also

Table 1. Isotropic shifts and n_λ values for 0.4 M $\Delta\text{-}[\text{Ni}(\text{en})_3]\text{X}_2$ at 301.5 K.^a

Solvent	δ_{ax}	δ_{eq}	$\Delta\delta^{\text{obs}}$	n_λ
X = Cl				
H ₂ O	67.8	107.2	39.4	0.62
HCONH ₂	57.5	118.8	61.3	0.69
X = NO ₃				
H ₂ O	71.4	103.4	32.0	0.60
HCONH ₂	61.9	112.8	50.9	0.66
Me ₂ SO	47.4	129.5	82.1	0.76
X = MeCO ₂				
H ₂ O	71.0	105.8	34.8	0.61
HCONH ₂	56.4	117.9	61.5	0.69
MeOH	49.2	129.4	80.2	0.75
X = BPh ₄ ^b				
MeCN			70.2	0.60
Me ₂ CO			50.1	0.66
THF ^c			50.8	0.66
HCONMe ₂			31.5	0.72
Me ₂ SO			87.8	0.78

^a Solutions prepared from isolated complex salt. ^b en resonances obscured by BPh₄ resonances and therefore only $\Delta\delta^{\text{obs}}$ could be determined accurately. ^c Tetrahydrofuran.

Table 2. Isotropic shifts and n_λ values for 0.4 M $\Delta\text{-}[\text{Ni}(\text{en})_3]\text{X}_2$ in presence of NaCl at 301.5 K.

[NaCl] (M)	δ_{ax}	δ_{eq}	$\Delta\delta^{\text{obs}}$	n_λ
X = Cl				
0.0	69.1	105.5	36.4	0.61
0.2	67.9	106.8	38.9	0.62
0.4	66.9	107.5	40.6	0.63
0.8	66.8	109.6	43.8	0.64
1.2	65.8	110.9	45.1	0.64
1.6	63.9	112.1	48.2	0.65
X = NO ₃				
0.0	71.3	103.2	31.9	0.60
0.4	69.7	105.6	36.0	0.61
1.6	67.5	108.6	41.1	0.63
2.0	64.9	110.9	46.0	0.64

investigated. Sodium chloride was found to have a significant effect on $\Delta\delta^{\text{obs}}$. The results are given in Table 2. However, other salts did not have a marked effect. The maximum concentration of salt added to $[\text{Ni}(\text{en})_3]\text{X}_2$ (0.4 M) and the observed change in $\Delta\delta^{\text{obs}}$ were as follows: for $\text{X}^- = \text{Cl}^-$, NaF, 0.8 M, 0.2; KF, 3.0 M, 2.7; NaNO_3 , 1.2 M, 0.3; NaNO_2 , 2.0 M, 1.4; Na_3PO_4 , 0.4 M, 0.4; NaClO_4 , 0.4 M, 0.0; for $\text{X}^- = \text{NO}_3^-$, KF, 1.6 M, 2.3; NaNO_3 , 1.2 M, 1.2; K_3PO_4 , 0.8 M, 1.3. These results of a concentration dependence study are given in Table 3. The study showed that the chemical shift difference for both the chloride and nitrate salts increased markedly with concentration. A similar concentration dependence study (0.4 to 1.6 M) with the mono complexes of 1,2-ethanediamine and 1,2-propanediamine showed no detectable change in the peak position. The same result was obtained when sodium chloride (0.2 to 1.2 M) was added to the mono complexes (0.4 M). For all of the above investigations with $[\text{Ni}(\text{en})_3]^{2+}$, the mean chemical shift for the axial and equatorial protons did not show a significant variation even for those systems where the individual chemical shifts showed marked changes.

The variable temperature spectra of $[\text{Ni}(\text{pn})_3](\text{MeCO}_2)_2$ and $[\text{Ni}(\text{dmbn})_3](\text{MeCO}_2)_2$ were also studied. Compared to the mono complexes with half-band widths of about 4 ppm, the tris complexes gave rather broad resonances, with half-band widths of the order of 40 ppm. As a result, the 'axial' protons could not be distinguished from other resonances. For $[\text{Ni}(\text{pn})_3]^{2+}$, the axial protons were assigned the same chemical shift as the methyl protons at 301.5 K. The equatorial proton resonance for $[\text{Ni}(\text{pn})_3]^{2+}$ was found to give a negative deviation

Table 3. Isotropic shifts and n_λ values of Δ - $[\text{Ni}(\text{en})_3]\text{X}_2$ as a function of concentration at 301.5 K.

Conc ^a (M)	δ_{ax}	δ_{eq}	$\Delta\delta^{\text{obs}}$	n_λ
X = Cl				
0.4	67.8	107.2	39.4	0.62
0.8	65.8	110.0	44.2	0.64
1.2	62.6	113.2	50.6	0.66
X = NO₃				
0.4	71.4	103.4	32.0	0.60
1.2	69.4	106.4	37.0	0.62
1.6	67.1	109.0	41.9	0.63

^a Solutions prepared from isolated complex salt.

