[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY OF CLARK UNIVERSITY]

Hydrolytic Tendencies of Metal Chelate Compounds. V. Hydrolysis and Dimerization of Copper(II) Chelates of 1,2-Diamines[1]

BY R. L. GUSTAFSON AND A. E. MARTELL

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Stability constants of the 1:1 Cu(II) chelates of N,N'-dimethylethylenediamine, N,N,N',N'-tetramethylethylenediamine, N-hydroxyethylethylenediamine, N,N'-dihydroxyethylethylenediamine, α,α'-dipyridyl and 1,10-phenanthroline are reported. The first and second hydrolysis constants of these chelate compounds are determined by potentiometric measurements of hydrogen ion concentration at 0.3, 25.0 and 42.5°. In all cases the monohydroxo chelate compounds were found to be in equilibrium with binuclear diolated forms. The equilibrium constants and the thermodynamic changes involved in hydrolysis and olation reactions are discussed in the light of the structures and other properties of the ligands and of the chelate compounds formed.

In a recent publication Courtney, *et al.*,[2] have reported equilibrium constants of the hydrolytic reactions of copper(II) chelates of five aliphatic polyamines. In the present paper the scope of this research is extended to include four additional bidentate ligands: N,N'-dimethylethylenediamine (DMEN), N,N,N',N'-tetramethylethylenediamine (TMEN), α,α'-dipyridyl (DIPY) and 1,10-phenanthroline (PHEN), and measurements are reported at temperatures of 0.3, 25.0 and 42.5°. Also, the work previously reported[2] for the copper(II) chelates of N-hydroxyethylethylenediamine (HEN) and N,N'-dihydroxyethylethylenediamine (2-HEN) at 25.0° has been extended to include data at the other two temperatures.

Experimental

Materials.—Samples of N-hydroxyethylethylenediamine and N,N'-dihydroxyethylethylenediamine obtained from Carbon and Carbide Chemical Co. were purified by fractional distillation and were then isolated as the dihydrochlorides. Samples of the dihydrochlorides of N,N'-dimethylethylenediamine and N,N,N',N'-tetramethylethylenediamine were prepared and recrystallized by conventional methods. The 1,10-phenanthroline monohydrochloride was obtained from the G. Frederick Smith Chemical Co. Standardization of the aqueous solutions of the above chelating agents was carried out by means of potentiometric titration with standard carbonate-free potassium hydroxide. A reagent grade sample of α,α,'-dipyridyl was obtained from the Fluka Chemical Co., Switzerland, and was used without further purification.

Potentiometric Titrations.—The calculation of the distribution of the various chelate species as a function of *p*H and of total metal ion concentration was carried out on the basis of potentiometric titrations of the metal chelate systems under investigation over a tenfold range of concentration in the manner previously described.[2] The hydrogen ion concentration was recorded with a Beckman Model G *p*H meter fitted with extension glass and calomel electrodes. The titrations were carried out in a multi-necked flask designed to accommodate a mercury seal stirrer, gas inlet and outlet tubes, microburet delivery tube and electrodes. The ionic strength was maintained relatively constant by using an electrolyte medium of 0.1 *M* potassium nitrate, and presaturated nitrogen was bubbled through the solutions during the course of the titrations to exclude carbon dioxide. Measurements were made at temperatures of 0.3, 25.0 and 42.5°.

Mathematical Treatment of Data

In all of the copper (II) chelates studied in this investigation, four species have been shown to exist: a diaquo chelate, $CuA(H_2O)_2^{2+}$, a monohydroxo compound,[3] $Cu[OH]A(H_2O)^{1+}$, a dihydroxo species, $Cu[OH]_2A$ and a dimer, $(Cu[OH]A)_2^{2+}$. The solution equilibria may be expressed in terms of the equations

