reaction 5 as compared with (4) is accepted as evidence that this reaction is accomplished by removal of a proton (and formation of a chelate ring) as shown in equation 5 rather than by the simple addition of the hydroxide ion as in reaction 4. A similar argument may be applied to equations 2 and 3, and it will be shown later[12] that the equilibrium constant for reaction 3 is greater than for (2).

The complex ion $Cu(en)_2(OH^-)^{+1}$ evidently undergoes no further reaction with strong base, even in 1 N solution.[9] The complex ion $Cu[hen(OH)hen(O^-)]^{+1}$ decomposes above pH 10 to form the product shown in equation 2 with one mole of amine being set free. The complex ion $Cu[hen(OH)_2]_2^{+2}$ reacts with sodium hydroxide but the type of complex shown by equations 4 and 5 is formed only to a limited extent. Instead, the decomposition of the 1:2 complex to form the product shown in equation 3 with the release of one mole of amine begins in the range of pH 8.5 to 9.0 which is at a lower concentration of base than is required for formation of the five-coördinate complex.

The 1:1 complexes of copper(II) ion and each of the amines en, hen(OH) and $hen(OH)_2$ may all be formed at pH 5.5 to 6. As more amine is added to solutions of these 1:1 complexes the second amine molecule is added to each below pH 7.5. The second amine molecule is not displaced from $Cu(en)_2^{+2}$ by 1 N sodium hydroxide. The ion $Cu[hen(OH)]_2^{+2}$ is so decomposed by 1 N sodium hydroxide, and $Cu[hen(OH)_2]_2^{+2}$ is decomposed by a much lower concentration of sodium hydroxide. For the tetraalkanol-substituted ethylenediamine there is no evidence for formation of a 1:2 complex. The reactions of equations 1, 2 and 3 all take place at about pH 7.0. The 1:1 complex of the tetraalkanol-substituted amine reacts with sodium hydroxide at a slightly lower pH.

The reactions which have been established between sodium hydroxide and the copper(II) ion complexes of ethylenediamine and of the three alkanol-substituted ethylendiamines form a groundwork for the interpretation of pH titration curves for a number of systems involving various metallic ions and a number of alkanol-substituted amines. Several such studies are included in an accompanying report.[12]

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[12] J. L. Hall, W. E. Dean and E. A. Pacofsky, THIS JOURNAL, **82**, 3303 (1960).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WEST VIRGINIA UNIVERSITY, MORGANTOWN, WEST VIRGINIA]

Metal Chelates of Alkanol-substituted Amines[1]

BY JAMES L. HALL, WARREN E. DEAN AND EDWARD A. PACOFSKY

RECEIVED SEPTEMBER 14, 1959

The chelate compounds formed between each of the metallic ions copper(II), nickel(II), cobalt(II), cadmium(II) and zinc(II) and each of seven different alkanol-substituted ethylenediamine molecules have been investigated by the potentiometric method of Bjerrum. The mono- and di-substituted amines form both 1:1 and 1:2 complexes with metallic ions.[2] In general the 1:1 complexes of these amines react with strong base either to form 1:2 complexes and the metallic hydroxides or to form uncharged chelate compounds by loss of protons from the 1:1 complexes. In several instances the 1:2 complexes are decomposed in alkaline solution to yield the same final product as for the 1:1 complexes. In general the chelates having the highest stability as shown by log K_1 have the lowest acidity as shown by pK_{A_1} and pK_{A_2}. The tetraalkanol-substituted amines form only 1:1 complexes with the metallic ions. In general 2-hydroxypropyl substitution leads to greater stability of the chelate compounds than does 2-hydroxyethyl substitution. For each amine, the order of stability of the complexes with the various metallic ions follows the usual order except that the cadmium(II) ion complexes of the tetraalkanol-substituted amines are more stable than would be anticipated.

Introduction

There is considerable evidence for the participation in chelation of the hydroxyl groups of certain alkanol-substituted amines. Such chelation may be expected if the nitrogen and oxygen atoms can be included in the same five-membered ring. Coördination of both nitrogen and oxygen atoms evidently is involved in the complex ions formed in solution and in the solid compounds formed between transition metal salts and the ethanolamines[3-6] and substituted ethanolamines.[7] A previous study in this Laboratory[8] has shown that the 1:1 copper(II) ion complex of a tetraalkanol-substituted ethylenediamine (4-hpn, included in Table I) acts in solution as a dibasic acid of appreciable strength. There is evidence to support the assumption that this acidic property is due to enhancement of the acidity of hydrogen atoms of the hydroxyl groups upon coördination of the oxygen atoms. Similar conclusions have been reached for the copper(II) ion complexes of hn[9] and 2-hn.[10] Martell, Chaberek, Courtney, Westerback and Hyytiainen[11] have considered the ques-

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[1] Supported by the Office of Ordnance Research, U. S. Army. From a portion of the Ph.D. Dissertation of W. E. Dean, West Virginia University, 1959.

