[Contribution from The College of Chemistry and Physics, The Pennsylvania State University]

Equilibrium Constants for the Formation of Complexes between Metal Ions and Polyamines[1,2]

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In order to obtain a comparison of the relative stability of complex ions containing chelate rings of more than five members, an attempt was made to obtain the formation constants of the complexes of copper(II), nickel, cobalt(II) and zinc ions with a series of polyamines. No formation constants could be obtained in the case of 1,4-butanediamine, N,N-dimethyl-1,3-propanediamine N-isopropyl-1,3-propanediamine and γ-aminopropylmorpholine with any of the four metal ions studied because precipitates appeared before appreciable coördination had occurred. Data were obtained for all four metal ions only with 2,2-dimethyl-1,3-propanediamine and histamine. Incomplete data were obtained for the complexes of 3,3′-diaminodipropylamine, 1,3-propanediamine and β-aminoethylmorpholine because of precipitation with one or more of the metal ions. Where data were available at two or more temperature ΔH and ΔS values were calculated for the reactions involved. In all cases the 6-membered rings were considerably less stable than the corresponding 5-membered rings and no complexes were formed with those amines which might form 7-membered chelate rings. Substitution on the nitrogen atom of the ligand caused a further decrease in stability except in the case of histamine.

Introduction

This paper reports a study of the formation constants of complexes of copper, nickel, cobalt and zinc ions with 1,3-propanediamine, 3,3′-diaminodipropylamine, 2,2-dimethyl-1,3-propanediamine, 1,-4-butanediamine, N,N-dimethyl-1,3-propanediamine, N-isopropyl-1,3-propanediamine, β-aminoethylmorpholine, γ-aminopropylmorpholine and histamine. The successive formation constants were determined by the method of Bjerrum.[4] Comparison of the values of the formation constants of the above complexes with data available for the complexes of the same metal ions with other amines[4–11] leads to a comparison of the stability of metal–amine complexes as a function of chelate ring size.

Experimental

3,3′-Diaminodipropylamine, N-isopropyl-1,3-propanediamine, N,N-dimethyl-1,3-propanediamine were gifts from the New Product Department of the American Cyanamid Company. 2,2 - Dimethyl - 1,3 - propanediamine dihydrochloride was prepared in this Laboratory by J. Rockett.[12] 1,3-Propanediamine dihydrochloride and β-aminoethylmorpholine were gifts of Professor T. S. Oakwood. 1,4-Butanediamine dihydrochloride and histamine dihydrochloride were purchased from the Eastman Kodak Company. γ-Aminopropylmorpholine was a gift of the Carbide and Carbon Chemicals Company. All the amines and amine salts were carefully repurified before use.

The general procedure was to pipet into the titration cell 75 ml. of a previously prepared solution containing a known concentration of metal salt, mineral acid and strong electrolyte (usually KNO_3). This solution was titrated with a solution of amine of known concentration. In the cases where a salt of the amine was used, this was weighed into the titration cell, 75 ml. of the metal ion solution added, and the resulting solution titrated with a standardized NaOH solution, thereby generating the free amine during the course of the titration. A nitrogen atmosphere was maintained over the solutions during the course of the titrations.

The *p*H measurements were made with the Beckman General Purpose Glass Electrode using a Beckman Calomel Electrode as reference electrode. Titrations were carried out at various temperatures obtained by use of a constant-temperature water-bath. The 30 ± 0.01° and 50 + 0.1° baths were controlled by mercury thermoregulators, while the 0 ± 0.1° bath was obtained by a water–crushed ice mixture. The *p*H readings at 0 and 50° were corrected using the formula supplied by the Beckman Instrument Company.

Aqueous solutions of the acids and metal salts used were prepared and analyzed by means of generally accepted methods. The *p*H-meter was standardized both before and after the titrations against buffer solutions prepared from National Bureau of Standards buffer salts. During the titrations the systems reached equilibrium as soon as the heat of reaction could be dissipated to the surroundings and the original temperature regained. This was practically instantaneous at 30 and 50°, but required about 10 min. at 0°.