Table 4. Isotropic shifts and n_λ values for $[\text{Ni}(\text{R-pn})_3]\text{X}_2$ at 301.5 K.^a

Solvent	$\delta_{\text{CH}_3}, \delta_{\text{ax}}$	δ_{eq}	$\Delta\delta^{\text{obs}}$	n_λ
X = Cl^b				
H ₂ O	19.1	157.4	138.3	0.94
HCONH ₂	16.0	153.2	137.2	0.93
X = NO₃^c				
HCONH ₂	15.9	153.7	137.7	0.93
Me ₂ SO	19.7	157.7	138.0	0.93
X = MeCO₂^c				
H ₂ O	17.9	157.1	139.2	0.94
MeOH	18.2	158.2	140.0	0.94
HCONH ₂	17.6	158.6	141.0	0.94

^a Solutions prepared from isolated complex salt. ^b At 0.4 M. ^c At 0.8 M.

from Curie Law confirming changes in conformer populations with temperature, whereas for $[\text{Ni}(\text{dmbn})_3]^{2+}$ the equatorial resonance δ 169.2 at 301.5 K strictly followed Curie behaviour consistent with the stereospecificity of this ligand. For $[\text{Ni}(\text{pn})_3]^{2+}$, assuming that $\delta \times T$ for the mean of the 'equatorial' and 'axial' resonances is independent of temperature, it is possible to estimate the $\delta \times T$ against T plot for the 'axial' proton. Spectra were also recorded for $[\text{Ni}(\text{pn})_3]^{2+}$ in a number of solvents. The results are presented in Table 4. The 'axial' proton's resonance was obscured by the methyl resonance and hence it was assigned the same chemical shift as the methyl.

The approximate rates of the $\Delta \rightleftharpoons \Lambda$ inversion were calculated for the aqueous solution containing 1.6 M NaCl and for the DMSO solution by using the equation,^{2,3}

$$k_i = (\pi/\sqrt{2})(\Delta\nu_{\text{ax,eq}}^2 - \Delta\nu_T^2)^{\frac{1}{2}} \quad (3)$$

where $\Delta\nu_{\text{ax,eq}}$ is the frequency separation in the absence of inversion and $\Delta\nu_T$ is the observed frequency separation at temperature T , both expressed in Hz. The experimental data and the calculated rates are given in Table 5. From these rates, the enthalpies and entropies of activation were calculated from a plot of $-R \ln(k_i h/kT)$ against T^{-1} according to the Eyring equation,

$$-R \ln(k_i h/kT) = \Delta H^\ddagger T^{-1} - \Delta S^\ddagger \quad (4)$$

Table 5. Rates of inversion for $\text{Ni(en)}_3\text{Cl}_2$. T is in K, $\Delta\nu_{\text{ax,eq}}$ and $\Delta\nu_T$ are in Hz, and k_i is in s^{-1} .

T	$\Delta\nu_{\text{ax,eq}}$	$\Delta\nu_T$	k_i
(a) 1.6 M NaCl			
345	33.90	32.2	2355
350	32.30	28.3	3459
355	30.99	22.3	4780
360	29.72	14.7	5738
362.5	28.96	9.7	6062
365	28.20	0	6265
(b) DMSO			
365	59.2	57.8	2843
370	57.3	53.5	4558
375	55.2	49.1	5603
380	53.2	41.8	7311
385	51.4	27.5	9647
390	49.7	13.9	10600
395	49.1	0	10907

The values obtained were for 1.6 M NaCl, $\Delta H^\ddagger$ $48.1 \pm 6.2 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger$ $-41.2 \pm 17.3 \text{ JK}^{-1} \text{ mol}^{-1}$, $\Delta G^\ddagger$ (300 K) $60.5 \pm 11.4 \text{ kJ mol}^{-1}$; for DMSO, $\Delta H^\ddagger$ $50.3 \pm 6.0 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger$ $-41.3 \pm 15.9 \text{ JK}^{-1} \text{ mol}^{-1}$, $\Delta G^\ddagger$ (300 K) $62.7 \pm 10.8 \text{ kJ mol}^{-1}$.

Insufficient data from both Reilley's investigations⁶ and this study of $[\text{Ni(en)}_3]^{2+}$ in water, prevented a calculation of enthalpies and entropies of activation in this solvent. However, the free energy of activation at coalescence was calculated from the Eyring equation from the rate estimated from eqn. (2). Both sets of data gave $\Delta G^\ddagger$ 65.7 kJ mol^{-1} at 374 K.

Conformation analysis - chemical shift method

Because the conformations interconvert rapidly, the observed chemical shifts, for example δH2 and δH3 for protons H2 and H3 in Fig. 3, are weighted averages of their values in the frozen λ and δ conformations.

$$\delta\text{H2} = n_\lambda \delta\text{H2}(\lambda) + n_\delta \delta\text{H2}(\delta) \quad (5)$$

$$\delta\text{H3} = n_\lambda \delta\text{H3}(\lambda) + n_\delta \delta\text{H3}(\delta) \quad (6)$$

where n_λ and n_δ are the mol fractions of the λ and δ conformations, respectively, and are related by

$$n_\lambda + n_\delta = 1 \quad (7)$$

abbreviating eqn. (1) to

$$\delta_i^{\text{iso}} = K_i T^{-1} \quad (8)$$

eqns. (5) and (6) can be expressed as

$$T\delta\text{H2} = n_\lambda K_{\text{H2}}(\lambda) + n_\delta K_{\text{H2}}(\delta) \quad (9)$$

$$T\delta\text{H3} = n_\lambda K_{\text{H3}}(\lambda) + n_\delta K_{\text{H3}}(\delta) \quad (10)$$