$$Cu(H_2O)_4^{2+} + A \rightleftharpoons CuA(H_2O)_2^{2+} + 2H_2O$$

$$K_{MA} = \frac{[CuA]}{[Cu][A]} \qquad (1)$$

$$CuA(H_2O)_2^{2+} \rightleftharpoons Cu[OH]A(H_2O)^{1+} + H^+$$

$$K_{M[OH]A} = \frac{[Cu[OH]A][H^+]}{[CuA]} \qquad (2)$$

$$CuA(H_2O)_2^{2+} \rightleftharpoons Cu[OH]_2A + 2H^+$$

$$K_{M[OH]_2A} = \frac{[Cu[OH]_2A][H^+]^2}{[CuA]} \qquad (3)$$

$$2CuA(H_2O)_2^{2+} \rightleftharpoons (Cu[OH]A)_2^{2+} + 2H^+ + 2H_2O$$

$$K_{(M[OH]A)_2} = \frac{[(Cu[OH]A)_2][H^+]^2}{[CuA]^2} \qquad (4)$$

$$2Cu[OH]A(H_2O)^{1+} \rightleftharpoons (Cu[OH]A)_2^{2+} + 2H_2O$$

$$K_d = \frac{[(Cu[OH]A)_2]}{[Cu[OH]A]^2} \qquad (5)$$

where A represents one of the ligands listed above. The amount and distribution of the various chelate species present under varying conditions of *p*H and total concentration may be calculated from the above equilibria with the relationships outlined in a previous paper.[2] Since the present data are to be correlated with kinetic data obtained from the Cu(II) chelate catalyzed hydrolysis of substituted phosphonofluoridates, it is necessary to consider the unbound Cu(II) ion as a significant constituent of the experimental solution. The metal chelate formation constant K_{MA} may be calculated from the expression

$$K_{MA} = \frac{T_A - X[A]}{X[A]^2} \qquad (6)$$

where

$$X = \frac{[H^+]^2}{K_1K_2} + \frac{[H^+]}{K_2} + 1 \qquad (7)$$

for the chelates of DMEN, TMEN, HEN and 2-HEN and

$$X = \frac{[H^+]}{K_1} + 1 \qquad (7')$$

for the chelates of DIPY and PHEN. T_A is the total concentration of ligand species present, and K_1 and K_2 are the first and second acid dissociation

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[1] This investigation was supported by a research grant, B-1171, from the National Institute of Neurological Diseases and Blindness, Public Health Service.

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

[3] Brackets around OH within the formula of a coördination compound indicate a hydroxyl ion bound directly to the metal ion, whereas a set of brackets enclosing the entire formula indicates molar concentration.

constants of the ligand, respectively. The concentration of the neutral species of the ligand [A] may be calculated by the relationship

$$[\mathrm{A}] = \frac{(2 - a)T_{\mathrm{A}} - [\mathrm{H}^+] + [\mathrm{OH}^-]}{\dfrac{2[\mathrm{H}^+]^2}{K_1K_2} + \dfrac{[\mathrm{H}^+]}{K_2}} \tag{8}$$

where a is equal to the number of moles of standard KOH added per mole of ligand. With equations 6–8 it was possible to calculate formation constants for the copper(II) chelates of DMEN, TMEN, HEN and 2-HEN. However since the copper(II) chelates of DIPY and PHEN are virtually completely formed even in acid solution, it was not possible to calculate K_{MA} in this manner. For a solution containing two moles of the acid form of the ligand per mole of copper(II) ion, the following equation applies

$$K_{\mathrm{MA}} = \frac{Y}{K_{\mathrm{MA_2}}[\mathrm{A}]^2(T_{\mathrm{M}} - aT_{\mathrm{A}} - [\mathrm{H}^+] + [\mathrm{OH}^-] + [\mathrm{A}] + Y)} \tag{9}$$

where

$$Y = \frac{K_{\mathrm{MA_2}}[\mathrm{A}](T_{\mathrm{A}} - [\mathrm{A}]X)}{2K_{\mathrm{MA_2}}[\mathrm{A}] + 1} \tag{10}$$

and $K_{\mathrm{MA_2}}$ is expressed by the equation

$$\mathrm{CuA^{2+} + A \rightleftarrows CuA_2{}^{2+}}$$

$$K_{\mathrm{MA_2}} = \frac{[\mathrm{CuA_2}]}{[\mathrm{CuA}][\mathrm{A}]} \tag{11}$$

From two sets of experimental data, it is possible to calculate K_{MA} and $K_{\mathrm{MA_2}}$ from equation 9.