[2] Ratios represent the relative proportions of the metallic ion and amine in that order.

[3] W. Hieber and E. Levy, *Ann.*, **500**, 14 (1933); *Z. anorg. allgem. Chem.*, **219**, 225 (1934).

[4] H. Brintzinger and B. Hesse, *ibid.*, **248**, 345, 351 (1941).

[5] P. S. James, Master's Thesis, West Virginia University, 1957.

[6] W. E. Dean, Master's Thesis, West Virginia University, 1956.

[7] Fr. Hein and W. Beerstecher, *Z. anorg. allgem. chem.*, **282**, 93 (1955).

[8] J. L. Hall, F. R. Jones, C. E. Delchamps and C. W. McWilliams, THIS JOURNAL, **79**, 3361 (1957).

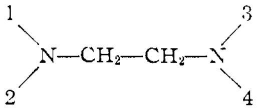
[9] J. L. Hall and W. E. Dean, *ibid.*, **80**, 4183 (1958).

[10] J. L. Hall and W. E. Dean, *ibid.*, **82**, 3300 (1960).

[11] A. E. Martell, S. Chaberek, Jr., R. C. Courtney, S. Westerback and H. Hyytiainen, *ibid.*, **79**, 3036 (1957). See this article for several references to previous work.

TABLE I

SUBSTITUTED ETHYLENEDIAMINE MOLECULES



$$^{1}_{2}\!>\!N{-}CH_2{-}CH_2{-}N\!<^{3}_{4}$$

etOH = $-C_2H_4OH$, iprOH = $-CH_2CHOHCH_3$

Abbreviations	Substituents 1	2	3	4	Name
hn or hen-OH	etOH	H	H	H	N-(2-Hydroxyethyl)-ethylenediamine
2-hn or 2-hen(OH)$_2$	etOH	H	H	etOH	N,N′-Di(2-hydroxyethyl)-ethylenediamine
hpn or hpen-OH	iprOH	H	H	H	N-(2-Hydroxypropyl)-ethylenediamine
2-hpn or 2-hpen(OH)$_2$	iprOH	H	H	iprOH	N,N′-Di(2-hydroxypropyl)-ethylenediamine
4-hn or 4-hen(OH)$_4$	etOH	etOH	etOH	etOH	N,N,N′,N′-Tetra(2-hydroxyethyl)ethylenediamine
hn-3-hpn or hen-OH-3-hpen(OH)$_3$	etOH	iprOH	iprOH	iprOH	N-(2-Hydroxyethyl)-N,N′,N′-tri(2-hydroxypropyl)ethylenediamine
4-hpn or 4-hpen(OH)$_4$	iprOH	iprOH	iprOH	iprOH	N,N,N′,N′-Tetra(2-hydroxypropyl)ethylenediamine

tion of participation of such alkanol hydroxyl groups in coördination and have concluded that the weight of evidence is in favor of direct coordination of the metallic ion by the hydroxyl group.

The detailed studies which have been made[5–10] of the copper(II) complexes of a mono-, a di- and a tetraalkanol-substituted ethylenediamine over a wide range of alkalinity afford a reasonable basis for the interpretation of the *p*H titration curves for the mixtures of metallic ion salts and the several different alkanol-substituted amines studied here.

The present report gives the results of a study, by a modification of the method of Bjerrum,[12] to determine the formation constants of the chelates formed between several different metallic ions and several different alkanol-substituted ethylenediamines. The reaction of each of the complexes with strong base is also described.

The amines used in the present work are listed in Table I. Each of these alkanol-substituted amine molecules may form two or more five-membered chelate rings with a metallic ion. The metallic ions included in the present study are copper(II), nickel(II), cobalt(II), cadmium(II) and zinc (II). In addition some qualitative studies were made with manganese(II) and iron(III) salts.

Experimental

The experimental method consisted of potentiometric titrations with sodium hydroxide, using the glass electrode, of the acidified solution of the chelating agent, in the absence of the metallic ion and in the presence of various proportions of the metallic ion. This is the method of Bjerrum[12] following a modification somewhat like that used by Chaberek and Martell.[13]

Apparatus and Procedure.—A Beckman Model G *p*H meter with extension electrodes was used to record the hydrogen ion concentrations. Titrations were performed in a 400 ml. tall form Berzelius beaker fitted with a plastic cover which had openings to accommodate a stirrer, the glass and calomel electrodes, the burette tip and nitrogen inlet and outlet tubes. The beaker was secured in a water bath maintained at a temperature of 25 ± 0.05°.

