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Empirical Force Field Calculations of Strain-Energy Contributions to the Thermodynamics of Complex Formation. 3. Chelate Effect in Complexes of Polyamines

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Empirical force field calculations are used to show that the steady decrease in enthalpy change on complex formation per nitrogen donor atom in complexes of polyamine ligands $H(NHCH_2CH_2)_xNH_2$, with Ni^{II} as x increases from 1 (en) to 4 (tetren), is due to cumulative ring strain. At the same time, this effect is partly offset by the increase in Ni–N bond strength in the absence of strain effects as the nitrogen donor changes from primary to secondary to tertiary. The opposing effects of cumulative ring strain and increasing bond strength of secondary relative to primary nitrogen donors coordinated to Ni^{II} produce a net decrease in ΔH on complex formation that almost exactly matches a term in ΔS present in the free energies of formation of the unidentate ammine complexes. This matching of terms makes analysis of the chelate effect in these polyamines appear much simpler than when the separate enthalpy and entropy contributions are examined.

Introduction

In the first two papers in this series[1,2] the difference in stability between analogous complexes of Ni^{II} containing on the one hand five-membered and on the other six-membered chelate rings formed with polyamine ligands was examined by means of semiempirical force field calculations. The program used for these calculations is that used by Snow,[3] and our modifications to it have also been described.[1,2] The program minimizes the conformational potential energy, U, of the molecule, taking into consideration contributions from bond-stretching, angle-bending, nonbonded, and torsional interactions. The necessary force constants have been tabulated in our first two papers.[1] The differences in stability between the five- and six-membered ring analogues is almost entirely an enthalpy effect,[4] which has been attributed to greater steric strain in the six-membered ring.[5,6] If it is assumed that the strain is an intramolecular phenomenon, so that solvent effects are not important, direct comparison should be possible of the difference in strain energy between the five- and six-membered ring analogues with the difference in their enthalpy changes on complex formation, ΔH, even though these have been measured in aqueous solution.[4] The conformational potential energy, U, must also be calculated for the free ligands, since these will not be the same and must contribute to the overall difference in ΔH. In Table I, only the difference in U for ethylenediamine (en) and 1,3-diaminopropane (pn) was calculated (0.37 kcal mol^{-1}),[7] and it was assumed that for other polyamine ligands, the effect of the addition of a methylene group to an ethylene bridge would also be to increase U by 0.37 kcal mol^{-1}. The comparison of the difference in ΔU and in ΔH for the five- and six-membered ring analogues is seen in Table I. The excellent agreement observed is highly encouraging, because Table I was regarded as a test of the usefulness of the type of calculations attempted here.

Table I. The Strain Energies, U, of Pairs of Otherwise Analogous Ni^{II} Complexes of Polyamines[a]

complex	U, kcal mol^{-1}	$-\Delta U_{5,6}$, kcal mol^{-1}	ΔH,[b] kcal mol^{-1}	$-\Delta(\Delta H)_{5,6}$, kcal mol^{-1}
$[Ni(en)(H_2O)_4]^{2+}$	1.14	1.53	−9.0	1.2
$[Ni(pn)(H_2O)_4]^{2+}$	3.04		−7.8	
$[Ni(en)_2(H_2O)_2]^{2+}$	3.35	3.07	−18.3	3.3
$[Ni(pn)_2(H_2O)_2]^{2+}$	7.16		−15.0	
$[Ni(en)_3]^{2+}$	4.57	7.44	−28.0	6.7
$[Ni(pn)_3]^{2+}$	13.12		−21.3	
$[Ni(dien)(H_2O)_3]^{2+}$	6.08	1.46	−11.9	1.3
$[Ni(dptn)(H_2O)_3]^{2+}$	8.28		−10.6	
$[Ni(dien)_2]^{2+}$	11.87	7.97	−25.3	7.7
$[Ni(dptn)_2]^{2+}$	21.32		−17.6	

[a] The polyamines are those in which the first member of the pair has all five-membered and the second member all six-membered chelate rings. The difference in U for each pair, $\Delta U_{5,6}$, is shown in the second column, corrected as described in the text for the extra strain induced in the free ligands by the presence of an extra methylene group in those forming six-membered rings. 0.37 kcal mol^{-1} is subtracted from U for the complex for each such extra methylene group. In the third column is shown ΔH for the formation of the complex in aqueous solution. The difference in ΔH for each pair must then be compared with $\Delta U_{5,6}$. [b] Reference 4.

In an examination of the chelate effect in complexes of polyamines, it had previously been noted[8] that the stability constants of the complexes of polyamines forming five-membered rings could be very simply related to the stability constants of the analogous ammonia complexes by eq 1. In

$$\log K_1(\text{polyamine}) = 1.152n \log K_1(NH_3) - \left(\sum_{i=1}^{n-1} i\right)\lambda + (n-1)\log 55.5 \quad (1)$$

eq 1, n is the number of nitrogen donor atoms, and the factor of 1.152, which is $pK_a(CH_3NH_2)/pK_a(NH_3)$, accounts for the inductive effect of the ethylene bridges. The $(n-1)$ log 55.5 term corrects for the asymmetry of the standard reference state.[9] The term in λ, where λ is simply $\log K - \log K_{n+1}$, accounts for the steady decrease in $\log K_n(NH_3)$ as n increases. The term $\log \beta_n(NH_3)$ could just as well have been used in

