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Stability Constants of Metal Coordination Compounds

Complexes of N-Ethylethylenediamine and 2-(Ethylthio)-Ethylamine

UNITED STATES DEPARTMENT OF THE INTERIOR

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Complexes of N-Ethylethylenediamine and 2-(Ethylthio)-Ethylamine

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STABILITY CONSTANTS OF METAL COORDINATION COMPOUNDS

Complexes of N-Ethylethylenediamine and 2-(Ethylthio)-Ethylamine

by

David J. MacDonald,[1] Alexander May,[1] and E. G. Baglin[2]

ABSTRACT

Stability constants, that is, equilibrium constants for complex-formation reactions, have been determined by a titrimetric method for complexes formed by the transition metal ions Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} with the structurally analogous bidentate ligands N-ethylethylenediamine and 2-(ethylthio)-ethylamine. The sulfur containing ligand was found to be the weaker of the two chelating agents for each of the four metals. Absorption spectra of the individual complexes have been determined in order to calculate their crystal field stabilization energies. The combined results suggest a linear relation between free energy of chelation and ionic radius of the metal ion.

INTRODUCTION

One phase of the Bureau of Mines research on the recovery of metal values from ores is directed toward fundamental studies in the coordination chemistry of ore processing. These studies are designed to obtain a better understanding of the relationships between a chelating ligand's structural and electronic features and its ability to function as a chelating agent for particular metal ions or groups of metal ions. The resulting data aid in determining the possibility of applying selected ligands in treating ores that do not lend themselves to conventional processing techniques, thus increasing the Nation's mineral resource potential.

The objectives of the present study were to compare the coordinating abilities of a sulfur atom and a nitrogen atom in molecules that were as nearly identical as possible in all other respects. This required the precise comparison of stability constants of one ligand with those of another analogous ligand under closely similar conditions. Because there are no comparable data in the existing literature, experiments were performed to obtain the data reported and analyzed here. These experiments were conducted at a uniform temperature of 25° C, and at low ionic strength, usually less than 0.1 $\underline{M}$. No added neutral electrolytes were used, in order to keep the ionic strength as low as possible, thereby minimizing the effect of deviations from ideality.

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[1] Research chemist.
[2] Chemist.

Several of the metal-ligand systems dealt with in this study have been investigated by others, but not under the uniform conditions of ionic strength and temperature necessitated by the present goal. For example, Basolo and Murmann (1)[3] determined stability constants for complexes formed by copper(II) and nickel(II) with N-ethylethylenediamine, but only in 0.50 M potassium nitrate solutions. In a similar study of the same complexes by Edwards (5), a supporting electrolyte of 1 M potassium chloride was used. However, the results obtained in these separate investigations were not identical, demonstrating that stability constants measured under conditions of widely differing ionic strength cannot be compared.

In addition to determining the stability constants, auxiliary data, which made it possible to determine the absorption spectra of individual complexes in solution, were obtained. A new method of data analysis was developed for this purpose. The molar extinction coefficient (or molar absorptivity) was derived for a single species at any given wavelength from the observed absorption spectrum of a mixture of complex species and from their individual concentrations as calculated from equilibrium data. By this means, it is possible to determine the extinction coefficients or absorption spectrum of a single species even when that species cannot be isolated from the mixture in which it occurs. This information is of value to the present investigation because the free energy of the chelation reaction can be corrected for the influence of crystal field stabilization energy. Use of this crystal field stabilization energy correction (as will be discussed later) constitutes an original contribution to the thermodynamics of chelation and thus increases the fundamental knowledge of coordination chemistry in ore processing.

THEORY

The sulfur and nitrogen atoms of the chelating agents used in this investigation differ in two important respects; namely, size and polarizability. These properties of the atoms are important because the chelating agent containing the larger-sized atom, for example, the sulfur atom would be expected to chelate better with a metal atom of larger size, while the analogous ligand containing only nitrogen donor atoms would be expected to chelate better with smaller metal atoms, other things being equal. The sulfur atom's greater polarizability enables it to coordinate more strongly with those metal atoms which themselves possess the greater polarizability.

This aspect of coordination chemistry is described by the hard and soft acid and base (HSAB) theory proposed by Pearson (8-9). According to this theory, the sulfur atom, being a soft base, coordinates best with a soft acid; and the nitrogen atom, being a hard base, coordinates best with a hard acid. Therefore, the transition metal elements for these experiments were selected so as to cover a range of acid hardness, varying from the borderline hardness of Ni^{2+} to the moderate softness of Cd^{2+}. A qualitative measure of Pearson's acid softness for a particular element is indicated by its atomic refractivity. Numerical values of this quantity for the transition metal elements used in

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[3] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

this study are shown in table 1. Although these data refer to the neutral atoms rather than to the 2^+ cations, it is very likely that the cations will show the same relative order of acid softness.

TABLE 1. - Atomic refractivities as related to acid hardness or softness[1]

Element	Atomic refractivity ($cm^3 \cdot mole^{-1}$)	Hardness or softness
Nickel........	6.5	Harder
Copper........	7.0	↓
Zinc..........	8.9	↑
Cadmium.......	12.7	Softer

[1] Data taken from reference 10.

Another measure of softness in accordance with the HSAB theory is given by Klopman's (6) "calculated softness character," symbolized by $E_m^{\ddagger}$ in table 2. Although a calculated softness character for Zn^{2+} was not included in Klopman's paper, it seems reasonable to expect that Zn^{2+} will be intermediate between Cu^{2+} and Cd^{2+} in this respect.

TABLE 2. - Calculated softness character for selected ions[1]

Ion	$E_m^{\ddagger}$ (ev)	Hardness or softness
Fe^{3+}.............	2.22	Hard
Sr^{2+}.............	2.21	Do.
Ni^{2+}.............	.29	Borderline
Cu^{2+}.............	-.55	Do.
Cd^{2+}.............	-2.04	Soft
Ag^{+}..............	-2.82	Do.

[1] Reference 7.

