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Complexes of Diethylenetriamine, 2-Aminoethyl Sulfide, Triethylenetetramine, and 1,8-Diamino-3,6-dithiaoctane

UNITED STATES DEPARTMENT OF THE INTERIOR

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Complexes of Diethylenetriamine, 2-Aminoethyl Sulfide, Triethylenetetramine, and 1,8-Diamino-3,6-dithiaoctane

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by

Alexander May[1] and David J. MacDonald[1]

ABSTRACT

In this Bureau of Mines publication stability constants for complexes of diethylenetriamine, 2-aminoethyl sulfide, triethylenetetramine, and 1,8-diamino-3,6-dithiaoctane with copper, nickel, zinc, and cadmium were determined. The amine complexes were found to be much more stable than the analogous thio complexes. The results are interpreted in terms of possible molecular structure of the complexes.

INTRODUCTION

One phase of 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 efforts are designed to obtain a better understanding of the relation between a ligand's structure and its ability to function as a chelating agent for a particular metal ion or group of metal ions. The results serve as an aid in predicting ligand structures which may be useful in treating ores that do not lend themselves to conventional processing techniques, thus increasing the Nation's mineral resource potential.

Specifically, the objective of this work was to compare the coordinating ability of secondary amines with that of analogous thio compounds. Names and formulas of the ligands with the symbols by which they will be identified throughout this report are as follows:

Symbol	Formula	Name
-N-N	$CH_3CH_2NH(CH_2)_2NH_2$	N-ethylethylenediamine
-S-N	$CH_3CH_2S(CH_2)_2NH_2$	2-ethylthio-ethylamine
N-N-N	$H_2N(CH_2)_2NH(CH_2)_2NH_2$	diethylenetriamine
N-S-N	$H_2N(CH_2)_2S(CH_2)_2NH_2$	2-aminoethyl sulfide
N-N-N-N	$H_2N(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$	triethylenetetramine
N-S-S-N	$H_2N(CH_2)_2S(CH_2)_2S(CH_2)_2NH_2$	1,8-diamino-3,6-dithiaoctane

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[1] Research chemist.

A report on the initial phase of this work by MacDonald, May, and Baglin (2)[2] describes the experimental methods, calculations, and stability constants for the complexes of -N-N and -S-N with Cu^{2+}, Ni^{2+}, Zn^{2+}, and Cd^{2+} in aqueous solution. The current study extends to complexes of these metals with N-N-N, N-S-N, N-N-N-N, and N-S-S-N, making possible a comparison of a set of bidentate ligands with sets of similar tridentate and tetradentate ligands.

Stability constants reported in the literature by different authors often are not strictly comparable because they are often determined under significantly different conditions. The stability constants determined in this study correspond to a uniform temperature of 25.0° C and an ionic strength of 0.1. Although many stability constants are reported in the literature and in the monograph by Sillén and Martell (5), few of these constants have been determined under conditions comparable to those adopted in this investigation. No suitable values determined under these conditions were found in the literature for complexes of N-S-S-N and no values determined under any conditions were found for the ligand N-S-N. Thus, the present study provides a self-consistent basis of comparison for these ligands and fills gaps in existing data.

Optical absorption spectra were also determined for the various complexes. Because calculation of stability constants requires use of an arbitrary assumption regarding the identities of the several complexes present in a given metal-ligand mixture, a separate procedure (2) was applied to determine the optical absorption spectra of each such complex. Although the computation of individual absorption spectra from the spectrum of a mixture requires an arbitrary assumption as to which complexes are present, the observation that a single set of assumed complexes leads to satisfactory agreement with experiment in both the stability constant computation and the absorption spectrum computation strongly suggests that the set of assumed complexes is the correct one.

EXPERIMENTAL

Chemicals

Diethylenetriamine, $C_4H_{13}N_3$, (N-N-N), was purchased and redistilled under helium at 18 to 22 torr. The fraction boiling from 99° C at 18 torr to 104° C at 22 torr was used.

2-Aminoethyl sulfide dihydrochloride, $C_4H_{12}N_2S \cdot 2HCl$, (N-S-N·2HCl), was prepared and purified by the method of Marxer and Miescher (3).

