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Anion Dependence of the Ring Conformational Equilibria of the Tris(ethylenediamine)nickel(II) Cation

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The temperature dependence of the nmr contact shifts of $Ni(en)_3X_2$ (X^- = nitrate, acetate, benzoate) in water, methanol, and DMSO is interpreted in terms of chelate ring conformational equilibria. A new type of behavior, which is attributed to the formation of multiple hydrogen bonds between cation and anion, is observed at low temperature in H_2O and CH_3OH. At high temperature in H_2O a correlation between the base strength of the anion and the parameters for ring inversion is observed. The large values of ΔH and ΔS for the ring conformational equilibria calculated in these systems suggest that association of cation and anion plays an important role in ethylenediamine ring conformational behavior.

Introduction

Recently there has been interest in studying the conformations of ethylenediamine chelates by nmr[1-3] and a recent review summarizes much of this work.[4] In a previous paper[5] we explored the role of solvent on the conformational equilibrium and concluded that the observed changes are primarily due to hydrogen bonding of the amine protons to the solvent. The solvents studied were DMSO and H_2O, both of which form strong hydrogen bonds, while the anions were carefully selected to minimize specific interactions with the cation. We wish to report here results which extend the earlier studies to include good hydrogen bonding anions.

One of the earliest reports of the influence of anions upon ring conformational equilibria in tris-ethylenediamine complexes was by Mason and Norman,[6] who observed changes in the visible circular dichroism of aqueous $Co(en)_3{}^{3+}$ to be dependent upon anion and anion concentration. Among the anions found to affect the circular dichroism were phosphate, sulfate, acetate, hydroxide, perchlorate, and the halides. The authors suggested that their liquid-phase observations could be explained by a hydrogen-bonding association of the anions with the cations which alters the ring conformational equilibria.

Raymond, *et al.*,[7,8] in crystal structure studies of $Cr(en)_3{}^{3+}$ found that the ring conformations were dependent on the anion type, with the anion $Ni(CN)_5{}^{3-}$ producing both $\Lambda(\delta\lambda\lambda)$ and $\Lambda(\delta\delta\lambda)$ configurations and the anion $Co(CN)_6{}^{3-}$ giving $\Lambda(\lambda\lambda\lambda)$. They explained their data in terms of the availability of the amine hydrogens for hydrogen bonding to the anions or H_2O of crystallization. A later X-ray structure of $Co(en)_3{}^{3+}$ with the $Cr(CN)_5NO^{3-}$ anion revealed a $\Lambda(\delta\lambda\lambda)$ conformation[9] while $Co(en)_3{}^{3+}$ with $Cu_2Cl_8{}^{4-}$ gave a $\Lambda(\lambda\lambda\delta)$ conformation.[10] However, other X-ray structures which show strong hydrogen bonding between the cation and anion in $[Ni(en)_3](NO_3)_2$,[11] $Ni(en)_3SO_4$,[12] $Cu(en)_3SO_4$,[13] $Co(en)_3(NO_3)_3$,[14] and $Co(en)_3{}^{3+}$ with $HPO_4{}^{2-}$ [15] all revealed the usual $\Lambda(\delta\delta\delta)$ configuration.

Some nmr evidence is available for the association of anions with tris-ethylenediamine complexes. Sudmeier and Blackmer observed[3] a temperature-dependent broadening in the nmr spectrum of $Rh(en)_3{}^{3+}$ upon addition of phosphate. Fung and Martin[16] have shown, by means of ^{59}Co and ^{31}P nmr, that $PO_4{}^{3-}$ associates with $Co(en)_3{}^{3+}$ in H_2O solution.

Both the crystal structure studies and the solution results suggest that anions, as well as solvents, are influencing the conformation of the ethylenediamine chelate. We undertook this work in order to elucidate better the effect anions have on ring conformation and the ring inversion equilibrium.

Experimental Section

Solvents. Deuterated MeOH, DMSO, and D_2O were obtained from Stohler Isotope Chemicals.

