(dipic)H$_2$O], 64440-67-1; H[VO(O$_2$)(dipic)H$_2$O], 64440-66-0; H$_2$O$_2$, 7722-84-1; III, 64475-65-6.

Supplementary Material Available: Table I giving elemental analyses of all complexes, Table II summarizing the vibrational spectra of complexes, and Tables III and IV giving rate constants of the first rapid stage and of the subsequent second and third stages for the reaction of trimeric [V(O)$_2$(dipic)]$_3$$^{3-}$ with H$_2$O$_2$, [H$^+$] = 1.0–0.1 M (5 pages). Ordering information is given on any current masthead page.

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Anion Dependence of Ring Conformational Equilibria of the Tris(ethylenediamine)nickel(II) Cation. 2. Effect of Anion Base Strength in Aqueous Solution

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The temperature dependence of the NMR contact shifts of [Ni(en)$_3$](RCO$_2$)$_2$ (R = Cl$_3$C, Cl$_2$HC, ClH$_2$C, and H) in water is interpreted in terms of the chelate ring conformational equilibria. As was found previously for acetate, benzoate, and nitrate, two separate equilibria are exhibited by these systems in the temperature range from 0 to 75 °C. For the high-temperature process a more precise correlation is observed in these new results between the base strength of the anion and the parameters for ring inversion. The large values of ΔH and ΔS for the high-temperature equilibrium are interpreted as the result of the breaking of hydrogen bonds and the dissociation of ion pairs. These observations and recent x-ray crystal results suggest that association of cation and anion plays an important role in ethylenediamine ring conformational behavior.

Introduction

The equilibrium that exists in solution between the δ and λ conformations in the five-membered chelate rings of tris-(ethylenediamine)metal complexes has been studied using the technique of NMR spectroscopy during the past decade.[2-4] An excellent review by Beattie[5] summarizes the methylene proton spectra of several [M(en)$_3$]$^{m+}$ complexes. In our studies of the dynamic NMR spectrum of the paramagnetic [Ni-(en)$_3$]$^{2+}$ complex we have found that solvents[6] and anions[7] can shift this equilibrium according to their ability to associate with or hydrogen bond to the cation. For example, at high temperature in aqueous solution the thermodynamic parameters for the δ ⇌ λ ring inversion observed for [Ni(en)$_3$]X$_2$ (X = acetate, benzoate, and nitrate) increase with the base strength of these anions.[7] The large values of ΔH and ΔS found for these systems suggest that association of cation and anion plays an important role in ethylenediamine ring conformational behavior. A subsequent x-ray crystal structure determination[8] of [Ni(en)$_3$](O$_2$C$_2$H$_3$)$_2$·2H$_2$O revealed the Λδδδ[9] configuration of the cation involved in several strong hydrogen bonds to acetate anions and solvate molecules.

While the three anions previously studied do differ in their base strength, their structural diversity precludes firmly ascribing the observed variation to a single parameter. In order to verify a correlation between anion base strength and the ring conformational equilibrium, we have extended our studies to include a series of [Ni(en)$_3$](RCOO)$_2$ compounds, where RCOO$^-$ is a carboxylate anion. These anions have a well-established trend in their base strength but no gross structural differences. We report here the results of this new study along with its comparison to our earlier work.

Experimental Section

Synthesis and Characterization of Compounds. [Ni(en)$_3$](O$_2$CH)$_2$, Tris(ethylenediamine)nickel(II) Formate. A saturated solution was prepared by adding 3.35 g (18 mmol) of nickel(II) formate dihydrate to approximately 90.0 mL of water at 75 °C. A 4-mL volume of 99% ethylenediamine (60 mmol) was slowly added with stirring, and the solution turned from light green to purple. Liquid volume was reduced to approximately 15 mL by warming on a vacuum roto evaporator, and the solution was then refrigerated at 10 °C for 24 h until a precipitate formed. This purple solid was collected and washed with ether; the approximate yield was 68%. This material is stable in aqueous solutions, but the solid is slightly hygroscopic and must be stored with a desiccant.