In calculating the species distribution as a function of $-\log[\mathrm{H}^+]$ and total metal species concentration, simultaneous solution of the equilibrium expressions 1–4 is time consuming and cumbersome; hence the following procedure was employed. With an estimated value of [CuA], the concentrations of the other chelate species were determined at the desired hydrogen ion concentration. The concentration of unbound copper(II) was calculated from the relationship

$$[\mathrm{Cu}] = \left(\frac{[\mathrm{CuA}]X}{K_{\mathrm{MA}}}\right)^{1/2} \tag{12}$$

By a method of successive approximations, such calculations were repeated until the total concentration of all species became equal to the total concentration of copper(II) compounds T_{M} in accordance with the equation

$$T_{\mathrm{M}} = [\mathrm{Cu}] + [\mathrm{CuA}] + [\mathrm{Cu[OH]A}] + [\mathrm{Cu[OH]_2A}] + 2[(\mathrm{Cu[OH]A})_2] \tag{13}$$

Values of ΔH, ΔF and ΔS for the hydrolysis and olation reactions were calculated with the usual relationships

$$\Delta H = \frac{2.303RT_1T_2(\log K_2 - \log K_1)}{T_2 - T_1}$$

$$\Delta F = -2.303\,RT\log K$$

$$\Delta S = \frac{\Delta H - \Delta F}{T}$$

Results and Discussion

Solution Equilibria.—The titration curves illustrated in Fig. 1 for the Cu(II)–TMEN chelate show that an increase in metal chelate concentration results in a shift of the buffer regions to lower *p*H values in the m interval from 2–3, where m represents the number of moles of potassium hydroxide added per mole of metal ion. The portion of the curves corresponding to m values from 0 to 2 indicates neutralization of the two moles of HCl present in the molecule. Beyond the crossover of the curves at $m = 3$, the second buffer region is displaced to higher *p*H values with a corresponding increase in the concentration of the metal chelate. Similar sets of titration curves were obtained for the copper(II) chelates of the other ligands studied. The greater requirement of base at a particular *p*H as a result of the higher concentration of metal chelate is an indication of the formation of a polymer of the type ($\mathrm{Cu[OH]A}_n{}^{n+}$). As is shown graphically in Fig. 2, a plot $[\mathrm{H}^+](T_{\mathrm{OH}} + [\mathrm{H}^+] - [\mathrm{OH}^-])/[\mathrm{CuA}]$ *vs.* $[\mathrm{CuA}]/[\mathrm{H}^+]$ results in a straight line, which verifies the assumption of a dimer of the Cu(II)–TMEN chelate compound. Similar plots were obtained for the other metal chelate systems investigated, but in some cases of dipyridyl–Cu(II) and of *o*-phenanthroline–Cu(II), the intercepts at $[\mathrm{CuA}]/[\mathrm{H}^+] = 0$ fell at values which were actually slightly below zero. For the other systems studied, intercepts at positive values were obtained, indicating extensive formation of the mononuclear monohydroxo chelates. Obviously some finite concentration, however small, of monohydroxo chelate species must exist in accordance with the equilibrium expression of equation 5. Although it is difficult to assign accurate values of $K_{\mathrm{M[OH]A}}$ for Cu–DIPY and Cu–PHEN in the cases where a negative value of the intercept was obtained, maximum values have been chosen based on the fact that intercepts below zero have no

TABLE I

EQUILIBRIUM CONSTANTS OF COPPER(II) CHELATES OF 1,2-DIAMINES

Ligand	log K_{MA}	$pK_{\mathrm{M[OH]A}}$	$pK_{\mathrm{M[OH]_2A}}$	$pK_{\mathrm{(M[OH]A)_2}}$	log K_{d}
		$t = 0.3°$			
DMEN	..	8.54	19.7	13.41	3.7
TMEN	..	8.34	19.0	13.26	3.4
HEN	..	7.69	18.1	13.7	1.7
2-HEN	..	7.64	17.43	13.2	2.1
DIPY	..	8.3	18.7	11.65	5.0
PHEN	..	8.3	...[a]	11.65	4.9
		$t = 25.0°$			
DMEN	9.72	8.09	18.2	12.41	3.8
TMEN	7.20	8.00	17.72	12.13	3.9
HEN	9.90	7.30	17.24	12.4	2.2
2-HEN	9.68	7.15	16.52	12.9	1.4
DIPY	6.33	7.9	17.67	10.81	5.0
PHEN	7.4	>7.8	17.3	10.67	>5.0
		$t = 42.5°$			
DMEN	..	7.83	18.1	11.87	3.8
TMEN	..	7.64	16.93	11.48	3.8
HEN	..	7.08	16.53	12.0	2.2
2-HEN	..	6.88	15.84	12.0	1.7
DIPY	..	>7.5	16.91	10.27	>4.7
PHEN	..	>7.3	17.13	10.32	>4.3

[a] Precipitation presumably of the neutral chelate species, $\mathrm{Cu[OH]_2A}$, occurred in the upper buffer region in all cases where the total metal chelate concentration was greater than 3×10^{-4} *M*.

