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Stability Constants of *N*-Methyl- and *N*-Ethyl-Substituted Diethylenetriamine Complexes of Copper(II)

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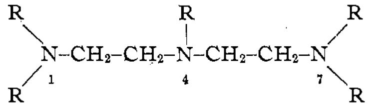
Proton stability constants for a series of eight *N*-methyl- and *N*-ethyl-substituted diethylenetriamines (Rdien) have been measured in aqueous solution. The first two constants, K_1 and K_2, can be predicted using an empirical method of Clark and Perrin. The third, K_3, can be estimated qualitatively. Stability constants, K_f, for the reaction of the Rdien ligands with Cu(II) to form $Cu(Rdien)^{2+}$ decrease linearly with increasing methyl or ethyl substitution on the terminal nitrogen atoms. Substitution at the central nitrogen does not affect the stability. Hydroxo stability constants, K_{OH}, for the reaction of $Cu(Rdien)^{2+}$ with OH^- to give $Cu(Rdien)(OH)^+$ are all very similar except that for $Cu(1,1,7,7\text{-}Et_4dien)(OH)^+$ which is unusually high.

Introduction

In the course of examining the catalytic properties of metal ion complexes in the hydrolysis of amino acid esters,[2] we turned to copper(II) complexes of N-substituted diethylenetriamine (Rdien), where the R



groups in the 1, 4, and 7 positions may be either H, CH_3, or C_2H_5. Before conducting the kinetic studies, it was necessary to know the equilibrium constants for the complexation of Cu(II) by the diethylenetriamines. Herein are reported the equilibrium studies.

There are three types of equilibria which were examined: first, the proton stability constants, K_1, K_2, and K_3, of the three nitrogen donor atoms in the Rdien ligands themselves

$$H^+ + Rdien \rightleftharpoons RdienH^+,\qquad K_1 = [RdienH^+]/[H^+][Rdien] \quad (1)$$

$$H^+ + RdienH^+ \rightleftharpoons RdienH_2^{2+},\qquad K_2 = [RdienH_2^{2+}]/[H^+][RdienH^+] \quad (2)$$

$$H^+ + RdienH_2^{2+} \rightleftharpoons RdienH_3^{3+},\qquad K_3 = [RdienH_3^{3+}]/[H^+][RdienH_2^{2+}] \quad (3)$$

second, the stability constants, K_f, for the formation of the $Cu(Rdien)^{2+}$ complexes

$$Cu^{2+} + Rdien \rightleftharpoons Cu(Rdien)^{2+},\qquad K_f = [Cu(Rdien)^{2+}]/[Cu^{2+}][Rdien] \quad (4)$$

and, third, the stability constants, K_{OH}, for the formation of the $Cu(Rdien)(OH)^+$ complexes

$$Cu(Rdien)^{2+} + OH^- \rightleftharpoons Cu(Rdien)(OH)^+,\qquad K_{OH} = [Cu(Rdien)(OH)^+]/[Cu(Rdien)^{2+}][OH^-] \quad (5)$$

Experimental Section

Materials.—The substituted diethylenetriamines were purchased from the Ames Laboratories, Milford, Conn. Their names will be abbreviated by indicating the R groups and their positions in the unsubstituted diethylenetriamine (dien); for example, 1,4-dimethyldiethylenetriamine will be given by 1,4-Me_2dien. All amines were purified by vacuum distillation through a 10-cm glass column under the following conditions of temperature and pressure (mm): 1-(Me)dien, 62° (3 mm); 1,4-Me_2dien, 84° (15 mm); 1,1-Me_2dien, 83° (13 mm);[3] 1,1,4,7,7-Me_5dien, 82.5° (13 mm);[4] 1,1-Et_2dien, 114° (23 mm);[3] 1,4,7-Et_3dien, 83° (3.5 mm); 1,1,7,7-Et_4dien, 120° (10 mm);[4] 4-Me-1,1,7,7-Et_4dien, 127° (13 mm). Where required, they were slowly redistilled on a platinum spinning-band column. Their purity was established by proton nmr or gas chromatography. They were stored at −78° in the dark in tightly stoppered glass containers.