[Ni(en)$_3$](O$_2$C$_2$H$_2$Cl)$_2$, Tris(ethylenediamine)nickel(II) Monochloroacetate. A 14-g (150 mmol) amount of crystalline monochloroacetic acid was dissolved in 15 mL of water, and nickel(II) carbonate was added in small portions with warming until effervescence was complete. Approximately 7.50 g (63 mmol) was required. On cooling, a green solid formed which was redissolved with 15 mL of 95% ethanol. This solution was cooled while 15 mL of ethylenediamine (207 mmol) was slowly added, resulting in precipitation of the purple product which was washed with ethanol and dried for 24 h in a vacuum desiccator at 47 °C; the approximate yield was 86%. This material is very hygroscopic to the point of decomposition, and aqueous solutions are unstable, turning from purple to blue in 3 to 4 weeks.

Table I. Characterization Data for a Series of [Ni(en)$_3$]$^{2+}$ Carboxylate Complexes

	[Ni(en)$_3$]- (O$_2$CH)$_2$· 0.5H$_2$O	[Ni(en)$_3$]- (O$_2$C$_2$H$_2$- Cl)$_2$	[Ni(en)$_3$]- (O$_2$C$_2$H- Cl$_2$)$_2$· 0.5H$_2$O	[Ni(en)$_3$]- (O$_2$C$_2$- Cl$_3$)$_2$· 0.5H$_2$O
Equivalent Conductance in Water at 25 °C in cm^2 equiv^{-1} Ω^{-1}				
$N \times 10^4$				
10	129.2	132.4	131.1	106.7
Elemental Analysis				
% C calcd	28.42	28.20	23.69	20.96
exptl	28.76	28.68	23.52	20.74
% H calcd	8.05	6.62	5.43	4.40
exptl	8.02	6.92	5.10	4.21
% N calcd	24.86	19.73	16.58	14.67
exptl	24.68	19.35	15.96	13.88
% Cl calcd		16.65	27.97	37.13
exptl		16.28	28.20	35.97
Infrared Spectrum in cm^{-1}				
ν(C=O)	1567	1590	1650	1650
Electronic Transitions in μm^{-1} at 0.100 M				
$^3A_{2g} \rightarrow {}^3T_{2g}$	1.08	0.93	1.12	1.13
Spin forbidden	1.31		1.27	1.26
$^3A_{2g} \rightarrow {}^3T_{1g}$ (F)	1.83	1.80	1.83	1.84
$^3A_{2g} \rightarrow {}^3T_{1g}$ (P)	2.87	2.96	2.87	2.87
Water Solubility Near Saturation in mol L^{-1}				
	1.89	2.94	1.26	0.41

[Ni(en)$_3$](O$_2$C$_2$HCl$_2$)$_2$, Tris(ethylenediamine)nickel(II) Dichloroacetate. Nickel(II) carbonate was added in small portions with warming to 20 mL of 7.6 M dichloroacetic acid (152 mmol) until effervescence was complete. Approximately 7.84 g (66 mmol) was necessary. A green, glass-like solid formed on cooling which was redissolved with 20 mL of 95% ethanol and placed in an ice bath while 15 mL (218 mmol) of ethylenediamine was slowly added. A purple precipitate formed which was filtered and washed with cold ethanol. The product was dried in air at room temperature and the approximate yield was 90%. The material is stable as a solid and in aqueous solution.

[Ni(en)$_3$](O$_2$C$_2$Cl$_3$)$_2$, Tris(ethylenediamine)nickel(II) Trichloroacetate. The procedure was similar to the synthesis described above using 5.07 g (43 mmol) of nickel(II) carbonate in 20 mL of 5.0 M trichloroacetic acid (100 mmol) and resulted in a 52% yield on precipitation with 9.5 mL (141 mmol) of ethylenediamine. This material was air-dried and is stable in aqueous solution.

Characterization data for these four compounds are given in Table I. The UV-visible spectra of the [Ni(en)$_3$]$^{2+}$ complexes are in good agreement with the literature values for solid [Ni(en)$_3$](ClO$_4$)$_2$,[10] given as 1.12, 1.27, 1.83, and 2.90 μm^{-1}. Instruments used in the characterization of compounds included a Model RC16B2 conductance bridge manufactured by Industrial Instruments and fitted with a platinum cell having a constant θ =0.1113 cm^{-1}, a Beckman Model IR-10 infrared spectrophotometer, and Cary 14 and Beckman Acta CIII UV-visible spectrophotometers. The solubility measurements were carried out on the Acta CIII instrument using the band at 1.83 μm^{-1} (ϵ_{max} = 6.40 L mol^{-1} cm^{-1}). Elemental analyses were performed by Chemalytics, Inc., Tempe, Ariz.