The ionic strength at the beginning of each titration was adjusted to 0.5 by addition of potassium nitrate. The initial concentration of the amine was ordinarily 0.004 *M* with enough nitric acid present to neutralize the amine and provide 0.002 *M* in excess. The initial volume was adjusted to 200 ml. of solution. Addition of approximately 1.0 *M* sodium hydroxide produced only a small dilution effect during titration. Presaturated nitrogen was passed through the vessel before and during the titration.

For solutions of ratio 1:1, both metallic ion and amine were initially 0.004 *M*. For the 1:2 solution the metallic ion concentration was 0.002 *M* and the amine concentration was 0.004 *M*. Solutions having a greater excess of amine are not included in the present report since higher complexes were not formed with a moderate excess of amine. It would be desirable, however, to have titration curves with an excess of amine for more precise determination of the formation constants of some of the 1:2 complexes.

Materials.—Copper(II) perchlorate hexahydrate and nickel(II) perchlorate hexahydrate were prepared from the corresponding reagent-grade carbonates as described previously.[14] Cobalt(II) perchlorate, manganese(II) perchlorate, iron(III) perchlorate, zinc(II) sulfate and cadmium sulfate were all obtained as hydrated, reagent-grade salts and were used without further purification. The 4-hpn, hn and 2-hn were the same as described previously.[8–10] The hpn and 4-hn were obtained from the Wyandotte Chemicals Corporation. The 2-hpn and hn-3-hpn were obtained from the Visco Products Co. In general, these amines were samples which had been prepared by the manufacturers' laboratories for research work. For some, vacuum distillations or recrystallizations were performed for further purification. For each the neutral equivalent of the material used corresponded very closely to the weighed amount.

Calculations

The equations for the determination of the stability constants are adapted from those of Bjerrum.[12] The particular equations used here were derived following the form given by Carlson, McReynolds and Verhoek.[15] Values of pK_{AH_1} and pK_{AH_2}, the dissociation constants for the conjugate acids of the amine, were determined from the titration curves of the amine in the absence of chelating metallic ions. These values are required for the calculation of the stability constants. They are of considerable interest in themselves and will be reported separately. From the titration curve of each metallic ion–amine mixture, values of pA and $\bar{n}$ were calculated and plotted. If the plot of $\bar{n}$ as a function of pA was distinctly stepwise, the values of log K_1 and log K_2 were taken as equivalent to pA at $\bar{n} = 0.5$ and $\bar{n} = 1.5$, respectively. If the curve was not stepwise, the values of the constants thus determined were used as approximate values from which the actual constants were calculated by the con-

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(12) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

(13) S. Chaberek, Jr., and A. E. Martell, THIS JOURNAL, **74**, 5052 (1952).

(14) J. M. Bolling and J. L. Hall, *ibid.*, **75**, 3953 (1953).

(15) G. A. Carlson, J. P. McReynolds and F. H. Verhoek, *ibid.*, **67**, 1334 (1945).

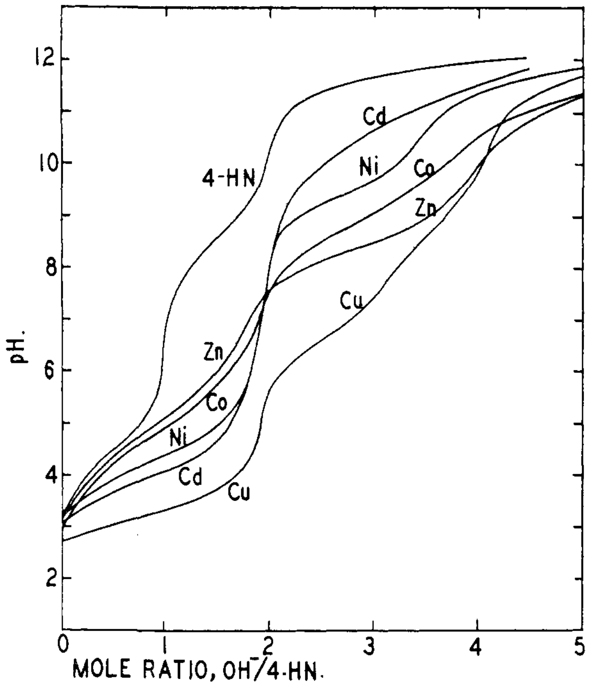

Fig. 1.—Potentiometric titration curves for 4-HN and for 1:1 mixtures of 4-HN and each of the ions: Cu(II), Ni(II), Co(II), Zn(II), and Cd(II).

vergence method of Carlson, McReynolds and Verhoek[15] or by solving the simultaneous equations given by Bjerrum.[12] The table of corrections given by Van Uitert, Fernelius and Douglas[16] is useful for this purpose.

