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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.

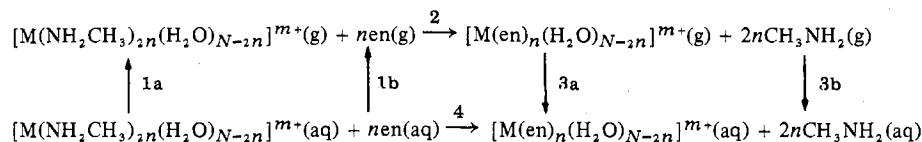
for the entropy of solvation of -28 eu/mol of methylamine, giving ΔS_{3b}° of $-56n$ eu, where n is the number of chelate rings formed in Scheme I.

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

Scheme I



the NH_2 torsion, giving 0.55 eu. The infrared data of methylamine have also been collected by Owens and Barker⁷ and agree with the results of Gray and Lord.⁶ The overall and reduced moments of inertia are calculated by using the bond distances and bond angles reported by Lide⁸ and the barrier to internal rotation estimated by Shimoda, Nishikawa, and Itoh.⁹ The entropy of internal rotation and the entropy of rotation of methylamine calculated from these data are given in Table I. The entropy of translation is calculated from the molecular weight. The value of $S^\circ_{\text{CH}_3\text{NH}_2(\text{g})}$ obtained by combining the entropies of translation, rotation, internal rotation, and vibration is in excellent agreement with the value obtained from the thermal data,^{10,11} Table I.

The spectrum of ethylenediamine was measured by Sabatini and Califano.¹² The vibrational entropy of ethylenediamine is calculated by using the vibrational fundamentals assigned there, except those due to NH_2 and NCCN torsions, giving 2.53 eu. The overall and reduced moments of inertia are calculated by using the structure parameters reported by Yokozeki et al.^{13,14} The barrier to internal rotation for NCCN torsion is estimated as 2.8 kcal.¹³ The barrier to internal rotation for NH_2 torsion of ethylenediamine is the same as that of ethylamine, 1.99 kcal.¹³ The entropy of rotation and the sum of the entropies of internal rotations are calculated from these data and given in Table I. The entropy of translation is calculated from the molecular weight. The value of $S^\circ_{\text{en}(\text{g})}$ obtained by combining all of these contributions, is given in Table I. It agrees with the value of Myers.²

The partial molar entropies of methylamine and ethylenediamine in aqueous solution can be calculated from the entropies of gaseous species and the entropies of solvation of these two compounds. For organic ligands, Cobble has given an empirical equation to calculate the partial molar entropies in aqueous solution.¹⁵ The value of the partial molar entropies of these two ligands in aqueous solution obtained by both methods are in good agreement and given in Table I. The value for en agrees with the value of Myers.²

The Difference between the Standard Entropies of the Gaseous Complexes. It is virtually impossible to calculate accurately the standard entropies of the gaseous complexes. However, we can estimate the entropy change of chelation, ΔS_2° , by evaluating the difference between the standard entropies of the gaseous complexes. The entropies of translation of these two gaseous complexes are virtually the same. The intrinsic entropies of rotation, which are defined as $S_{\text{rot}} + R \ln(\text{symmetry number})$, of these two species are also the same, and the difference between the rotational entropies of these two species is due only to the different symmetry numbers of these species. This difference is defined as the symmetry effect of chelation on the entropy of rotation of the complexes. If both of the structure and the percentages of the isomers of the complexes are known, the symmetry effect for Scheme I can be obtained by eq 3, where R is the gas

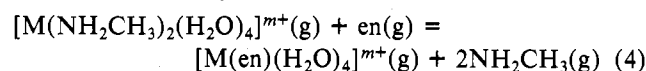
$$\Delta S_{\text{sym}} = R \left(\sum_{i=1}^{n_i} P_i \ln a_i - \sum_{j=1}^{n_j} P_j \ln a_j \right) \quad (3)$$

constant, n_i and n_j are the number of isomers of $[\text{M}(\text{NH}_2\text{CH}_3)_{2n}(\text{H}_2\text{O})_{N-2n}]^{m+}(\text{g})$ and the number of isomers of $[\text{M}(\text{en})_n(\text{H}_2\text{O})_{N-2n}]^{m+}(\text{g})$, respectively, P_i and P_j are the fraction of the isomer i of $[\text{M}(\text{NH}_2\text{CH}_3)_{2n}(\text{H}_2\text{O})_{N-2n}]^{m+}(\text{g})$ and the fraction of the isomer j of $[\text{M}(\text{en})_n(\text{H}_2\text{O})_{N-2n}]^{m+}(\text{g})$,

