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- (32) Our calculations not only place the energy of the D_{4d} structure significantly above the D_{2d} or C_{2v} , but also fail to place the D_{4d} structure at a relative minimum. The more open D_{4d} structure could have some entropic stabilization but probably not more than a few to 10 cal/(K mol), but even this stabilization would not give relative stability for D_{4d} at room temperature. An estimate of the entropy difference between the two solution-state forms observed by NMR² can be obtained by assuming concentration ratios of 95:5 at -32 °C and 5:95 at 46 °C. This assumption yields $\Delta H^\circ = 13$ kcal/mol and $\Delta S^\circ = 45$ cal/(K mol). Although this ΔH° value is consistent with a previous estimate,³³ this large ΔS° value seems inconsistent with simple face opening and may indicate some form of ion pairing with concomitant loss of freedom and desolvation of ions. This large entropy change further supports our arguments based upon energetic calculations in making less likely the occurrence of the D_{4d} structure as a stable intermediate.
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Symmetry and Isomer Concepts in the Evaluation of Statistical Factors

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Symmetry and isomer concepts are considered in the general evaluation of statistical factors in coordination reactions. If A and B are different monodentate ligands and all of the $(N-n)B$'s in the reagent and all of the $(n+1)A$'s in the product of the reaction $MA_nB_{N-n} + A = MA_{n+1}B_{N-n-1} + B$ are structurally or energetically equivalent, the sum of the symmetry and isomer effects of this reaction is equal to $R \ln [(N-n)/(n+1)] + C$, the statistical factor obtained by the Brønsted method, where C is a constant for the difference in the symmetry of the free ligands, A and B. If the B's in the reagent are not structurally or energetically equivalent, and all of the A's in the product are structurally or energetically equivalent, the sum of the symmetry and isomer effects of this reaction is smaller than $R \ln [(N-n)/(n+1)] + C$. If the A's in the product are not structurally or energetically equivalent, and all of the B's in the reagent are structurally or energetically equivalent, the sum of the symmetry and isomer effects of this reaction is larger than $R \ln [(N-n)/(n+1)] + C$.

I. Introduction

Statistical factors have long been used in correlating ionization constants of acids,^{1,2} rate constants,³ and stability constants of metal complexes.^{4,5} Benson³ termed the earlier statistical factors "the intuitive Brønsted method" and showed that the symmetry corrections derived from statistical mechanics can be equivalent to those obtained by this intuitive method. This is true only if there are no isomers present in the system. It is shown in the present work that, when isomers are present, the statistical factor is the sum of the symmetry effect and the isomer effect. Although the statistical factors in current use⁶ are satisfactory for monodentate ligands when no isomers are present, this is not the case for octahedral or square-planar complexes to which the factors are frequently applied unless there is no preference for cis or trans positions. Two recent papers^{7,8} also pointed out that the Brønsted method for obtaining statistical factors is not general. For polydentate ligands the attempt by Sen⁹ to extend the Brønsted method is unsatisfactory because of his oversimplifications. In general, it is necessary to consider the isomer effect to give the correct evaluation of statistical factors. The term "symmetry and isomer effects or contributions" stands for the longer phrase "the entropy change owing to symmetry and isomer effects" in this paper.

II. Theory

The symmetry number σ "is the number of nonequivalent ways in which the atoms of the molecule can be interchanged by rigid rotation of the molecule in space and remain completely indistinguishable from some other such orientational rearrangement".¹⁰ If a complex $M(ABC\dots)$ has a coordination number N and has N different ligands, then there are $N!$ arrangements of the ligands in the complex. The isomer number r is the total number of geometric and optical isomers of the complex. The isomers (in toto) of $M(ABC\dots)$ can be

rotated to give the $N!$ possible arrangements. The number of rotational operations needed, for each isomer considered separately, equals the symmetry number for MA_N , provided the coordination number and geometry of MA_N and $M(ABC\dots)$ are the same. Thus