Carbonate-free NaOH was standardized against dried potassium acid phthalate and the $Cu(NO_3)_2$ solutions were standardized by titration with EDTA using murexide indicator, according to the method of Schwarzenbach.[5] Doubly distilled water was used in making all solutions.

pH Measurements.—All titrations were done with a Radiometer TTT1C titrator using a SBU1 syringe buret (0.5-ml capacity) and a TTA31 microtitration assembly. The pH meter was standardized with buffers at pH 4.01, 7.00, and 10.00 at 25.0°. To convert the hydrogen ion activity (pH) to hydrogen ion concentrations (pH_c), a solution of 0.0100 *M* HCl and 0.100 *M* KNO_3 was titrated. The hydrogen ion concentration (pH_c) was calculated assuming complete dissociation of the HCl. At high pH readings, known added NaOH and K_w were used to calculate pH_c. The value of K_w (1.615×10^{-14}) was calculated at ionic strength 0.11 from data given for KBr solutions.[6] (Data were not available for KNO_3 solutions.) The deviations between the meter readings (pH) and actual hydrogen ion concentrations (pH_c) in the acid region were less than 0.02 unit. At pH 11.5, a total deviation of 0.10 unit was found and was applied as a linear correction from pH 7 to 11.5.

In all titrations Radiometer Type K101/3 liquid junction saturated calomel and Beckman Type E-2 miniature glass electrodes were used. Solutions were maintained under a nitrogen atmosphere during titrations by bubbling in prepurified nitrogen which had been passed through concentrated aqueous NaOH. The temperature of all solutions was held at 25.0° by circulating constant-temperature water through the water-jacketed titration cell.

Titrations of $RdienH_3^{3+}$.—In order to evaluate the proton stability constants, K_1, K_2, and K_3, 10-ml solutions of $RdienH_3^{3+}$ were titrated with 0.2 *M* NaOH. The titrated solutions were approximately 9.5×10^{-3} *M* in Rdien and 28.5×10^{-3} *M* in standard HNO_3 and contained sufficient KNO_3 so that the average ionic strength of the solution during the titration was 0.11. A typical titration curve is shown for 1,4-$Me_2dienH_3^{3+}$ in Figure 1.

Titration of $RdienH_3^{3+}$ and Cu^{2+}.—The determinations of the equilibrium constants K_f and K_{OH} were done by titrating with NaOH 10-ml aqueous solutions of 9×10^{-3} *M* $Cu(NO_3)_2$, 9×10^{-3} *M* Rdien, 27×10^{-3} *M* HNO_3, and sufficient KNO_3 to

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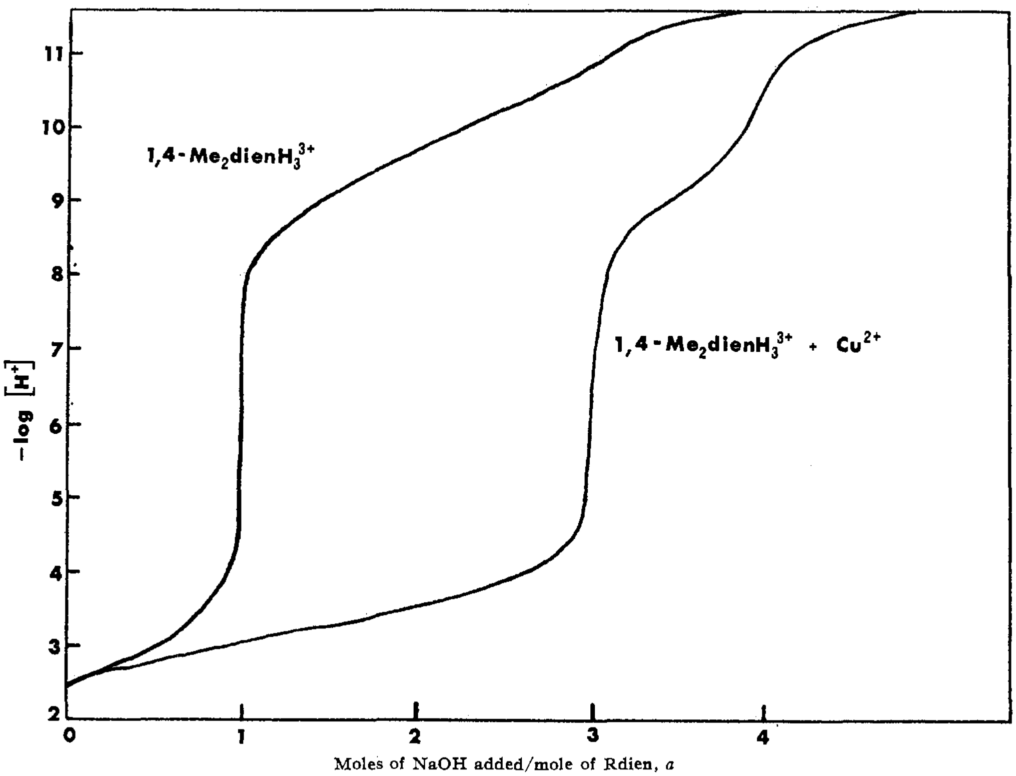