Triethylenetetramine dihydrosulfate dihydrate, $C_6H_{18}N_4 \cdot 2H_2SO_4 \cdot 2H_2O$, (N-N-N-N·$2H_2SO_4 \cdot 2H_2O$), was purchased and used without further purification.

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

1,8-Diamino-3,6-dithiaoctane dihydrochloride, $C_6H_{16}N_2S_2 \cdot 2HCl$, (N-S-S-N·2HCl), was prepared and purified by the method of Dwyer and Lyons (1).

Results of elemental analyses of these reagents, as shown in table 1, suggests a satisfactory degree of purity.

TABLE 1. - Elemental analyses

Compound	C, pct		H, pct		Cl, pct		N, pct		S, pct	
	Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found
$C_4H_{13}N_3$............	46.57	46.39	12.70	12.62	-	-	40.73	39.63	-	-
$C_4H_{12}N_2S$ 2HCl......	24.88	24.80	7.31	7.37	-	-	14.50	14.47	16.60	16.48
$C_6H_{18}N_4 \cdot 2H_2SO_4 \cdot 2H_2O$	19.04	19.16	6.93	6.46	-	-	-	-	16.95	14.01
$C_6H_{16}N_2S_2 \cdot 2HCl$.....	28.46	28.47	7.16	7.30	28.00	28.01	11.06	10.28	25.32	24.87

The copper, nickel, zinc, cadmium, potassium hydroxide, and hydrochloric acid solutions were prepared from copper sulfate pentahydrate and cadmium of ACS reagent grade and 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[3] (Ser. No. 122834), 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 (±0.1° 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. This was equipped with 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 path lengths were used.

Experimental Procedure--Stability Constants

For a typical experiment, 1 to 2 millimoles of a ligand substance was weighed to the nearest 0.1 milligram and placed in the jacketed titration vessel; or, for the ligand substance diethylenetriamine, a known volume of a standard acidified solution of the ligand was pipeted into the jacketed titration vessel.

In experiments designed to determine the acid dissociation constants of protonated forms of a ligand, the ligand substance was titrated with a 1.000-N potassium

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

hydroxide solution after sufficient water had been 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 ligand substance 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 held beneath the surface of the solution. The pH of the system was measured by means of appropriate electrodes immersed in the solution, readings being taken after the addition of each increment of potassium hydroxide solution. Before beginning each titration, sufficient time was allowed to ensure 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 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 precisely known quantity of a soluble transition metal salt generally used in such quantity as to ensure the presence of slightly more than two moles of the bidentate ligand substance per mole of metal ions. 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. Other essential input data concerned the total concentration of metal ions, ligand substance, acid, and total volume, each referring to conditions prior to the addition of titrant.

These data were processed with a Xerox Data Systems Sigma 7 computer, using the computer program SCOGS (4) (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.

Experimental Procedure--Absorption Spectra

Absorption spectra of appropriate metal-ligand mixtures were measured by use of solutions adjusted to have pH sufficient to provide significant concentrations of the complexes whose individual spectra were desired.

The final concentrations of the metal and ligand in these solutions were calculated on the assumption that the volumes of the ligands were insignificant and 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 several days' interval, so fresh solutions were prepared and the spectra run as soon as possible, generally within 1 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 absorption spectra of such mixtures were measured from 400 nm to 800 nm at 25° C with the Cary recording spectrophotometer.

Optical extinction coefficients of Cu(II) and Ni(II) complexes of N-N-N-N and N-S-S-N were not determined in this way. Only one complex species was found for Cu(II) with each of these two ligands. For Ni(II) only one complex species was detected with N-S-S-N and two complex species with N-N-N-N. The absorption spectra of these complexes could therefore be determined directly by use of solutions whose pH had been adjusted to the point at which the desired complex was predominant.

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:

$$\varepsilon_c = \frac{A_c}{l[C]}, \tag{1}$$

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

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

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

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

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

$$A = \log \frac{I_0}{I}, \tag{2}$$

where I_0 = intensity of incident radiation,

and I = intensity of transmitted radiation.