Preparation of Complexes. Tris(ethylenediamine)nickel(II) benzoate, $Ni(en)_3(OBz)_2$, was prepared by adding excess ethylenediamine to a mixture of the solid nickel benzoate and methanol and extracting the complex into methanol, followed by evaporation of the methanol. $Ni(en)_3(acetate)_2$ was prepared in the same manner as $Ni(en)_3(OBz)_2$. $Ni(en)_3(NO_3)_2$ was prepared by adding excess ethylenediamine to an aqueous solution of $Ni(NO_3)_2$. $Ni(en)_3(NO_3)_2$ precipitated out upon addition of acetone. All complexes gave satisfactory chemical analysis. Electronic spectra obtained on a Cary Model 14 for the various solvent–anion combinations showed agreement with solid $Ni(en)_3(ClO_4)_2$.[17]

Nmr spectra were obtained for saturated solutions using a Varian HA-100 modified to obtain side bands of variable frequency up to 40 kHz. At least three spectra were taken at each temperature and the average values are reported here. Isotropic shifts were measured in ppm downfield from the diamagnetic $Zn(en)_3{}^{2+}$. Probe temperature was measured as previously described.[18]

Data reduction was carried out as previously described[5] but was initially unsuccessful over the complete temperature range for certain anion–solvent combinations. To test whether ΔS and ΔH remain constant as a function of temperature, plots were made of $-\ln K$ *vs.* $1/T$ using our values of ΔS and ΔH over the temperature range for which acceptable fits could be obtained and comparing this calculated line with values obtained at each data point by setting

$$K = (1 - f)/(1 + f) \qquad (1)$$

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$$f = \frac{K_{bb}' - K_{aa}'}{K_b - K_a} \qquad (2)$$

where K is the equilibrium constant, $K_b - K_a$ is the shift-temperature product difference for two types of protons in the "frozen conformation" and is constant with temperature, and $K_{bb}' - K_{aa}'$ is the difference in the shift-temperature product actually measured. Equations 1 and 2 are a rearrangement of the equation developed by Reilley and coworkers.[19] The resulting plot for Cl^- is shown in Figure 1, and it is obvious that all the data fall on a single straight line. However the plot for OAc^- shown in Figure 2 is not linear and, therefore, more than one equilibrium must be important over the complete temperature range. Results similar to the OAc^- case are obtained for OBz^- and NO_3^- ions in H_2O and OBz^- in CH_3OH.

To obtain ΔH, ΔS, and $K_b - K_a$ for both the high- and low-temperature equilibria, the following manipulation of data was carried out. First we assumed the equation

$$K_{bb}' - K_{aa}' = (K_b - K_a)[2/(1 + K) - 1] \qquad (3)$$

to remain valid and obtained values for $K_b - K_a$, ΔH, and ΔS over the entire temperature range. Using these values we obtained a plot of $-\ln K$ *vs.* $1/T$ (see Figure 2). Then using those points which seem to fall in a straight line, new values of $K_b - K_a$, ΔH, and ΔS, were calculated using eq 3 for both of the straight-line portions of the curve. With these new values of $K_b - K_a$, ΔH, and ΔS, we again made $-\ln K$ *vs.* $1/T$ plots. This procedure was repeated until self-consistency was achieved for each straight-line portion. An example of the resulting $-\ln K$ *vs.* $1/T$ plots for OAc^- in the high- and low-temperature regions are shown in Figures 3a and b.

A measurement of the amount of ring pucker can be obtained from the dihedral angle which the axial methylene proton makes with the C-N-Ni plane. These were calculated from the values of $K_b - K_a$ as described previously,[5] using a shift of −300 ppm for a proton at $\theta = 180°$ as observed by Wandiga, Sarmeski, and Urbach.[20] In all cases $\theta_{eq} - \theta_{ax}$ is between 113 and 117°, which is close to the expected dihedral angle of 120° which results from tetrahedral, or nearly so,[21] HCH angles.

A short comment is necessary here on the assumptions that have been made in the manipulation of the data. The first important assumption is that we consider only $\delta \longleftrightarrow \lambda$ conversion, not $\lambda\lambda\lambda \longleftrightarrow \lambda\lambda\delta \longleftrightarrow \lambda\delta\delta \longleftrightarrow \delta\delta\delta$ conversion, and as a consequence we obtain only average values of these equilibria. This is due to the fact that the contact shift depends only on the conformation of a single ring and does not directly depend on the other rings of the complex. Our values for ring pucker represent an average for the various conformations possible. Further, we have assumed that one value of $K_b - K_a$ describes both the δ and λ ring conformations, although this is probably not true. Finally, the data manipulation outlined above assumes that only one process occurs at low temperature while a different equilibrium operates at high temperature. The assumption that these two equilibria do not interfere with each other may not be correct and casts some doubt on the numbers we have obtained.