EXPERIMENTAL

Chemicals

2-(Ethylthio)-ethylamine hydrochloride, ($CH_3CH_2SCH_2CH_2NH_2 \cdot HCl$), ($C_4H_{12}ClNS$); and N-ethylethylenediamine, ($CH_3CH_2NHCH_2CH_2NH_2$), ($C_4H_{12}N_2$) were purchased and used without further purification. Their purity was verified by elemental analysis, and the respective calculated theoretical and experimentally determined percentages of each element are as follows:

Compound	Analysis				
Calculated for $C_4H_{12}ClNS$..	C, 33.72	H, 9.06	Cl, 24.88	N, 9.83	S, 22.51
Found for $C_4H_{12}ClNS$.......	C, 33.81	H, 8.51	Cl, 24.60	N, 9.59	S, 22.89
Calculated for $C_4H_{12}N_2$....	C, 54.00	H, 14.51	-	N, 31.49	-
Found for $C_4H_{12}N_2$.........	C, 54.38	H, 13.91	-	N, 31.59	-

Copper sulfate pentahydrate and cadmium chloride were both ACS reagent grade.

Zinc chloride, nickel sulfate, potassium hydroxide, and hydrochloric acid were obtained as prestandardized concentrated solutions.

Deionized water, free of CO_2, was used in the preparation of all solutions.

Instruments

Measurements of pH were made with a Radiometer Type TTT1d pH meter,[4] used with a Radiometer Type G202C glass electrode and a Radiometer Type K401 fiber junction calomel reference electrode. The solutions containing the electrodes were maintained at a constant temperature ($\pm 0.1^\circ$ C) by circulating water from a constant temperature bath through jacketed titration vessels. The assembly, comprised of the pH meter and electrodes, was calibrated against reference buffer solutions based on U.S. National Bureau of Standards Certified Buffers. A two-point buffer adjustment procedure was used to compensate for any variation in the sensitivity of the glass electrode. The pH measurements were accurate within 0.02 pH.

Volumes of reagents used were measured with Class A volumetric pipets or with a glass plunger micrometer buret having an accuracy of 0.02 to 0.04 percent.

A Cary Model 15 recording spectrophotometer was used for all optical absorbance measurements. It was equipped with a Cary Model 1115 repetitive scan accessory, a Cary Model 1116 program timer, and a thermostatable cell jacket for temperature control of the absorbance cells. A constant temperature circulator supplied water through the cell jacket at 25° C. Cylindrical absorption cells of 1.00- and 5.00-cm pathlengths were used.

Experimental Procedure--Stability Constants

For each experiment, 1 to 2 millimoles of the ligand substance 2-(ethylthio)-ethylamine hydrochloride was weighed to the nearest 0.1 milligram and placed in the jacketed titration vessel; or, for the ligand substance N-ethylethylenediamine, a known volume of a standard solution (0.1890 $\underline{F}$ N-ethylethylenediamine and 0.500 $\underline{N}$ total acidity) was pipeted into the jacketed titration vessel.

In experiments designed to determine the acid dissociation constants of protonated forms of the ligand, the ligand substance was titrated with a 1.000 $\underline{N}$ potassium hydroxide solution after sufficient water was added to bring the total volume of the system to a known volume in the range of 25 to 30 ml before addition of the titrant. The volume of the solution made by adding a known volume of water to a 1- or 2-millimole quantity of

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[4] Reference to specific brands is made for identification only and does not imply endorsement by the Bureau of Mines.

2-(ethylthio)-ethylamine hydrochloride was assumed to be the same as the volume of the water used. The potassium hydroxide solution was added to the acidified ligand solution in 0.05- or 0.02-ml increments with continuous mechanical stirring, through a fine-tipped delivery tube dipped beneath the surface of the solution. The pH of the system was measured by means of appropriate electrodes immersed in the solution, after the addition of each increment of potassium hydroxide solution. Before beginning each titration, sufficient time was allowed to insure that the solution in the titration vessel had become thermally equilibrated with the temperature-regulated water being circulated through the jacket of the vessel. The heat of neutralization during the titration was considered to be too small to upset the thermal equilibration under these conditions. Because the top of the titration vessel was closed off from the atmosphere, leaving a dead air space of only about 10-ml volume above the solution, blanketing the solution with inert gas to exclude atmospheric CO_2 was unnecessary.

In experiments designed to determine metal complex stability constants, a similar procedure was followed, but with the inclusion of a known volume of a stock solution made from the chloride or sulfate salt of the transition metal, generally used in such quantity as to insure the presence of slightly more than two moles of the bidentate ligand substance per mole of metal ions. At the concentrations used, complexing of the metal ions by chloride or sulfate is too slight to interfere with determination of stability constants. Thus, there would be an ample amount of ligand present to form a 2:1 complex and thereby preclude the undesired consumption of titrant by metal-ion hydrolysis.

Data Processing--Stability Constants

The immediate result of the experimental work consisted of a set of measurements of the pH of the system. Each pH value corresponded to a value of the volume of potassium hydroxide titrant added. Further data essential to the calculation were obtained prior to the addition of titrant. These data consisted of the known total concentration of metal ions, ligand substance, and total acid, plus the total volume.

These data were processed with a Xerox Data Systems Sigma 7 computer, using the computer program SCOGS (11) (acronym for Stability Constants of Generalized Species). The program employs a nonlinear least-squares method to calculate in an iterative process those numerical values of the complex-ion stability constants which provide the best possible agreement between the observed experimental data and the corresponding calculated quantities.

Available on request from the senior author[5] is a computer-produced listing of all the titration data for each metal-ligand system and the derived quantities calculated from these data.

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[5] Computer listing available from D. J. MacDonald, Reno Metallurgy Research Center, 1605 Evans Ave., Reno, Nev. 89505.

Experimental Procedure--Absorption Spectra

This phase of the work involved the use of the following solutions:

1. A solution prepared by dissolving 0.6659 gram of N-ethylethylenediamine in 100.0 ml of water; 15.0 ml aliquots of this solution were placed in the thermostated Radiometer titration vessel at 25° C and adjusted to pH values of 6.38 and 11.08 with 1.000 N HCl. The pH of all the following solutions were adjusted in the same manner.