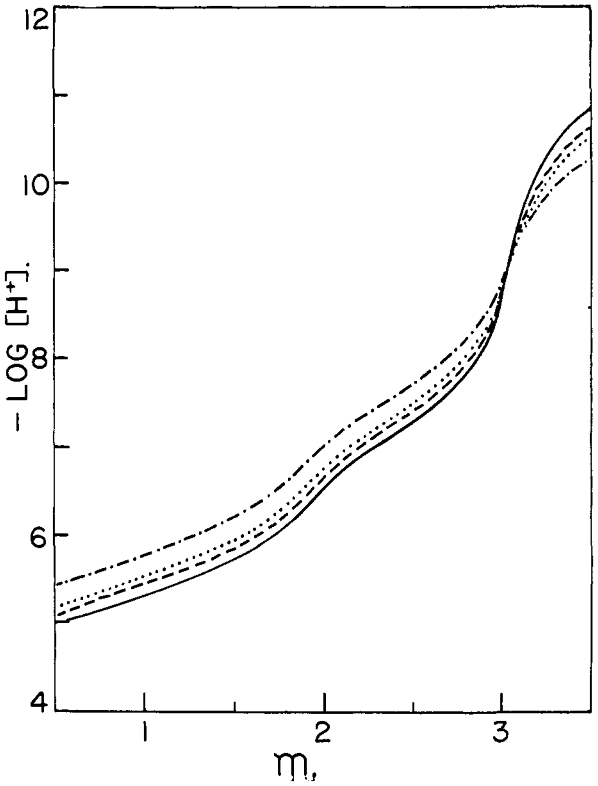


Fig. 1.—Potentiometric titration of solutions of copper(II) N,N,N′,N′-tetramethylethylenediamine chelates. $T_A/T_M = 1$. Concentrations: solid line, 9.88×10^{-3} *M;* dashed line, 5.12×10^{-3} *M;* dotted line, 3.07×10^{-3} *M;* dot-dash line, 1.02×10^{-3} *M;* $t = 25.0°$; $\mu = 0.10$ (KNO_3).

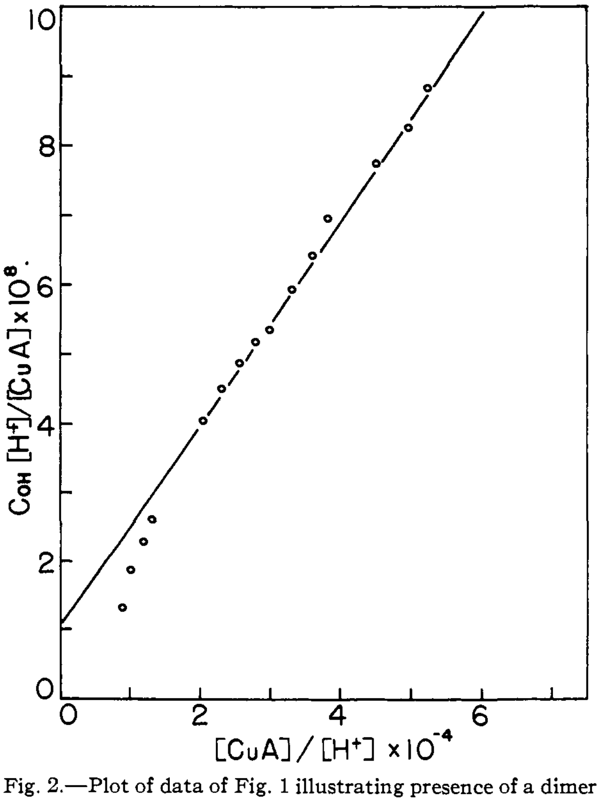


Fig. 2.—Plot of data of Fig. 1 illustrating presence of a dimer of copper(II)–N,N,N′,N′-tetramethylethylenediamine.