Figure 1.—Upper curve: titration of 9×10^{-3} *M* $1,4\text{-}Me_2dienH_3^{3+}$ with NaOH. Lower curve: titration of 9×10^{-3} *M* $1,4\text{-}Me_2dienH_3^{3+}$ and equimolar Cu^{2+} with NaOH.

give an average ionic strength of 0.13. The lower curve in Figure 1 is typical of these titration curves.

Results

Evaluation of K_1, K_2, and K_3.—These constants, defined by eq 1–3, were calculated from data such as are shown in the upper curve of Figure 1. Each titration was repeated four to seven times to ensure reproducibility of the results. Each curve shows an end point after the addition of 1 equiv of base and then another very gradual break after 2 additional equiv. The region preceding the first end-point rise corresponds to the removal of a proton from the central nitrogen (the 4 position) of $RdienH_3^{3+}$ to give $RdienH_2^{2+}$, in which the terminal nitrogens are protonated. Prue and Schwarzenbach[7] suggested that electrostatic repulsion between the protonated nitrogens would favor protonation at the 1 and 7 positions in $dienH_2^{2+}$. Subsequently Ciampolini and Paoletti[8] used ΔH data for reaction 3 to support the suggestion that the proton on the central nitrogen in $dienH_3^{3+}$ is removed first. Since the titration curves of all of the Rdien molecules studied here have the same basic features, it is presumed that K_3 is associated with the removal of a proton from the central nitrogen atom in all cases.

The removal of the two remaining protons in $RdienH_2^{2+}$ at much higher pH is associated with equilibrium constants K_1 and K_2, which are both very similar in magnitude.

The method of Schwarzenbach[9] was used to calculate K_1, K_2, and K_3. In deriving the expression used in making the calculations, A will represent Rdien and HA, H_2A, and H_3A the protonated forms.

The total amine concentration, C_A, is defined as

$$C_A = \sum_{j=0}^{m} [H_jA] = [A] + [HA] + [H_2A] + [H_3A] \qquad (6)$$

and the total acid concentration present, $[H]_t$, as

$$[H]_t = C_A(m - a) = [H] - [OH] + \sum_{j=1}^{m} j[H_jA] \qquad (7a)$$

or

$$C_Ag = \sum_{j=1}^{m} j[H_jA] \qquad (7b)$$

where $g = m - a + ([OH] - [H])/C_A$, m is the maximum number of protons the molecule can accept, and a is the apparent neutralization point of the acid and is defined as the number of moles of NaOH per mole of amine which has been added at that point in the titration. The quantity [H] is directly measurable as pH_c, and [OH] is obtained from it and the ion product for water, K_w.