2. A solution consisting of 0.4166 gram of N-ethylethylenediamine dissolved in 100.0 ml of water; 5-ml portions of this solution plus 10 ml of 0.0400 F $CuSO_4$ solution were adjusted to pH values of 3.98, 5.20, 6.60, and 10.81 with 1.000 N HCl.

3. Solutions prepared by taking 10.00-ml aliquots of solution 1 plus 5.00 ml of 0.0681 F $NiSO_4$ solution and adjusting the pH to 5.98 and 7.01 with 1.000 N HCl and adjusting the pH to 9.01 and 10.50 with 1.000 N KOH. Since the $NiSO_4$ solution had an acidity of 0.0977 N hydrogen ion, pH adjustment with KOH was required for the higher pH values.

4. A solution consisting of 1.6178 grams of 2-(ethylthio)-ethylamine hydrochloride dissolved in 100.0 ml of water; 15.00-ml aliquots of this solution were adjusted to pH values of 8.08 and 9.00 with 1.000 N KOH.

5. A solution prepared by dissolving 0.4694 gram of 2-(ethylthio)-ethylamine hydrochloride in 50.0 ml of water; 10.00-ml aliquots of this solution plus 5.00 ml of 0.0400 F $CuSO_4$ solution were adjusted to pH values of 4.29, 4.91, and 5.41 with 1.000 N KOH.

6. Solutions prepared by taking 10.00-ml aliquots of solution 4 plus 5.00 ml of 0.0681 F $NiSO_4$ and adjusting the pH to 6.82 and 7.11 with 1.000 N KOH.

The final concentrations of the metal and ligand in these solutions were calculated on the assumption that the volumes of the initial ligand solutions, metal solutions, and acid and base used in adjusting the pH were additive. Preliminary experiments showed that some of the absorption spectra changed over a several days' interval, so fresh solutions were prepared and the spectra run as soon as possible, generally within an hour after preparation. The concentrations of metal and ligand selected were in the same ratios as the ratios of metals to ligands used in determining the stability constants with the SCOGS program. The total concentrations of these solutions differed slightly from that of the stability constant solutions in order to obtain suitable absorption spectra.

The solutions were made as indicated above and their absorption spectra were measured from 400 nanometers (nm) to 800 nm at 25° C on the Cary recording spectrophotometer.

The extinction coefficients determined were those of the following:

N-ethylethylenediamine and its singly protonated and doubly protonated conjugate acids;

N-ethylethylenediaminecopper(II) ion, bis(N-ethylethylenediamine)copper(II) ion, tris(N-ethylethylenediamine)copper(II) ion, and copper(II) ion;

N-ethylethylenediaminenickel(II) ion, bis(N-ethylethylenediamine)nickel(II) ion, tris(N-ethylethylenediamine)nickel(II) ion, and nickel(II) ion;

2-(ethylthio)-ethylamine and its singly protonated conjugate acid,
2-(ethylthio)-ethylaminecopper(II) ion, bis[2-(ethylthio)-ethylamine]copper(II) ion, and tris[2-(ethylthio)-ethylamine]copper(II) ion;

and 2-(ethylthio)-ethylaminenickel(II) ion and bis[2-(ethylthio)-ethylamine]-nickel(II) ion.

No extinction coefficients were determined for zinc and cadmium complexes because these are colorless.

Calculations--Extinction Coefficients

The optical extinction coefficient of a colored compound or ion at a given wavelength of light is a characteristic constant of the compound or ion.

The optical extinction coefficient is defined by the equation:

$$\varepsilon_c = \frac{A_c}{1[C]} , \qquad (1)$$

where ε_c = extinction coefficient of species C (also referred to as molar absorptivity) with dimensions of $\underline{M}^{-1}$ cm^{-1},

A_c = absorbance of species C (also referred to as absorbancy or optical density) dimensionless,

1 = length (cm) of the optical path through the solution containing species C,

and [C] = concentration of C in moles per liter ($\underline{M}$).

The absorbance of a solution or any transparent medium can be measured directly by use of a spectrophotometer and is defined as:

$$A = \log \frac{I_o}{I} , \qquad (2)$$

where I_0 = intensity of incident radiation,

and I = intensity of transmitted radiation.

The total absorbance of a solution containing i species is:

$$\frac{A}{1} = \varepsilon_1 [C_1] + \varepsilon_2 [C_2] + \varepsilon_3 [C_3] + \ldots\ldots\ \varepsilon_i [C_i]. \qquad (3)$$

The absorbance is a function of the wavelength of the incident radiation (as is the extinction coefficient for each species).

The present method for determining extinction coefficients is based on equation 3, on absorbance measurements, and on the results of the SCOGS computer program (11). The concentrations of each species present at every pH value used in the titrimetric input data are calculated and printed out by the SCOGS program. The absorbance and length of optical path at selected pH values are measured. Thus, all quantities in equation 3 are known except the extinction coefficients. By selecting a number of pH values from the SCOGS data corresponding to the number of species present, a set of simultaneous equations are derived with sufficient data to solve for the extinction coefficients.

The criterion of pH selection was that the concentration of each species forming the main diagonal coefficient in each row of simultaneous equations under consideration should be greater than the sum of the concentrations of all other species in that row. This criterion results from the Gauss-Seidel (7, 12) iteration method of solving simultaneous equations, which was used to solve equation 3.

Variations in developing the sets of simultaneous equations were used as a check on the method and to obtain coefficients which cause the Gauss-Seidel iteration method of solving simultaneous equations to converge to a solution. The extinction coefficients of the uncomplexed metal ion, the free ligand, and the protonated ligand species were determined separately. These results were included in equation 3 as constants when solving for the extinction coefficients of the metal-ligand species.

RESULTS

Stability Constants

The numerical values of the logarithms of the stability constants for the various complexes as determined in this study, together with the corresponding standard deviations, are shown in table 3. The stability constants tabulated below are defined as follows:

For a metal ion M and a neutral, deprotonated ligand L,

$$\beta_1 = [ML]/[M][L],$$

$$\beta_2 = [ML_2]/[M][L]^2,$$

and

$$\beta_3 = [ML_3]/[M][L]^3,$$

where square brackets denote the concentration in gram-moles per liter.