The total absorbance of a solution containing i species is:

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

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

The present method for determing extinction coefficients is based on equation 3, on absorbance measurements, and on the results of the SCOGS computer program (4). 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 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 to converge satisfactorily. The extinction coefficients of the uncomplexed metal ion, the free ligand, and 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 series.

RESULTS

Table 2 shows numerical values of logarithms of the stability constants for the various complexes as determined in this study, together with their standard deviations. For a metal ion M, and a neutral, deprotonated ligand L, the stability constants are defined as follows:

$$\beta_1 = [ML]/[M][L], \qquad (4)$$

$$\beta_2 = [ML_2]/[M][L]^2, \qquad (5)$$

$$\beta_3 = [ML_3]/[M][L]^3, \qquad (6)$$

$$\beta_4 = [ML_4]/[M][L]^4. \qquad (7)$$

The protonation constants are also defined as above with the metal ion, M, being replaced by the proton, H. There are two species in table 2, MLOH and MHL, which contain either a hydroxide group, OH^-, or an extra proton, H^+.

The stability constants for these species are defined as:

$$\beta = [MLOH]/[L][M][OH^-] \text{ for MLOH,} \tag{8}$$

$$\beta = [MHL]/[L][M][H^+] \text{ for MHL.} \tag{9}$$

The square brackets denote molar concentration.

TABLE 2. - Stability constants

Cation	Stability constants	Complex	Cation	Stability constants	Complex
LIGAND: N-N-N			LIGAND: N-N-N-N		
H^+	$\log \beta_1 = 9.929 \pm 0.008$	HL	H^+	$\log \beta_1 = 10.006 \pm 0.007$	HL
	$\log \beta_2 = 18.981 \pm 0.007$	H_2L		$\log \beta_2 = 19.428 \pm 0.005$	H_2L
	$\log \beta_3 = 23.230 \pm 0.011$	H_3L		$\log \beta_3 = 26.729 \pm 0.009$	H_3L
				$\log \beta_4 = 31.145 \pm 0.012$	H_4L
Cu^{++}	$\log \beta_1 = 15.615 \pm 0.021$	ML	Cu^{++}	$\log \beta_1 = 20.750 \pm 0.050$	ML
	$\log \beta_2 = 20.198 \pm 0.072$	ML_2			
	$\log \beta_1 = 7.750 \pm 0.095$	MLOH			
Ni^{++}	$\log \beta_1 = 10.232 \pm 0.040$	ML	Ni^{++}	$\log \beta_1 = 14.194 \pm 0.052$	ML
	$\log \beta_2 = 18.149 \pm 0.062$	ML_2		$\log \beta_2 = 17.503 \pm 0.147$	ML_2
Cd^{++}	$\log \beta_1 = 7.493 \pm 0.026$	ML	Cd^{++}	$\log \beta_1 = 10.675 \pm 0.045$	ML
	$\log \beta_2 = 12.469 \pm 0.035$	ML_2		$\log \beta_2 = 12.709 \pm 0.192$	ML_2
Zn^{++}	$\log \beta_1 = 8.730 \pm 0.029$	ML	Zn^{++}	$\log \beta_1 = 11.802 \pm 0.043$	ML
	$\log \beta_2 = 13.205 \pm 0.046$	ML_2		$\log \beta_1 = 2.012 \pm 0.099$	MLOH
LIGAND: N-S-N			LIGAND: N-S-S-N		
H^+	$\log \beta_1 = 9.675 \pm 0.006$	HL	H^+	$\log \beta_1 = 9.564 \pm 0.004$	HL
	$\log \beta_2 = 18.390 \pm 0.004$	H_2L		$\log \beta_2 = 18.404 \pm 0.003$	H_2L
Cu^{++}	$\log \beta_1 = 9.004 \pm 0.016$	ML	Cu^{++}	$\log \beta_1 = 10.598 \pm 0.010$	ML
Ni^{++}	$\log \beta_1 = 7.019 \pm 0.009$	ML	Ni^{++}	$\log \beta_1 = 7.186 \pm 0.016$	ML
	$\log \beta_2 = 12.676 \pm 0.010$	ML_2			
Cd^{++}	$\log \beta_1 = 4.889 \pm 0.012$	ML	Cd^{++}	$\log \beta_1 = 4.867 \pm 0.024$	ML
	$\log \beta_2 = 7.825 \pm 0{,}018$	ML_2		$\log \beta_1 = 12.276 \pm 0.063$	MHL
Zn^{++}	$\log \beta_1 = 5.054 + 0.021$	ML	Zn^{++}	$\log \beta_1 = 5.067 \pm 0.070$	ML
	$\log \beta_2 = 7.902 \pm 0.035$	ML_2		$\log \beta_2 = 7.445 \pm 0.105$	ML_2