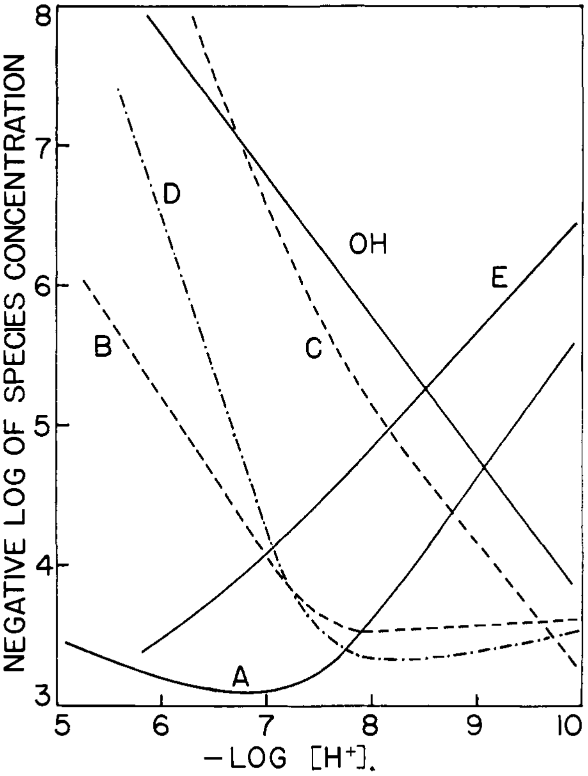


Fig. 3.—Graph showing distribution of copper(II)–N,N,N′,N′-tetramethylethylenediamine chelate as a function of the hydrogen ion concentration: A, diaquo chelate, $[CuA^{2+}]$; B, monohydroxo chelate, $[Cu[OH]A^{1+}]$; C, dihydroxo chelate, $[Cu[OH]_2A^0]$; D, dimer, $[(Cu[OH]A)_2^{2+}]$; E, free copper(II); OH, hydroxyl ion. $t = 25.0°$; $\mu = 0.10$ (KNO_3).

physical meaning and the assumption that the negative intercept is a consequence of the order of probable error in determining $K_{M[OH]A}$ by extrapolation. The equilibrium constants for all of the systems investigated at temperatures of 0.3, 25.0 and 42.5° are listed in Table I.

The most striking result of the equilibrium studies is the relatively high dimerization tendencies in the cases of the copper(II) chelates of dipyridyl and *o*-phenanthroline. By comparing the values of the dimerization constants K_d in Table I with the values of the acid dissociation constants of the various ligands listed in Table II, it may be seen that the chelates of dipyridyl and *o*-phenanthroline, which are by far the least basic and hence the weakest donors of the six ligands investigated, dimerize to the greatest extent. It would perhaps be expected that in a chelate compound in which the

TABLE II

ACID DISSOCIATION CONSTANTS OF LIGANDS

$t = 25.0°$: $\mu = 0.10$ (KNO_3)

Ligand	pK_1	pK_2
DMEN	7.01	9.88
TMEN	5.90	9.14
HEN	6.49	9.52
2-HEN	6.26	9.24
DIPY	4.45	..
PHEN	4.95	..

TABLE III

VALUES OF ΔH^0(KCAL./MOLE) FOR HYDROLYSIS AND DIMERIZATION REACTIONS OF Cu(II) CHELATES

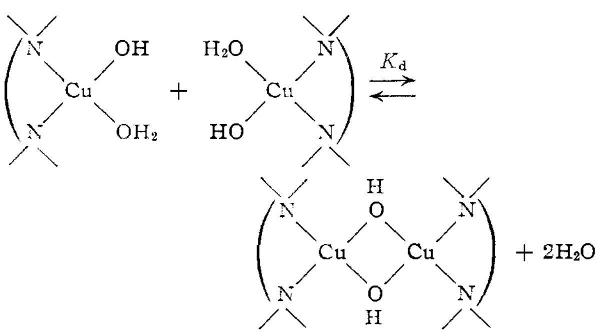
Ligand	$\Delta H^0(K_{M[OH]A})$	$\Delta H^0(K_{M[OH]A_2})$	ΔH^0 (K_d)
DMEN	+6.6 ± 0.2	+14.4 ± 0.6	+1.0 ± 0.4
TMEN	+7 ± 1	+16.6 ± 0.4	+3 ± 3
HEN	+5.7 ± 0.2	+15 ± 3	+4 ± 3
2-HEN	+7.1 ± 0.3	+13 ± 6	−1 ± 7
DIPY	+<8	+12.9 ± 0.2	−<0.6
PHEN	+<10	+12 ± 2	−<4