Combining eq 1, 2, 3, 6, and 7b yields

$$g + (g - 1)[H]K_1 + (g - 2)[H]^2K_1K_2 + (g - 3)[H]^3K_1K_2K_3 = 0 \qquad (8)$$

When one of the constants is sufficiently different from the other two (as K_3 is in the present situation), eq 8 will reduce to only two significant terms, those involving the members, $[H]^j\bar{K}_j$ and $[H]^{j-1}\bar{K}_{j-1}$. Division of this result by $[H]^{j-1}\bar{K}_{j-1}$ gives

$$(g - j + 1) + (g - j)[H]K_j = 0 \qquad (9)$$

which can be used to calculate K_3.

Using eq 9, K_3 was evaluated by computer from six to ten points in the buffer region lying between a values of 0.3 and 0.7. As in all of the calculations in this

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[9] G. Schwarzenbach, *Helv. Chim. Acta*, **33**, 947 (1950).

TABLE I

EXPERIMENTAL VALUES[a] OF K_1, K_2, K_3, K_f, AND K_{OH} AT 25.0°

Rdien	Log K_1	Log K_2	Log K_3	Log K_f	Log K_{OH}
dien	9.89 ± 0.01	9.06 ± 0.01	4.27 ± 0.01	15.91 ± 0.03	5.17 ± 0.06
1-(Me)dien	9.86 ± 0.06	9.18 ± 0.02	3.30 ± 0.03	15.32 ± 0.03	5.07 ± 0.08
1,4-Me_2dien	10.03 + 0.02	9.35 ± 0.02	2.82 ± 0.03	15.11 + 0.02	4.79 ± 0.04
1,1-Me_2dien	9.62 ± 0.06	8.63 ± 0.05	3.62 ± 0.04	14.33 ± 0.04	5.32 ± 0.11
1,1,4,7,7-Me_5dien	9.22 ± 0.01	8.41 ± 0.03	2.09 ± 0.03	12.16 ± 0.03	5.14 ± 0.04
1,1-Et_2dien	9.90 ± 0.08	9.10 ± 0.03	3.93 ± 0.05	13.17 ± 0.11	5.44 ± 0.11
1,4,7-Et_3dien	10.13 ± 0.02	9.37 ± 0.02	2.93 ± 0.02	13.17 ± 0.08	5.21 ± 0.14
1,1,7,7-Et_4dien	9.78 ± 0.04	9.03 ± 0.02	3.39 ± 0.04	10.43 ± 0.03	6.18 ± 0.03
4-Me-1,1,7,7-Et_4dien	9.71 ± 0.03	9.02 ± 0.01	2.29 ± 0.03	≤9.15	

[a] The ionic strength was adjusted with KNO_3 to 0.13. Error limits are standard deviations.

communication, concentrations of species were corrected for changes in volume caused by the addition of NaOH. From the values of K_3 at the different points, a standard deviation was determined for each average K_3. These results are given in Table I.

For the calculation of K_1 and K_2, which have similar values, eq 8 reduces to only three terms

$$\frac{g-1}{(g-2)[\mathrm{H}]} = -K_2 - \frac{g}{(g-2)[\mathrm{H}]^2}\frac{1}{K_1} \qquad (10)$$

Using a least-squares iterative computer program, eq 10 was fitted where $(g - 1)/(g - 2)[\mathrm{H}]$ was the dependent variable and $g/(g - 2)[\mathrm{H}]^2$ the independent variable. In most cases less than ten iterations were necessary to achieve a convergence value of 10^{-6}. Data used in these calculations were taken from the region lying between a values of 1.3 and 2.7. The calculated K_1 and K_2 constants are presented in Table I.

Evaluation of K_f and K_{OH}.—The constants K_f and K_{OH} as defined in eq 4 and 5 were calculated from titration data such as are shown in the lower curve of Figure 1. The curves typically show an initial region at low pH where the upper and lower curves are the same and the proton from the central nitrogen of $\mathrm{RdienH_3}^{3+}$ is being removed. Beyond 1 equiv of base, there is a buffer region until 3 equiv is added. In this region the deep blue $\mathrm{Cu(Rdien)}^{2+}$ forms. At still higher pH, a short buffer region up to the addition of 4 equiv of NaOH indicates the formation of the hydroxo complex $\mathrm{Cu(Rdien)(OH)}^+$.