The acid dissociation constants of the amines were determined in similar titrations using barium ion, a non-coördinating ion, in place of the coördinating metal ions.

Data and Results

Dissociation Constants of the Amines.—The results are given in Table I.

Table I

Acid Dissociation Constants of Some Amines in Solutions 1.0 M in KNO_3 and 0.01 M in Ba^{++}

Amine	HNO_3, M	Temp., °C.	pK_{AH_3}	pK_{AH_2}	pK_{AH}
3,3′-Diaminodipropylamine	0.0509	0	8.98	10.77	11.70
	.0483	30	8.02	9.70	10.70
	.0509	50	7.62	9.19	10.12
1,3-Propanediamine	.0509	0		9.95	11.60
	.0509	30		8.95	10.54
	.0509	50		8.38	9.32
2,2-Dimethyl-1,3-propanediamine	.0509	0		9.07	11.22
	.0242	30		8.18	10.22
	.0509	50		7.55	9.65
β-Aminoethylmorpholine	.0509	30		4.84	9.45
Histamine	.0509	30		6.38	9.86
	.0509	50		6.01	9.27

Formation Constants of the Complexes.—The *p*H measurements were used to calculate the $\bar{n}$ and A values for formation curves. A typical set of formation curves is shown in Fig. 1. From these

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[2] A portion of a thesis presented by George B. Hares in partial fulfillment of the requirements for the degree of Doctor of Philosophy. January, 1952.

[3] Chemistry Department: University of Pittsburgh, Pittsburgh 13, Pennsylvania.

[4] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

[5] G. A. Carlson, J. P. McReynolds and F. H. Verhoek, This Journal, **67**, 1334 (1945).

[6] R. V. Bruehlman and F. H. Verhoek, *ibid.*, **70**, 1401 (1948).

[7] H. B. Jonassen, R. B. LeBlanc and R. M. Rogan, *ibid.*, **72**, 4968 (1950).

[8] J. E. Prue and G. Schwarzenbach, *Helv. Chim. Acta*, **33**, 985 (1950).

[9] G. Schwarzenbach, *ibid.*, **33**, 974 (1950).

[10] J. E. Prue and G. Schwarzenbach, *ibid.*, **33**, 995 (1950).

[11] J. E Pure and G. Schwarzenbach, *ibid.*, **33**, 963 (1950).

[12] J. Rockett, M.S. Thesis, The Pennsylvania State College, June, 1948.

curves the formation constants given in Tables II–IV were calculated. For certain combinations of amine and cation it is not possible to determine the formation curve because precipitates form before appreciable coördination takes place. This situation obtains for 1,4-butanediamine, N,N-dimethyl-1,3-propanediamine, N-isopropyl-1,3-propanediamine and γ-aminopropylmorpholine with all four metal ions studied. Cobalt and zinc gave precipitates at 0 and 30° with 1,3-propanediamine and at 30° with β-aminoethylmorpholine. Copper and nickel gave precipitates with 1,3-propanediamine only at 50°, but the data for nickel at 0° were not considered reliable. Precipitation occurred with 2,2-dimethyl-1,3-propanediamine only for zinc at 50°.

TABLE II

FORMATION CONSTANTS OF SEVERAL AMINE COMPLEXES WITH VARIOUS BIVALENT METAL IONS

Amine	Temp.	°C.	Cu^{++}	Ni^{++}	Co^{++}
3,3′-Diaminodipropylamine	0	log K_1	15.75	10.25	7.51
	30	log K_1	14.25	9.09	6.63
	50	log K_1	13.66	8.88	6.36
1,3-Propanediamine	0	log K_1	10.74	7.00	..
		log K_2	8.05	4.92	
	30	log K_1	9.62	...	..
		log K_2	7.00	...	..
β-Aminoethylmorpholine	30	log K_1	6.60	3.78	..
		log K_2	3.96	...	..