By addition and subtraction of eqns. (9) and (10), the following equations are obtained:

$$T(\delta\text{H2} + \delta\text{H3}) = n_\lambda K_{\text{H2}}(\lambda) + n_\lambda K_{\text{H3}}(\lambda) + n_\delta K_{\text{H2}}(\delta) + n_\delta K_{\text{H3}}(\delta) \quad (11)$$

$$T(\delta\text{H2} - \delta\text{H3}) = n_\lambda K_{\text{H2}}(\lambda) - n_\lambda K_{\text{H3}}(\lambda) + n_\delta K_{\text{H2}}(\delta) - n_\delta K_{\text{H3}}(\delta) \quad (12)$$

Reilley made the assumptions that $K_{\text{H2}}(\lambda) = K_{\text{H3}}(\delta)$ and $K_{\text{H3}}(\lambda) = K_{\text{H2}}(\delta)$, which imply that the hyperfine coupling constants for H2(λ) and H3(δ) and for H3(λ) and H2(δ) are identical. These assumptions are used here, but their validity will be discussed later. Taking eqns. (11) and (12), and utilizing relation (7) and the above assumptions, the final equations can be expressed as

$$T(\delta\text{H2} + \delta\text{H3}) = K_{\text{H2}}(\lambda) + K_{\text{H3}}(\lambda) \quad (13)$$

$$T(\delta\text{H2} - \delta\text{H3}) = (2n_\lambda - 1)\{K_{\text{H2}}(\lambda) - K_{\text{H3}}(\lambda)\} \quad (14)$$

According to eqn. (13), the product of the temperature and the mean of the chemical shifts for H2 and H3 should be independent of temperature.

From eqn. (8)

$$K_{\text{H2}}(\lambda) - K_{\text{H3}}(\lambda) = T\{\delta\text{H2}(\lambda) - \delta\text{H3}(\lambda)\} \quad (15)$$

and eqn. (14) can be rearranged to give

$$n_\lambda = 0.5[1 + (\delta\text{H2} - \delta\text{H3})/(\delta\text{H2}(\lambda) - \delta\text{H3}(\lambda))] \quad (16)$$

or more simply

$$n_\lambda = 0.5[1 + \Delta\delta^{\text{obs}}/\Delta\delta^{\text{int}}] \quad (17)$$

where $\Delta\delta^{\text{int}}$ is the intrinsic chemical shift difference between axial and equatorial protons in the frozen conformation.

The values of n_λ and hence values of the equilibrium constant, $K_{\lambda\delta}$, and the free energy difference for the $\lambda \rightleftharpoons \delta$ equilibrium can be calculated from the experimental data if a value for $\Delta\delta^{\text{int}}$ is known. Ho and Reilley determined $\Delta\delta^{\text{int}}$ to be 182 at 305.1 K for $[\text{Ni}(\text{N},\text{N}'\text{-dmen})(\text{OH}_2)_4]^{2+}$ by an indirect method based on the assignment of a contact shift of 6 ppm for the "frozen" axial proton.⁵ This value was chosen because it was the value found for the ethylenic axial proton in $[\text{Ni}(\text{edta})]^{2-}$. The value of $\Delta\delta^{\text{int}}$ 182 yielded a good straight-line plot for $\log K_{\lambda\delta}$ against T^{-1} . However, it was found that the correlation coefficient for the fit of Ho and Reilley's data to a straight line approached unity as $\Delta\delta^{\text{int}}$ was allowed to increase to unrealistic values. Further, $[\text{Ni}(\text{edta})]^{2-}$ is a very poor model compound because the nitrogens are tertiary and the diamine chelate ring in that complex is under considerable strain, which is relieved by the chelate ring being flattened compared to the bidentate situation.²⁴ For $[\text{Ni}(\text{en})_3]^{2+}$, Ho and Reilley determined a value of $\Delta\delta^{\text{int}}$ 152 at 305.1 K by using a similar least squares fit method.⁶

In this paper, complexes of 3,3-dimethyl-1,2-butanediamine were used as models to determine $\Delta\delta^{\text{int}}$ for primary amines. The *tert*-butyl group stereospecifically restricts the conformation to λ for the (*R*) configuration.²⁵ In this conformation with the *tert*-butyl group equatorial the geometry of the ring is virtually identical to the related 1,2-ethanediamine chelate ring, and substituted diamine chelates where the substituents are equatorial.²⁵ The axial and equatorial proton resonances were found to obey Curie Law strictly, consistent with the stereospecificity of this ligand (Fig. 2). The values of $\Delta\delta^{\text{int}}$ determined from $[\text{Ni}(\text{dmbn})\text{S}_4]^{2+}$ were for water 159.6, methanol 162.2, and DMSO 163.6 at 300 K. In the spectrum of $[\text{Ni}(\text{dmbn})_3]^{2+}$ the resonance for the axial protons was not observed, but the equatorial proton had δ 169.2 at 301.5 K compared to δ 170.9 for $[\text{Ni}(\text{dmbn})(\text{OH}_2)_4]^{2+}$. It was assumed therefore that $\Delta\delta^{\text{int}}$ is the same for the mono and tris complexes. The value of $\Delta\delta^{\text{int}}$ 159.6 at 300 K which corresponds to 158.8 at the ambient temperature of 301.5 K was also used for the tris complexes in methanol and DMSO because, in contrast to the mono complexes, the solvents are not in the primary coordination sphere.