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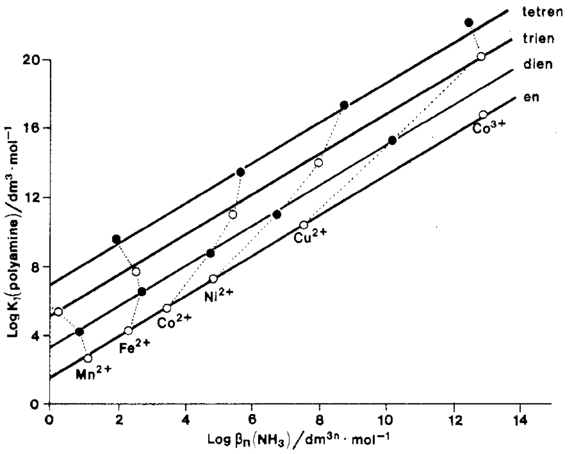

Figure 1. Plot of log K_1(polyamine) vs. log $\beta_n(NH_3)$ for complexes of various metal ions with n-dentate polyamine ligands forming five-membered rings on complex formation. The lines drawn have the slopes of 1.152 and intercepts of $(n - 1)$ log 55.5 expected from eq 1 in the text. Dotted lines connect points for the same metal ion with different polyamines.

the place of n log $K_1(NH_3)$ in eq 1, dropping the term in λ, but expression of eq 1 in the form shown is more convenient for the following discussion. In Figure 1 eq 1 is plotted to show graphically how well it relates log K_1(polyamine) to log β_n-(NH_3). The lines drawn have the expected intercepts of $(n - 1)$ log 55.5 and have slopes of 1.152. For Mn^{II} and Fe^{II}, λ has been set at 0.5, which is the value found for other M^{II} ions.

The connection between eq 1 and calculations of U for polyamine complexes is that, whereas the latter calculations show that very large increases in U can occur on complex formation with polyamines (more than 10 kcal mol^{-1}), no specific allowance for this is made in eq 1. An indication of where eq 1 makes allowance for this strain energy can be found by looking at the enthalpy changes produced by the formation of the complexes involved. For the ammonia complexes, it is found that ΔH_n for the addition of successively more ammonias to the metal ion is very nearly constant[4] and that, as would be expected from its interpretation as a statistical effect,[10] the steady decrease in log K_n with increasing n is due to an unfavorable entropy contribution. On the other hand, this unfavorable contribution to log K_1(polyamine) with increasing number of chelate rings is entirely an enthalpy effect.[4] This suggests strongly that the term in λ in eq 1 does not have the same significance for the polyamines as it does for the ammonia complexes. It is reasonable that no unfavorable entropy contribution from the term in λ should occur for the polyamines. In the ammonia complexes it relates to the decreasing probability of separate ammonia molecules attaching themselves to the metal ion as successively more are attached, but the polyamine is a single particle, and no such statistical effect is observed. It is felt that it is the term in λ in eq 1 that is accommodating the increase in the change in U on complex formation as successively more chelate rings are added to the polyamine complex. For a test of this hypothesis, U has been calculated for the Ni^{II} complexes, and also for the free ligands, in the series of polyamines en, dien, trien, tetren, and penten (abbreviations as in Table V), and also U for the hexaaquo ion $[Ni(H_2O)_6]^{2+}$ has been calculated so that ΔU for the reaction could be calculated:

$$\begin{array}{ccccc} M & + & L & \xrightarrow{\Delta U} & ML \\ U_M & & U_L & & U_{ML} \end{array}$$

In order to translate eq 1 entirely into enthalpy terms, the $(n - 1)$ log 55.5 term should fall away, since it is an entropy contribution. The term in λ might also have been expected to fall away, but as seen from this discussion it persists, although now with a different significance. Finally, the inductive effects of the ethylene bridges must in some way be allowed for as was done by the introduction of the factor of 1.152 into eq 1. This factor was estimated[8] from linear free energy relationships (LFER) of log β_n(amine) for various metal ions, where the amines were unidentate, e.g., anilines, pyridines, and ammonia, vs. ligand pK_a. A simple factor of pK_a-(CH_3NH_2)/p$K_a(NH_3)$ could be used, because the LFER pass very close to the origin of the diagram. From past experience with linear enthalpy relationships (LER)[11] we note that these do not tend to pass through the origin of the diagram, so that a simple factor of $\Delta H(CH_3NH_2^+)/\Delta H(NH_4^+)$ cannot be used, but rather an LER must be completely established. We have determined stability constants and enthalpy changes on complex formation with Ni^{II} and combined them with data already in the literature in order to construct the required LER. The reason ΔH for the formation of the methylamine complexes themselves cannot be used directly is that the free methyl group produces a large steric destabilization. This makes comparison with the polyamine, where this destabilization is much smaller, inappropriate.[8] At the same time it renders the complexes of methylamine so unstable to hydrolysis that, except in rare cases such as Ag^I, a calorimetric study of them would be impossible.

In this study, then, the aims are to see whether an equation of the same form as eq 1 can be used to correlate enthalpy changes on complex formation for polyamine complexes and if the decrease in ΔH per nitrogen donor atom as more rings are added can be related to cumulative steric strain.