TABLE III

FORMATION CONSTANTS OF COMPLEXES OF 2,2-DIMETHYL-1,3-PROPANEDIAMINE WITH VARIOUS BIVALENT METAL IONS

		0°	30°	50°
Cu^{++}	log K_1	10.95	9.94	9.41
	log K_2	8.25	7.45	6.86
Ni^{++}	log K_1	7.22	6.59	6.23
	log K_2	4.99	4.41	4.15
Co^{++}	log K_1	5.41	4.88	4.38
	log K_2	3.52	3.07	ppt.
Zn^{++}	log K_1	5.58	5.21	
	log K_2	5.58	5.20	

TABLE IV

FORMATION CONSTANTS OF COMPLEXES OF HISTAMINE WITH VARIOUS BIVALENT METAL IONS

		30°	50°
Cu^{++}	log K_1	9.60	
	log K_2	6.49	
Ni^{++}	log K_1	6.87	6.50
	log K_2	4.96	4.78
	log K_3	3.08	2.83
Co^{++}	log K_1	5.34	5.10
	log K_2	3.75	3.32
	log K_3	1.88	1.56

The plots of log K_N *vs.* $1/T$ for the complexes for which data are available at three temperatures were found to be linear within the limits of error. The thermodynamic quantities calculated from these data are presented in Table V. The ΔF values were calculated from the constants determined at 30°. The ΔH values are the average of the values calculated for the intervals 0–30° and 30–50°. The ΔS values were calculated from the ΔF and ΔH values in the table. The additional values for other complexes in Table V were calculated from constants determined at two temperatures. The ΔF values are considered reliable to *ca.* + 0.2 kcal. The average error in the ΔH values is probably *ca.* ± 2 kcal., and for the ΔS values it is probably *ca.* ± 7 cal./degree. The errors are discussed more fully elsewhere.[13]

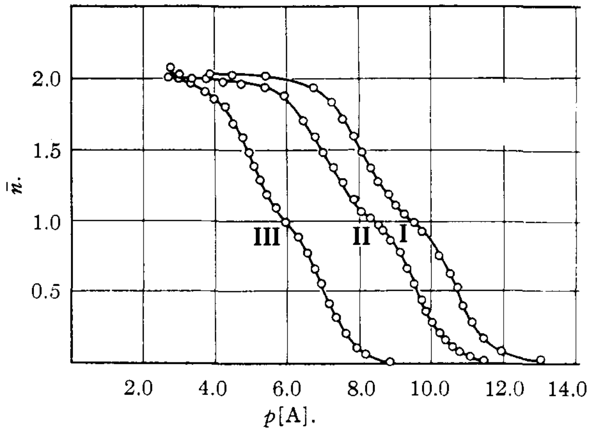

Fig. 1.—Formation curves for complexes of 1,3-propanediamine: I, Cu^{++} at 0°; II, Cu^{++} at 30°; III, Ni^{+} at 0°.

TABLE V

THERMODYNAMIC QUANTITIES FOR THE STEPWISE FORMATION OF VARIOUS COMPLEXES AT 30°

Ligand	Metal ion	n value	$-\Delta F$, kcal./mole	$-\Delta H$, kcal./mole	ΔS, cal./degree-mole
3,3′-Diaminodipropylamine	Cu^{++}	1	19.7	16	+12
	Ni^{++}	1	12.6	10	+ 9
	Co^{++}	1	9.2	9	+ 1
1,3-Propanediamine	Cu^{++}	1	13.3	14	− 3
		2	9.7	13	−12
2,2-Dimethyl-1,3-propanediamine	Cu^{++}	1	13.8	12	+ 7
		2	10.3	12	− 7
	Ni^{++}	1	9.1	8	+ 3
		2	6.0	7	− 3
	Co^{++}	1	6.8	7	0
		2	4.2	6	− 6
	Zn^{++}	1	7	5	+ 8
		2	7	5	+ 8
Histamine	Ni^{++}	1	9.5	8	+ 5
		2	6.9	4	+10
		3	4.3	6	− 6
	Co^{++}	1	7.4	5	+ 8
		2	5.2	10	−16
		3	2.6	7	−15

Discussion

Although data could not be obtained in some cases because of the formation of hydroxides or basic precipitates, the appearance of such a precipitate is itself an indication of low stability. Precipitation occurred most often for the metal ions giving less stable complexes (Zn and Co) and for all four metal ions precipitation occurred more often at the higher temperatures where the complexes are less stable.