The value of $\Delta\delta^{\text{int}}$ for a secondary nitrogen donor was calculated using $\Delta\delta^{\text{int}}$ for a primary nitrogen and the $\Delta\delta^{\text{obs}}$ values for the primary and secondary

nitrogens from the *N*-methyl-1,2-ethanediamine complex. This yielded 196.2, 207.4, and 212.1 for water, methanol and DMSO solutions, respectively, at 300 K.

The complex $[\text{Ni}(\text{tmpn})\text{S}_4]^{2+}$ was used as the model for the determination of $\Delta\delta^{\text{int}}$ for tertiary nitrogens. It has been found to exist exclusively in the conformation with the methyl equatorial because in the alternative conformation there is a severe 1,3-diaxial interaction between methyl groups.¹ Because of insolubility problems, the value for aqueous solution could not be determined, but in methanol and DMSO the values were 119.1 and 122.4, respectively, at 300 K. Based on the trend in $\Delta\delta^{\text{int}}$ values with solvent for the primary and secondary nitrogens, the value in water for the tertiary would be of the order of 113. Separate signals were observed for the axial and equatorial NCH_3 groups in $[\text{Ni}(\text{tmpn})\text{S}_4]^{2+}$. The separation (MeOH , 15.5; Me_2SO , 12.8 at 300 K) gives $\Delta\delta^{\text{int}}$ for $\text{N}(\text{CH}_3)_2$. The value in water would be approximately 18.

With these above values of $\Delta\delta^{\text{int}}$, n_λ was computed from eqn. (17), and from this, $K_{\lambda\delta}$ and ΔG were calculated at each temperature, and ΔH and ΔS were determined from a plot of $-R \ln K$ against T^{-1} using a weighted least-squares method of analysis. The results are summarized for the mono complexes in Table 6. For the tris complexes, the free energy differences for the equilibria

$$\Delta(\lambda\lambda\lambda) \rightleftharpoons \Delta(\lambda\lambda\delta) \quad (\Delta G_1^\circ)$$

$$\Delta(\lambda\lambda\lambda) \rightleftharpoons \Delta(\lambda\delta\delta) \quad (\Delta G_2^\circ)$$

$$\Delta(\lambda\lambda\lambda) \rightleftharpoons \Delta(\delta\delta\delta) \quad (\Delta G_3^\circ)$$

can be approximated by assuming that the free energy for each $\lambda \rightleftharpoons \delta$ interconversion has the same energy:

$$\Delta G_1^\circ = \Delta G^\circ - RT \ln 3 \quad (18)$$

$$\Delta G_2^\circ = 2\Delta G^\circ - RT \ln 3 \quad (19)$$

$$\Delta G_3^\circ = 3\Delta G^\circ \quad (20)$$

where ΔG° is calculated directly from n_λ and $RT \ln 3$ is a statistical entropy term. The results from this study are presented in Table 7, which also includes published data for these systems.

Table 6. Conformational analysis data, for $[\text{NiLS}_4]^{2+}$. ΔH and ΔG (300 K) are in kJ mol^{-1} and ΔS is in $\text{J K}^{-1} \text{mol}^{-1}$, n_λ at 300 K.

S	n_λ	ΔH	ΔS	ΔG
L = pn				
H ₂ O	0.95	8.1 ± 0.3	$+2.0 \pm 0.7$	7.5 ± 0.5
MeOH	0.95	^a	^a	7.2 ± 0.7
Me ₂ SO	0.93	5.5 ± 0.2	-2.8 ± 0.4	6.3 ± 0.3
L = men				
H ₂ O	0.71	2.1 ± 0.1	-0.3 ± 0.3	2.2 ± 0.2
MeOH	0.72	2.2 ± 0.2	0.0 ± 0.5	2.2 ± 0.2
Me ₂ SO	0.76	2.7 ± 0.1	-0.8 ± 0.3	2.9 ± 0.2
L = een ^b				
H ₂ O	0.68	1.7 ± 0.2	-0.5 ± 0.6	1.9 ± 0.4
L = N,N'-dmen				
H ₂ O	0.80	2.2 ± 0.1	-3.9 ± 0.2	3.4 ± 0.2
MeOH	0.82	1.2 ± 0.1	-8.4 ± 0.2	3.7 ± 0.2
Me ₂ SO	0.82	2.2 ± 0.1	-5.2 ± 0.4	3.8 ± 0.2
L = trmen ^c				
H ₂ O	0.74 ^d			2.6 ± 0.6^e

^a Variable temperature data too inaccurate for meaningful ΔH and ΔS values. ^b N-Ethyl-1,2-ethanediamine with chemical shift data taken from Ref. 5. ^c N,N,N'-Trimethyl-1,2-ethanediamine with chemical shift data taken from Ref. 5 at 305.1 K. ^d ± 0.04 (NMe, 0.73; ¹NCH₂, 0.78; ²NCH₂, 0.70). ^e NMe, 2.5; ¹NCH₂, 3.2; ²NCH₂, 2.2.