$$r_{M(ABC\dots)}\sigma_{MA_N} = N! \quad (1)$$

A compound which has no geometric or optical isomers is defined as type I and can have the general formula $M(A_aB_bC_c\dots)$. The total number of ways to arrange aA , bB , and cC around the central atom is $N!/(a!b!c!\dots)$. In this case $r = 1$ by definition. The single isomer can be rotated to obtain the total number of arrangements, and the number of rotational operations needed equals $\sigma_{MA_N}/\sigma_{MA_aB_bC_c\dots}$, where again N is the same for MA_N and for $MA_aB_bC_c\dots$ and the geometry is the same. Therefore

$$\frac{N!}{a!b!c!\dots} = \frac{\sigma_{MA_N}}{\sigma_{MA_aB_bC_c\dots}} \quad (2)$$

and from eq 1 it follows that

$$r_{M(ABC\dots)}\sigma_{MA_aB_bC_c} = a!b!c!\dots \quad (3)$$

Consider the reaction in eq 4, where A and B are mono-



dentate groups and the structure and coordination number remain unchanged. The symmetry effect of the reaction, ΔS^{sym} , is

$$\Delta S^{\text{sym}} = -R \ln \frac{\prod \sigma_{\text{products}}}{\prod \sigma_{\text{reactants}}} \quad (5)$$

When eq 3 is used for the symmetry number for type I compounds, eq 6 is obtained, where C is a constant for the

$$\Delta S^{\text{sym}} = -R \ln \left[\frac{(n+1)!(N-n-1)!}{r_{M(\text{ABC}\dots)}} \right] + R \ln \left[\frac{n!(N-n)!}{r_{M(\text{ABC}\dots)}} \right] + C \quad (6)$$

difference in the symmetry of the free ligands, A and B. This equation simplifies to eq 7 which is equivalent to the statistical

$$\Delta S^{\text{sym}} = R \ln \frac{N-n}{n+1} + C \quad (7)$$

factor in common textbook use⁶ and is valid only for type I compounds.

A compound which has geometric or optical isomers is defined as a type II compound. If in reaction 4 the reactant is type I and the product is type II, then eq 7 is no longer valid. This will be the case if the reactant, $\text{MA}_n\text{B}_{N-n}$, contains rotationally nonequivalent B ligands. If there are x B's in $\text{MA}_n\text{B}_{N-n}$ which are rotationally equivalent, and if one of these x B's is substituted by A, one of the isomers, $[\text{M}(\text{A}_{n+1}\text{B}_{N-n-1})]_x$, is formed. So long as this restriction holds, $[\text{MA}_{n+1}\text{B}_{N-n-1}]_x$ can be treated as a type I compound. Without this restriction, the total number of ways to arrange $(n+1)\text{A}$ and $(N-n-1)\text{B}$ is $N!/[(N-n-1)!(n+1)!]$. With the above restriction, the number of allowable arrangements is reduced by a factor of $x/(N-n)$. In this case, the isomer number is 1. This single isomer can be rotated to obtain the total number of arrangements, and the number of rotational operations needed equals $\sigma_{\text{MA}_n\text{B}_{N-n}}/\sigma_x$, where again N is the same for MA_N and for $\text{MA}_{n+1}\text{B}_{N-n-1}$ and the geometry is the same. Therefore

$$\frac{N!}{(N-n-1)!(n+1)!} \frac{x}{N-n} = \frac{\sigma_{\text{MA}_n\text{B}_{N-n}}}{\sigma_x} \quad (8)$$