In general the 1:1 complexes of the metallic ions and the alkanol-substituted amines act as dibasic acids with strong base. From the titration curve for this stepwise reaction may be calculated the successive ionization constants of the acid. These are expressed as pK_{A_1} and pK_{A_2}.

Results and Discussion

Some of the titration curves for the various amines and mixtures of amines and metallic ions are shown in Figs. 1 to 5, inclusive. The curves for copper(II) ion and 2-hn which are included in Fig. 2 will be used to show in detail how qualitative and quantitative information may be derived from the curves. After this explanation, the remaining discussion will be divided to give, first, a discussion of the complexes of the tetra-alkanol-substituted amines and second, a discussion of the remaining complexes, considering each metallic ion separately.

Interpretation of Curves.—In all of the plots given in this report, the zero of the X-axis is placed at the end point which represents the neutralization of the excess nitric acid of the solution. For the copper(II) curves of Fig. 2, the "b" curve, as with all similar sets of curves, is for the solution in which the metallic ion to amine ratio is 1:2 and the "a" curve is for the ratio 1:1. The amine concentration is constant for all three titrations. If only a 1:1 complex were formed between copper(II) ion and 2-hn, the 1:2 curve, b, should be approximately mid-way between the 2-hn and 1:1 (a) curves at all values of pH as it would be simply an average of the two. Since the 1:2 curve is not mid-way in the low range of pH, it is evident that a complex other than 1:1 is formed and it is known from previous work[10] that this is the 1:2 complex. Above a pH of about 9.5, the 1:2 curve is midway between the other two. The previous work[10] shows that in such alkaline solution the 1:2 complex is decomposed leaving a 1:1 complex which has reacted with the strong base and the amine salt or, above pH 10.5, free amine in the solution.

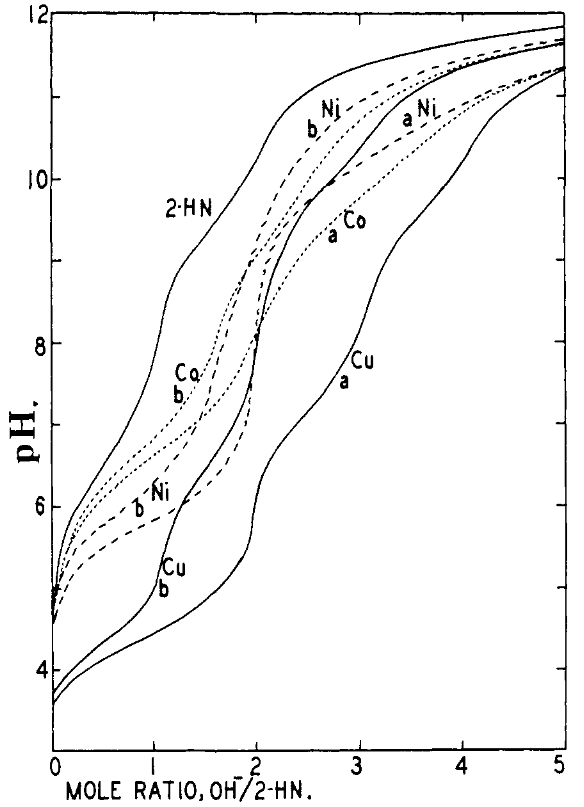

Fig. 2.—Potentiometric titration curves for of 2-HN and for 1:1 (curve a) and 1:2 (curve b) mixtures of the ions Cu(II), Ni(II), and Co(II) with 2-HN.