Experimental Section

Formation Constants and Calorimetry. Materials. Stock solutions of $Ni(NO_3)_2$ were made up from Merck "pro analysi" grade $Ni(NO_3)_2 \cdot 6H_2O$ and were analyzed by titration against a standard solution of EDTA.[12] Stock solutions of HNO_3 were standardized against freshly recrystallized borax. The ligands used were aniline (AN), 4-(dimethylamino)pyridine (DMAP), and 3-cyanopyridine (CN-py). AR grade AN was purchased from BDH and was purified by distillation from zinc dust under reduced pressure. DMAP was obtained from Merck and used without further purification. CN-py (Merck) was purified by zone refining under nitrogen. This was done because it is not sufficiently basic for standardization with acid. Other ligand stock solutions were standardized by titration with standard HNO_3.

Potentiometric Titration (DMAP and AN). All measurements were made at 298.15 ± 0.05 K. The ionic strength was adjusted to 0.1 M with AR grade KNO_3 purchased from Hopkins and Williams or with the nitrate salt of the protonated ligand. The pK_a's of the ligands, and their formation constants with Ni^{II}, were determined with a Radiometer type G202B glass electrode, together with the reference electrode and titration cell described previously.[13] Values of the pK_a were calculated from the potentiometric data by using the MINIQUAD program, and values for the stability constants with Ni^{II} were calculated by using LETAGROP ETITR.[15] Corrections were made for other reactions occurring in the experiments, i.e., hydrolysis of Ni^{II}, by using the stability constants shown in Table II. Also shown in Table II are the values of log K determined in this study.

Spectrophotometric Studies (CN-py). Attempts to measure stability constants for the Ni^{II}CN-py system potentiometrically were ruled out by the low basicity (pK_a = 1.64[16]) of the ligand. Spectrophotometric measurements were made on a series of solutions with total Ni^{II} concentrations of 0.0333 M and a total CN-py concentration varying from 0 to 0.4 M at 385 and 365 nm. A Zeiss M4 QIII spectrophotometer was used with 5-cm quartz cells, thermostated to 25 ± 0.1 °C. All the species involved were found to absorb in the region used for the study. Stability constants were calculated from the spectrophotometric data with the LETAGROP SPEFO program.[17] The data were consistent with the presence of the ML complex only, giving log K_1 = 1.23 ± 0.03.

Calorimetry. The enthalpy changes on complex formation were determined with the titration calorimeter described previously,[18] and enthalpy changes on complex formation, $\Delta H_f{}^\circ$, were also calculated

Table II. Thermodynamic Functions for Protonation and Complex Formation with Ni^{II} of Various Amine Ligands[a]

cation	ligand	complex	log β (lit.)	log β (lit.)	$\Delta G°$, kcal mol^{-1}	$\Delta H°$, kcal mol^{-1}	$\Delta S°$, dig^{-1} mol^{-1}	$\Delta H°$, kcal mol^{-1}
H^+	aniline	HL	4.54 ± 0.02	4.601[b,c]	−6.19 ± 0.03	−7.24	−3.6	−7.31[c]
H^+	4-(dimethylamino)pyridine	HL	9.55 ± 0.02	9.57[b,d]	−13.03	−11.4 ± 0.8	5.4	−10.8[d,e]
		H_2L	10.5 ± 0.4					
H^+	3-cyanopyridine	HL		1.64[f]				−1.0[f]
H^+	OH^-	HL		13.78[g]				−13.49[g]
Ni^{2+}	aniline	ML	1.6 ± 0.4		−2.2 ± 0.5	+0.1 ± 0.6	7.5 ± 2	
Ni^{2+}	4-(dimethylamino)pyridine	ML	2.70 ± 0.02		−3.68 ± 0.03	−6.0 ± 0.7	−8 ± 2	
Ni^{2+}	3-cyanopyridine	ML	1.23 ± 0.03		−1.68 ± 0.04	−1.1 ± 0.1	2 ± 0.2	
Ni^{2+}	OH^-	ML		4.14[b,h]				1.20[b,h]

[a] At 25 °C and in 0.1 M KNO_3 as determined in this work, together with literature values for comparison. Also shown are thermodynamic functions, e.g., hydrolysis of Ni^{2+}, taken into account during the course of our experiment. [b] $\mu = 0$. [c] Reference 4. [d] Reference 20. [e] Reference 2. [f] Reference 16. [g] Reference 21. [h] Reference 22.

Table III. Final Energy Terms (kcal mol^{-1}) from the Energy Minimizations of the Free Ligands and Ni^{II} Complexes of the Polyamines en through pn and the Aquo Ion $[Ni(H_2O)_6]^{2+}$

complex or ligand	bond length deformns	nonbonded interactions	valence angle deformns	torsional strain	total strain, *U*
en	0.07	1.40	0.14	0.01	1.62
dien	0.17	2.62	0.32	0.02	3.13
trien	0.28	3.84	0.49	0.04	4.64
tetren	0.37	5.03	0.66	0.05	6.10
penten	1.31	9.54	3.45	1.76	16.07
$[Ni(en)(H_2O)_4]^{2+}$	0.20	−0.48	0.71	0.71	1.14
$[Ni(dien)(H_2O)_3]^{2+}$	0.36	0.54	3.11	2.07	6.08
$[Ni(trien)(H_2O)_2]^{2+}$	0.46	1.05	3.54	4.39	9.44
$[Ni(tetren)(H_2O)]^{2+}$	0.61	2.43	4.56	8.46	16.07
$[Ni(penten)]^{2+}$	1.28	6.26	9.68	10.75	27.98
$[Ni(H_2O)_6]^{2+}$	0.18	−1.32	0.05	0.0	−1.09
$[Ni(en)_2(H_2O)_2]^{2+}$	0.19	0.25	1.46	1.46	3.35
$[Ni(en)_3]^{2+}$	0.18	0.32	1.87	2.20	4.57
$[Ni(dien)_2]^{2+}$	0.74	1.49	5.42	4.21	11.87