TABLE IV

VALUES OF ΔF^0 AND ΔS^0 FOR HYDROLYSIS AND DIMERIZATION REACTIONS OF Cu(II) CHELATES AT VARIOUS TEMPERATURES

Reaction	ΔF^0 (kcal./mole) 0.3°	ΔF^0 (kcal./mole) 25.0°	ΔF^0 (kcal./mole) 42.5°	ΔS^0 (cal./mole/deg.) 0.3°	ΔS^0 (cal./mole/deg.) 25.0°	ΔS^0 (cal./mole/deg.) 42.5°
			Cu(II)-DMEN			
$K_{M[OH]A}$	+10.69	+11.04	+11.31	−15.0	−14.9	−14.9
$K_{(M[OH]A)_2}$	+16.78	+16.93	+17.15	− 8.7	− 8.5	− 8.7
K_d	− 4.6	− 5.2	− 5.5	+20	+21	+21
			Cu(II)-TMEN			
$K_{M[OH]A}$	+10.44	+10.92	+11.04	−13	−13	−13
$K_{(M[OH]A)_2}$	+16.60	+16.55	+16.58	± 0.0	± 0.0	± 0.0
K_d	− 4.3	− 5.3	− 5.5	+27	+28	+27
			Cu(II)-HEN			
$K_{M[OH]A}$	+ 9.62	+ 9.96	+10.2	−14.3	−14.3	−14.3
$K_{(M[OH]A)_2}$	+17.1	+16.9	+17.3	− 8	− 6	− 7
K_d	− 2.1	− 3.0	− 3.2	+22	+23	+23
			Cu(II)-2-HEN			
$K_{M[OH]A}$	+ 9.56	+ 9.76	+ 9.94	− 9.0	− 8.9	− 9.0
$K_{(M[OH]A)_2}$	+16.5	+17.6	+17.3	−12	−15	−14
K_d	− 2.6	− 1.9	− 2.5	+ 6	+ 3	+ 5
			Cu(II)-DIPY			
$K_{M[OH]A}$	+10.4	+10.8	+>10.8	−>9	−>9	−>9
$K_{(M[OH]A)_2}$	+14.58	+14.75	+14.84	− 6.1	− 6.3	− 6.1
K_d	− 6.3	− 6.8	−>6.8	+>19	+>21	+>20
			Cu(II)-PHEN			
$K_{M[OH]A}$	+10.4	+>10.6	+>10.5	−>1	−>2	−>2
$K_{(M[OH]A)_2}$	+14.58	+14.56	+14.91	− 9	− 9	− 9
K_d	− 6.1	−>6.8	−>6.2	+>8	+>9	+>7

copper(II) ion forms weaker bonds with a ligand, the metal would have greater affinity for an additional donor group such as a hydroxyl ion. The formation of a monohydroxo chelate may be considered to be the first step in dimer formation, which proceeds according to the reaction



For the less stable chelates (dipyridyl and *o*-phenanthroline) there is greater affinity of the monohydroxo chelate for an additional donor atom than is true of the analogous chelates of the aliphatic diamines; hence dimer formation takes place more easily in the case of the aromatic compounds.

Whereas the stabilities of the aquo chelates of DMEN and TMEN are markedly different, these compounds are observed to undergo dimerization to approximately the same degree and to a much greater extent than the chelates of HEN and 2-HEN. Examination of the first and second dissociation constants shows that the hydrolytic tendency of Cu–TMEN is considerably greater than that of Cu-DMEN. This difference would be expected in view of the weaker affinity of the TMEN ligand for the metal ion. The fact that Cu–TMEN does not dimerize to a greater extent than does the chelate of the dimethyl substituted analog probably may be attributed to the greater steric repulsions of the larger number of methyl substituents in the former case.

Only a small degree of dimerization is observed for the monohydroxo chelates of Cu-HEN and Cu-2-HEN. While this effect may be explained partly by steric considerations, it is felt that the primary influence is the direct binding of the ethoxide group (or groups) to the central metal ion as discussed previously,[2] thus preventing dimerization except by dissociation of the ethoxide–metal linkage.