For both the 1:1 and 1:2 curves for copper(II) and 2-hn solutions, the break between pH 5 and pH 6 represents completion of the formation of the Cu(2-hn)$^{+2}$ complex ion according to the equation

$$\mathrm{Cu^{+2} + (2\text{-}hn)H_2^{+2} + 2\ OH^- \longrightarrow Cu(2\text{-}hn)^{+2} + 2\ H_2O}$$

For each titration the amount of base required at this end-point was equal to twice the number of moles of amine coördinated. For the 1:1 curve the breaks at about pH 8 and 10.2 represent the completion, in successive steps, of the following two reactions

$$\mathrm{Cu[2\text{-}hen(OH)_2]^{+2} + OH^- \longrightarrow Cu[2\text{-}hen(OH)(O^-)]^{+1} + H_2O}$$

$$\mathrm{Cu[2\text{-}hen(OH)(O^-)]^{+1} + OH^- \longrightarrow Cu[2\text{-}hen(O^-)_2]^0 + H_2O}$$

At each of these end-points the amount of base

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(16) L. G. Van Uitert, W. C. Fernelius and B. E. Douglas, THIS JOURNAL, **75**, 457 (1953).

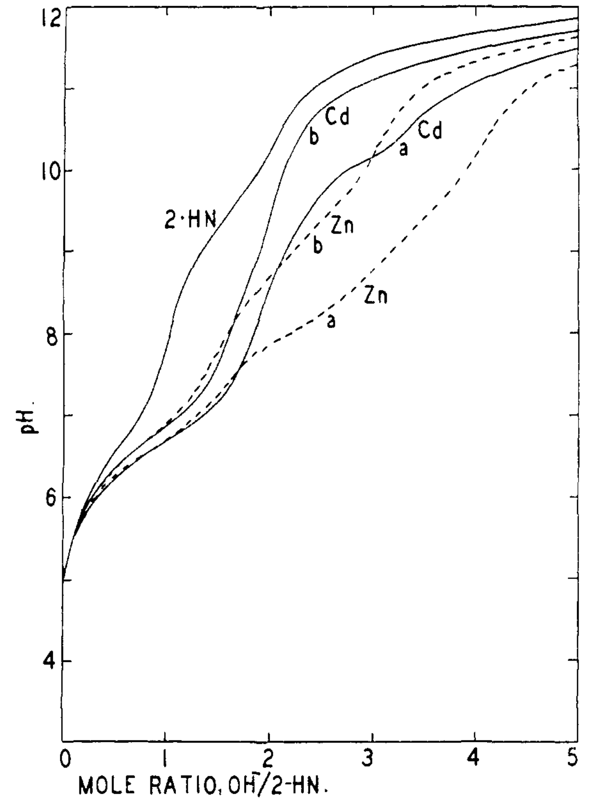

Fig. 3.—Potentiometric titration curves for 2-HN and for 1:1 (curve a) and 1:2 (curve b) mixtures of the ions Cd(II), and Zn(II) with 2-HN.

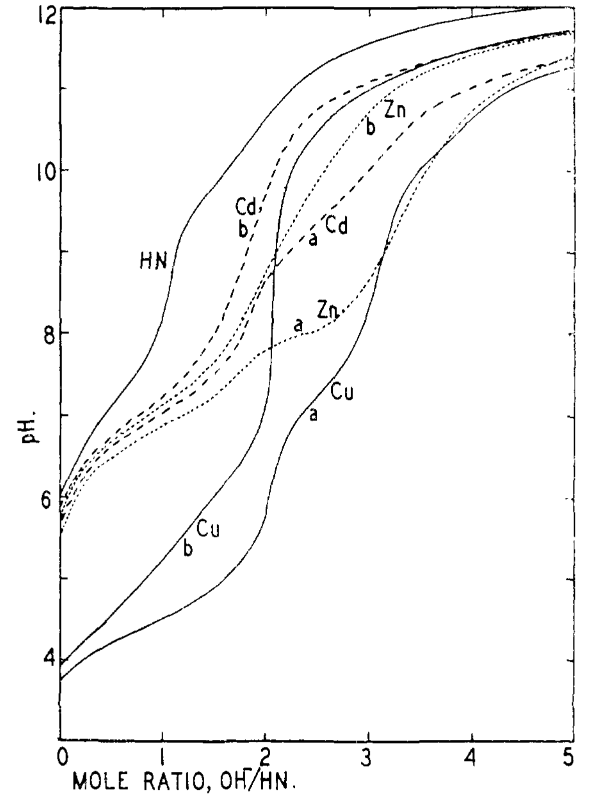

Fig. 4.—Potentiometric titration curves for HN and for 1:1 (curve a) and 1:2 (curve b) mixtures of the ions Cu(II), Cd(II) and Zn(II) with HN.

required is two equivalents greater than that required to bring the amine salt to the same *p*H. That is, for each, the horizontal displacement between the 2-hn and 1:1 curves at these points is equal to two equivalents of base per mole of copper(II) ion. This is the amount of base required to produce each complex from an amine solution at that particular *p*H. It follows that if there were no reaction of the 1:1 complex with base, the 1:1 and 2-hn curves should converge above *p*H 10.5.