The monochloroacetate compound shows an anomalously low frequency of 0.93 μm^{-1} for the Dq band, $^3A_{2g} \rightarrow {}^3T_{2g}$; within 24 h of preparing the aqueous solution this band shifts even lower to 0.81 μm^{-1}. This decomposition leads within a few weeks to a blue colored solution which is probably due to the formation of bis(ethylenediamine)nickel(II)L$_2$, where L is H$_2$O, O$_2$C$_2$H$_2$Cl$^-$, or an amine carboxylate condensation product. Over the same interval the equivalent conductance of this solution was found to increase approximately 31%. A brown decomposition product will form in a few days if solid [Ni(en)$_3$](O$_2$C$_2$H$_2$Cl)$_2$ in a closed container is left in a humid atmosphere. Similar behavior has been found for [Ni(en)$_3$](O$_2$C$_2$H$_3$)$_2$·2H$_2$O.[8] Both of these compounds are very hygroscopic and have a very large solubility in water.

NMR Measurements. The proton magnetic resonance spectra of the [Ni(en)$_3$]$^{2+}$ carboxylate complexes were obtained from saturated aqueous solutions prepared with 99.8% deuterium oxide (Wilmad Glass Co., Buena, N.J.). The molar concentrations of these solutions are given in Table I. NMR spectra were obtained using a Varian HA-100 spectrometer modified with external amplification and audio oscillation in order to generate sidebands of variable frequency up to 40 kHz. The spectrometer was equipped with a V6040 temperature controller, and the spectra were recorded sweeping the magnetic field at a resonating frequency of 100.0 MHz. The large residual HDO resonance of these solutions appeared as the solvent peak, and spectral calibration was achieved using its first downfield sideband. Isotropic shifts were measured in ppm downfield from the diamagnetic [Zn(en)$_3$]$^{2+}$. Temperature was measured by means of a Digitec Series 590 thermocouple permanently mounted in the probe[11] and precalibrated with Varian temperature calibration samples and charts prepared from the work of van Geet.[12] Errors in sample temperature were estimated at ± 0.1°C.

Nuclear magnetic resonance spectra of each of the [Ni(en)$_3$]-(RCOO)$_2$ salts freshly dissolved in D$_2$O show the characteristic doublet for the methylene protons of the tris complex but, in addition, show a smaller peak in the center of this doublet which is attributed to the bis complex[2] in which an ethylenediamine ligand has been replaced by water molecules or anions. This occurs to a much lesser extent when formate is the anion and can be eliminated in all the solutions by adding excess ethylenediamine to the dissolved salt. However, data collection was performed on solutions containing only the dissolved salts.
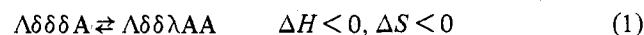
Results

For each compound three spectra were obtained at each temperature, and the average values for the recorded axial, σ_a, and equatorial, σ_b, methylene proton contact shifts are given in Table II. Values for ΔH, ΔS, and ΔG were obtained by a fit of the calculated shift-temperature product difference,[2] $K_b - K_a$, to the corresponding observed values as previously described.[6,7] The experimental values of $K_b - K_a$ and those calculated for the best fit are listed in Table II. The thermodynamic parameters obtained from this analysis at selected temperatures are presented in Table III for each of the compounds in this study.

As was observed with the anions acetate, benzoate and nitrate, two separate equilibria, one at high and one at low temperature, are found for each of the anions studied here. The data in Table II which were used for the high- and low-temperature fits are so designated, and the thermodynamic parameters in Table III are also separated into these two groups.

Discussion

The data in Table III are consistent with several earlier hypotheses[7] concerning the anion dependence of the ring conformational equilibrium of the [Ni(en)$_3$]$^{2+}$ cation in aqueous solution. For example, at lower temperatures ion pairing would be expected to be more prevalent and result in the formation of multiple hydrogen bonds between the carboxylate anions and a particular complex cation. This is indicated by the proposed[7] equilibrium 1, where AA indicates

$$\Lambda\delta\delta\delta A \rightleftarrows \Lambda\delta\delta\lambda AA \qquad \Delta H < 0, \Delta S < 0 \qquad (1)$$

two hydrogen bonds to a single anion and A indicates a singly hydrogen-bonded anion. Equilibrium 1 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. In agreement, the low-temperature results in Table III show negative ΔH and negative ΔS values for each of the anions studied. Also, there is very little divergence between the values which would probably be the case in adding one more hydrogen bond to an already formed ion pair.
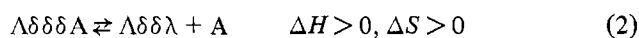
As the temperature of the system is increased, a crossover from the low-temperature behavior to the high-temperature behavior occurs at about 30 °C in H$_2$O. In the higher temperature regions for all anions studied, we find large positive values for ΔH and ΔS which are strikingly dependent