Results and Discussion

The measured values for the contact shifts of $Ni(en)_3{}^{2+}$ have been deposited in the microfilm edition (see paragraph at end of paper regarding supplementary material). The values of ΔH, ΔS, ΔG, and $K_b - K_a$ obtained from the data analysis are presented in Table I. Figure 4 contains plots of $T\delta$ *vs.* T for the NO_3^- system in H_2O. Similar plots for the other new systems can be found in the microfilm edition. Curvature at the higher temperatures is due to $\Delta \longleftrightarrow \Lambda$ configurational interconversion of the metal ion and these points are not included in the calculations. Examination of the data shows small but significant differences in contact shifts for different anions in the same solvent, demonstrating that anions do have an effect on the conformational equilibria.

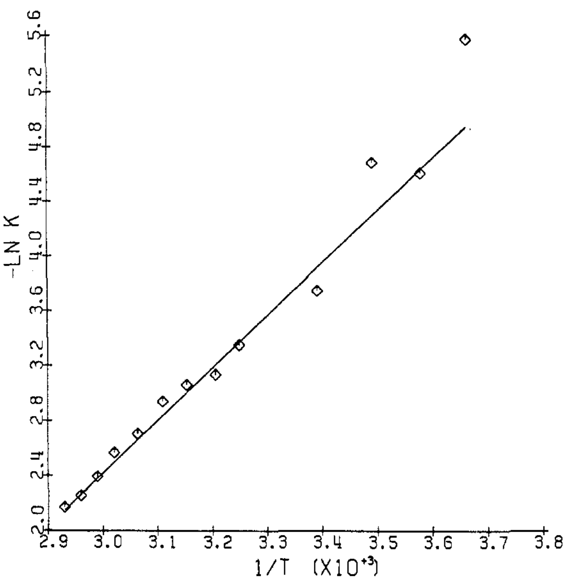

Figure 1. Plot of $-\ln K$ *vs.* $1/T$ (°K) for tris(ethylenediamine)nickel(II) chloride in water. The scatter at low temperature (270°K) probably is due to increased solvent viscosity.

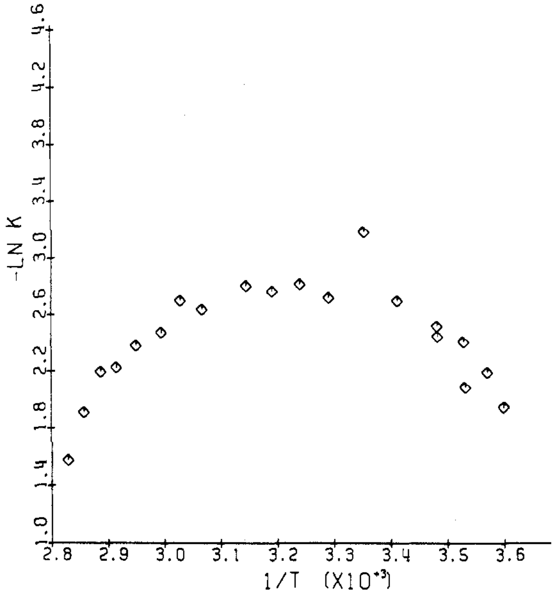

Figure 2. Plot of $-\ln K$ *vs.* $1/T$ (°K) for tris(ethylenediamine)nickel(II) acetate where $K_B - K_A$ was obtained from a fit of all data over entire temperature range.

The data for NO_3^-, OAc^-, and OBz^- in H_2O and for OBz^- in CH_3OH exhibit a behavior not found previously as is illustrated by Figure 4. In all of these systems at low temperature the $T\delta$ curves for the axial and equatorial protons begin to curve toward each other, rather than continue their divergence as observed for the chloride system. This behavior is more obvious in the van't Hoff plots, examples of which appear in Figures 2 and 3 where it is clear that two different equilibria, one at high and one at low temperature, are being observed. As outlined below, we believe that this low-temperature behavior is due to the formation of two hydrogen bonds between amine protons on different rings and two oxygens of the NO_3^-, OAc^-, or OBz^- anions. Since the Cl^- ion is a monoatomic moiety, its ability to form such multiple hydrogen bonds is restricted and the behavior associated with these multiple hydrogen bonds is not observed.