For the 1:2 curve, copper(II) ion and 2-hn, the break at about *p*H 8 represents the formation of $Cu(2\text{-hn})_2{}^{+2}$ according to the equation

$$Cu(2\text{-hn})^{+2} + (2\text{-hn})H^{+1} + OH^- \longrightarrow [Cu(2\text{-hn})_2]^{+2} + H_2O$$

Since, at this *p*H, the amine is in the form (2-hn)-H^{+1}, only one additional equivalent of base is required for each mole of amine coördinated. At the end-point for the 1:2 curve just below *p*H 10.5 the following reaction is completed

$$Cu[2\text{-hen}(OH)_2]_2{}^{+2} + 2\,OH^- \longrightarrow Cu[2\text{-hen}(O^-)_2]^0 + 2\,H_2O + 2\text{-hn}$$

This is in agreement with the horizontal spacing between the 2-hn and 1:2 curves.

Complexes of the Tetraalkanol-substituted Ethylenediamines.—Figure 1 shows the titration data for each of the metallic ions and 4-hn in 1:1 ratio. The corresponding curves for 4-hpn and hn-3-hpn are quite similar in form to the ones shown in Fig. 1. The step which appears at about mole ratio 3.5 for the Ni(II) and 4-hn system is less distinct for the systems involving this metal and 4-hpn and hn-3-hpn. The steps in the titration curves for Cu(II) with 4-hpn and with hn-3-hpn which appear at mole ratios 3 and 4 are somewhat more distinct than the ones shown in Fig. 1 for Cu(II) with 4-hn. Other differences in the curves for the three amines are largely ones of vertical displacement and result in the differences in the numerical constants given in Table II. The curve for 4-hpn and copper(II) ion was given previously by Hall, Jones, Delchamps and McWilliams.[8] This curve was rerun for exact determination of values for Table II. In the previous work there was no evidence of complexes being formed between the metallic ion and the amine in other than 1:1 ratio. In the present work this is verified for all the tetraalkanol-substituted amines studied. Except for small differences in the values of the constants the behavior of these three amines is similar.

For the metallic ions investigated, the order of decreasing stability with the tetraalkanol-substituted ethylenediamines for the 1:1 complexes is Cu(II) > Cd(II) > Ni(II) > Co(II) > Zn(II). This is the usual order[17] except the cadmium complex is more stable than would be predicted.

The titration curves for the tetra-substituted amines, with the exception of the copper(II) curves,

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(17) D. P. Mellor and L. Maley, *Nature*, **161**, 436 (1948).

do not show distinct steps after the formation of the 1:1 complex and this indicates that, for the various reactions occurring after the 1:1 complex is formed, a succeeding reaction is initiated before the preceding one is completed. These reactions may include the removing of one or two of the hydrogen atoms of the coördinated alcohol groups or may represent decomposition of the complex with the formation of the metallic hydroxide or a basic salt as precipitate.

TABLE II

VALUES OF LOG K_1, LOG K_2, pK_{A_1} AND pK_{A_2}

Metal ion	Ligand	Log K_1	Log K_2	pK_{A_1}	pK_{A_2}	pH, first precpt.[b]
Cu(II)	hn	10.11	7.51	7.21	10.12	
	2-hn	9.77	5.84	7.18	9.43	
	2-hpn	11.01	5.63	7.34	9.58	
	4-hpn	9.75		6.77	8.97	
	hn-3-hpn	9.36				7.1
	4-hn	8.52				7.7
	hpn	10.40	7.40	7.59	10.08	
Ni(II)	hn	6.66	5.80			7.2
	2-hn	6.67	4.2[a]			7.5
	2-hpn	6.84	4.1			7.0
	4-hpn	7.65		9.76	11.22	
	hn-3-hpn	7.25				9.2
	4-hn	6.27		9.26		9.3
Co(II)	hn	4.87	5.0[a]	9.07		10.0
	2-hn	5.13	4.0[a]			8.8
	2-hpn	5.02	4.5			8.5
	4-hpn	6.33		8.99	10.21	
	hn-3-hpn	5.96		8.93	10.12	
	4-hn	5.04		8.56	9.76	
Zn(II)	hn	4.75	5.4[a]	8.05		8.2
	2-hn	4.79	4.3[a]	8.23		8.8
	2-hpn	5.12	4.45			8.0
	4-hpn	6.09				8.2
	hn-3-hpn	5.67				6.8
	4-hn	4.74				7.9
Cd(II)	hn	4.93	4.3[a]			8.8
	2-hn	5.07	3.8[a]			9.1
	2-hpn	5.33	3.3[a]			9.0
	4-hpn	7.80				9.5
	hn-3-hpn	7.73				9.4
	4-hn	7.04				9.2

[a] Approximate value. Further action with base is indicated before complete formation of the 1:2 complex. [b] These pH values are for titration of the 1:1 mixtures. For the 1:2 mixtures of the mono- and disubstituted amines precipitates were formed only for the Cd(II) and hn system at pH 9.8 and for the Cd(II) and 2-hn system at pH 10.5. Also the 1:2 mixture of Zn(II) and 2-hn showed a slight turbidity at pH 11.0.