To facilitate interpretation of the results, the stability constants from the present study and from the initial investigations (2) are given in table 3. Three stability constants have been omitted from the table, because they have a stoichiometry not comparable with that of the other species on table 3. The three species are as follow: MLOH for Cu^{2+} plus N-N-N; MLOH for Zn^{++} plus N-N-N-N; and MHL for Cd^{++} plus N-S-S-N.

TABLE 3. - Summary of stability constants

Ligand	HL, log β_1	H_2L, log β_2	H_3L, log β_3	H_4L, log β_4	CuL, log β_1	CuL_2, log β_2	CuL_3, log β_3	NiL, log β_4
-N-N	10.2	17.4	(1)	(1)	9.5	17.2	18.7	6.1
-S-N	9.4	(1)	(1)	(1)	5.4	10.1	14.1	2.8
N-N-N	9.9	19.0	23.2	(1)	15.6	20.2	(1)	10.2
N-S-N	9.7	18.4	(1)	(1)	9.0	(1)	(1)	7.0
N-N-N-N	10.0	19.4	26.7	31.1	20.8	(1)	(1)	14.2
N-S-S-N	9.6	18.4	(1)	(1)	10.6	(1)	(1)	7.2

Ligand	NiL_2, log β_2	NiL_3, log β_3	CdL, log β_1	CdL_2 log β_2	CdL_3, log β_3	ZnL, log β_1	ZnL_2, log β_2	ZnL_3 log β_3
-N-N	10.6	13.7	4.7	8.1	9.4	4.6	8.7	9.4
-S-N	5.2	(1)	2.7	4.4	(1)	(1)	(1)	(1)
N-N-N	18.1	(1)	7.5	12.5	(1)	8.7	13.2	(1)
N-S-N	12.7	(1)	4.9	7.8	(1)	5.1	7.9	(1)
N-N-N-N	17.5	(1)	10.7	12.7	(1)	11.8	(1)	(1)
N-S-S-N	(1)	(1)	4.9	(1)	(1)	5.1	7.4	(1)

[1] No complex formed.

Wavelengths of the principal absorption peaks in the 400 nm to 700 nm range are shown in table 4.

TABLE 4. - Wavelength of principal absorption peaks in the UV-visible region for complexes of Cu^{2+} and Ni^{2+}

Ligand	Complex	Wavelength (nanometers)	
		Cu^{2+}	Ni^{2+}
N-N-N	ML	610	590
N-N-N	ML_2	620	520
N-N-N	MLOH	650	-
N-S-N	ML	670	590
N-S-N	ML_2	-	550
N-N-N-N	ML	580	566
N-N-N-N	ML_2	-	543
N-S-S-N	ML	617	576

DISCUSSION

Data in table 3 show that the number of protonated species is the same for each ligand as the number of amino groups in the ligand. The thio group remains unprotonated and has little effect on the stability of the protonated species. The basicities of the ligands are somewhat similar and thus are not a major factor in the variations in stability of the metal coordination species. In every case where both amino and thio complexes are formed, the stability of the complex containing a secondary amino group is greater than that of the analogous ligand containing a thio group (2).