TABLE 3. - Stability constants at 25° C

Ligand	Log β_1	Log β_2	Log β_3
A. CATION Ni^{2+}			
N-Ethylethylenediamine......	6.136±0.011	10.639±0.021	13.74±0.14
2-(Ethylthio)-ethylamine....	2.828±0.007	5.252±0.008	No complex
B. CATION Cu^{2+}			
N-Ethylethylenediamine......	9.547±0.006	17.196±0.008	18.56±0.23
2-(Ethylthio)-ethylamine....	5.369±0.015	10.035±0.054	14.43±0.15
C. CATION Zn^{2+}			
N-Ethylethylenediamine......	4.611±0.016	8.658±0.030	No complex
2-(Ethylthio)-ethylamine....	No complex	No complex	No complex
D. CATION Cd^{2+}			
N-Ethylethylenediamine......	4.807±0.024	8.322±0.044	10.01±0.37
2-(Ethylthio)-ethylamine....	2.719±0.005	4.451±0.009	No complex
E. CATION H^+			
N-Ethylethylenediamine......	10.220±0.004	17.367±0.006	-
2-(Ethylthio)-ethylamine....	9.366±0.003	No complex	-

Table 3 also includes values (part E) for the free ligand protonation constants as determined in these studies. The protonation constants are related to the base strength of the ligands and are essential to evaluation of the metal-ligand stability constants by the method used. The base strength is expressed in terms of the protonation constant or the stability constant for formation of the conjugate acid. In studies using 2-(ethylthio)-ethylamine, no result is expected for β_2. Although the primary amine group in that compound is protonated readily, the only other possible site for protonation, namely the sulfur atom, is not susceptible to protonation in dilute aqueous solution.

Absorption Spectra

The extinction coefficients of each individual metal-ligand species are presented in figures 1 through 4, which are graphs of extinction coefficients versus wavelength. The crystal field splitting energy and crystal field stabilization energy (to be discussed later) were calculated in accordance with the methods described by Drago (4) and by Basolo and Pearson (2). These results are given in table 4.

TABLE 4. - Crystal field stabilization energies (CFSE) and crystal field splitting energy (10 Dq)

Species	Maximum, nm	10 Dq		CFSE	
		kcal/mole	cm^{-1}	kcal/mole	cm^{-1}
N-ETHYLETHYLENEDIAMINE PLUS COPPER(II)					
ML	670	42.65	14,925	25.60	8,955
ML_2	560	51.03	17,857	30.63	10,714
ML_3	550	51.96	18,182	31.19	10,909
N-ETHYLETHYLENEDIAMINE PLUS NICKEL(II)					
ML	620	46.09	16,129	55.34	19,355
ML_2	570	50.13	17,544	60.19	21,053
ML_3	580	49.27	17,241	59.15	20,689
2-(ETHYLTHIO)-ETHYLAMINE PLUS COPPER(II)					
ML	720	39.69	13,889	23.83	8,333
ML_2	580	49.27	17,241	29.58	10,345
ML_3	650	43.96	15,385	26.39	9,231
2-(ETHYLTHIO)-ETHYLAMINE PLUS NICKEL(II)					
ML	630	45.36	15,873	54.46	19,048
ML_2	([1])	-	-	-	-

[1] No maximum could be detected.

DISCUSSION

Stability Constants

Numerical values of the stability constants, as shown in table 3, follow usually expected trends, with successively larger values for successive steps of complexation, and with values for the four metals increasing in the order $Zn^{2+} < Cd^{2+} < Ni^{2+} < Cu^{2+}$, thereby indicating the general validity of the results.

The result for protonation of 2-(ethylthio)-ethylamine provides substantial support for a prediction by Clark and Perrin (3) that a typical primary amine will have log β = 10.77 and that its base strength will be diminished by 1.4 log units if an alkylthio group is located two carbon atoms away from the base center. According to this prediction, 2-(ethylthio)-ethylamine should have log β_1 = 9.37. By actual experiment, the value was found to be log β_1 = 9.366.