Comparison of the dimerization constants K_d with the formation constants K_{MA} of Table I indicates that in general, the copper(II) chelates having the lowest stability dimerize to the greatest extent, provided that: (1) the ligands employed are bidentate, and (2) no unfavorable steric effects are involved. This generality may be extended to the hydrolysis of the aquo copper(II) ion studied by

Berecki-Biedermann,[4] who found that the equilibrium constants for the reactions

$$Cu^{2+} + H_2O \rightleftharpoons Cu[OH]^{1+} + H^+$$

and

$$2Cu^{2+} + 2H_2O \rightleftharpoons Cu[OH]_2Cu^{2+} + 2H^+$$

correspond to pK values of 8.0 and 10.6, respectively. These results indicate the value of log K_d to be 5.4. Thus there is more extensive polymerization in the case of the aquated copper(II) ion than for the chelates of dipyridyl and *o*-phenanthroline, the ligands having the weakest coördinating tendencies of the ligands studied.

By the use of the equilibrium data of Table I, it is possible to determine species distribution as a function of total metal or ligand concentration and hydrogen ion concentration. A sample plot of $-\log[H^+]$ *vs.* the negative logarithm of the various species concentrations for 1.0×10^{-3} *M* Cu(II) and TMEN at 25° is shown in Fig. 3. Here it may be seen that the concentration of the dihydroxo chelate increases with increasing *p*H, mainly at the expense of the diaquo chelate. In this case, the concentrations of the monohydroxo chelate and dimer remain relatively constant in the $-\log[H^+]$ range 8–10. For many of the other copper(II) chelate systems studied, the concentrations of the dimer and of monohydroxo chelate reach a maximum at $-\log[H^+]$ 8–8.5 and the contributions of these species fall off sharply on either side of this region.

Thermodynamic constants calculated from the data of Table I for reactions 2, 4 and 5 are listed in Tables III and IV. Considerable deviations were observed in some cases because of the lack of accuracy of values of $K_{M[OH]A}$ for chelates of dipyridyl and *o*-phenanthroline (which contain only a small proportion of monohydroxo species in equilibrium with the dimer) and of values of $K_{(M[OH]A)_2}$ for chelates of HEN and 2-HEN (which contain only a small proportion of dimer in equilibrium with the monohydroxo species). Since values of log K_d are determined from the differences of two large quantities according to the equation

$$\log K_d = 2pK_{M[OH]A} - pK_{(M[OH]A)_2}$$

they may be considered to be reliable only to the first decimal place and hence have been rounded off in Table I.

The small, almost negligible values of ΔH^0 in Table III and the relatively large values of ΔS^0 in Table IV indicate that the driving force in the formation of the dimer from the monohydroxo chelate compound is primarily an entropy effect. As is indicated in the equation for this reaction illustrated above, the increase in entropy with dimerization probably is due for the most part to the negative entropy contribution of the coördinated water molecules in the hydroxo chelate, and the entropy increase which results when the restraint on these coördinated water molecules is removed as they are released to the solvent when dimerization occurs.

WORCESTER, MASS.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE PENNSYLVANIA STATE UNIVERSITY]

A Thermodynamic Study of Some Metal–Amine Coördination Compounds[1]

BY G. H. MCINTYRE, JR., B. P. BLOCK AND W. CONARD FERNELIUS

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A method is presented by which activity formation constants and free energy, enthalpy and entropy changes can be obtained for the coördination of amines to metal ions. Values for these quantities from 10 to 40° in 10° intervals are presented for the reaction of nickel(II) ion with ethylenediamine (en) and N-methylethylenediamine (Meen); copper(II) ion with en, Meen, diethylenetriamine (dien), 4-amino-2-thiabutane (Maes) and 1,8-diamino-3,6-dithiaoctane (diames); and zinc ion with en, Meen and dien. Values for the proton–amine formation constants for these amines also are given. Relations of the enthalpy changes for the different ligand-metal associations are discussed.

Introduction

During the past dozen years many measurements of formation constants have been made.[2]

While the data are very useful, they would be vastly more so if (1) they included values for the heats of reaction as well as free energies and (2) the formation constants were true thermodynamic values instead of *molarity quotients*[3] valid only at a definite ionic strength. The first limitation has been stressed by Bjerrum[4] and by Burkin.[5]

The latter points out the need for ΔH values in determining bond strengths. A few investigators have reported calorimetrically measured heats of reaction.[6–9]

Several others have made equilibrium measurements over a limited range of temperatures (0–50° as a maximum) and used these data to calculate ΔH.[10–19] Still others have been concerned with ob-

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[1] From a dissertation submitted by G. H. McIntyre, Jr., in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June 1953. Presented in preliminary form at the 124th meeting of the American Chemical Society, Chicago, Illinois, September 11, 1953.

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