Table II. Chemical Shifts of Aqueous [Ni(en)₃]²⁺ Carboxylate Complexes as a Function of Temperature

Temp, °C	σ_a, ppm	σ_b, ppm	$K_b - K_a$, ppm K Calcd	$K_b - K_a$, ppm K Exptl	Deviation, %
		[Ni(en)₃](O₂CH)₂			
0.3	-72.3 (5)	-114.8 (11)	10875.63	11629.01	-6.93
3.5	-73.2 (2)	-114.0 (15)	10886.73	11301.70	-3.81
6.5	-74.4 (15)	-111.3 (8)	10896.32	10307.34	5.41
9.5ᵃ	-74.1 (22)	-112.8 (19)	10905.20	10942.79	-0.34
11.9ᵃ	-73.3 (15)	-111.5 (20)	10911.81	10885.48	0.24
15.6	-72.3 (21)	-108.7 (21)	10921.25	10524.94	3.63
20.5ᵃ	-71.1 (11)	-108.0 (7)	10932.52	10860.34	0.66
24.8ᵃ	-70.5 (12)	-107.4 (12)	10941.39	11000.61	-0.54
30.5	-69.0 (9)	-103.3 (1)	10951.82	10419.75	4.86
32.0	-68.3 (3)	-103.6 (2)	10487.09	10759.28	-2.60
37.8ᵇ	-68.8 (4)	-102.3 (5)	10423.83	10416.51	0.07
42.5	-67.8 (4)	-99.7 (6)	10350.67	10068.91	2.72
47.4ᵇ	-66.9 (4)	-99.0 (5)	10246.29	10271.69	-0.25
53.0ᵇ	-66.5 (6)	-97.4 (6)	10080.50	10054.87	0.25
58.8ᵇ	-64.5 (3)	-94.1 (2)	9839.84	9846.63	-0.07
65.0	-64.2 (4)	-93.6 (1)	9480.80	9935.52	-4.80
		[Ni(en)₃](O₂C₂H₂Cl)₂			
0.4ᵃ	-105.5 (8)	-135.9 (6)	8245.15	8309.34	-0.78
4.5ᵃ	-102.4 (3)	-132.0 (7)	8392.82	8202.05	2.27
7.1ᵃ	-100.9 (1)	-131.8 (8)	8479.20	8653.28	-2.05
9.9ᵃ	-99.5 (11)	-129.2 (5)	8566.40	8391.29	2.04
14.3ᵃ	-97.9 (10)	-128.4 (8)	8692.36	8760.04	-0.78
18.0ᵃ	-95.7 (5)	-126.4 (4)	8788.75	8954.90	-1.89
22.0ᵃ	-94.2 (2)	-124.0 (2)	8884.14	8801.67	0.93
25.9ᵃ	-93.2 (7)	-123.1 (2)	8969.24	8927.83	0.46
31.5ᵇ	-86.1 (1)	-119.8 (2)	10377.91	10277.36	0.97
37.5ᵇ	-85.1 (1)	-118.0 (7)	10345.75	10221.63	1.20
43.5ᵇ	-83.2 (7)	-116.7 (8)	10302.88	10611.57	-3.00
50.3ᵇ	-82.2 (2)	-114.3 (4)	10237.64	10373.68	-1.33
55.9ᵇ	-81.3 (3)	-111.6 (6)	10167.29	9977.77	1.86
60.6ᵇ	-80.9 (4)	-110.8 (5)	10094.13	9983.13	1.10
65.1ᵇ	-79.3 (3)	-108.9 (2)	10009.89	10012.20	-0.02
70.4ᵇ	-78.9 (1)	-107.9 (5)	9890.05	9951.61	-0.62
		[Ni(en)₃](O₂C₂HCl₂)₂			
-0.5ᵃ	-75.5 (7)	-114.2 (2)	10487.10	10545.82	-0.56
3.2ᵃ	-75.1 (14)	-112.6 (15)	10515.13	10372.51	1.36
6.2ᵃ	-73.6 (5)	-111.6 (5)	10536.12	10616.41	-0.76
9.2	-72.7 (14)	-111.1 (18)	10555.64	10859.46	-2.88
12.4	-72.3 (6)	-107.6 (15)	10575.03	10085.05	4.63
15.7	-72.1 (6)	-106.7 (11)	10593.59	9987.27	5.72
16.6ᵇ	-69.8 (7)	-112.7 (1)	12144.23	12437.52	-2.42
21.1ᵇ	-69.3 (4)	-110.0 (2)	12016.45	12009.81	0.06
25.3ᵇ	-68.1 (7)	-107.9 (19)	11886.32	11866.37	0.17
30.7ᵇ	-67.1 (8)	-105.0 (18)	11702.98	11513.18	1.62
35.8ᵇ	-66.3 (5)	-103.0 (7)	11512.70	11343.09	1.47
39.4ᵇ	-66.4 (4)	-102.0 (6)	11368.11	11156.46	1.86
45.3ᵇ	-65.3 (9)	-99.4 (7)	11112.43	10842.58	2.43
50.4ᵇ	-64.1 (8)	-98.5 (14)	10872.48	11114.58	-2.23
55.7ᵇ	-63.7 (8)	-97.1 (6)	10604.42	10974.05	-3.49
60.8ᵇ	-63.6 (6)	-95.0 (2)	10328.56	10497.71	-1.63
65.5ᵇ	-63.2 (4)	-92.7 (6)	10059.02	9977.98	0.80
71.0ᵇ	-62.8 (4)	-90.5 (5)	9725.36	9555.32	1.75
		[Ni(en)₃](O₂C₂Cl₃)₂			
30.6ᵇ	-69.1 (7)	-105.9 (13)	11208.88	11192.88	0.14
37.0ᵇ	-69.1 (9)	-105.1 (3)	11184.40	11175.01	0.08
42.2ᵇ	-68.1 (6)	-103.7 (9)	11163.34	11227.09	-0.57
47.8ᵇ	-67.0 (12)	-101.6 (5)	11139.45	11101.02	0.35
53.4	-67.1 (7)	-102.5 (22)	11114.36	11549.74	-3.92
58.9	-65.7 (5)	-101.1 (2)	11088.52	11766.52	-6.11
65.5	-64.6 (14)	-99.7 (1)	11055.96	11913.03	-7.75