DISCUSSION

The assumptions that $K_{\text{H}_2}(\lambda) = K_{\text{H}_3}(\delta)$ and $K_{\text{H}_3}(\lambda) = K_{\text{H}_2}(\delta)$ imply the dihedral angle between Ni–N and say C–H_{ax} in a λ conformation is identical to the same dihedral angle in a δ conformation. For an achiral ligand this will of course be valid, but for chiral ligands such as pn, men, N,N'-dmen, and trmen this need not necessarily be correct. In fact, conformational-energy minimization calculations have shown, for example for R-pn chelate rings, that, whereas in the λ conformation with the methyl equatorial, the two ring carbons are equidistant from the NMN plane, in the δ conformation the unfavourable interactions between the axial methyl and the apical ligand are minimized by the ring adopting a conformation in which the two ring carbons are unsymmetrically located with respect to the NMN plane.²¹ In addition, conformations with axial substituents tend to be flattened to minimize non-bonded interactions. Both of these factors would remove this above dihedral angle equality. For M–N 200 pm, for which the energy minimization calculations were conducted, the inequality is marked, but for longer M–N bond lengths as apply here (Ni–N, ~ 210 pm) it becomes less significant. The error in the results due to this cannot be estimated, but it will be of little importance for the N,N'-dimethyl-1,2-ethanediamine and 1,2-ethanediamine complexes which maintain symmetric conformations for both δ and λ chelate rings.

Table 7. Conformational analysis data for $\Delta\text{-}[\text{NiL}_3]\text{Cl}_2$. Solvent is water unless stipulated, ΔH and ΔG (301.5 K) are in kJ mol^{-1} , ΔS is in $\text{J K}^{-1} \text{mol}^{-1}$, and n_λ is at 301.5 K.

Conc (M)	n_λ	ΔH	ΔS	ΔG	ΔG_1	ΔG_2	ΔG_3
L = en							
0.4 ^a	0.63	1.5	0.8	1.3	–1.4	–0.1	+3.9
0.4 ^{b,c}	0.62	1.3	0.3	1.2	–1.5	–0.3	+3.6
0.8 ^d	0.97	31.9	76.4	9.0	+6.3	+15.3	+27.0
0.8 ^{e,c}	0.65	2.0	1.8	1.5	–1.2	+0.3	+4.5
0.8 ^{f,c}	0.64	^g	^g	1.4	–1.3	+0.1	+4.2
0.4 ^{f,c,h}	0.65	2.0	1.6	1.5	–1.2	+0.3	+4.5
^{d,i}	0.98	24.4	49.6	9.5	+6.8	+16.3	+28.5
^{e,c,i}	0.79	4.2	3.0	3.3	+0.6	+3.9	+9.9
L = pn							
0.8 ^{f,c}	0.94	5.0	–5.9	6.8	+4.1	+10.9	+20.4

^a Results from Ref. 6. ^b Data from Ref. 6. ^c Results calculated with $\Delta\delta^{\text{int}}$ 158.8. ^d Results from Ref. 9. ^e Data from Ref. 9 for 305 to 340 K. ^f Current data. ^g Insufficient data points for accurate values. ^h Solution contained 1.6 M NaCl. ⁱ Me₂SO solution at unknown concentration.

The results for $[\text{Ni}(\text{R-pn})\text{S}_4]^{2+}$ have two surprising features. Firstly, the n_λ and associated $\Delta G_{\lambda\delta}$ values are higher than the values obtained by the coupling constant method for $[\text{Co}(\text{R-pn})(\text{NH}_3)_4]^{3+}$ (n_λ 0.72, ΔG 2.37 kJ mol⁻¹) and $[\text{Co}(\text{R-pn})\text{CN}_4]^-$ (n_λ 0.83, ΔG 3.97 kJ mol⁻¹).¹ Energy-minimization calculations had suggested that the non-bonded interactions between an apical water molecule and an axial methyl group attached to a five-membered diamine chelate are less than for an apical ammonia or a cyanide.²⁵ Further, as the metal–ligand bond lengths for nickel(II) are greater than for cobalt(III), the axial methyl is further away from an apical ligand in the nickel(II) complex, and therefore, unfavourable interactions should be reduced.¹ No explanation for the above result can be offered at this stage. The second surprising feature, which was also observed for the other diamines, was that for the methanol and DMSO systems the $\delta \times T$ values for the average of the axial and equatorial CH chemical shifts increased with temperature. This indicates the presence of a second equilibrium with the species favoured at higher temperatures having a larger contact shift. Several processes such as ion-pairing, hydrogen-bonding, dissociation, and paramagnetic-diamagnetic equilibria can be discounted. Ion-pairing is not affecting the spectra because the spectrum of $[\text{Ni}(\text{en})(\text{OH}_2)_4]^{2+}$ is independent of added chloride ion. As hydrogen-bonding decreases with increasing temperature, the observed larger contact shifts at higher temperature would suggest that, if a solvated–unsolvated equilibrium is important, the unsolvated species has the larger contact shift. However, DMSO has been found to solvate at the NH_2 of coordinated diamines more strongly than water,¹⁷ and yet the contact shifts in DMSO are greater than in water. Therefore, the results cannot be explained by a solvated–unsolvated equilibrium. Similarly, dissociation and paramagnetic-diamagnetic equilibria would give the opposite result to what was observed.