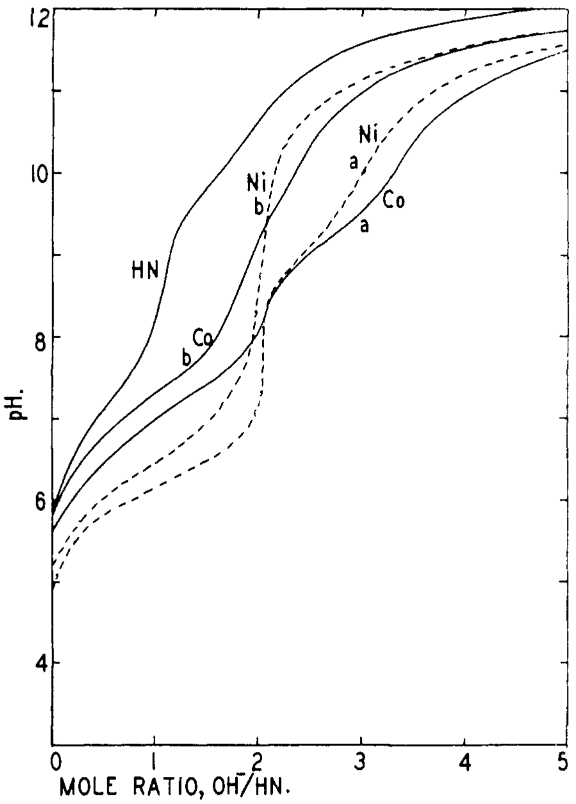

Fig. 5.—Potentiometric titration curves for HN and for 1:1 (curve a) and 1:2 (curve b) mixtures of the ions Co(II) and Ni(II) with HN.

The close approach of the titration curve for a metallic ion-amine mixture to the curve for the amine only at a pH below that at which the free amine is formed shows decomposition of the complex. For cadmium, for example, the close approach of the 4-hn and 1:1 curves (Fig. 1) at a pH of 9 indicates decomposition of the 1:1 complex. On the other hand, for zinc, the large amount of base required at high values of pH indicates formation of the zincate ion after displacement of the amine from the complex. The overlap of reactions and the formation of precipitates prevents the determination of many of the pK_{A_1} and pK_{A_2} values.

An examination of the log K values of the complexes of 4-hpn, 4-hn and hn-3-hpn shows approximately constant differences between the log K values for each metal with the same two amines. The exception is for the complexes of cadmium(II) ion for which the differences are smaller. It is noted that cadmium is in a different period of the periodic table from the other metals studied and has an ionic radius about 20% higher than the others.

It is observed that for all the metallic ions, substitution of 2-hydroxypropyl groups on the amine molecule leads to greater stability of the resulting complexes than does 2-hydroxyethyl substitution. The cobalt(II) complexes of the tetraalkanol-substituted ethylenediamines were the only ones in addition to the copper(II) and 4-hn complex which did not form precipitates as base was added. As a result these are the only ones of this series for which pK_{A_1} and pK_{A_2} values are available for all three amines.

Complexes of Mono- and Dialkanol Substituted Ethylenediamines.—Figures 3 and 4 show the titration curves for 1:1 and 1:2 ratios of the various metallic ions and 2-hn. Corresponding curves for

2-hpn are in general similar but show the differences which lead to the differences in the constants shown in Table II. Likewise the titration curves for the systems involving hn are shown in Figs. 4 and 5 but the results for the Cu(II)-hpn system are shown only in the table.

Copper(II) Complexes.—The copper(II) ion complexes of hn and 2-hn have been studied in detail previously[9,10] and the titration curves for copper(II) ion and 2-hn mixtures were used above to illustrate the details of the present analysis. For hpn and 2-hpn, as for hn and 2-hn, there is a 1:2 chelate formed at intermediate values of pH which decomposes at a higher pH. There is a general relation that the 1:1 chelate having the highest stability as shown by log K_1 has the lowest acidity as shown by pK_{A_1} and pK_{A_2}. The ligands containing the 2-hydroxypropyl groups form more stable complexes than do those containing 2-hydroxyethyl groups. In one respect the copper(II) complexes generally are different from those of the other metals studied. For the copper(II) complexes the amines having one and two N-alkanol substituents form more stable complexes than do those with four such substituents. For the other metallic ions studied the converse is generally but not always true.