Table II. Entropy Changes for Scheme I (eu)

	ΔS_{1b}	ΔS_2	ΔS_{3b}	ΔS_4
octahedral complexes $n = 1$	36	27	-56	7
octahedral complexes $n = 2$	72	>54	-112	>14
tetrahedral complexes $n = 1$	36	25	-56	5
tetrahedral complexes $n = 2$	72	>50	-112	>10

respectively, and a_i and a_j are the symmetry number of the isomer i of $[\text{M}(\text{NH}_2\text{CH}_3)_{2n}(\text{H}_2\text{O})_{N-2n}]^{m+}(\text{g})$ and the symmetry number of the isomer j of $[\text{M}(\text{en})_n(\text{H}_2\text{O})_{N-2n}]^{m+}(\text{g})$, respectively. As an example, consider reaction 4. There are two



isomers possible for $[\text{M}(\text{en})(\text{H}_2\text{O})_4]^{m+}$. The symmetry number of both isomers is 2. Schwarzenbach, Milyukov, Ashcroft, and Mortimer¹⁷⁻¹⁹ have pointed out that in the complex $[\text{M}(\text{NH}_3)_2(\text{H}_2\text{O})_4]^{2+}$ the two ammonia molecules are probably trans to each other. In view of the steric effect, we may predict that the trans isomer is the predominant species of $[\text{M}(\text{NH}_2\text{CH}_3)_2(\text{H}_2\text{O})_4]^{m+}$.

The symmetry entropy gain due to the complexes in this reaction is about 2.6 eu. In general, the symmetry number of the octahedral or square-planar complex containing chelate rings is smaller than the symmetry number of the corresponding complex containing only monodentate ligands. Therefore, the symmetry factor of the complexes makes a positive contribution to the entropy change of chelation. In the case of tetrahedral complexes $[\text{M}(\text{NH}_2\text{CH}_3)_2(\text{H}_2\text{O})_2]^{m+}$ and $[\text{M}(\text{en})(\text{H}_2\text{O})_2]^{m+}$ there is no symmetry entropy gain, since the symmetry number of these complexes is the same.

The isomer effect of chelation can be obtained by eq 5,

$$\Delta S_{\text{isom}} = R \left(\sum_{i=1}^{n_i} P_i \ln P_i - \sum_{j=1}^{n_j} P_j \ln P_j \right) \quad (5)$$

where P_i and P_j are the fraction of the isomer i of $[\text{M}(\text{NH}_2\text{CH}_3)_{2n}(\text{H}_2\text{O})_{N-2n}]^{m+}(\text{g})$ and the fraction of the isomer j of $[\text{M}(\text{en})_n(\text{H}_2\text{O})_{N-2n}]^{m+}(\text{g})$, respectively.

For reaction 4, the entropy gain due to the isomer factor is 1.3 eu. In the case of tetrahedral complexes, there are two isomers, the δ and λ forms for $[\text{M}(\text{en})(\text{H}_2\text{O})_2]^{m+}$. If we assume an equal distribution of these forms, the entropy gain owing to the isomer effect for the reaction $[\text{M}(\text{NH}_2\text{CH}_3)_2(\text{H}_2\text{O})_2]^{m+}(\text{g}) + \text{en}(\text{g}) = [\text{M}(\text{en})(\text{H}_2\text{O})_2]^{m+}(\text{g}) + 2\text{NH}_2\text{CH}_3(\text{g})$ is 1.4 eu. In general, the isomer factor often makes a positive contribution to ΔS° in chelation reactions.

The vibrational entropy of $[\text{M}(\text{en})_n(\text{H}_2\text{O})_{N-2n}]^{m+}(\text{g})$ is slightly larger than that of $[\text{M}(\text{NH}_2\text{CH}_3)_{2n}(\text{H}_2\text{O})_{N-2n}]^{m+}(\text{g})$ due to the bending of the chelate rings.²⁰ The frequency of this bending is about the same as the NCCN bending of ethylenediamine.²⁰ The difference between the vibrational entropies of these two complexes is about 1.4n eu.