Upon examining models of $Ni(en)_3{}^{2+}$ one discovers that the distances between amine protons differ on conversion from $\Lambda\delta\delta\delta$, the form calculated to be the more stable,[22,23] to $\Lambda\lambda\lambda\lambda$. On comparison of distances and directional factors,

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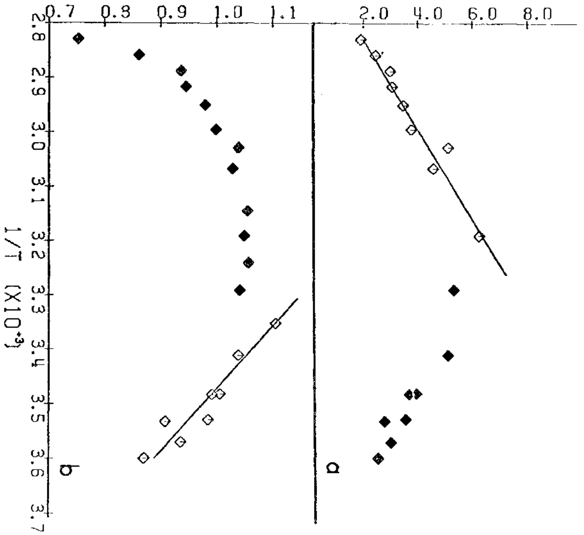

Figure 3. Plot of $-\ln K$ *vs.* $1/T$ (°K) in high- (a) and low-temperature (b) regions for tris(ethylenediamine)nickel(II) acetate in water. The lines were calculated from ΔH and ΔS obtained from the data fit in the respective temperature regions. The solid points were not used to obtain the fit.

one finds that there is a possibility of two simultaneous hydrogen bonds being formed between the cation and such Lewis bases as nitrate, acetate, or benzoate which have two or more oxygens. Multiple hydrogen bonding between axial hydrogens (such as 1HB and 4HB in Figure 5) and PO_4^{3-} oxygens has been postulated as a stabilizing influence for the $\Lambda\delta\delta$ conformation on the basis of the circular dichroism of aqueous $Co(en)_3^{3+}$ [6] and has been found to occur in a crystal structure.[15] There is, however, considerable difference in the distance between the oxygen atoms of PO_4^- and NO_3^-. These distances as well as those between various protons of tris-ethylenediamine complexes are summarized in Table II.[8,11,15,24-26] Those distances which are longer than 3.0 Å are not listed. We have included only those pairs of N-H's which point in approximately the same direction so that two simultaneous hydrogen bonds to one anion could be formed. There are other short distances which were omitted because the N-H's point in quite different directions.

From the data in Table II we notice that the oxygen-oxygen distances of NO_3^-, OAc^-, and OBz^- are similar so that we might expect that they will produce similar conformational behavior. We notice that the pairs which provide the best match of distances are 1HA-3HA, from two δ rings, and 2HB-6HB, involving a $\delta\lambda$ ring pair. These $\delta\lambda$ interactions are further favored by the fact that the N-H bonds are inclined toward each other, so that the most favorable interaction will occur with oxygens somewhat closer together than the H-H distance. We conclude that the simultaneous formation of two hydrogen bonds by NO_3^-, OAc^-, and OBz^- at low temperatures will favor the $\delta\delta\lambda$ conformation. We note that Gollogy, *et al.*,[22] calculated the difference in energy between $\delta\delta\delta$ and $\delta\delta\lambda$ to be small and that Sudmeier and Blackmer,[3] from an analysis of the J coupling of $Rh(en)_3^{3+}$, con-

Table I. Thermodynamic and Ring Pucker Parameters for the Ring Conformational Equilibria of $Ni(en)_3{}^{2+}$