ᵃ Indicates data point used in low-temperature fit. ᵇ Indicates data point used in high-temperature fit.

on the anion's base strength. This can be explained[7] by equilibrium 2, which allows the dissociation of several anions

$$\Lambda\delta\delta\delta A \rightleftharpoons \Lambda\delta\delta\lambda + A \qquad \Delta H > 0, \Delta S > 0 \qquad (2)$$

and solvent molecules which are hydrogen bonded to the cation. 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. The trends reflected in these values at high temperature are directly related to the increasing affinity of the anions for protons. This is well-illustrated by the plots in Figure 1 of ΔH and ΔS vs. the pK_a of the conjugate acids of the anions.

The conformational equilibrium of aqueous [Ni(en)₃]²⁺ in the presence of a variety of anions has been reported previously.[6,7] For example, both chloride and nitrate anions yield enthalpies and entropies of the magnitudes found for the carboxylate compounds listed in Table III. The ΔH for chloride is 7.6 (1) kcal mol⁻¹ and ΔS is 18.2 (3) eu over the entire temperature range from 0 to 70 °C. Nitrate shows larger values, $\Delta H = 18.1$ (7) kcal mol⁻¹ and $\Delta S = 49$ (2) eu, over the range from 30 to 70 °C. Even though it is difficult to place an exact measurement of the difference in the base strength between Cl⁻ and NO₃⁻, this tends to be in agreement with our conclusion that, by increasing the number and strength of the hydrogen bonds to amine protons, a better acceptor anion will yield higher ΔH and ΔS values for the ring conformational equilibrium. Nitrate exhibits another equilibrium for the low-temperature range in which ΔH and ΔS are negative but are much smaller ($\Delta H = -0.312$ (4) kcal mol⁻¹ and $\Delta S = -1.82$ (1) eu) than the low-temperature values given in Table III. Except for the very large $K_b - K_a = 57\,700$ (600) ppm K of nitrate at low temperature, these values (13 900 (100) and 10 700 (100) ppm K for Cl⁻ and NO₃⁻, respectively) in the high-temperature range are quite comparable to those in Table III.