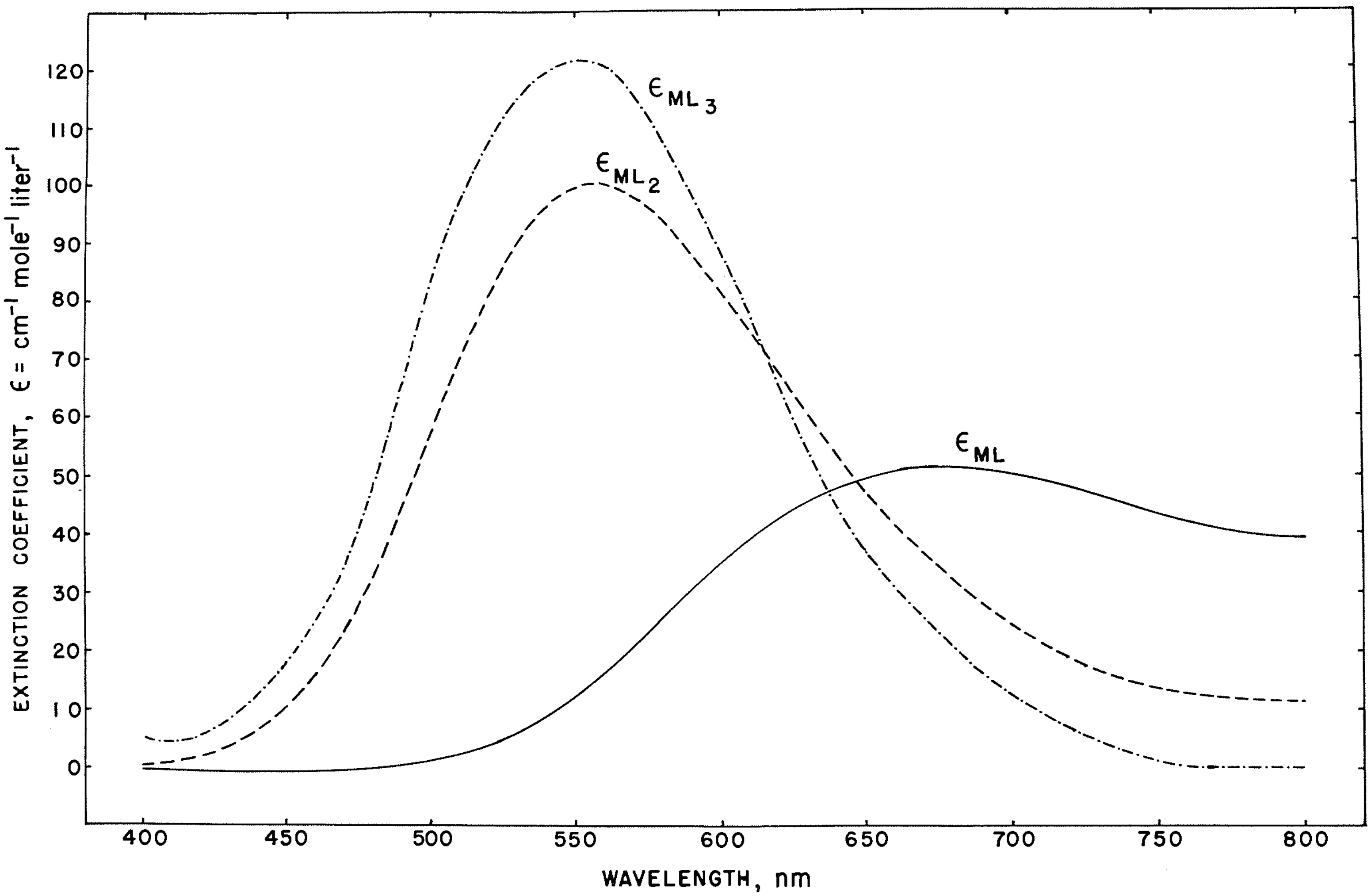

FIGURE 1. - Extinction Coefficients of N-Ethylethylenediamine Coordination Species With Copper(II).

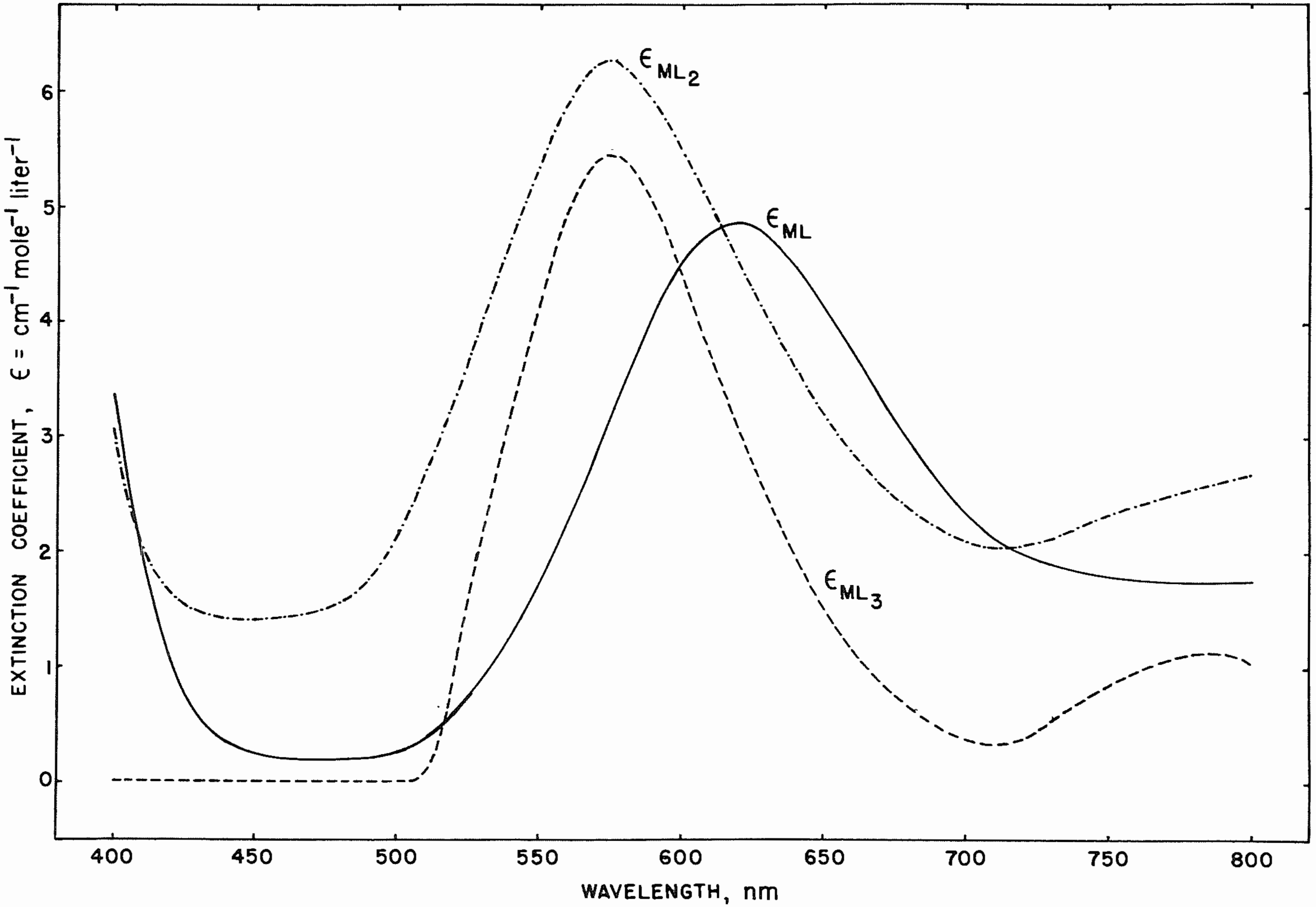

FIGURE 2. - Extinction Coefficients of N-Ethylethylenediamine Coordination Species With Nickel(II).