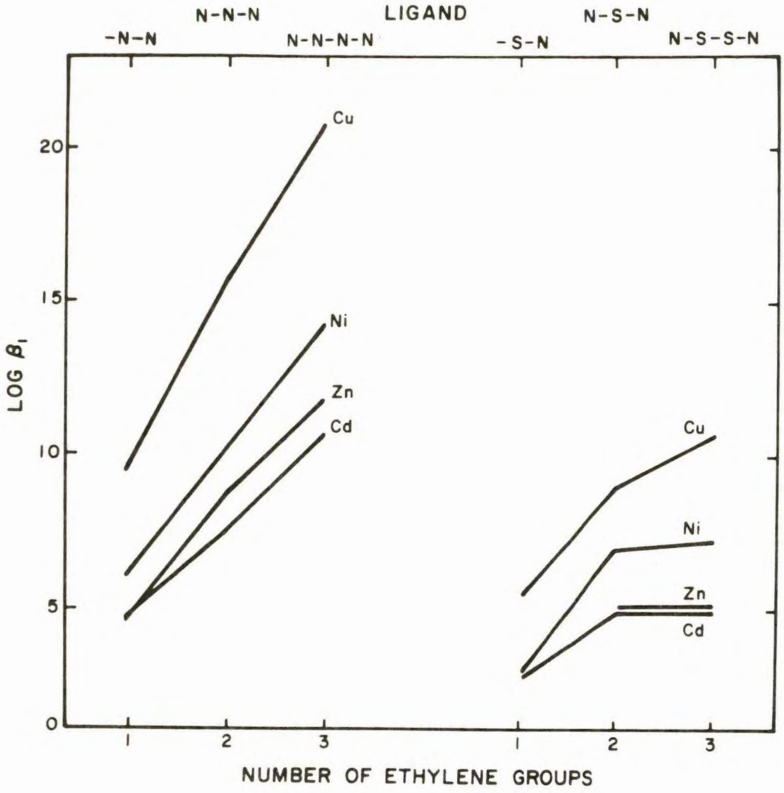

FIGURE 1. - Stability constants versus number of ethylene groups.

The general relationships and trends in the values of the stability constants can be seen in figure 1, which is a plot of log β_1 against the number of ethylene groups, $-(CH_2)_2-$, in the ligand, emphasizing the contrast between the secondary amines and the analogous sulfides. Similar plots are obtained for higher order β values. Table 3 and figure 1 show that the order of stability is: Cu > Ni > Zn > Cd; tetradentate > tridentate > bidentate, and secondary amino compounds > thio compounds.

At the outset, it was assumed that N-S-S-N would act as a tetradentate ligand analogous to N-N-N-N. Therefore, finding no ML_2 complexes formed between N-S-S-N and Cu^{2+}, Ni^{2+}, or Cd^{2+} was as expected, although it did seem odd that the log β_1 values for complexes of N-S-S-N were so much smaller than those for analogous complexes of N-N-N-N. But quite unexpected was the discovery of an ML_2 complex between N-S-S-N and Zn^{2+} in the absence of any such ML_2 complex between N-N-N-N and Zn^{2+}. Another unexpected observation was the formation of a protonated form of the ML complex between N-S-S-N and Cd^{2+}, which must mean that only one of the amine groups was coordinated to the Cd^{2+}, leaving the other amine group free to accept a proton. These observations, when considered all together, strongly suggest that the N-S-S-N molecule is only a bidentate ligand, unlike N-N-N-N which may function as a bidentate, tridentate, or tetradentate ligand. In the case of the Ni^{2+}, Zn^{2+}, and Cd^{2+} complexes, it is noteworthy that the ML complexes of N-S-N have essentially the same log β_1 values as the ML complexes of N-S-S-N. This strongly suggests that both these ligands may be only bidentate, having structures as in figures 2C and 2D. The observation of a larger value for log β_2 in $Zn^{2+}(N\text{-}S\text{-}N)_2$ than in $Zn^{2+}(N\text{-}S\text{-}S\text{-}N)_2$, while not conclusive, is at least consistent with this hypothesis in that the latter complex would be subject to greater steric hindrance.