The ring conformational equilibria that result in aqueous solutions of [Ni(en)₃](OBz)₂ and [Ni(en)₃](OAc)₂ have also been examined,[7] and a more direct comparison with the results presented in Table III can be made for these compounds. For each of these systems two equilibria are found over the temperature range from 0 to 70 °C. Below 30 °C both benzoate and acetate produce negative values for both ΔH and ΔS which are slightly smaller than the same parameters given for the carboxylate systems listed in Table III. Although scatter in the data for benzoate in this temperature range produced parameters of low reliability, ΔH was given as -1.67 (8) kcal mol⁻¹ with $\Delta S = -11.2$ (3) eu; for acetate ΔH is -1.74 (3) kcal mol⁻¹ and $\Delta S = -8.05$ (6) eu. These values are in relative agreement with our earlier discussion in which equilibrium 1 was invoked to explain the cation–anion interactions and conformer interconversions that could give rise to such negative parameters.
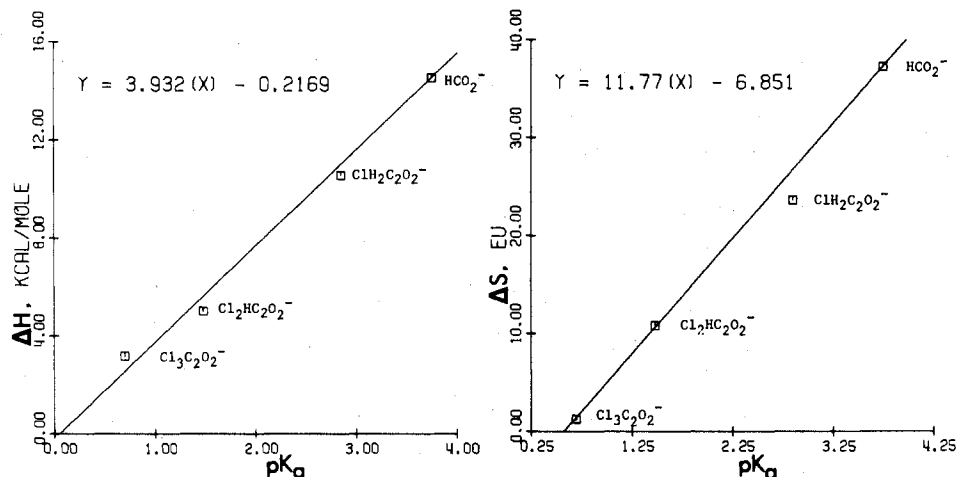
The $K_b - K_a$ value for benzoate below 30 °C is 13 400 (200) ppm K and is similar to values in Table III; the acetate $K_b - K_a$ at low temperature was found to be a rather high value of 26 700 (600) ppm K. Above 30 °C the $K_b - K_a$ value for the ring conformational equilibrium of the benzoate system is 12 500 (200) ppm K and that for the acetate system is 12 900 (100) ppm K, which are both in relative agreement with high-temperature values in Table III. The $K_b - K_a$ parameter indicates the extent of the ring puckering in the system under study[6] and would be expected to vary only over a small range. We have assumed[7] that one value of $K_b - K_a$ describes both the δ and λ ring conformations, although this is probably not true. Thus, the anomalously large $K_b - K_a$ values found at low temperature for nitrate and acetate may be the result of a rather large degree of ring puckering in [Ni(en)₃]²⁺ cations, in which all of the chelate rings have predominantly the same conformation.

Finally, the high-temperature thermodynamic parameters for the benzoate and acetate systems can be correlated with the data for the other carboxylate anions using the plots in Figure 1. The pK_a at 25 °C of the conjugate acid of benzoate

Table III. Thermodynamic Parameters for the Ring-Inversion Equilibrium in Aqueous $[Ni(en)_3]^{2+}$ Carboxylate Complexes[a]