Solvent	Anion	Temp range, °C	$10^3(K_b - K_a)$	ΔH, kcal/mol	ΔS, eu	δ_{eq},[b] ppm	δ_{ax},[b] ppm	θ_{eq},[b] deg	θ_{ax},[b] deg	$\Delta G(25°)$, kcal/mol
D_2O	Chloride[a]	+0.2 to +68.2	13.9 ± 0.1	7.6 ± 0.1	18.2 ± 0.3	−109.6 ± 0.4	−63.2 ± 0.4	232.8 ± 0.1	117.3 ± 0.1	2.2 ± 0.2
D_2O	Acetate	+4.7 to +25.2	26.7 ± 0.6	−1.74 ± 0.03	−8.05 ± 0.06	−135 ± 2	−46 ± 2	227.8 ± 0.3	113.0 ± 0.5	0.66 ± 0.05
		+30.7 to +69.8	12.9 ± 0.1	24.0 ± 0.7	64 ± 2	−111.5 ± 0.4	−68.3 ± 0.4	232.4 ± 0.1	118.5 ± 0.1	4.9 ± 1.3
D_2O	Benzoate	+9.9 to +27.7[c]	13.4 ± 0.2	−1.67 ± 0.08	−11.2 ± 0.3	−112.0 ± 0.8	−67.1 ± 0.8	232.3 ± 0.2	118.2 ± 0.2	1.7 ± 0.2
		+27.7 to +69.2	12.5 ± 0.2	11.0 ± 0.2	27.7 ± 0.5	−112.2 ± 0.7	−70.3 ± 0.7	232.3 ± 0.2	119.0 ± 0.2	2.7 ± 0.4
D_2O	Nitrate	−0.4 to +25.4	57.7 ± 0.6	−0.312 ± 0.004	−1.82 ± 0.01	−186 ± 2	−8 ± 2	218.1 ± 0.4	99.4 ± 1.2	0.23 ± 0.01
		+31.2 to +65.8	10.7 ± 0.1	18.1 ± 0.7	49 ± 2	−107.2 ± 0.3	−71.3 ± 0.3	233.3 ± 0.1	119.2 ± 0.1	3.6 ± 1.3
MeOD	Benzoate	−31.7 to −11.8[c]	31.4 ± 0.5	−2.20 ± 0.06	−14.4 ± 0.3	. . .	. . .	. . .	. . .	. . .
		−16.7 to +54.7	31.8 ± 0.3	2.50 ± 0.03	3.8 ± 0.1	−143.6 ± 1.0	−36.9 ± 1.0	226.2 ± 0.2	110.5 ± 0.3	1.2 ± 0.2
DMSO-d_6	Nitrate	+1.8 to +84.6	35.8 ± 0.06	1.17 ± 0.04	0.00 ± 0.08	−151 ± 2	−31 ± 2	224.8 ± 0.4	108.8 ± 0.7	1.17 ± 0.06
DMSO-d_6	Tetraphenylborate[a]	+20.1 to +88.3	30.0 ± 0.3	5.8 ± 0.1	11.8 ± 0.3	−136.8 ± 1.0	−36.8 ± 1.0	227.5 ± 0.2	110.6 ± 0.3	2.3 ± 0.2

[a] Data from ref 5. [b] At 25°. [c] Scatter of data in this temperature range produces parameters of low reliability.

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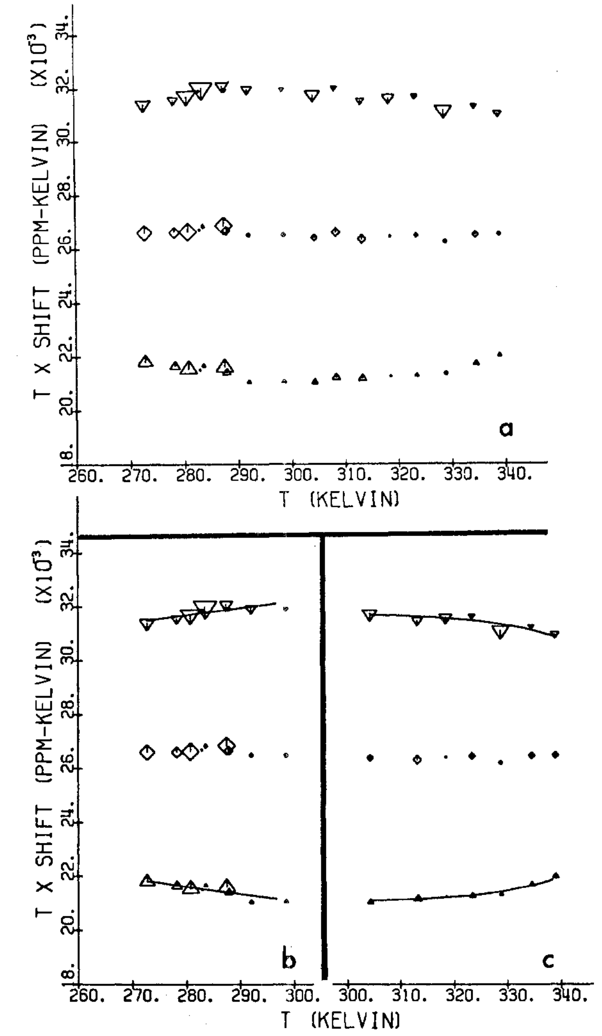