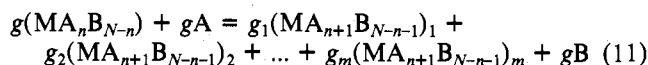
and from eq 1 it follows that

$$\frac{r_{M(\text{ABC}\dots)}}{(N-n-1)!(n+1)!} \frac{x}{N-n} = \frac{1}{\sigma_x} \quad (9)$$

or

$$\sigma_x = \frac{(N-n)!(n+1)!}{r_{M(\text{ABC}\dots)}x} \quad (10)$$

Equation 10 indicates that the symmetry number of the x isomer of $\text{MA}_{n+1}\text{B}_{N-n-1}$ equals the factorial expression on the right-hand side divided by the x number of B's (as defined earlier) and the isomer number for the same geometry when all of the ligands are different. For the reaction



where g is Avogadro's number and g_i is g times the mole fraction of isomer i , the sum of the symmetry and isomer effects is

$$\Delta S_{n+1}^{\text{sym+iso}} = -k \ln [(\sigma_1/\sigma_w)^{g_1}(\sigma_2/\sigma_w)^{g_2}\dots(\sigma_m/\sigma_w)^{g_m}] + k \ln \frac{g!}{g_1!g_2!\dots g_m!} + C \quad (12)$$

where σ_w is the symmetry number of the reactant, k is the Boltzmann constant, and C is a constant for the difference in the symmetry of the free ligands, A and B. The term $S^{\text{sym+iso}}$ can be treated as a continuous function of g_i , and the maximum of the function can be calculated by eq 13.

$$d(\Delta S_{n+1}^{\text{sym+iso}}) = 0 \quad (13)$$

This equation means the value of the symmetry and isomer effects of this reaction remains unchanged when one molecule of $(\text{MA}_{n+1}\text{B}_{N-n-1})_1$ is changed to one molecule of

$(\text{MA}_{n+1}\text{B}_{N-n-1})_2$; at the maximum of the function, we get

$$-k \ln [(\sigma_1/\sigma_w)^{g_1}(\sigma_2/\sigma_w)^{g_2}\dots(\sigma_m/\sigma_w)^{g_m}] + k \ln \frac{g!}{g_1!g_2!\dots g_m!} + C = -k \ln [(\sigma_1/\sigma_w)^{g_1-1}(\sigma_2/\sigma_w)^{g_2+1}\dots(\sigma_m/\sigma_w)^{g_m}] + k \ln \frac{g!}{(g_1-1)!(g_2+1)!\dots g_m!} + C \quad (14)$$

From eq 14 and 10, it can be shown that

$$\frac{g_1}{x_1} = \frac{g_2+1}{x_2} \quad (15)$$

Since $g_2 \gg 1$ or $g_2+1 \approx g_2$, then

$$\frac{g_1}{x_1} = \frac{g_2}{x_2} \quad (16)$$

where x_1 is the number of B's in the reactant, which can be substituted by A to form isomer 1, $[\text{MA}_{n+1}\text{B}_{N-n-1}]_1$, etc., and where x_2 is similarly defined for isomer 2. Repeating the above procedure, we get

$$\frac{g_1}{x_1} = \frac{g_2}{x_2} = \dots = \frac{g_k}{x_k} \quad (17)$$

This equation means when the mole fraction of isomer i is proportional to x_i , the sum of the symmetry and isomer effects of this reaction is a maximum. This statement is the same as saying that the sum of the symmetry and isomer effects is a maximum when all of the B's in the reactant, $\text{MA}_n\text{B}_{N-n}$, have the same probability of being changed by A. The sufficient condition of all of the B's in the reactant having the same probability to be changed by A is that all of these B's are structurally or energetically equivalent. In this case, the maximum value of the sum of symmetry and isomer effects of reaction 4 is given by eq 18. This equation is obtained from

$$(\Delta S_{n+1}^{\text{sym+iso}})_{\text{max}} = R \ln \frac{N-n}{n+1} + C \quad (18)$$

eq 3, 10, 12, and 17, as well as Stirling's approximation. This equation means if the B's in the reactants are totally energetically equivalent, K_{n+1} is proportional to $N-n$, the number of B's in $\text{MA}_n\text{B}_{N-n}$ and inversely proportional to $n+1$, the number of A's in $\text{MA}_{n+1}\text{B}_{N-n-1}$. If the B's in the reactants are not totally energetically equivalent, the sum of the symmetry and isomer effects of this reaction is smaller than $R \ln [(N-n)/(n+1)] + C$. How much smaller it is depends upon the distributions of the isomers of $\text{MA}_{n+1}\text{B}_{N-n-1}$.