When methyl substitution is on the N, the energy difference between the axial and equatorial conformations is markedly less than for the C-substituted chelates as predicted by the energy-minimization calculations.^{21,25} The *men*, *een*, and *trmen* systems had similar n_λ and $\Delta G_{\lambda\delta}$ values. The *N,N'*-*dmen* system gave larger values for these two parameters because the equilibrium is between two equatorial methyls and two axial methyls. Based on n_λ for the racemic isomer and the racemic:*meso* isomer ratio, it is possible to calculate the relative

populations of the conformations with two equatorial methyls, one equatorial and one axial methyl, and two axial methyls. The ratios at 300 K were found to be 1:0.96:0.25 in water, 1:0.56:0.22 in methanol, and 1:0.72:0.22 in DMSO. These yield free energy differences between the di-equatorial configuration and the equatorial-axial configuration of 0.1 kJ mol⁻¹ in water, 1.5 kJ mol⁻¹ in methanol, and 0.8 kJ mol⁻¹ in DMSO. The *meso* equatorial-axial configuration is stabilized relative to the di-equatorial configuration by a probability entropy term ($RT \ln 2$) of 1.7 kJ mol⁻¹ at 300 K, and when this is taken into account, the energy difference between an axial and an equatorial *N*-methyl group for *N,N'*-*dmen* does not differ markedly from the corresponding energy for the *men*, *een* and *trmen* systems.

Statistically significant differences were found in the thermodynamic parameters for the mono complexes in different solvents. However, because of the complexity of the systems possessing different unidentate ligands and with the possibility of different degrees of solvation at the NH protons, it has not been possible to interpret these differences in the energies.

The observed rate constants for the inversion of the coordinated secondary nitrogen in the DMSO solutions of the mono complexes of *N*-methyl-1,2-ethanediamine and *N,N'*-dimethyl-1,2-ethanediamine are of a similar order of magnitude when the difference in the temperatures and the statistical factor for the two-centre inversion in the latter ligand are taken into account. The observed rates of inversion in DMSO must be higher than in water because the separations of the axial and equatorial resonances are smaller in water and yet no evidence for inversion was obtained up to 373 K. From the study of $[\text{Co}(\text{NH}_3)_4(\text{men})]^{3+}$,²⁶ $[\text{Pt}(\text{en})(\text{men})]^{2+}$,²⁷ $[\text{PtCl}_2(\text{en})(\text{men})]^{2+}$,²⁹ and $[\text{Co}(\text{NO}_2)_2(\text{men})_2]^+$,²⁸ Buckingham and coworkers have proposed that the nitrogen inversion proceeds *via* a deprotonated intermediate. The above greater rate of inversion in DMSO than in water (pH ~8) could therefore be associated with the higher basicity of DMSO.²⁹

Values of n_λ and the free energies, ΔG_1 , ΔG_2 and ΔG_3 , have been determined by the coupling constant method for the tris(1,2-ethanediamine) complexes of cobalt(III), rhodium(III), and ruthenium(II).¹ The results for cobalt(III) were in excellent agreement with values obtained by an indirect method³⁰ based on the concentrations of the

various isomers of $[\text{Co}(\text{R-pn})(\text{S-pn})_{3-i}]^{3+}$, which had been prepared under equilibrium conditions and separated chromatographically. For the above three complexes in water at about 300 K, n_λ values of between 0.64 and 0.70 were found. Similar values were found for $[\text{Ni}(\text{en})_3]^{2+}$ in the present study from the current data and the data of Ho and Reilley⁶ and Cramer⁹ (Table 7). Ho and Reilley's calculative procedure had yielded a similar result,⁶ but Cramer⁹ had determined an n_λ value of 0.98.

For $[\text{Ni}(\text{en})_3]^{2+}$ in DMSO, Cramer determined a similar value for n_λ to that in water even though $\Delta\delta^{\text{obs}}$ in the two solvents differed markedly.⁹ He rationalized this result on the basis of a proposed difference in ring pucker in the two solvents due to the strong hydrogen-bonding interactions between the complex and DMSO. The proposed greater ring pucker in this solvent would make the $\text{Ni}-\text{N}-\text{C}-\text{H}_{\text{eq}}$ dihedral angle closer to 180° , which is the optimum angle for electron delocalization, thus making $\Delta\delta^{\text{obs}}$ and $\Delta\delta^{\text{int}}$ larger in DMSO. However $[\text{Ni}(\text{pn})_3]^{2+}$ does not show a similar large variation in $\Delta\delta^{\text{obs}}$ with solvent (Table 4), and hence the observed differences between the water and DMSO solution spectra of $[\text{Ni}(\text{en})_3]^{2+}$ are not derived from differences in ring pucker, but result from differences in $\Delta G_{\lambda\delta}$. Cramer's method of calculation is therefore called into question.

At 301.5 K and 0.4 M concentration in water $\Delta[\text{Ni}(\text{en})_3]^{2+}$ yields for $\lambda \rightleftharpoons \delta$ ΔH 1.3 kJ mol⁻¹, ΔS +0.3 JK⁻¹ mol⁻¹, and ΔG 1.2 kJ mol⁻¹. The low ΔS value suggests there is not a marked difference in the solvation of the λ and δ conformations by water as the vibrational entropy term is expected to be small.¹⁴ At 0.8 M concentration, both the ΔH and ΔS values are increased. Similar values for ΔH and ΔS were obtained at 0.4 M concentration in the presence of 1.6 M NaCl. Both results suggest that there is stronger ion association for the λ conformation.* Further evidence for this can be gained from Tables 2 and 3. The value of n_λ increased from 0.60 with no chloride in solution to 0.65 with 2.4 M chloride, and it increased by 0.04 from 0.4 M complex to 1.2 M complex.