Figure 4. Temperature dependence of methylene proton contact shifts for tris(ethylenediamine)nickel(II) nitrate in water: (a) all data points; (b) low-temperature fit; (c) high-temperature fit. For each temperature the points designated with squares are not observed but are averages of the other two. The size of the symbols is proportional to the standard deviation of the data.

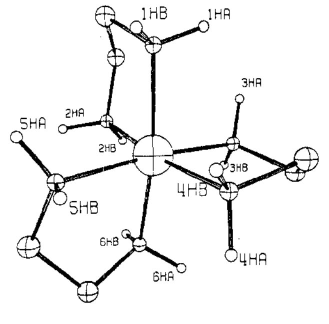

Figure 5. View of a tris(ethylenediamine)metal cation exhibiting $\Lambda\delta\delta\lambda$ conformation from data in ref 8.

cluded that the $\delta\delta\lambda$ form was the most abundant in solution. The postulated formation of multiple hydrogen bonds by anions such as NO_3^- is supported by the X-ray structure of $Co(en)_3(NO_3)_3$.[14] There the nitrate ions form multiple hydrogen bonds of both the 1HA-3HA and 1HB-4HB types, with the latter type forming somewhat stronger overall interactions than the former. Since the H-H distances in the $\delta\lambda$ pairs fall between the 1HA-3HA and 1HB-4HB distances, multiple hydrogen bonds of significant strength between

Table II. Various Internuclear Distances in $M(en)_3$ Complexes and Anions

Identity[a]	Conformn	Dist, Å	Remarks	Ref
1HA-3HA[a]	$\delta\delta$	2.26	Λ-Cr(en)$_3^{3+}$	8
1HB-4HB[a]	$\delta\delta$	2.66	Λ-Cr(en)$_3^{3+}$	8
1HB-5HB[b]	$\lambda\delta$	2.59	Λ-Cr(en)$_3^{3+}$	8
2HA-5HA[a]	$\delta\lambda$	2.56	Λ-Cr(en)$_3^{3+}$	8
2HB-6HB[a]	$\delta\lambda$	2.35	Λ-Cr(en)$_3^{3+}$	8
4HA-6HA[b]	$\lambda\delta$	2.41	Λ-Cr(en)$_3^{3+}$	8
1HA-3HA[a]	$\delta\delta$	2.36	Λ-Co(en)$_3^{3+}$	24
1HA-3HA[b]	$\lambda\lambda$	2.62	Λ-Co(en)$_3^{3+}$	24
Anion oxygen-oxygen distances				
PO_4^{3-}		2.50		24
HPO_4^{2-}		2.42		15
NO_3^-		2.20		11
OAc^-		2.23		25
OBz^-		2.23[c]		26

[a] $\Lambda(\delta\delta\lambda)$; see Figure 5. [b] $\Lambda(\lambda\lambda\delta)$; all rings are inverted with respect to Figure 5. [c] Obtained by considering an average between both *p*-bromo- and *p*-chlorobenzoic acid carbon-oxygen distances.

chelate rings should also be expected for the mixed conformers.