For the reaction $\text{MA}_n\text{B}_{N-n} + \text{A} = \text{MA}_{n+1}\text{B}_{N-n-1} + \text{B}$, if all of the B's of the reactants are rotationally equivalent and the A's of the products are not rotationally equivalent, $\text{MA}_{n+1}\text{B}_{N-n-1}$ is of type I and $\text{MA}_n\text{B}_{N-n}$ is of type II (a mixture of isomers). The conclusion of this case when all of the A's of the product are energetically equivalent is that the sum of the symmetry and isomer effects of this reaction is equal to $R \ln [(N-n)/(n+1)] + C$, which is again equivalent to the statistical effect found in textbooks. When the A's of the product are not totally energetically equivalent, the sum of the symmetry and isomer effects is larger than $R \ln [(N-n)/(n+1)] + C$ (i.e., in this case this is the minimum value for $\Delta S_{n+1}^{\text{sym+iso}}$).

III. Conclusion

The statistical factor should be evaluated as the sum of symmetry and isomer effects. However, scientists often use the statistical factors obtained by the Brönsted method,^{1,6} which are not general. It is instructive to show why they are not general and how to use them correctly. The reaction $\text{MA}_n\text{B}_{N-n} + \text{A} = \text{MA}_{n+1}\text{B}_{N-n-1} + \text{B}$ is considered as an ex-

ample. There are four possible cases.

Case 1. Both the reactant, MA_nB_{N-n} , and the product, $MA_{n+1}B_{N-n-1}$, are type I compounds. In this case, the isomer contribution is zero. The statistical factor obtained by the Brönsted method,^{1,6} $R \ln [(N-n)/(n+1)] + C$, is the same as the statistical factor obtained by the symmetry contribution.

Case 2. If the reactant, MA_nB_{N-n} , is type I and the product, $MA_{n+1}B_{N-n-1}$, is type II, the statistical factor obtained by the Brönsted method, $R \ln [(N-n)/(n+1)] + C$, is true only if all of the B's in the reactant, MA_nB_{N-n} , have the same probability of being changed by A. Since we cannot find any example that all of the B's in MA_nB_{N-n} have the same probability of being changed by A in the real system in this case, we may conclude that $R \ln [(N-n)/(n+1)] + C$ is larger than the correct statistical factor, the sum of the symmetry and isomer contributions, in this case.

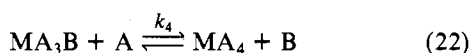
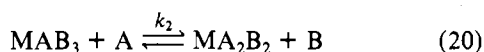
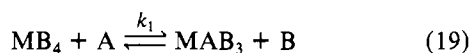
Case 3. In this case the reactant, MA_nB_{N-n} , is type II and the product, $MA_{n+1}B_{N-n-1}$, is type I. This is the reverse situation of case 2. The reverse reaction, $MA_{n+1}B_{N-n-1} + B = MA_nB_{N-n} + A$, is of case 2 type. According to the conclusion of case 2, the statistical factor of this reverse reaction, $-\Delta S_{n+1}^{\text{sym+iso}}$, should be equal to or smaller than the term obtained by the Brönsted method, $R \ln [(n+1)/(N-n)] - C$. Therefore, the statistical factor of the forward, case 3 reaction, $\Delta S_{n+1}^{\text{sym+iso}}$, should be equal to or larger than, $R \ln [(N-n)/(n+1)] + C$, the term obtained by the Brönsted method. Therefore, $R \ln [(N-n)/(n+1)] + C$ is the correct statistical factor only if all of the A's in the product, $MA_{n+1}B_{N-n-1}$, have the same probability of being changed by B. Since we cannot find any example that all of the A's in $MA_{n+1}B_{N-n-1}$ have the same probability of being changed by B in the real system in this case, we may conclude that $R \ln [(N-n)/(n+1)] + C$ is smaller than the correct statistical factor, the sum of the symmetry and isomer contributions, in this case.