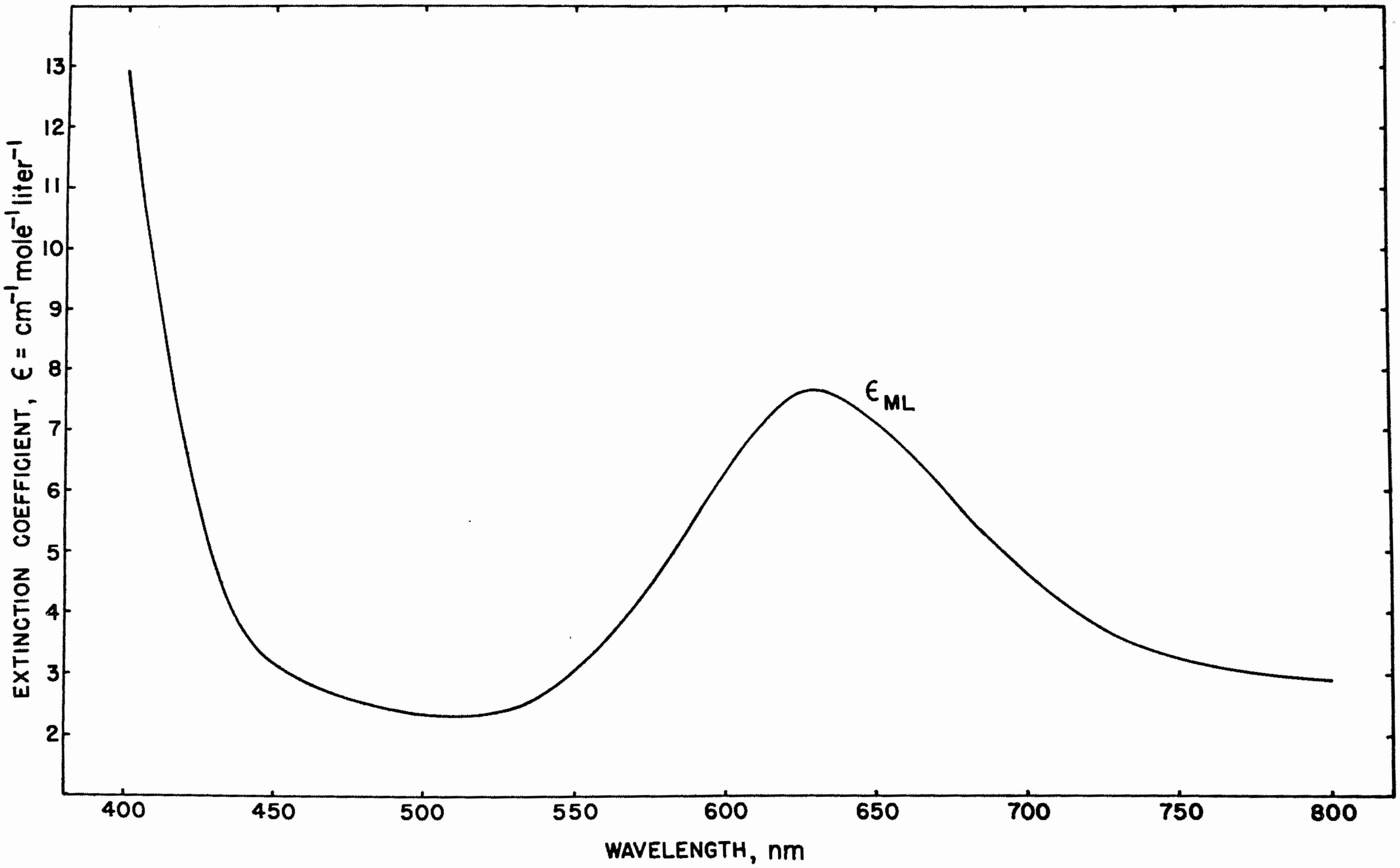

FIGURE 3. - Extinction Coefficients of 2-(Ethylthio)-ethylamine Coordination Species With Nickel(II).