from the calorimetric data and known stability constants by using the LETAGROP KALLE program.[19] In the same way as for the potentiometric measurements, corrections were made, for example, for hydrolysis of Ni^{2+} by using the enthalpy changes listed in Table II.

Force Field Calculations. The energy minimization procedure and details of the force field, and of the computer program, have previously been described.[2] All force constants used in the present calculations are the same as those tabulated previously.[1,2] It is best to use trial coordinates from the actual crystal structures, as this will tend to minimize the chances of the program finding false energy minima. Where the Ni^{II} structures were not available, coordinates from the Co^{III} structures have been used. Coordinates for $[Ni(en)(H_2O)_4]^{2+}$ were those taken from the structure of $[Ni(en)(H_2O)_4](NO_3)_2$.[23] For $[Ni(dien)(H_2O)_3]^{2+}$ trial coordinates were generated by disregarding one dien ligand in the structure[6] of $[Ni(dien)_2](ClO_4)_2$ and replacing it with three water molecules. Coordinates for $[Ni(trien)(H_2O)_2]^{2+}$ were obtained from the structure[24] of L-β_2-(*R*,*R*,*S*)-[Co(trien)(*S*-Pro)]$^{2+}$, the L-proline (*S*-Pro) group being disregarded and replaced with two water molecules. Coordinates for $[Co(tetren)Cl]^{2+}$ were used for $[Ni(tetren)(H_2O)]^{2+}$, and those from $[Co(penten)]^{2+}$ [25] were used for $[Ni(penten)]^{2+}$.

For the free ligands, the structure of en is known.[26] The structures of the other polyamines dien through tetren were generated from this structure by adding the required number of methylene and amine groups so as to preserve the linear *n*-alkane type of structure found for en[26] and pn.[27] The free ligand penten presents rather more of a problem, and the best that we could do in this instance was to take the coordinates from the crystal structure of dirubidium dihydrogen ethylenediaminetetraacetate dihydrate.[28] The oxygens from the carboxylate groups were disregarded, and the SHELL-X[29] program was used to convert the carboxylate carbon into a methylene group by the addition of two hydrogens and the addition subsequently of an amine group to each such methylene group, including the lone electron pairs on the nitrogen atoms. Disregard of the rubidium atoms and the crystal waters left the trial coordinates for the free penten ligand. Coordinates for $[Ni(H_2O)_6]^{2+}$ were available directly from the reported[30] structure of $[Ni(H_2O)_6](ClO_4)_2$. In all cases where hydrogen positions were not reported, these coordinates were generated by using SHELL-X.[29] The values of *U* calculated for all these free ligands and Ni^{II} complexes are shown in Table III.

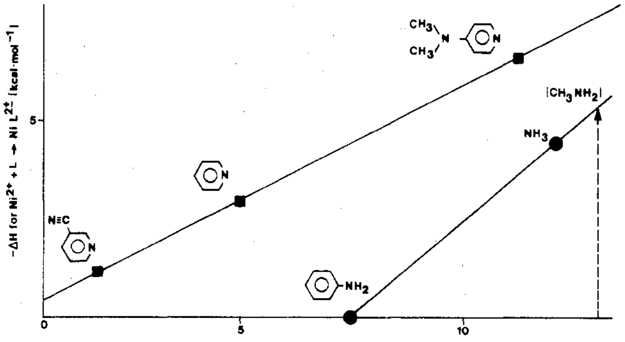

Figure 2. Linear enthalpy relationship for the enthalpy change on complex formation of Ni^{II} with a selection of unidentate amines vs. the enthalpy change on protonation of the same ligands. The dotted line indicates the expected position of the hypothetical strain-free Ni^{II} complex with methylamine.

Discussion

In Figure 2 is shown the plot of ΔH for the protonation of the unidentate amines studied vs. ΔH for the formation of the Ni^{II} complex. Although a single LFER is observed for these ligands with Ni^{II} and the proton, this is not found to be the case with the enthalpy change on complex formation. As found previously,[11] the behavior of free energy changes on complex formation presents a simpler picture of these reactions than that gained from the examination of the enthalpy and entropy contributions separately. If one can be so bold as to draw lines through three and two points, respectively, then it would appear that two separate LERs exist, one containing heterocyclic and the other nonheterocyclic nitrogen donors. This is not really surprising if it is considered that in the gas phase pyridine is a stronger base than ammonia,[31] as is also the case in solvents of low dielectric constant with neutral Lewis acids.[32] The solvation effects that are involved in making