Case 4. Both the reactant and the product are type II compounds. The mathematical methods, arguments, and conclusions of cases 2 and 3 can be modified and extended to get the following conclusions. If all of the B's in the reactant, MA_nB_{N-n} , have the same probability of being changed by A, and all of the A's in the product, $MA_{n+1}B_{N-n-1}$, have the same probability of being changed by B, the term obtained by the Brönsted method, $R \ln [(N-n)/(n+1)] + C$, is equal to the sum of the symmetry and isomer contributions, the correct statistical factor. Since this seems unlikely to happen in the real system in this case, we may conclude that the term obtained by the Brönsted method, $R \ln [(N-n)/(n+1)] + C$, is meaningless in this case.

Therefore, $R \ln [(N-n)/(n+1)] + C$ can be used as the statistical factor in case 1, but it is too large in case 2, too small in case 3, and meaningless in case 4. A sum of the symmetry and isomer contributions should be used as the statistical factor.

IV. Examples

1. Complex Formations with Monodentate Ligands. For square-planar complexes, reactions 19–22 are taken as examples. MA_4 , MA_3B , MAB_3 , and MB_4 are of type I, while



MA_2B_2 , a mixture of *cis*- MA_2B_2 and *trans*- MA_2B_2 , is of type II. The comparison between the statistical effects in current

Table I. Comparison of Statistical Effects in Current Use and Statistical Effects Derived from the Symmetry and Isomer Concepts for the Reactions of Square-Planar Complexes

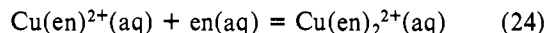
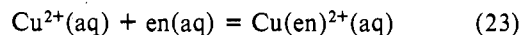
	statistical effect in current use	statistical effect derived from symmetry and isomer concepts
ΔS_1^{stat}	$R \ln 4 + C$	$R \ln 4 + C$
ΔS_2^{stat}	$R \ln 3/2 + C$	$<(R \ln 3/2 + C)$
ΔS_3^{stat}	$R \ln 2/3 + C$	$>(R \ln 2/3 + C)$
ΔS_4^{stat}	$R \ln 1/4 + C$	$R \ln 1/4 + C$

Table II. Experimental Values for the Entropy Changes in the Reactions of Ethylenediamine with Cu^{2+} and $Cu(en)^{2+}$ in Aqueous Solution

$Cu^{2+}(\text{aq}) + \text{en}(\text{aq}) = Cu(\text{en})^{2+}(\text{aq}) \quad \Delta S_1$			
$Cu(\text{en})^{2+}(\text{aq}) + \text{en}(\text{aq}) = Cu(\text{en})_2^{2+}(\text{aq}) \quad \Delta S_2$			
$\Delta S_1, \text{eu}$	$\Delta S_2, \text{eu}$	$\Delta S_1 - \Delta S_2, \text{eu}$	ref
6.0	-0.1	6.1	12
5	0	5	13
5.4	0.9	4.5	14
1.3	-2.0	3.3	15
5	0	5	16
9.0	3.7	5.3	17
		av 4.9	

use and those derived from the symmetry and isomer concepts is shown in Table I.