Complex	ΔH, kcal mol^{-1}	ΔS, eu	$10^{-3}(K_b - K_a)$, ppm K	Error,[b] %	pK_a[c]
		High Temperature			
$[Ni(en)_3](O_2C_2Cl_3)_2$	3.2 (1)	1.2 (4)	11.42 (5)	0.34	0.70
$[Ni(en)_3](O_2C_2HCl_2)_2$	5.0 (1)	10.8 (3)	13.1 (3)	1.90	1.48
$[Ni(en)_3](O_2C_2H_2Cl)_2$	10.6 (4)	24 (1)	10.5 (2)	1.51	2.85
$[Ni(en)_3](O_2CH)_2$	14.55 (4)	37.3 (1)	10.60 (2)	0.18	3.75
		Low Temperature			
$[Ni(en)_3](O_2C_2HCl_2)_2$	-2.7 (2)	-17.4 (6)	10.9 (1)	0.95	1.48
$[Ni(en)_3](O_2C_2H_2Cl)_2$	-3.14 (5)	-15.9 (2)	10.2 (2)	1.56	2.85
$[Ni(en)_3](O_2CH)_2$	-3.0 (3)	-20 (1)	11.06 (6)	0.48	3.75

[a] Standard deviations (in parentheses) are in units of the last digit. [b] Root mean square of the deviation (%) in Table II. [c] For the conjuate acid of the anion.

Figure 1. Plots of ΔH and ΔS of the ring-inversion equilibrium vs. anion conjugate acid pK_a from data in Table III.

is 4.19 while that for acetate is 4.75. According to the equation for the line in Figure 1, the expected enthalpies at these pK_a values are 16.3 and 18.5 kcal mol^{-1}, respectively. The experimental values are 11.0 (2) kcal mol^{-1} for benzoate and 24.0 (7) kcal mol^{-1} for acetate. Similarly, the expected ΔS values are 42.5 eu for benzoate and 49.1 eu for acetate. The experimental values are 27.7 (5) eu for benzoate and 64 (2) eu for acetate. The experimental parameters for the benzoate system fall below the lines in each of the graphs in Figure 1 since both the experimental ΔH and the experimental ΔS are about 35% less than their calculated counterparts. The experimental ΔH and ΔS for the acetate system are both 30% greater than their calculated values and, if plotted, would fall above the respective extrapolated lines in Figure 1. These deviations appear to be systematic rather than random and remain unexplained. The low values for benzoate could perhaps result from a hydrophobic effect of the aromatic ring that prohibits optimum ion pairing in aqueous solutions, thereby reducing hydrogen-bond formation. Also, the structural difference of benzoate is probably large enough to allow its omission from the comparison of the other carboxylate anions. This is not true for acetate, however, and its deviations from the expected values are more difficult to rationalize. We can only suggest that acetate represents the upper limit at which equilibrium 2 may be invoked. For anions with a base strength like that of acetate or larger, equilibrium 3 may occur,

$$\Lambda\delta\delta\delta AA \rightleftarrows \Lambda\delta\delta\lambda + A \qquad \Delta H > 0, \Delta S > 0 \qquad (3)$$

in which the dissociation of a doubly hydrogen-bonded anion, AA, would result in higher enthalpy and entropy values than those expected from equilibrium 2. The x-ray crystal structure[8] of $[Ni(en)_3](OAC)_2 \cdot 2H_2O$ supports this rationale. In the solid state we have found both acetate anions doubly hydrogen

bonded to amine protons of the cation in the $\Lambda\delta\delta\delta$ configuration.

The correlation reported here between the thermodynamic parameters which characterize the ring conformational equilibrium of $[M(en)_3]^{m+}$ complexes and the base strength of the counterion supports our contention[6,7] that the ring conformational equilibrium of such complexes is dominated by the effects of hydrogen bonding of the cation to anions and to the solvent. It appears that such effects must be considered when studying the conformations of ethylenediamine rings.

References and Notes

(1) This paper is abstracted from a dissertation submitted to the Graduate Division of the University of Hawaii by J.T.H. in partial fulfillment of the requirements for the Doctor of Philosophy Degree in Chemistry.
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(9) There are eight isomers: Λδδδ, Λδδλ, Λδλλ, Λλλλ, Δλλλ, Δλλδ, Δλδδ, and Δδδδ. Absolute configuration about the metal has been designated Λ or Δ where the view down the threefold axis of the complex forms a left-handed or right-handed propeller, respectively. In the Λ configuration, the δ ring conformation is achieved when the carbon–carbon bond is nearly parallel to the threefold axis, and the λ ring conformation is assigned where this bond forms an oblique angle with the C_3 axis. Due to identical conformational stabilities of their mirror image set, the discussion has been limited to only the first set of four conformers in the above list.
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