In order to explain our data, we propose the equilibria

$$\delta\delta\delta A \longleftrightarrow \delta\delta\lambda AA \quad \Delta H < 0 \quad \Delta S < 0 \tag{4}$$

$$\delta\delta\lambda AA \longleftrightarrow \delta\delta\lambda A \quad \Delta H > 0 \quad \Delta S > 0 \tag{5}$$

$$\delta\delta\delta A \longleftrightarrow \delta\delta\delta + A \quad \Delta H > 0 \quad \Delta S > 0 \tag{6}$$

$$\delta\delta\delta A \longleftrightarrow \delta\delta\lambda + A \quad \Delta H > 0 \quad \Delta S > 0 \tag{7}$$

$$\delta\delta\delta \longleftrightarrow \delta\delta\lambda \quad \Delta H > 0 \quad \Delta S > 0 \tag{8}$$

where AA indicates two hydrogen bonds to a single anion and A indicates a singly hydrogen bonded anion. Equation 4 thus represents a singly bonded anion forming a second hydrogen bond, accompanied by a $\delta \rightarrow \lambda$ inversion. This hydrogen-bond formation gives a negative ΔH and the loss of rotational freedom of the anion gives a negative ΔS. Equation 6 merely represents the breaking of the hydrogen bond between the cation and anion, without effect on ring conformation, while eq 5 represents the breaking of one of two hydrogen bonds again without effect on ring conformation. Equation 7 represents a dissociation of a hydrogen bond which does alter a ring conformation, while eq 8 is completely independent of the anion. Solvation has been neglected in all cases, but the solvent influence must be kept in mind since it may be more important in eq 8 than is the energy difference between the gas-phase δ and λ rings.[5] In eq 5-8 the positive ΔH's and ΔS's are caused by breaking hydrogen bonds to anions or, in the case of (8), to the solvent. Models also show that the dissociation of either solvent or anion upon change in ring conformation, which is proposed in eq 7 and 8, will occur becuase the equatorial amine protons in the λ conformation are not available for hydrogen bonding due to those steric interactions with the methylene protons of neighboring chelate rings which make the λ conformation less stable.[22,23] The models also show that this amine proton is accessible in the δ conformation.

We can also consider an equilibrium

$$\delta\delta\delta A \longleftrightarrow \delta\delta\lambda A \tag{9}$$

in which ring conformational change occurs without dissociation of an anion. However the large ΔH and the large variations between anions and solvents suggest that such an equilibrium is not the dominating influence.

Of the equilibria listed above our method is directly sensitive only to those which involve any change in the ring conformations, *i.e.*, (4), (7), and (8). However, as we shall see (5) and (6) have an important indirect influence on our results.

We will start our examination of the data with a limiting case. It seems likely that in methanol, a weak hydrogen-bonding solvent, at low temperature we would find (4) to be the predominant observable equilibrium. Unfortunately, the low-temperature (below $-20°$) results in methanol are so scattered that the values for ΔH and ΔS presented in Table I are of questionable reliability. Still the $-\ln K$ *vs.* $1/T$ plots do show a small negative ΔH and a small negative ΔS, as one would expect for eq 4. As the temperature is raised, equilibrium 5 will be driven to the right, eliminating equilibrium 4, so that the high-temperature values will be due to equilibria 7 and 8. Since methanol is less basic than OBz^-, most of the cations will remain hydrogen bonded to the OBz^- anions, so that equilibrium 7 will not be important. We attribute the small ΔH and ΔS values observed at high temperature to equilibrium 8, with the major contribution to these values due to dissociation of some weakly held solvent upon change of ring conformation.

Turning to the low-temperature data in H_2O we notice that for OBz^-, OAc^-, and NO_3^- the results in Table I are very similar to the low-temperature results for OBz^- in methanol. This indicates that equilibrium 4 is the important one at low temperature in H_2O, as expected. For all of these systems we notice large values of $K_b - K_a$, which indicate a high degree of ring pucker. This is expected from the model we have proposed, in that 2HB and 6HB in Figure 5 are favorably oriented to form simultaneous hydrogen bonds to two anion oxygens only when the rings are very puckered.

As the temperature of these systems is increased, a crossover from the low-temperature behavior to the high-temperature behavior occurs at about 30° in H_2O. This is in a temperature region where many kinds of anomalous behavior, thought to be due to H_2O structure changes, have been claimed.[27] This suggests that the change in the ring conformational behavior may be associated with a change in H_2O structure. Such a change in H_2O structure could perhaps favor the formation of multiple hydrogen bonds between the cation and anion, producing the behavior we observe at low temperature.