The accurate estimation of the entropy of internal rotation of the complex $[\text{M}(\text{NH}_2\text{CH}_3)_{2n}(\text{H}_2\text{O})_{N-2n}]^{m+}(\text{g})$ is virtually impossible because of the paucity of experimental data. The internal rotational entropy due to each methyl group in the complex is about the same as that of the free ligand. As an approximation, 1.8 eu is used. From the reduced moment of inertia, we estimate that the entropy of each of the internal rotations around the N-M bonds in $[\text{M}(\text{NH}_2\text{CH}_3)_2(\text{H}_2\text{O})_{N-2}]^{m+}(\text{g})$ is between 5 and 7 eu. Let us use 6 eu as an

Table III. Entropy Data for Chelation Reactions in Aqueous Solution at 25 °C (eu)

reaction	S°_{exptl}	S°_{calcd}	
		octahedral complexes	tetrahedral complexes
$\text{Cd}(\text{NH}_2\text{CH}_3)_2^{2+} + \text{en} = \text{Cd}(\text{en})^{2+} + 2\text{NH}_2\text{CH}_3$	5, ^a 7 ^b	7	5
$\text{Cd}(\text{NH}_2\text{CH}_3)_4^{2+} + 2\text{en} = \text{Cd}(\text{en})_2^{2+} + 4\text{NH}_2\text{CH}_3$	19 ^{a,b}	>14	>10

^a From ref 21. ^b From ref 22.

Table IV. Factors Influencing the Entropy Change of Chelation for Octahedral Complexes in Aqueous Solution

factor	contribution		total value, eu
	from free ligands, eu	from complexes, eu	
solvation	-20	0	-20
translation	34.1	0	34.1
intrinsic rotation	14.4	0	14.4
symmetry	1.4	2.6	4.0
isomer	0	1.3	1.3
vibration	-1.4	1.4	0
internal rotation	-11.2	-15.6	-26.8

approximation. When n is 2 or 3, it is less than 6 eu due to larger steric effects.

$S^\circ_{[\text{M}(\text{NH}_2\text{CH}_3)_2(\text{H}_2\text{O})_{N-2}]^{m+}(\text{g})}$ is much larger than $S^\circ_{[\text{M}(\text{en})_n(\text{H}_2\text{O})_{N-2n}]^{m+}(\text{g})}$ mainly due to the internal rotational entropy factor. For octahedral complexes and $n = 1$, the value of the difference $S^\circ_{[\text{M}(\text{NH}_2\text{CH}_3)_2(\text{H}_2\text{O})_4]^{m+}(\text{g})} - S^\circ_{[\text{M}(\text{en})(\text{H}_2\text{O})_4]^{m+}(\text{g})}$ is about 10.3 eu. In the case of $n = 2$, the difference is expected to be much smaller than 20 eu, because of the hindered internal rotations around the M-N bonds. For tetrahedral complexes and $n = 1$, the value of the difference $S^\circ_{[\text{M}(\text{NH}_2\text{CH}_3)_2(\text{H}_2\text{O})_2]^{m+}(\text{g})} - S^\circ_{[\text{M}(\text{en})(\text{H}_2\text{O})_2]^{m+}(\text{g})}$ is about 12.8 eu. In the case of $n = 2$, the difference is expected to be much smaller than 25 eu, because of the hindered internal rotations around the M-N bonds.

Entropy Change for the Reaction in Eq 1 in the Gas Phase and in Aqueous Solution. We are now ready to combine all of the contributions of entropy to the process of chelation in a Born-Haber-type analysis. For octahedral and tetrahedral complexes the results are given in Table II. These calculated values are in excellent agreement with the experimental results given in Table III. It is notable that the internal rotational factor in the case of $n = 2$ is not double that of $n = 1$, so the entropy change of chelation at $n = 2$ is much more than double that at $n = 1$.

Discussion

Factors Involved in Determining Entropies of Metal Chelate Formation. The magnitudes of the factors involved in determining the entropy change for the reaction of octahedral complexes and at $n = 1$ are given in Table IV.