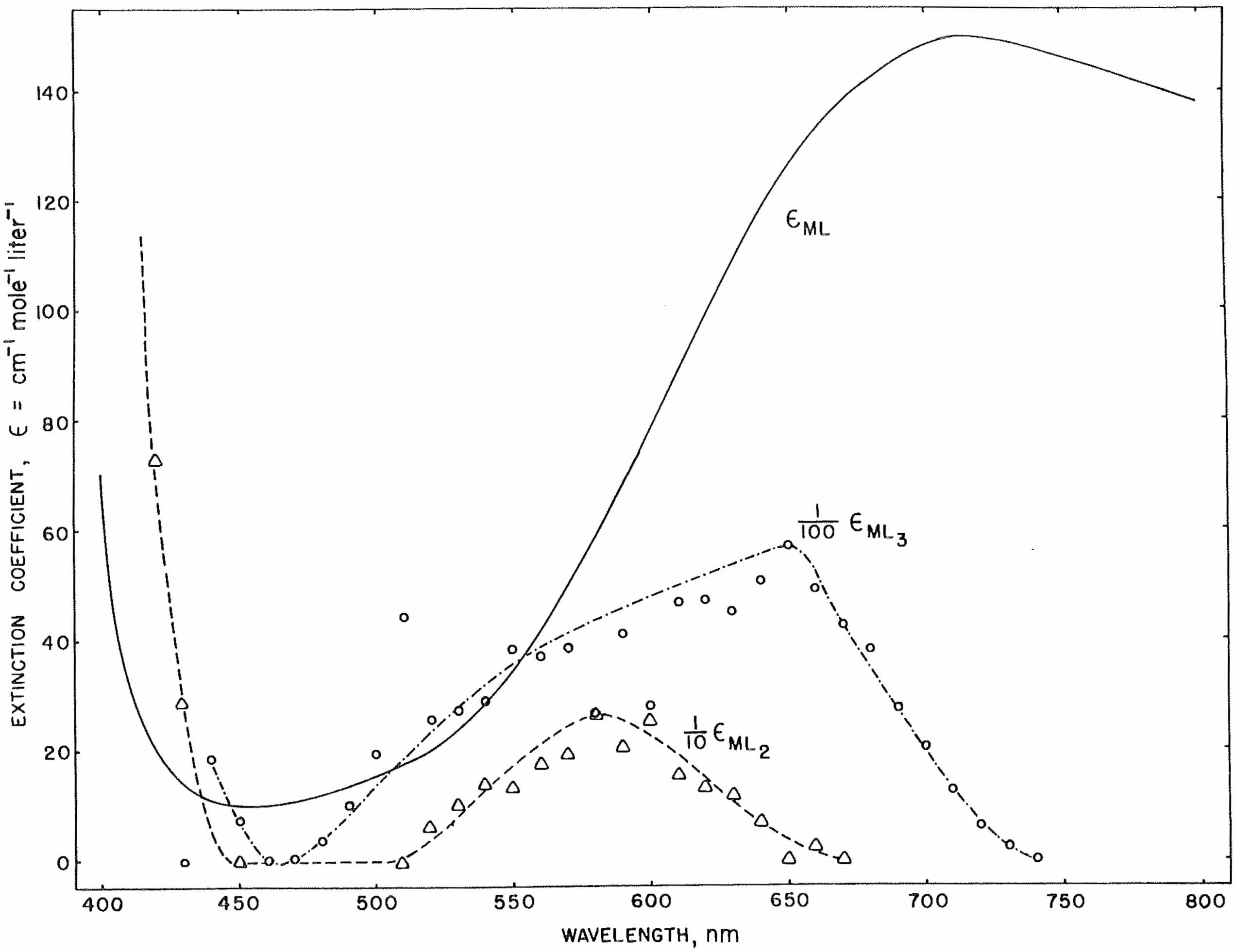

FIGURE 4. - Extinction Coefficients of 2-(Ethylthio)-ethylamine Coordination Species With Copper(II).

It is noteworthy that the difference in basicity between the two ligands, using data from part E of table 3, for example, 10.220 - 9.366 = 0.854, is much smaller than the corresponding difference between metal-ligand stability constants. These differences are tabulated for each metal in table 5, and as shown, the Δ log β_1 for the proton is much smaller than those of Ni^{2+}, Cu^{2+}, and Cd^{2+}. This strongly suggests that the observed difference in complexing ability between these two ligands cannot be ascribed to a difference in basicity alone. Evidently, the secondary nitrogen atom of the N-ethylethylenediamine molecule coordinates a metal atom much more strongly than does the secondary sulfur atom of the 2-(ethylthio)-ethylamine molecule. As would be predicted by the HSAB theory, this difference is least for Cd^{2+}, the softest of the Lewis acids involved. If still softer metal cations were used (such as Hg^{2+}), cations might conceivably be found for which the sulfur-containing ligand would be a stronger chelating agent than its nitrogen-containing analog.

TABLE 5. - Differences in stability constants for comparable complexes of N-ethylethylenediamine and of 2-(ethylthio)-ethylamine (log β for N-ethylethylenediamine minus log β for 2-(ethylthio-ethylamine))

Cation	Δ Log β_1	Δ Log β_2	Δ Log β_3
Ni^{2+}	3.31	5.39	-
Cu^{2+}	4.18	7.16	4.1
Cd^{2+}	2.09	3.87	-
H^+	.85	-	-

Thermodynamics of Complex Formation

Under the isothermal and isobaric conditions of these experiments, the stability constant of a given reaction is related to its standard Gibbs free energy change according to the relation

$$\Delta G° = -RT \ln \beta,$$

where R is the ideal gas constant and T is the absolute temperature.

At 25° C, this expression reduces to

$$\Delta G° = -1.364 \log_{10} \beta \text{ (kcal·mole}^{-1}).$$

For example, on this basis, the Gibbs free energy change for the reaction producing the N-ethylethylenediaminecopper(II) complex is found to be -13.02 kcal $mole^{-1}$.

Part of the free energy of chelation depends on the electric field intensity experienced by the nonbonding electrons of the metal ion in the transition-metal complex. This contribution to the overall free energy of a coordination compound is referred to as the crystal field stabilization energy (CFSE). The magnitude of the CFSE depends on the number of d-subshell electrons in the metal ion, and on the intensity and symmetry of the electric field imposed on the ion by its surroundings. For the complexes involved in this investigation, the CFSE can be calculated from a knowledge of the absorption spectra, the assumed electron configurations, and the assumed octahedral symmetry. For Ni^{2+}, with its d^8 configuration, the CFSE for an octahedral complex is equal to 12 Dq, where the quantity 10 Dq corresponds to the crystal field splitting energy. For Cu^{2+}, with a d^9 configuration, the CFSE in an octahedral complex equals 6 Dq. In the case of Zn^{2+} and Cd^{2+}, their closed subshell d^{10} electron configurations result in CFSE equal to zero regardless of their environment. Even though the CFSE involves only those d-subshell electrons described as nonbonding electrons in the terminology of the molecular orbital theory, it is a very substantial quantity of energy, amounting to 29.2 kcal·$mole^{-1}$ for hydrated Ni^{2+}. In general, the CFSE is large enough so that its influence on the thermodynamics of chelation cannot be ignored.

In particular, the difference in CFSE between complexes of N-ethylethylenediamine and 2-(ethylthio)-ethylamine must be accounted for in a comparison of stability constants for those ligands. When this difference in CFSE is added to the free energy difference, the sum represents the stereochemical contribution to the energy of chelation excluding the undesired electronic contribution. This pure stereochemical energy of chelation, and the values from which it is derived, is shown in table 6.

TABLE 6. - Stereochemical free energy of chelation

Ion	Log β_1 (N)[1]	Log β_1 (S)[2]	Δ Log β_1	$\Delta\Delta G$[3] (kcal/mole)	Δ CFSE (kcal/mole)	Stereochemical $\Delta\Delta G$ (kcal/mole)
Cu^{2+}	9.547	5.369	4.178	-5.699	1.87	-3.83
Ni^{2+}	6.136	2.828	3.308	-4.512	.88	-3.63
Cd^{2+}	4.807	2.719	2.088	-2.848	.00	-2.85

[1] For complexing with N-ethylethylenediamine.
[2] For complexing with 2-(ethylthio)-ethylamine.
[3] $\Delta\Delta G = -1.364\ \Delta \log \beta$.