2. Complex Formations with Bidentate Ligands. Reactions 23 and 24 are used as an example to show the validity of the



sum of symmetry and isomer effects as the statistical factor. For eq 23 the following calculations can be made:

The symmetry numbers of tetragonal $Cu^{2+}(\text{aq})$, en , and $Cu(\text{en})^{2+}$ are 8, 2, and 2, respectively. The symmetry effect of reaction 23 is

$$-R \ln 2 + R \ln 2 + R \ln 8 = 4.1 \text{ eu} \quad (25)$$

If we assume an equal distribution of the δ and λ forms of $Cu(\text{en})^{2+}$, the isomer effect of reaction 23 is

$$+R \ln 2 = 1.4 \text{ eu} \quad (26)$$

Therefore the sum of symmetry and isomer effects equals 5.5 eu.

The ratio of $[\delta\delta\text{-}Cu(\text{en})_2^{2+}]/[\delta\lambda\text{-}Cu(\text{en})_2^{2+}]$ evaluated by Corey and Bailar¹¹ is 5. For eq 24 the symmetry number and the distribution of isomers are as follows:

species	symmetry no.	relative distribution
$Cu(\text{en})^{2+}$	2	
en	2	
$\delta\delta\text{-}Cu(\text{en})_2$	4	5
$\lambda\lambda\text{-}Cu(\text{en})_2$	4	5
$\delta\lambda\text{-}Cu(\text{en})_2$	2	1

The symmetry effect of eq 24 is $-5/11R \ln 4 - 5/11R \ln 4 - 1/11R \ln 2 + R \ln 2$, which equals 0.1 eu. The isomer effect of eq 24 is $-5/11R \ln 5/11 - 5/11R \ln 5/11 - 1/11R \ln 1/11 + 1/2R \ln 1/2 + 1/2R \ln 1/2$, which equals 0.5 eu. The sum of the symmetry and isomer effects of eq 24 equals 0.6 eu.

The difference of $\Delta S_1^{\text{sym+iso}}$ and $\Delta S_2^{\text{sym+iso}}$ for eq 23 and 24 equals 5.5 eu - 0.6 eu or 4.9 eu. The values of $\Delta S_1 - \Delta S_2$ obtained by experiments under various conditions¹²⁻¹⁷ are shown in Table II. The average value of $\Delta S_1 - \Delta S_2$ is in good agreement with $\Delta S_1^{\text{sym+iso}} - \Delta S_2^{\text{sym+iso}}$. The sum of symmetry and isomer effects should be used as the statistical factor in this case. On the other hand, the value of $\Delta S_1 - \Delta S_2$ predicted by Sen was 2.8 eu⁹ and that predicted by Powell and Curtis was 3.2 eu.¹⁸

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The Entropy Effect of Chelation

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A detailed analysis of the entropy change of chelation of a typical reaction $[M(NH_2CH_3)_2n(H_2O)_{N-2n}]^{m+}(aq) + nen(aq) = [M(en)_n(H_2O)_{N-2n}]^{m+}(aq) + 2nNH_2CH_3(aq)$ reveals five entropy factors as significant. The magnitudes of these factors have been evaluated by statistical mechanical methods. Combining these contributions yields the entropy change of chelation which agrees satisfactorily with the experimental values. In general, the entropy effect of chelation in the gas phase can be described as a combined effect of the three positive contributions $\Delta S_{\text{translation}}$, $\Delta S_{\text{intrinsic rotation}}$, and $\Delta S_{\text{symmetry and isomer}}$ and a negative contribution, $\Delta S_{\text{internal rotation}}$. The entropy change of chelation in aqueous solution will differ significantly from that in the gas phase or in organic solvents.

Introduction

The entropy effect of chelation is more complicated than that described as due to the entropy increase resulting from the fact that more molecules of monodentate ligand are liberated than molecules of chelating ligand are used in the reaction, as Martell¹ and Myers² have pointed out. In order to understand more thoroughly the entropy concepts of chelate ring formation and the nature, significance, and magnitude of each of the important entropy factors, a typical example, Scheme I, is studied in detail.