In the higher temperature regions in H_2O and for all anions studied we find low values of $K_b - K_a$ and large positive values for ΔH and ΔS. As is the case in MeOH, at higher temperature, equilibrium 5 would be driven to the right thus eliminating equilibrium 4. The marked anion dependence of ΔH and ΔS rules out equilibrium 8 as the dominating influence, leaving equilibrium 7 as the only observable one remaining. The small value for $K_b - K_a$ indicates a nearly flat ring which is favorable for hydrogen bonding to the anions and to H_2O.[5] The large positive values for ΔH indicate that several hydrogen bonds are broken during the process and the large values for ΔS indicate that several anions or solvent molecules gain translational degrees of freedom. These values are in accord with equilibrium 7 when we allow the dissociation of several anions and solvent molecules which are hydrogen bonded to the cation.

The ΔH and ΔS values at high temperature in H_2O show a correlation with the base strength of the anions. Thus the weakest base, Cl^-, shows the smallest ΔH and ΔS while the strongest base, OAc^-, produces the largest values. While the values for NO_3^- and OBz^- indicate that one of them is out of line, work with a series of carboxylate anions in which the structure is held constant and the anion base strength is varied[28] indicates that such correlation does hold. In order to account for this correlation, especially the increase in ΔS with base strength, it is necessary to invoke equilibrium 6. As the base strength increases, equilibrium 6 will shift to the left so that more anions will be hydrogen bonded to the cation. This would increase the proportion of molecules which can participate in equilibrium 7 as well as increase the number of anions hydrogen bonded to each cation. Then upon ring inversion more anions will be dissociated and a larger positive ΔS will result. Remembering that our data yield an average value for ΔH and ΔS, then the increasing base strength, by way of equilibrium 6, shifts the values of ΔH and ΔS from those expected for equilibrium 8 toward those expected for equilibrium 7.

For $Ni(en)_3(Ph_4B)_2$ in DMSO, little specific interaction between anion and cation is expected and the values observed have been attributed to solvation of the cation by DMSO.[5] When $Ni(en)_3(NO_3)_2$ is dissolved in DMSO, the NO_3^- ion has little affinity for the solvent and would be expected to cling closely to the cation. The very small value of ΔS indicates no dissociation of anion or solvent upon ring inversion, a condition which is favored by the aprotic nature of the solvent. The small positive ΔH would then be either due to the difference in energy of the δ and λ ring conformers or due to slight weakening of the hydrogen bonds upon ring inversion. These results are consistent with equilibrium 9.

A referee has pointed out that there is an interesting inverse relationship between the ratios of $K_b - K_a$ and the dielectric constant ϵ for the OBz^- anion in D_2O and MeOD, *i.e.*, $\epsilon_{D_2O}/\epsilon_{MeOD} = 77.9/32.6 = 2.38$ and $(K_b - K_a)_{MeOD}/(K_b - K_a)_{D_2O} = 31.4/13.4 = 2.34$, which is the expected result for a specific association. However for the NO_3^- salts there is a direct relationship, *i.e.*, $\epsilon_{D_2O}/\epsilon_{DMSO} = 77.9/49 = 1.59$ and $(K_b - K_a)_{D_2O}/(K_b - K_a)_{DMSO} = 57.7/35.8 = 1.61$, which must require some other explanation. Studies in other solvents would be interesting, but the fact that high concentrations of salt are necessary for the nmr experiment will make such studies difficult.

From the results presented here, it is apparent that the ring conformational equilibria of $Ni(en)_3^{2+}$ are dependent upon the type of anion as well as its strength as a base. In order to rationalize the data a number of hydrogen-bonding equilibria have been invoked. Hydrogen bonding of the cation to the anion or the solvent appears to be the dominant factor in determining ethylenediamine ring conformational equilibria.

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Registry No. $Ni(en)_3^{2+}$, 15390-99-5; $Ni(en)_3(acetate)_2$, 14837-12-8; $Ni(en)_3(OBz)_2$, 51806-34-9; $Ni(en)_3(NO_3)_2$, 14405-81-3.

Supplementary Material Available. Figures 1A–4A and Table IA, all showing the temperature dependence of methylene proton contact shifts for $Ni(en)_3^{2+}$ complexes in various solvents, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-2208.

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