Although chloride ion affected the conformer populations, a number of other anions including

phosphate had no significant effect. The circular dichroism spectrum of $\Delta[\text{Co}(\text{en})_3]^{3+}$ in aqueous solution has been found to change markedly on the addition of phosphate.^{31,32} The changes have been explained previously in terms of the phosphate hydrogen-bonding to the cation along the complex's C_3 axis: in the $\Delta(\lambda\lambda\lambda)$ configuration three NH_{eq} protons are oriented approximately parallel to the C_3 axis and ideally situated for hydrogen-bonding to the phosphate, whereas in the $\Delta(\lambda\lambda\delta)$, $\Delta(\lambda\delta\delta)$ and $\Delta(\delta\delta\delta)$ configurations the protons are said to be less ideally oriented for a three-pronged hydrogen-bonding interaction. It is claimed that this results in the conformational equilibrium being shifted towards the λ conformation with an associated change in the circular dichroism. However, as pointed out by Sarneski and Urbach, such an interaction renders each nitrogen asymmetric with the same absolute configuration and this will have a major effect on the observed circular dichroism.³³ Further, the differences in the H—H separations for $\Delta(\lambda\lambda\lambda)$ and $\Delta(\lambda\lambda\delta)$ are relatively slight and the differences in the hydrogen-bonding between phosphate and these two configurations would not be marked. Nevertheless, NMR data confirm for $[\text{Co}(\text{en})_3]^{3+}$ and $[\text{Rh}(\text{en})_3]^{3+}$ that phosphate does increase n_λ , although the errors in n_λ are sufficiently large to make the actual magnitude of the increase uncertain: at 290 K $[\text{Rh}(\text{en})_3]^{3+}$ $[\text{PO}_4^{3-}]\text{O}$, n_λ 0.64 ± 0.06 ; $[\text{PO}_4^{3-}]$ 0.1 M, n_λ 0.68 ± 0.06 ; $[\text{Co}(\text{en})_3]^{3+}$ $[\text{PO}_4^{3-}]\text{O}$, n_λ 0.70 ± 0.07 ; $[\text{PO}_4^{3-}]$ 0.1 M, n_λ 0.73 ± 0.05 ; $[\text{PO}_4^{3-}]$ 0.3 M, n_λ 0.83 ± 0.08 . Chloride on the other hand, has a much smaller effect on the CD of $\Delta[\text{Co}(\text{en})_3]^{3+}$,³² consistent with the fact that the association constant for chloride with $[\text{Co}(\text{en})_3]^{3+}$ is an order of magnitude less than for phosphate.³⁴ In addition, the effect chloride has on the relative rotational strengths of the $^1A_1 \rightarrow ^1E$ and $^1A_1 \rightarrow ^1A_2$ components of the $^1A_{1g} \rightarrow ^1T_{1g}$ cubic absorption band differs from that of phosphate suggesting that the type of interaction is different for the two anions in solution.

Based on the above results for $[\text{Co}(\text{en})_3]^{3+}$ and $[\text{Rh}(\text{en})_3]^{3+}$ and the significant effect of chloride with $[\text{Ni}(\text{en})_3]^{2+}$ it had been anticipated that the addition of phosphate to $[\text{Ni}(\text{en})_3]^{2+}$ would induce large changes in the contact shifts of the ring protons. The observed changes were in fact zero for a 1:1 ratio of $[\text{Ni}(\text{en})_3]\text{Cl}_2$ and phosphate, and 1.29 ppm for a 1:2 ratio of $[\text{Ni}(\text{en})_3](\text{NO}_3)_2$ and phosphate. This latter result reflects a change in n_λ of less than 0.01. For the dipositive cation, ion association would

* Cramer and Harris claimed that their larger observed chemical shift differences compared to the previous results of Ho and Reilley⁶ were caused by a small amount of excess diamine.⁹ It has been shown here that the contact shifts for $[\text{Ni}(\text{en})_3]^{2+}$ are independent of 1,2-ethanediamine up to a 100% excess.

be less than for the tripositive $[\text{Co}(\text{en})_3]^{3+}$, and therefore a smaller change in n_λ would be expected for $[\text{Ni}(\text{en})_3]^{2+}$. However, the question that remains to be answered is why chloride was found here to have a much larger effect with $[\text{Ni}(\text{en})_3]^{2+}$ than phosphate and other anions such as fluoride, nitrate and perchlorate. One possible answer to this question relates to the interaction of the anions with the solvent, water. An investigation of the infrared and Raman OH stretching and librational bands of simple salt solutions has yielded the following order for anion-water interactions:³⁵

At the high concentrations of the complex salts of the present study, the number of water molecules per ion would be significantly less than for the CD, the diamagnetic NMR and the ion-association constant studies, and the number could be of the order of 16 or less. The degree of hydration of Cl^- would be very low compared to PO_4^{3-} and under these circumstances the chloride may be able to form a contact ion-pair with the complex which differs in stability for the δ and λ configurations. For ClO_4^- , the hydration is less than for Cl^- but it is known to form very unstable ion-pairs.³⁶ $[\text{Ni}(\text{en})_3](\text{NO}_3)_2$ showed a concentration dependence but this was less than for the chloride (Table 3), consistent with the above order.