As found previously[10,11] for the Cu^{2+}–dien reaction, the bis complex $\mathrm{Cu(dien)_2}^{2+}$ will not be present in measurable concentrations in the solutions studied here. Likewise protonated species such as $\mathrm{Cu(dienH)}^{3+}$ and $\mathrm{Cu(dienH_2)}^{4+}$ are absent. Finally, polymeric species of $\mathrm{Cu(dien)(OH)}^+$ have not been reported[10] to be present in solutions of Cu^{2+} and dien. Due to their negligible concentrations, none of these species has been considered in the calculations of K_f and K_{OH}.

The method of Prue and Schwarzenbach[7] was applied to the evaluation of K_f. The following set of equations was first used to calculate K_e for the reaction

$$\mathrm{Cu}^{2+} + \mathrm{RdienH_2}^{2+} \overset{K_e}{\rightleftharpoons} \mathrm{Cu(Rdien)}^{2+} + 2\mathrm{H}^+ \qquad (11)$$

$$\mathrm{Cu_{TOT}} = c = [\mathrm{Cu}] + [\mathrm{CuA}] \qquad (12)$$

$$\mathrm{A_{TOT}} = c = \alpha[\mathrm{H_2A}] + [\mathrm{CuA}] \qquad (13)$$

$$\mathrm{H_{TOT}} = cg = \beta[\mathrm{H_2A}] \qquad (14)$$

where

$$\alpha = 1/[\mathrm{H}]^2K_1K_2 + 1/[\mathrm{H}]K_2 + 1 + [\mathrm{H}]K_3$$

and

$$\beta = 1/[\mathrm{H}]K_2 + 2 + 3[\mathrm{H}]K_3$$

and g is defined in eq 7b. From eq 12–14, the unknowns $[\mathrm{H_2A}]$, $[\mathrm{Cu}]$, and $[\mathrm{CuA}]$ can be calculated as cg/β, $\alpha cg/\beta$, and $c - \alpha cg/\beta$, respectively. These quantities, together with the appropriate $[\mathrm{H}^+]$, can be combined to obtain K_e of eq 11

$$K_e = \frac{[\mathrm{H}^+]^2\left\{c - \dfrac{\alpha cg}{\beta}\right\}}{\left(\dfrac{\alpha cg}{\beta}\right)\left(\dfrac{cg}{\beta}\right)} = \frac{[\mathrm{H}^+]^2[\mathrm{CuA}^{2+}]}{[\mathrm{Cu}^{2+}][\mathrm{H_2A}]} \qquad (15)$$

Using a computer program, values of K_e were calculated at several points in the titration between a values of 1.3 and 2.7.

Since reaction 11 may be expressed as a combination of reactions 1, and 2, 4, their equilibrium constants must be related as

$$K_e = \frac{K_f}{K_1K_2} \qquad (16)$$

Using the experimental values of K_e, K_1, and K_2, eq 16 allows the calculation of K_f (Table I).

The K_f value reported for 4-Me-1,1,7,7-Et_4dien in Table I is an upper limit, since the measurement was complicated by precipitation near pH 5.8, and only a few points were available for the stability constant calculations.

Although Prue and Schwarzenbach[7] were able to determine K_f values for dien with Ni^{2+} and Zn^{2+} also, our attempts with these metals using the ligands 1,1,7,7-Et_4dien and 1,1-Et_2dien gave hydroxide precipitates of the metal at pH values lower than are required for complex formation. In nonaqueous solvents, 1,1,7,7-Et_4dien and 1,1,4,7,7-Me_5dien are known[12,13] to form complexes.

The constant K_{OH} for equilibrium 5 was obtained by first determining the acid dissociation constant, K_d, for the reaction

$$\mathrm{Cu(Rdien)(OH_2)}^{2+} \overset{K_d}{\rightleftharpoons} \mathrm{Cu(Rdien)(OH)}^+ + \mathrm{H}^+ \qquad (17)$$

Equation 9, which was also used for determining K_3, facilitated the calculation of K_d using data of the type given in the lower curve of Figure 1 between a values of 3.3 and 3.7. Since equilibrium 17 may be written in terms of equilibrium 5 and K_w for water, K_d may be expressed as

$$K_d = K_{OH}K_w \qquad (18)$$

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From this equation K_{OH} values were calculated and together with their standard deviations are given in Table I.