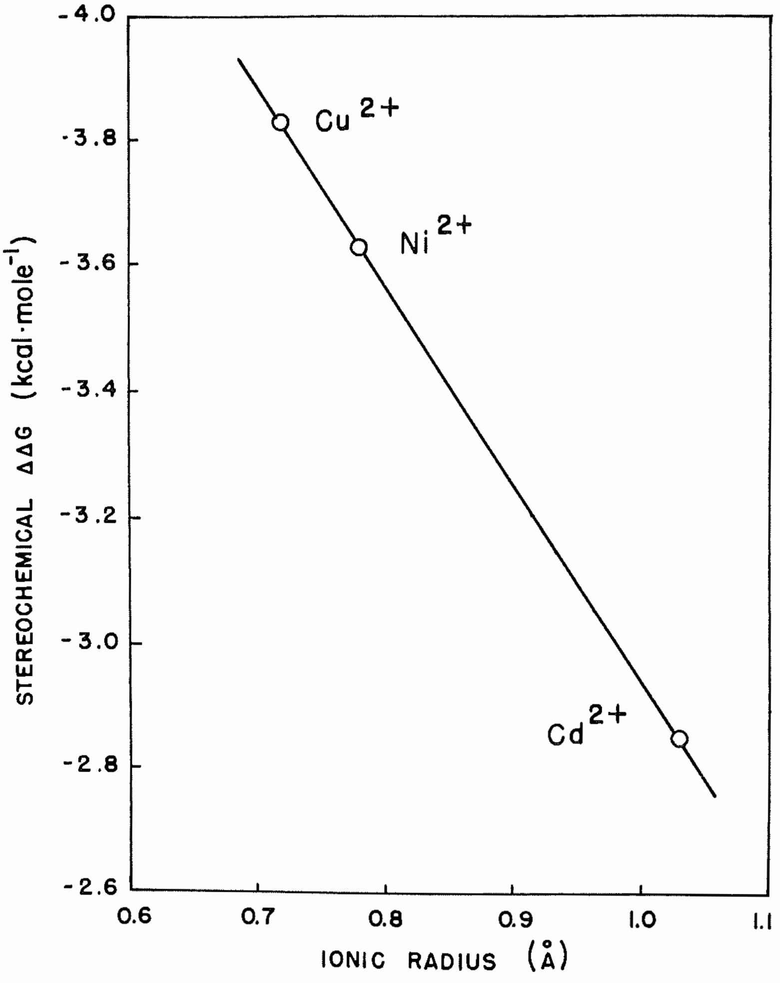

FIGURE 5. - Stereochemical ΔΔG Versus Ionic Radius.

In figure 5, these values of stereochemical free energy change have been plotted versus the ionic radius of Cu^{2+}, Ni^{2+}, and Cd^{2+} [using data from reference (2)]. The graph shows an apparent linear free energy relationship between free energy change and ionic radius, with a slope of 3.16 $kcal \cdot mole^{-1} \cdot angstrom^{-1}$. The present data are not extensive enough to establish this relationship as a general rule, but they may encourage a search for similar results in other metal-ligand systems. At present, this proposed relationship must be considered somewhat speculative.

Absorption Spectra

The present method allows definite assignment of each spectrum to the corresponding individual species. Because of this, the crystal field stabilization energy may be found for each species. In contrast to this, an actual spectrum as observed is the sum of the contributions of all the species; the shape and wavelength of the maximum is pH-dependent. The reason for the pH-dependency is that the equilibrium shifts to favor the formation of one or more species. By material balance and chemical reasoning a guess may be made as to which species, ML for example, is predominately responsible for a given maximum at a given pH. However, this method of assigning a maximum to a given species fails completely in the case of ML_2 and ML_3 in figures 1 and 2. The maxima for these species occur so close together that no assignment to the individual species can be made from the actual spectrum as observed. Thus, the present method yields information about individual species which is impossible to obtain otherwise.

The extinction coefficients for all species except bis[2-(ethylthio)-ethylamine]copper(II) and tris[2-(ethylthio)-ethylamine]copper(II), ML_2 and ML_3 in figure 4, produced smooth curves when plotted against wavelength. In these two exceptions, there was considerable scatter of the data. Bis[2-(ethylthio)-ethylamine]nickel(II) had extinction coefficients of zero from 400 to 800 nm.

Many spectra were recorded and calculations made on the 2-(ethylthio)-ethylamine system with copper(II) and nickel(II) in an effort to improve the results, but without success. Finally, the SCOGS output was examined, showing that the concentrations of the species for which erratic results were obtained were very small compared to the total concentration of other species which contribute to the absorbance. For example, $[ML_3]/([ML] + [ML_2] + [Cu(II)])$ for 2-(ethylthio)-ethylamine with copper(II) equaled only 0.003. The same type of ratio for the species for which consistent results were obtained ranged from 0.1 to 59.6. When a species contributes a very small amount to the total absorbance, erratic results can be caused by very small errors of measurement. The results for bis[2-(ethylthio)-ethylamine]nickel(II) are probably actually zero absorbance, because no positive results appeared as would be expected from random errors alone.

To check on the accuracy of the present method of measuring extinction coefficients, 41 measurements each of $\epsilon_{Cu^{2+}}$ and $\epsilon_{Ni^{2+}}$ were made with the ligand N-ethylethylenediamine. These results were compared with direct measurements of $\epsilon_{Cu^{2+}}$ and $\epsilon_{Ni^{2+}}$ made in the absence of a ligand. Assuming there were no errors in the direct measurements, the standard deviation of a single observation of ϵ was 0.26 for Cu^{2+} and 0.20 for Ni^{2+}.

CONCLUSIONS

Precise numerical values were determined for the stability constants of all the complexes formed between the analogous ligands N-ethylethylenediamine and 2-(ethylthio)-ethylamine and the metal ions Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+}. Absorption spectra and crystal field stabilization energies were also determined for each of the above-mentioned complexes containing copper or nickel.

The nitrogen-containing ligand was found to be the stronger of the two chelating agents for each of the four metals. Data on stability constants were combined with crystal field stabilization energy data to yield corrected values of the differences between free energies of formation of analogous complexes of the two ligands. These corrected stereochemical free energy differences were tentatively interpreted via a linear correlation with the ionic radius of the chelated metal ion.

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