$[\text{Ni}(\text{en})_3]^{2+}$ in DMSO showed a marked increase in n_λ over the aqueous solution (Tables 1 and 6). For the $\lambda \rightleftharpoons \delta$ equilibrium, both ΔH and ΔS were more positive, consistent with DMSO binding more strongly to the NH_2 groups in the λ configuration. The equatorial NH protons are readily accessible in both the δ and λ conformations, but for the Δ configuration the axial NH protons for a δ conformation are less accessible for solvation due to their interactions with other atoms in the molecule. The greater donor power of DMSO therefore stabilizes the λ more than water. In Table 1, n_λ values are given for a number of solvents and counter ions. The trend in n_λ values for the non-aqueous solvents follows the order of the donor number for the solvents: MeCN 14.1,²⁹ Me₂CO 17.0,²⁹ thf 20.0,²⁹ HCONH₂ 24.7,³⁷ HCON(Me)₂ 26.6,²⁹ Me₂SO 29.8.²⁹ Water with a donor number of 18.0 gives a smaller n_λ value than would be expected.

The inversion of $[\text{Ni}(\text{en})_3]^{2+}$ in water, in 1.6 M NaCl and DMSO was studied at elevated tempera-

tures. Ho and Reilley determined a free energy of activation of 65.7 kJ mol⁻¹ at 374 K for the water solution.⁶ The other two solvents yielded similar values: 1.6 M NaCl $\Delta G^\ddagger_{374}$ 63.5 kJ mol⁻¹, Me₂SO $\Delta G^\ddagger_{374}$ 65.7 kJ mol⁻¹. Insufficient data points were available for the water solution to calculate $\Delta H^\ddagger$ and $\Delta S^\ddagger$ but these were obtained for the 1.6 M NaCl and the DMSO solutions. These values are in excellent agreement indicating that the same mechanism is occurring in both solvents, and that the solvent does not play a dominant role in the formation of the activated complex. This is consistent with the non-bond-rupture twist mechanism proposed by Ho and Reilley.⁶ The large negative entropy of activation has also previously been associated with a twist mechanism.³⁸

Zamaraev has proposed that a Karplus-type equation could be applied to the proton contact shifts of diamine chelate rings to estimate the degree of ring pucker:¹²

$$A_i = B_0 + B_2 \cos^2 \theta_i \quad (21)$$

where A_i is the hyperfine coupling constant, B_0 and B_2 are constants, and θ the dihedral angle between the Ni-N-C and N-C-H planes (Fig. 4). Experimental evidence for radicals with rigid geometries has led to the conclusion that B_0 is much less than B_2 .³⁹ This allows the approximation,

$$A_i \approx B_2 \cos^2 \theta_i \quad (22)$$

and the formulation of the equation,

$$\delta_{ax}/\delta_{eq} = \cos^2 \theta_{ax}/\cos^2 \theta_{eq} \quad (23)$$

Eqn. (23) yields four values for the angle θ : θ , $\pi - \theta$, $\pi + \theta$, and $2\pi - \theta$. In calculations the intrinsic contact shifts must be employed; not shifts that are weighted because of the conformational equilibrium present. The intrinsic contact shifts for the axial and equatorial protons for 3,3-dimethyl-1,2-butane-diamine are 11.8 and 170.7 ppm at 300 K, and 7.4 and 126.5 ppm at 300 K for *N,N,N',N'*-tetramethyl-1,2-propanediamine. These shifts give θ values of approximately 76° for both rings. This angle was chosen in preference to the remaining three because of the correspondence to the angle of 78° found in the solid state for $[\text{Ni}(\text{en})_3](\text{MeCO}_2)_2 \cdot 2\text{H}_2\text{O}$.⁴⁰ The fact the two rings gave similar values for θ shows that the interactions of axial *N*-methyl groups are not sufficiently strong to cause significant flattening

of the chelate ring. The intrinsic contact shifts for the axial and equatorial protons in $[\text{Ni}(\text{dmbn})_3]^{2+}$ also gave a value of 76° for θ . The correspondence between this value for the tris(diamine) complex in solution and the value determined by X-ray analysis for the above crystalline complex suggests that the interactions of the solvent do not significantly affect the degree of pucker of the chelate rings.

Cramer studied the degree of pucker of the diamine chelates using an equation similar to (21) in which A_i was replaced by δ_i .⁹ He assumed a value of zero for B_0 and estimated a value of B_2 using a contact shift of 300 ppm and a θ value of 180° as found for the α -imino proton of *cis,cis*-1,3,5-tris(pyridine-2-carbonimino)cyclohexanenickel(II).⁴¹ Knowing B_2 , the dihedral angles were calculated from the individual contact shifts. Three points arise from Cramer's use of this method. Firstly, the hyperfine coupling constant and not the contact shift is related to the dihedral angle.¹² Secondly, the delocalization of electron density to the α -imino proton in the above compound is influenced by the presence of π -bonding in the ligand framework, which will increase the contact shift relative to the σ -bonded situation.⁴² Finally, of the angles 63, 117, 243, and 297° which were solutions for Cramer's equation, he chose 117° , a value dictated by his previous theory that chelate rings are much flatter in solution than in the solid state. A dihedral angle of 117° implies that the ring is approaching planarity which is most unlikely considering the high energy of that conformation.

Acknowledgements. The authors gratefully acknowledge financial support from the Australian Research Grants Committee.

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Received June 2, 1978.