Table IV. Values of ΔH(polyamine) (kcal mol^{-1}) Generated by Eq 2 for Ni^{2+} and Co^{2+} Polyamine Complexes Containing Five-Membered Rings, together with Experimental Values for Comparison

		en	dien	trien	tren[a]	tetren	penten
		Ni^{2+} Complexes					
$\Delta H_1°$	calcd	−8.9	−12.5	−15.5	−15.5	−17.9	−19.7
	obsd	−9.0	−11.9	−14.0	−15.2	−18.4	−19.7
$\Delta H_2°$	calcd	−17.91	−25.0				
	obsd	−18.3	−25.3				
$\Delta H_3°$	calcd	−26.7					
	obsd	−28.0					
		Co^{2+} Complexes					
$\Delta H_1°$	calcd	−7.1	−9.7	−11.8	−11.8	−13.2	−14.1
	obsd	−6.9	−8.2	−10.7	−10.7	−13.9	−14.8
$\Delta H_2°$	calcd	−14.2	−19.4				
	obsd	−14.0	−18.4				
$\Delta H_3°$	calcd	−21.2					
	obsd	−22.2					

[a] Tris(2-aminoethyl)amine.

Table V. Comparison of the Overall Change in Strain Energy on Complex Formation, ΔU[a]

complex	term in λ_H, kcal mol^{-1}	ΔU,[c] kcal mol^{-1}	term in λ_H[b]
$[Ni(en)(H_2O)_4]^{2+}$	0.59	0.61	0.61
$[Ni(dien)(H_2O)_3]^{2+}$	1.77	4.04	3.47
$[Ni(trien)(H_2O)_3]^{2+}$	3.54	5.89	6.94
$[Ni(tetren)(H_2O)]^{2+}$	5.90	11.06	11.00
$[Ni(penten)]^{2+}$	8.85	13.0	

[a] For Ni^{II} complexes with the series of polyamines $H(NHCH_2CH_2)_yNH_2$ ($y = 1$ = en, $y = 2$ = dien, $y = 3$ = trien, $y = 4$ = tetren) with the term in λ_H in eq 2 = 0.59 kcal mol^{-1}. [b] Corrected for secondary nitrogen atoms. [c] Overall change in strain energy.

pyridine a weaker base than ammonia in water must produce very large enthalpy and entropy effects that result in the split LER seen in Figure 2. Further studies of these unidentate amines have shown that such a split LER is obtained with all metal ions but that the split is much smaller with pairs of metal ions that are more similar in size (steric effects?) such as Ag^I and Hg^{II}. If the heterocyclic bases are excluded, an LER remains containing aniline and ammonia, from which it is seen that the inductive-effect factor (f) for Ni^{II} in eq 2 should have

$$\Delta H(\text{polyamine}) = nf\Delta H_1(\text{NH}_3) + \Big(\sum_{i=1}^{n-1} i\Big)\lambda_H \qquad (2)$$

a value of 1.16. From the discussion below it can be seen that the implicit assumption that ΔH for the protonation of alkylamines in aqueous solutions is a good measure of their basicity, because the proton is free of steric hindrance, is incorrect. Estimation of the enthalpy change on complex formation for the Ni^{II} methylamine complexes as in Figure 2 will, therefore, not yield strain-free values as hoped. Empirically, as shown in Table IV, a best-fit value of f in eq 2 is found to be higher at 1.19, and λ_H, the value of λ appropriate to enthalpy rather than free energies, is found to be 0.59 kcal mol^{-1} for both Ni^{II} and Co^{II}. Prediction of ΔH(polyamine) using eq 2 in Table IV is seen to be reasonable.

Although, as can be seen from the discussion below, eq 2 neglects an important change that takes place as further rings are added to the polyamine, the term in λ_H still represents a good measure of the decrease in ΔH per nitrogen atom as more rings are added to the polyamine complex. This decrease is being ascribed to strain effects, and as a starting point the magnitude of the term in λ_H in Table IV for each complex should be compared with the value of ΔU that has been calculated. The values of ΔU in Table V rise with increasing number of chelate rings in the same way as does the term λ_H but are much larger than this term. It is quite possible that this disagreement arises from theoretical difficulties involved in making comparisons such as those in Table IV, discussed below, or even from error in the force field. The standard deviation between ΔU and ΔH in Table I is only 0.5 kcal mol^{-1}, whereas the discrepancies in Table V are as much as 4 kcal mol^{-1}. The answer could lie in the fact that the difference in bond strength between primary, secondary, and tertiary amines is being neglected. This is not important in calculations for five- and six-membered rings, because the number of primary and secondary nitrogens in the two complexes being compared is always the same. When the chelate effect in free energy terms only is examined, the difference in basicity between primary, secondary, and tertiary nitrogens does not seem important, because the pK_a's in water[33] do not differ very much: $pK_a(CH_3NH_2) = 10.6$, $pK_a[(CH_3)_2NH] = 10.8$, $pK_a[(CH_3)_3N] = 9.9$. However, in the gas phase the order of basicity increases,[34] $CH_3NH_2 \ll (CH_3)_2NH \ll (CH_3)_3N$, and the relative decrease in basicity in water is ascribable to weaker solvation of the protonated relative to the nonprotonated amine as more methyl groups are added.[33] This weaker solvation is most reasonably interpreted in terms of steric repulsion between the methyl groups on the amine and the water of solvation around the proton. This is reflected in the steadily more unfavorable enthalpy change (ΔH) on protonation as more methyl groups are added (CH_3NH_2 −13.29, $(CH_3)_2NH$ −12.04, and $(CH_3)_3N$ −8.8 kcal mol^{-1}),[33] and bonds between the proton and water are broken by steric interaction with these methyl groups. At the same time, more water molecules are released on protonation of the amine, so that a steadily more favorable entropy contribution is observed as more methyl groups are added, and this partly counteracts the unfavorable enthalpy contribution, but not enough to allow observation of the true gas-phase basicity order for the methyl-substituted amines. Even methylamine must experience this steric effect to a certain degree, so that the inductive-effect parameter in Figure 2 will be underestimated.