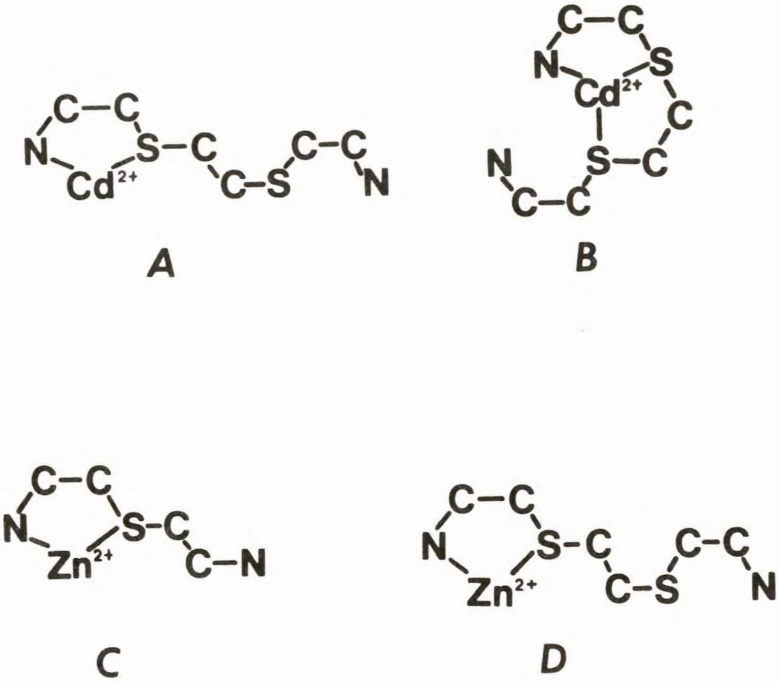

FIGURE 2. - Possible structures of complexes formed by Cd^{2+} and Zn^{2+} with N-S-N and N-S-S-N. (Hydrogen atoms omitted for clarity.)

The secondary amine ligands are structurally analogous to the thio-containing ligands. Differences in stabilities of these two classes of compounds are a measure of the coordinating ability of the secondary amino groups, -NH-, compared to that of the thio groups, -S-. These results are given in table 5, in which log K_3 = log β_3 - log β_2, and log K_2 = log β_2 - log β_1. Thus, K_2 and K_3 measure the changes in stability produced by adding a second and third ligand to species already containing one and two ligands, respectively. Table 5 shows that the secondary amino group enhances the stability relative to the thio group by factors of $10^{2.5}$ to $10^{5.3}$ for β_1 and by factors of $10^{1.7}$ to $10^{3.0}$ for K_2, but apparently decreases the stability for K_3. With only a single datum available for K_3, no general conclusions on this point are possible. The greater stability of the secondary amine complexes is probably due to the formation of five-membered chelate rings which are more favored by the particular covalent radius and electronegativity of nitrogen rather than that of sulfur.

TABLE 5. - Coordinating ability of -NH- compared to that of -S-

Ligands	Δ log β_1			
	Cu^{+2}	Ni^{+2}	Zn^{+2}	Cd^{+2}
-N-N minus -S-N............	4.1	3.3	(1)	2.0
N-N-N minus N-S-N..........	6.6	3.2	3.6	2.6
1/2(N-N-N-N minus N-S-S-N).	5.1	3.5	3.35	2.9
Average..............	5.3	3.3	3.5	2.5
	Δ log K_2 [2]			
-N-N minus -S-N............	3.0	2.1	(1)	1.7
N-N-N minus N-S-N..........	(1)	2.2	1.7	2.1
Average..............	3.0	2.2	1.7	1.9
	Δ log K_3 [3]			
-N-N minus -S-N............	-2.5	(1)	(1)	(1)

[1] Complex not formed.

[2] Δ log K_2 means log K_2 for -N-N minus log K_2 for -S-N.

[3] Δ log K_3 means log K_3 for -N-N minus log K_3 for -S-N.

CONCLUSIONS

The order of stabilities of the complexes considered in this study is Cu > Ni > Zn > Cd; tetradentate > tridentate > bidentate; and secondary amino compounds > thio compounds.

N-S-N and N-S-S-N complexes of Ni, Cu, Zn, and Cd appear to have similar structures, probably bidentate, in which only one amino nitrogen and the sulfur atom nearest to it are acting as donor atoms.

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