Discussion

Proton Stability Constants, K_1, K_2, and K_3.—Proton stability constants have been reported previously for dien,[7,11,14–17] 1,1,4,7,7-Me$_5$dien,[18] and 1,1,7,7-Et$_4$dien.[19] Where measurements have been made at an ionic strength near 0.1, our results are in good agreement with literature values for dien. In the case of 1,1,7,7-Et$_4$dien, the literature values[19] for K_1, K_2, and K_3 are 9.66, 8.62, and 3.55, respectively. Although K_1 and K_3 are in agreement with the values in Table I, K_2 differs significantly. The discrepancy appears to lie in the different equations which we and Margerum and coworkers[19] have used. We have not been able to derive their equation.

As noted previously, the constants K_1 and K_2 are similar in magnitude and are associated with the protonation of the most basic nitrogen atoms in Rdien, *i.e.*, the 1 and 7 atoms. The K_3 proton stability constant is much lower and corresponds to protonation of the nitrogen in the 4 position. The values of K_1, K_2, and K_3 depend upon the number of methyl or ethyl groups bonded to the nitrogen atoms as well as the number of nitrogen atoms which are protonated. Clark and Perrin[20] have developed an empirical method of predicting the pK_a (*i.e.*, log K_1, log K_2, or log K_3) of substituted amines. Table II gives an example of the method for 1,4,7-Et$_3$dien. The prediction of the most basic nitrogen in unprotonated 1,4,7-Et$_3$dien is made by assuming that the terminal nitrogen groups are derivatives of Et$_2$NH (pK_a = 11.15) and the central nitrogen of Et$_3$N (pK_a = 10.72). These pK_a values are then adjusted for substituents bonded to the ethyl groups. For example, the terminal Et$_2$NH groups have an –NR$_2$ group bonded two carbons distant from the nitrogen. This –NR$_2$ group reduces the pK_a of the terminal nitrogen by −0.9 unit. Other substituent effects are calculated similarly. Where there are two equivalent nitrogen atoms, a statistical factor of 0.30 (log 2) is also included in the calculation. As seen in part a of Table II, the first proton is predicted to go on the 1 and 7 nitrogens with a pK_a of 10.44; the second proton (part b) completes the protonation at the 1 and 7 positions with a pK_a of 9.50; the third proton (part c) goes on the 4 nitrogen with a pK_a of 3.52. Similar estimations of K_1, K_2, and K_3 have been made for the other Rdien amines; these together with the positions of protonation are given in Table III. Although the typical pK_a and ΔpK_a values for substituents used by Clark and Perrin (footnote *a*, Table II) were taken from data measured at 20°, these values also fit our data at the slightly higher temperature of 25°.

TABLE II

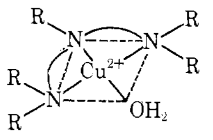
SAMPLE CALCULATION OF PREDICTED VALUES OF K_1, K_2, AND K_3 FOR 1,4,7-Et$_3$dien BY THE METHOD OF CLARK AND PERRIN