In comparisons of ΔU with the term in λ_H for Ni^{II} complexes the fact is then being neglected that in the *absence* of steric effects secondary Ni–N bonds should be stronger than primary bonds. Support for this idea can be obtained from the compilations of Drago and Wayland[32] of E and C values for primary, secondary, and tertiary amines and for $[Cu(hfac)_2]$ (hfac = hexafluoroacetylacetonate anion). $[Cu(hfac)_2]$ is the Lewis acid which in Drago's compilation most closely resembles a metal ion such as Ni^{II} in the gas phase. With Drago's E and C equation, the heat of reaction (ΔH) of $[Cu(hfac)_2]$ with methylamines can be calculated as −12.64 (CH_3NH_2), −15.91 ($(CH_3)_2NH$), and −18.89 ($(CH_3)_3N$) kcal mol^{-1} in the *absence* of steric effects. (Because of steric effects[32] ΔH is in fact found to be less exothermic than that calculated for $(CH_3)_3N$.) It seems reasonable by comparison to adopt the correction in Table V that the Ni–N bond is 1.7 kcal mol^{-1} more exothermic in secondary, as compared to primary, nitrogen-donor atoms in the *absence* of steric effects. The calculations in Table V have already taken steric effects into account, and so ΔH in Table V should be made exothermic by 1.7 kcal mol^{-1} for each secondary nitrogen present. This would bring down the discrepancies for cases involving secondary nitrogen donors to the same level of deviation as that observed in Table I. The same improvement can be achieved by assuming that tertiary nitrogens form Ni–N bonds 2.1 kcal mol^{-1} more exothermic than primary nitrogens. However, this result depends heavily on the calculated value of U for the free ligand penten. The coordinates for this ligand were taken from those for EDTA, and it is quite possible that the value of U for penten is incorrect because it is in the wrong conformation. Drago's E and C parameters suggest that the

Table VI. ΔH Calculated As Described in the Text[a]

		$[Ni(en)(H_2O)_4]^{2+}$	$[Ni(dien)(H_2O)_3]^{2+}$	$[Ni(trien)(H_2O)_2]^{2+}$	$[Ni(tetren)(H_2O)]^{2+}$	$[Ni(en)_2(H_2O)_2]^{2+}$	$[Ni(dien)_2]^{2+}$	$[Ni(en)_3]^{2+}$
ΔH	calcd	−8.91	−11.94	−16.55	−17.84	−17.84	−25.26	−27.75
	obsd	−9.0	−11.9	−14.0	−18.3	−18.30	−25.3	−28.0

[a] This is done by summation of the appropriate number of contributions from primary and secondary Ni–N bonds and subtraction of ΔU calculated from Table III. This is compared with the observed ΔH for the formation of Ni^{II} complexes with polyamines.[4]

increases in passing from primary to secondary and from secondary to tertiary aliphatic amines should be approximately equal, so that a better value for the increase in exothermicity on passing from primary to tertiary would probably be closer to 3 kcal mol^{-1}. For the macrocyclic effect[35] the difference in exothermicity between Ni–N bonds with primary, and with secondary, nitrogens has important consequences in that a macrocycle such as cyclam (1,4,8,11-tetraazacyclotetradecane) has four secondary nitrogens, whereas its open-chain analogue 2,3,2-tet (1,4,8,11-tetraazaundecane) has two primary and two secondary nitrogens. This will be discussed more fully in a subsequent paper in this series.

In Table VI is calculated ΔH for the Ni^{II} complexes of linear polyamines en through tetren by according a $\Delta H = -4.8$ kcal mol^{-1} per primary nitrogen present, and, at 1.7 kcal mol^{-1} more exothermic, a $\Delta H = -6.5$ kcal mol^{-1} for each secondary nitrogen present. From this total is subtracted ΔU calculated for each complex, taken from Table III. The agreement between the calculated and observed ΔH values is, apart from the case of the trien complex, excellent. At this point it is concluded that eq 1 works because the entropy term in λ, present in the formation constants of the unidentate amines, is mimicked by the enthalpy term in λ_H in eq 2. The term in λ_H in eq 2 works reasonably well because it is matched by the difference in two opposing contributions. First, a decrease in exothermicity is produced by an increase in ΔU as the number of chelate rings is increased, and this is opposed by the favorable contribution produced by the steadily increasing number of secondary nitrogens as the number of rings increases. Equations 1 and 2 also work when tertiary nitrogens are introduced. The introduction of a tertiary nitrogen requires that two secondary nitrogens be replaced by one more exothermic tertiary and one less exothermic primary nitrogen. A failure of eq 1 is that it underestimates log β_y(polyamine) values for $y > 1$. For example, it might be expected that log β_2(en) = 1.152 log $\beta_4(NH_3)$ + 2 log 55.5, but this consistently underestimates log β_2(en) by an amount corresponding to about 2λ. The reason for this now becomes clear. For eq 1 to work the fortuitous match between the term in λ and that in λ_H is required. When the second en is added, however, λ_H *is not* cumulative, whereas in the unidentate ammines the term in λ *is* cumulative, so that the match between the terms in λ and λ_H is lost. The decrease in log K_y(polyamine) for $y > 1$ is also an entropy effect and can be understood as a statistical effect, as in the case of the unidentate amines.