The coordination number of the metal is N , en is ethylenediamine, and the entropy terms are

$$\Delta S_4^\circ = \Delta S_{1a}^\circ + \Delta S_{1b}^\circ + \Delta S_2^\circ + \Delta S_{3a}^\circ + \Delta S_{3b}^\circ \quad (1)$$

where ΔS_4° is the entropy of chelation in aqueous solution, which can be measured experimentally, and ΔS_2° is the entropy of chelation in the gas phase, estimated theoretically. This study reveals a decisive factor, the sum of symmetry and isomer effects, which has heretofore been overlooked or not considered as being important.

Estimation of Entropy Factors

Solvational Factor of Chelation. It is not possible to measure directly the thermodynamic data of the formation of the complex in the gas phase; the available data are for the reaction in aqueous solution. The solvational entropy effect of chelation, ΔS_{solv} , is defined as the difference between the entropy of chelation in aqueous solution and that in the gas phase.

$$\Delta S_{\text{solv}} = \Delta S_4^\circ - \Delta S_2^\circ = \Delta S_{1a}^\circ + \Delta S_{1b}^\circ + \Delta S_{3a}^\circ + \Delta S_{3b}^\circ \quad (2)$$

The standard states are as follows: entropies of solution are for 1 m ideal solutions, entropies of ideal gases are at 1 atm (all at 298 K). Westheimer and Ingraham³ give an experimental value of 36 eu/mol for ΔS_{1b}° . The entropy of solvation for methylamine can be calculated from its heats of formation in the gas phase and in solution⁴ and the partial pressure of the gas above its aqueous solution.⁵ These data lead to a value

Table I. Entropy Data of Gaseous Ligands at 25 °C and 1 Atm and Partial Molar Entropies of Ligands in Aqueous Solution at 25 °C

	methylamine	ethylene-diamine
Entropy Data of Gaseous Ligands, eu		
entropy of translation	36.06	38.03
entropy of rotation	19.39	23.03
entropy of internal rotation	1.83	14.89
entropy of vibration	0.55	2.53
S°_{g} obtained in this work	57.83	78.48 ^a
S°_{g} from references	57.98, ^b	57.73 ^c
Partial Molar Entropies of Ligands, eu		
S°_{aq} obtained in this work	30	43
S°_{aq} obtained using Cobble's equation ^d	29 ^d	45 ^e

^a This agrees with Myers' value.² ^b From ref 10. ^c From ref 11. ^d From ref 15. ^e From ref 16.

for the entropy of solvation of -28 eu/mol of methylamine, giving ΔS_{3b}° of $-56n$ eu, where n is the number of chelate rings formed in Scheme I.

The radii of $[M(NH_2CH_3)_2n(H_2O)_{N-2n}]^{m+}$ and $[M(en)_n(H_2O)_{N-2n}]^{m+}$ are approximately the same. The Born equation predicts that these two ions have the same entropy of solvation, $\Delta S_{1a}^\circ = -\Delta S_{3a}^\circ$. The total solvational entropy effect of chelation $\Delta S_{1a}^\circ + \Delta S_{1b}^\circ + \Delta S_{3a}^\circ + \Delta S_{3b}^\circ$ is equal to $-20n$ eu. Therefore, the solvational entropy effect makes a negative contribution to the formation of chelate rings in this reaction.

Standard Entropies of Gaseous Ligands. The entropy of chelation in the gas phase, ΔS_2° , is equal to $2nS^\circ_{\text{CH}_3\text{NH}_2(\text{g})} + S^\circ_{[M(en)_n(H_2O)_{N-2n}]^{m+}(\text{g})} - nS^\circ_{\text{en}(\text{g})} - S^\circ_{[M(NH_2CH_3)_2n(H_2O)_{N-2n}]^{m+}(\text{g})}$. In order to evaluate the value of ΔS_2° , the standard entropies of gaseous ligands are calculated by statistical mechanical methods.

The vibrational spectrum of methylamine has been measured by Gray and Lord.⁶ The entropy of vibration of methylamine can be calculated from the fundamentals, omitting