The 1:1 titration curves for copper(II) ion with hn and 2-hn have been given previously by Courtney, Gustafson, Chaberek and Martell.[18] For hn, log K_1 was given as 9.90 and pK_{A_1} was given as 7.30. For 2-hn the corresponding values reported were 9.68 and 7.15. Also reported were values of pK_{A_1} plus pK_{A_2} of 17.24 and 16.52 for Cu(hn)$^{+2}$ and Cu(2-hn)$^{+2}$, respectively. The corresponding totals from the present work are 17.33 and 16.61, respectively. Evidence was also presented[18] to show that the 1:1 complexes between copper(II) ion and hn and 2-hn each have a tendency to form dimers in solution. Similar dimerization had been shown previously to take place for certain substituted ethanolamines[7] and has been discussed in regard to copper(II) complexes of monoethanolamine[5] and of diethanolamine.[6]

Nickel(II) Complexes.—The nickel(II) ion forms 1:1 and 1:2 complexes with the three mono- and dialkanol-substituted amines studied. There is no evidence for a 1:3 complex. As was shown by Edwards,[19] the Ni(hn)$^{+2}$ chelate reacts with one mole of sodium hydroxide to form the 1:2 complex and nickel(II) hydroxide which precipitates. At a pH of 11.5 the spacing between the hn and 1:1 curves (Fig. 5) indicates that the 1:2 complex has reacted with almost two more equivalents of base per mole of nickel(II) ion in solution. To a certain extent for the Ni(II) and hn systems and to a greater extent for the Ni(II) and 2-hn and Ni(II) and 2-hpn systems the reaction of base with the 1:2 complex is initiated before formation of the 1:2 complex is completed. Hence the values given in Table II for log K_2 are approximate. It is evident that these complexes are considerably weaker than the corresponding copper(II) ion complexes.

Cobalt(II) Complexes.—The cobalt(II) ion complexes of the mono- and disubstituted amines differ from the corresponding nickel(II) ion complexes in one important respect. Although the stability constants are lower, there is no tendency for the 1:1 complexes to precipitate cobalt(II) hydroxide upon addition of sodium hydroxide. The curve for the 1:1, Co(II):hn, mixture shows a distinct step so that a reliable value of pK_{A_1} was obtained.

Zinc(II) Complexes.—The 1:1 complexes formed between zinc(II) ion and hn, 2-hn and 2-hpn each decompose at approximately pH 8, evidently forming the 1:2 complexes and zinc(II) hydroxide. The curves for the 1:2 mixtures approach the corresponding curves for the copper(II) ion mixtures at high pH indicating that the final complex has reacted with two equivalents of hydroxide ion per mole of zinc(II) ion. It is not possible to determine from the present data whether or not the complex contains one or two amine molecules. Courtney, Gustafson, Chaberek and Martell[20] state that zinc(II) ion forms weak, easily disproportionated chelates with hn and 2-hn but do not give titration curves or stability constants.

Cadmium(II) Complexes.—As has been noted above the cadmium(II) ion complexes of 4-hn, 4-hpn and hn-3-hpn have unexpectedly high values of log K. The values of log K_1 for the cadmium(II) complexes of hn, 2-hn and 2-hpn, however, fall in the usual order with respect to the other metallic ions studied. All of the complexes of the cadmium(II) ion appear to be decomposed almost completely at about pH 10 yielding free amine and cadmium(II) hydroxide.

Other Metals.—The complexes of manganese(II) and iron(III) ions of some of these amines were investigated. It was found that the manganese(II) complexes were so slightly formed that it was impossible to calculate stability constants. The iron(III) ion formed ferric hydroxide at such a low pH as to mask all that might have occurred thereafter.

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[18] R. C. Courtney, R. L. Gustafson, S. Chaberek, Jr., and A. E. Martell, THIS JOURNAL, **81**, 519 (1959).

[19] L. J. Edwards, Doctor's Dissertation, University of Michigan, Ann Arbor, Michigan, 1950. Publication number 2586.

[20] R. C. Courtney, R. L. Gustafson, S. Chaberek, Jr., and A. E. Martell, THIS JOURNAL, **80**, 2121 (1958).