One can see that the compensation for the opposing effects of ΔU and the greater exothermicity of the increasing number of secondary nitrogens present as the number of chelate rings increases, which allows eq 1 and 2 to work, is fortuitous, by considering six-membered rings. Here the values of ΔU are larger, producing the well-known destabilization of complexes of the polyamines produced by steric strain. The term in λ in eq 1 no longer matches the term in λ_H in eq 2, so that the stabilities are now lower than those predicted by eq 1. The mathematical form of the term in λ, however, is still appropriate for the reproduction of all these effects. All that is necessary is the addition of 0.7 to λ in eq 1 (in equations[8] for polyaminopolycarboxylates as well) for the reproduction of log K_1 for ligands containing all six-membered rings. In Table VII are reproduced calculated and observed log K_1 values for polyamines containing all six-membered rings for a variety of metal ions. In ligands containing both five- and six-membered rings the situation becomes more complex, as alternating five- and six-membered rings lead to strain release relative to systems containing five- or six-membered rings only.[2]

Table VII. Calculated and Observed Values of log K_1(L) for Complexes of Polyamines with Six-Membered Rings Only[a]

		Ni^{II}	Co^{II}	Cu^{II}	Zn^{II}
L = NH_3		2.71	2.10	4.1	2.18
L = pn	calcd	6.78	5.34	9.98	5.56
	obsd	6.31		9.75	
L = dptn	calcd	9.25	7.13	14.05	7.41
	obsd	9.19	7.01	14.2	7.92
L = trpn	calcd	10.51	7.69	16.91	8.07
	obsd	10.48	7.81	17.05	9.32

[a] With eq 1 and a value of λ of 1.2. Also shown are the values of log $K_1(NH_3)$ used for each metal ion shown in the table. All constants are from ref 4. Conditions are 25 °C and $\mu = 0.1$. Abbreviations: pn = 1,3-diaminopropane, dptn = iminobis(3-aminopropane), trpn = *N,N'*-bis(3-aminopropyl)trimethylenediamine.

One of the difficulties associated with the relation of calculated values of U directly to the thermodynamics is that they refer to hypothetical nonvibrating molecules at 0 K—zero-point and thermal energies have not been included.[36] Zero-point and thermal energies make large contributions to $\Delta H_f°$ at room temperature, and can, for example, override U in deciding which one of two conformers is stable at room temperature.[36] Thus, in the absence of evidence from Drago's[32] E and C equation and gas-phase basicities of methyl-substituted amines,[34] it would have been more difficult to ascribe the greater magnitude of ΔU as compared with the term in λ_H in Table V to greater exothermicity of secondary relative to primary Ni–N bonds. It could possibly have been ascribed to a systematic change in the thermal and zero-point energy contribution in passing from the complexes of en to tetren. The good agreement observed in Table I suggests, in addition, that these energies do not make a large contribution to the overall thermodynamics. Supporting evidence for the greater exothermicity of the Ni–N bond when N is secondary as compared with primary comes from the formation constants of the two ligands HEEN ($HOCH_2CH_2NHCH_2CH_2NH_2$) and OBEN ($NH_2CH_2CH_2OCH_2CH_2NH_2$) with Ni^{II}. It is found that the Ni^{II} complex of HEEN is more stable[4] than that of OBEN by 1.6 kcal mol^{-1}. It would not be expected that ΔU for the two complexes would be very different. Normally, creation of a secondary nitrogen means addition of an extra chelate ring, so that the increase in exothermicity is canceled by the increase in ΔU caused by the extra ring. In HEEN and OBEN, the number of rings is the same, but primary and secondary oxygens and nitrogens are exchanged. It would appear that the nitrogen benefits more than the oxygen on changing from primary to secondary in its bond formation with the Ni^{II}. Because the secondary Ni–O bond should also become more exothermic, the 1.6 kcal mol^{-1} must be regarded as the lower limit of the increased exothermicity of secondary relative to primary nitrogens in Ni–N bonds.

A further difficulty is that the calculations are for a single conformer only, and at room temperature the free ligands in particular must be a mixture of conformers. This effect might account for the poor agreement observed in Table VI for trien. The complex has been given the *R,R,S* conformation, whereas a higher value of *U* is found for the *S,S,S* conformation, which largely removes the discrepancy. The *S,S,S* conformation could exist for entropy reasons, rather than those of strain. Greater simplicity, however, will be observed in examining the free energies because of compensation effects. Increasing numbers of conformers of the free ligand will make the enthalpy change on complex formation more exothermic because there will be more high-energy forms of the free ligand present but at the same time will increase the configurational entropy of the free ligand, and so make the entropy change less favorable. The same argument applies in reverse to the metal complex formed. Thus we see that ΔH° for the formation of the [Ni(trien)] complex is less favorable than predicted in both Tables IV and VI, and yet the free-energy change appears "normal" in Figure 1.