The data of Myers² show that $\Delta S^\circ_{\text{soln}}$ for $\text{Cd}(\text{H}_2\text{NMe})_4^{2+}$ and $\text{Cd}(\text{en})_2^{2+}$ are the same. This would no doubt be true of the coordinated species in Scheme I. The large negative solvational entropy factor is mainly due to the difference in solvational entropies of the ligands and the different standard states employed; entropies of solution are for 1 m ideal solutions, whereas entropies of ideal gases are at 1 atm. The difference in solvational entropies of the ligands is probably due to the fact that the hydrophobic exterior of two uncoordinated methylamines is larger than that of an uncoordinated ethylenediamine. For similar systems, we may expect a negative solvational entropy contribution in chelation reactions in aqueous solution for the same reasons. The solvation factor in organic solvents will be less significant than in aqueous solution. Thus, the entropy change of chelation in the gas

phase or in an organic solvent will be larger than that in aqueous solution.

The other factor which gives a large negative contribution to ΔS° in chelation reactions is the internal rotational term. Not only the internal rotations of the free ligands but also the internal rotations in the complex containing monodentate ligands are lost in the chelation process. As an example, let us consider Scheme I, where there are five degrees of freedom of internal rotation lost for each chelate ring formed. The loss of internal rotational entropy explains the decreasing magnitude of the entropy term with increasing ring size.^{23,24}

The net increase in the number of unbound ligands in the chelation process explains the large positive contributions to the ΔS° term due to the favorable translational and intrinsic rotational entropy factors.

The two positive contributions to the ΔS° term, $\Delta S_{\text{translation}}$ and $\Delta S_{\text{intrinsic rotation}}$, cancel out almost exactly the two negative contributions, $\Delta S_{\text{solvation}}$ and $\Delta S_{\text{internal rotation}}$ in Scheme I in aqueous solution at $n = 1$. Therefore the last significant factor, the sum of symmetry and isomer effects, plays an important role and cannot be overlooked in the chelation process.

In general, the complex system containing chelate rings can have conformational geometrical and optical isomers. The number of the possible isomers of the complex system containing chelate rings is often larger than the number of the possible isomers of the corresponding complex system containing only monodentate ligands. Furthermore, the symmetry number of the complex containing chelate rings is often smaller than the symmetry number of the complex containing only monodentate ligands. One of these two effects may be unfavorable in some chelation reactions, but the sum nearly always makes a positive contribution to ΔS° in the chelation process.

On the basis of the detailed entropy analysis of this typical reaction, we obtain a few general conclusions that are helpful in understanding the entropy effect of chelation.

1. 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 the negative contribution, $\Delta S_{\text{internal rotation}}$.

2. The solvational factor is important. The entropy change of chelation reaction in aqueous solution will differ significantly from that in the gas phase. In aqueous solution, the solvational factor often makes a negative contribution to ΔS° in the chelation reaction.

3. An unfavorable entropy change is possible in chelation reactions. As an example, the formation of large chelate rings results in a serious loss in the entropy of internal rotation.

Registry No. NH_2CH_3 , 74-89-5; en, 107-15-3.

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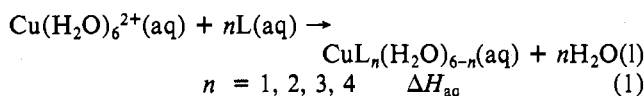
Thermodynamic and Spectroscopic Parameters in Metal Complexes: Extension of a Linear Relationship to Nickel(II) Derivatives

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A previous correlation between the thermodynamic heat of formation in aqueous solution of some 30 copper(II) complexes and their electronic band maxima has been extended to nickel(II) and iron(II). Three alternative correlations are reported from some 40 nickel(II) complexes containing one to six amine ligands. These involve correlations with directly observable transition energies and also with a calculated function based on the orbital angular overlap model. The difference ($\sigma_N - \sigma_O$) is shown to correlate well with $-\Delta H_f$ in substituted complexes. Although only very limited data are available, iron(II) amine derivatives exhibit similar behavior. It is shown that outer-sphere solvation energies cancel, fortuitously, from this correlation. These studies now permit the derivation of heats of formation of amine complexes of copper(II), nickel(II), and possibly iron(II) with reasonable accuracy.