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(13) E. Gonick, W. C. Fernelius and B. E. Douglas, THIS JOURNAL, **76**, 4673 (1954).

The considerable decrease in the stability of the complex as the size of the chelate ring increases from five to six members is shown by the comparison of the data in Table II for 1,3-propanediamine with data for ethylenediamine.[4] The decreased stability is shown by the smaller formation constants for copper and nickel and the fact that cobalt and zinc gave precipitates. Only two molecules of 1,3-propanediamine were coördinated while three molecules of ethylenediamine and 1,2-propanediamine are coördinated by the same metal ions. The lower coördination number with 1,3-propanediamine is probably due partly to the lower affinity for each molecule of ligand, but probably to a greater extent to spatial limitations.

The same relative stability is found for the comparison of the complexes of terdentate amines which form 5- and 6-membered chelate rings. The formation constants of 3,3′-diaminodipropylamine complexes (Table II) are smaller than those of the corresponding 2,2′-diaminodiethylamine complexes.[7] The complexes of 3,3′-diaminodipropylamine contain only one molecule of amine in comparison with two molecules of 2,2-diaminodiethylamine.

The separation of the amino groups by four carbon atoms in 1,4-butanediamine and γ-aminopropylmorpholine resulted in the precipitation of each of the four metal ions before appreciable coördination occurred. Solid coördination compounds of copper with 1,4-butanediamine and 1,6-hexanediamine were obtained by Pfeiffer and co-workers[14] in alcoholic solution, but the compounds were unstable in water.

The copper and nickel complexes of 2,2-dimethyl-1,3-propanediamine were more stable than those of 1,3-propanediamine and the cobalt and zinc complexes of the former ligand were stable in water below 50°. Cobalt and zinc gave precipitates with 1,3-propanediamine even at the lower temperatures. The increased stability of the 2,2-dimethyl-1,3-propanediamine complexes cannot be explained on the basis of the inductive effects of the methyl groups because the basicity of the ligand toward the proton is actually less than that of 1,3-propanediamine. The heats of formation of the 2,2-dimethyl-1,3-propanediamine complexes are slightly less than those of the 1,3-propanediamine complexes.

Although the differences in the ΔH values are not outside the average experimental error given, the difference is probably significant for two closely related complexes. Heats of formation and free energy changes are usually lower for ligands of lower basicity, but the ΔF values are slightly, but significantly, greater for the 2,2-dimethyl-1,3-propanediamine complexes. The reversal in the value of ΔF is due to the entropy effects. Since the ligands are very similar and the $\bar{n}$ value is the same in each case, it would seem that the difference in entropy might lie in the differences in the interaction of the complexes with the solvent. Frank and Evans[15] have proposed an explanation which can be extended to lead one to expect that the entropy change accompanying the formation of the more "hydrocarbon-like" complexes such as those of 2,2-dimethyl-1,3-propanediamine might be considerably more favorable due to the lesser tendency to create an ice-like structure in the solvent.

The only N-substituted-1,3-diamine studied which would form complexes under the conditions used was histamine. Histamine is peculiar not only in that the formation constants of its complexes are greater, except for Cu^{++}, than those of any other 1,3-diamine studied (Table IV), but also in that the complexes of histamine with Ni^{++} and Co^{++} contain three molecules of amine.[16] This phenomenon probably is due to the steric effect of the pyrazole ring.

The formation curve of Ni^{++} with β-aminoethylmorpholine and the blue-green color of the complex in solution indicate that only one molecule of the amine per metal ion was coördinated. It is unusual that although only one molecule of diamine was coördinated no precipitate formed during the titration.

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[14] P. Pfeiffer, A. Böhm and E. Schmitz, *Naturwissenschaften*, **35**, 190 (1948).

[15] H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 531 (1954).

[16] Since this work was completed additional formation constants have been published by B. L. Mickel and A. C. Andrews, THIS JOURNAL, **77**, 323, 5291 (1955), for histamine complexes of Ni^{++}, Cu^{++} and Co^{++} at 0 and 25°. The values reported agree very well with those given in Table IV although the temperature is different.