In a recent paper,[37] it was very correctly pointed out that the thermodynamics of the chelate effect in the gas phase might not bear much resemblance to the chelate effect as observed in aqueous solution. It was estimated that in the gas phase the enthalpy of formation of CuL_2^{2+} was 3.7 kcal mol^{-1} more endothermic when L = en as compared with the case where L = pn. This was cited as demonstrating that the assumption that the M–N bonds in the two complexes are of essentially the same bond strength is erroneous. In fact, the difference in strain energy for the pair of analogous Ni^{II} complexes, which is not likely to be very different from the Cu^{II} case, is 3.1 kcal mol^{-1}. One must add the qualification that, once the correction for the difference in ΔU has been made, the bond strengths would appear to be very nearly identical. A further point is that the enthalpy of formation of $[Cd(CH_3NH_2)_4]^{2+}$ in the gas phase was estimated to be considerably more favorable than for $[Cd(en)_2]^{2+}$, once more being cited as evidence to show that the Cd–N bond strengths were not the same. It was stated[37] that models showed that the strain in $[Cd(en)_2]^{2+}$ was small. This conclusion could only have been reached if a carbon atom were used to represent the tetrahedral Cd^{2+} ion, for, with the longer Cd–N as compared to the C–N bond length, the strain becomes enormous.[8] This is seen to be true for $M(en)_2$ complexes of tetrahedral ions from the crystal structure[38] of $[Hg(en)_2]^{2+}$, where the N–M–N bond angle, for example, is 78° instead of the 109° expected for tetrahedral geometry. In square-planar Cu^{II} this angle[39] is distorted only to 84° instead of the expected 90°. Thus, the evidence cited[37] tends to support the idea that the M–N bonds are of the same strength, once account has been taken of differences in strain energies. A further point that has been raised in our work is that account must be taken of the difference in primary, secondary, and tertiary nitrogen donor atoms.

Equation 1 and its extension to formation constants of complexes of polyaminopolycarboxylates[8] have been used to estimate[8,41] log $K_1(NH_3)$ values for metal ions such as Fe^{3+} or Pb^{2+}, the ammine complexes of which are hydrolyzed in water. These estimated log $K_1(NH_3)$ values proved important in analyzing[40] formation constants in aqueous solution with an equation of the form of the *E* and *C* equation of Drago.[32] Since this paper has shown that the significance of λ in eq 1 is largely steric, the assumptions which were made as to how λ should be estimated[8,40] for complexes of metal ions for which log $K_1(NH_3)$ is unknown are likely to be in error to a certain extent. As will be discussed in a future paper, the way in which λ has so far been estimated has to be reconsidered. One must add, though, that fortunately our estimates of log $K_1(NH_3)$ for hydrolysis-prone ammine complexes are not very sensitive to the estimated value of λ, so that the conclusions[40] based on these estimates are not materially altered.

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Registry No. $[Ni(pn)(H_2O)_4]^{2+}$, 31082-54-9; $[Ni(en)_2(H_2O)_2]^{2+}$, 15554-67-3; $[Ni(pn)_2(H_2O)_2]^{2+}$, 46140-10-7; $[Ni(en)_3]^{2+}$, 15390-99-5; $[Ni(pn)_3]^{2+}$, 18347-71-2; $[Ni(dien)(H_2O)_3]^{2+}$, 15662-52-9; $[Ni(dptn)(H_2O)_3]^{2+}$, 54866-08-9; $[Ni(dien)_2]^{2+}$, 19358-75-9; $[Ni(dptn)_2]^{2+}$, 46933-28-2; $[Ni(en)(H_2O)_4]^{2+}$, 15615-30-2; $[Ni(trien)(H_2O)_2]^{2+}$, 15662-53-0; $[Ni(tetren)(H_2O)]^{2+}$, 15662-54-1; $[Ni(penten)]^{2+}$, 70879-08-2; $[Ni(H_2O)_6]^{2+}$, 15365-79-4; $[Ni(tren)(H_2O)_2]^{2+}$, 36470-72-1; $[Co(en)(H_2O)_4]^{2+}$, 70832-90-5; $[Co(en)_2(H_2O)_2]^{2+}$, 23523-26-4; $[Co(en)_3]^{2+}$, 15390-99-5; $[Co(dien)(H_2O)_3]^{2+}$, 69567-86-8; $[Co(dien)_2]^{2+}$, 23624-01-3; $[Co(trien)(H_2O)_2]^{2+}$, 29871-98-5; $[Co(tren)(H_2O)_2]^{2+}$, 62866-31-3; $[Co(tetren)(H_2O)]^{2+}$, 28747-59-3; $[Co(penten)]^{2+}$, 70832-91-6; aniline, 62-53-3; 4-(dimethylamino)pyridine, 1122-58-3; 3-cyanopyridine, 100-54-9; en, 107-15-3; dien, 111-40-0; trien, 112-24-3; tetren, 112-57-2; penten, 4067-16-7; pn, 109-76-2; dptn, 56-18-8; trpn, 4605-14-5; pyridine, 110-86-1; NH_3, 7664-41-7; CH_3NH_2, 74-89-5; Ni, 7440-02-0; Co, 7440-48-4; Cu, 7440-50-8; Zn, 7440-66-6; Mn, 7439-96-5; Fe, 7439-88-5.

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