We have recently discussed a relationship³ observed between the heat of formation, in aqueous solution, of a series of copper(II) amine derivatives (eq 1) and the band energy of the maximum intensity absorption in their crystal field spectrum (eq 3, 4), i.e., for the process



we find, for ammonia

$$-\Delta H_{\text{aq}}^{\circ} = 4.90\nu(\text{d-d}) - 61.01 \quad (2)$$

and for polyamines in general

$$-\Delta H_{\text{aq}}^{\circ} = 4.33\nu(\text{d-d}) - 54.43$$

$$\Delta H^{\circ} \text{ in kcal mol}^{-1} \text{ and } \nu(\text{d-d}) \text{ in cm}^{-1} \times 10^3 \quad (3)$$

Some 30 amine complexes including simple ammonia derivatives, $\text{Cu}(\text{NH}_3)_x(\text{H}_2\text{O})_{6-x}$, linear tetradentate amines, and also macrocyclic derivatives⁵ were shown to obey these closely similar relationships. It was demonstrated that complexes were well behaved if there was free access for water molecules to occupy both axial sites of the molecule. In addition to providing a pragmatic procedure for evaluating heats of formation in aqueous solution, such studies should lead to a better understanding of such factors as outer-sphere solvation (hydration) energy and strain energy.

Of longer term importance is the eventual derivation of fundamental gas-phase thermodynamic data by spectroscopic methods.

Experimental Section

Much of the calorimetric and spectroscopic data were obtained from the literature as referenced in Table I.

Data for the 1:1, 2:1, and 3:1 ligand-to-metal ratio complexes of ethylenediamine (en), 1,3-propylenediamine (tn), 2,2'-bipyridyl (bpy), 2-aminomethylpyridine (2-AMP), and 2-aminoethylpyridine (2-AEP) were obtained by the following general procedure. The NiL_3^{2+} species were prepared in the solid state from nickel nitrate or perchlorate with the corresponding diamine in ethanol solution. In the case of 2-AEP only the bis ligand complex could be prepared. Satisfactory nickel

analyses were obtained to ensure purity.

Approximately 2×10^{-2} M solutions of these complexes were made up in aqueous solution, and their spectra recorded (Perkin-Elmer/Hitachi PE 340 or Beckman DK2A spectrometer). Calculated amounts of solid hydrated nickel nitrate or perchlorate were then added to these solutions to generate solutions in which the ligand to metal ratio was 2:1 and 1:1. These solutions were left overnight to achieve equilibrium, and their spectra then recorded. Such a procedure will not provide a solution containing solely the NiL_2^{2+} or NiL^{2+} aquated species but rather a mixture depending upon the relative stability constants. However, calculation (using data from ref 6) shows that each of these solutions contains primarily the desired species (Table II).

Results and Discussion

A considerable body of calorimetric data exists for nickel(II). However, it is not obvious how this may be correlated with the corresponding spectroscopic data. We must therefore seek a general model for correlating thermodynamic and spectroscopic data, which could be used for any metal. The orbital angular overlap model^{7,8} would appear to provide such a procedure, and we return therefore to the copper(II) relationship to develop this aspect.

Consider a general copper amine complex $\text{CuN}_x^E(\text{H}_2\text{O})_{4-x}^E(\text{H}_2\text{O})_2^A$ where N represents the ligating nitrogen atoms in the molecular plane and E and A represent equatorial and axial sites, respectively. We make the reasonable assumption that π bonding is not important in these complexes, though this may not be true for strongly π accepting ligands such as biguanide. There is also the pragmatic reason that there generally exist insufficient data to calculate the extent of any π bonding in these systems.

In seeking a general treatment we also neglect any off-diagonal contribution to the energy of the d states. Such contributions will arise in some of the less symmetric complexes but are not expected to be very important.

The crystal field maximum used earlier³ generally corresponds to the $xz, yz \rightarrow x^2 - y^2$ transition. By use of an orbital angular overlap approach with the assumptions outlined above, the (xz, yz) pair of orbitals may be assumed to remain degenerate and to possess an energy of zero with respect to the