	Assumed position of protonation 1	4	7
(a) Addition of First Proton, $\mathrm{CH_3CH_2\underset{1}{N}(H)CH_2CH_2\underset{4}{N}(CH_2CH_3)CH_2CH_2\underset{7}{N}(H)CH_2CH_3}$			
Typical value of pK_a[a]	11.15	10.72	11.15
Statistical correction	+0.30		+0.30
Effect of NR$_2$ group, 2 carbons distant	−0.9		−0.9
Effect of NHR groups, 2 carbons distant		−1.8	
Effect of NHR group, 4 carbons and 1 nitrogen distant	−0.11		−0.11
Predicted value of pK_a (*i.e.*, log K_1)	10.44	8.92	10.44
(b) Addition of Second Proton, $\mathrm{CH_3CH_2\underset{1}{N}(H)CH_2CH_2\underset{4}{N}(CH_2CH_3)CH_2CH_2\underset{7}{\overset{+}{N}}(CH_2CH_3)H_2}$			
Typical value of pK_a[a]	11.15	10.72	
Statistical correction	−0.30		
Effect of NR$_2$ group, 2 carbons distant	−0.9		
Effect of NHR group, 2 carbons distant		−0.9	
Effect of $\overset{+}{N}H_2R$ group, 2 carbons distant		−3.6	
Effect of $\overset{+}{N}H_2R$ groups, 4 carbons and 1 nitrogen distant	−0.45		
Predicted value of pK_a (*i.e.*, log K_2)	9.50	6.22	
(c) Addition of Third Proton, $\mathrm{CH_3CH_2\underset{1}{\overset{+}{N}}(H_2)CH_2CH_2\underset{4}{N}(CH_2CH_3)CH_2CH_2\underset{7}{\overset{+}{N}}(CH_2CH_3)H_2}$			
Typical value of pK_a[a]		10.72	
Effects of $\overset{+}{N}H_2R$ groups, 2 carbons distant		−7.2	
Predicted value of pK_a (*i.e.*, log K_3)		3.52	

[a] Typical pK_a values of amines: $C_2H_5NH_2$, 10.81; $(C_2H_5)_2NH$, 11.15; $(C_2H_5)_3N$, 10.72; $(C_2H_5)_2CH_3N$, 10.46; $C_2H_5(CH_3)_2N$, 10.16. $-\Delta_pK_a$ values of substituents (two carbon atoms from basic center): NH$_2$, 0.8; NHR, NR$_2$, 0.9; NH$_3^+$, NR$_3^+$, 3.6.

The agreement between the predicted (Table III) and the experimental (Table I) values of K_1 and K_2 is about what Clark and Perrin had found with other amines, *i.e.*, within 0.4 log unit. While K_3 is predicted to be much lower than K_1 and K_2, as is observed, only half of the predicted values fall within 0.4 log unit of the experimental K_3 values. The others differ by as much as 1.2 log units. It is not clear why the predictions are not reliable for K_3, and there seem to be no obvious reasons for the discrepancies.

Copper(II) Stability Constants, K_f.—The geometry of the Cu(Rdien)$^{2+}$ complexes presumably involves meridional coordination of the three nitrogen donors in the square plane with water occupying the other position(s)



This structure is supported by X-ray structural investigations of [Cu(dien)$_2$]Br$_2$·H$_2$O[21] and [Cu(dien)$_2$](NO$_3$)$_2$.[22]

The value of K_f for dien in Table I is in very good agreement with previous determinations[7,11,14,16,17] at similar

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TABLE III

PREDICTED VALUES OF K_1, K_2, AND K_3 BY THE METHOD OF CLARK AND PERRIN[a]

Rdien	Log K_1	Log K_2	Log K_3
dien	10.10 (1, 7)	9.15 (7, 1)	3.95 (4)
1-(Me)dien	10.30 (1), 9.99 (7)	9.45 (7), 9.65 (1)	3.95 (4)
1,4-Me_2dien	10.00 (1), 9.79 (7), 9.76 (4)	9.45 (7), 9.65 (1)	3.26 (4)
1,1-Me_2dien	9.80 (7), 9.45 (4)	8.81 (1)	3.95 (4)
1,1,4,7,7-Me_5dien	9.45 (1, 7) (1, 7)	8.51 (7, 1)	3.26 (4)
1,1-Et_2dien	9.80 (7), 9.72 (1)	9.37 (1) 9.46 (7)	3.95 (4)
1,4,7-Et_3dien	10.44 (1, 7)	9.50 (7, 1)	3.52 (4)
1,1,7,7-Et_4dien	10.01 (1, 7)	9.07 (7, 1)	3.95 (4)
4-Me-1,1,7,7-Et_4dien	10.01 (1, 7)	9.07 (7, 1)	3.26 (4)

[a] The site of protonation is given in parentheses.

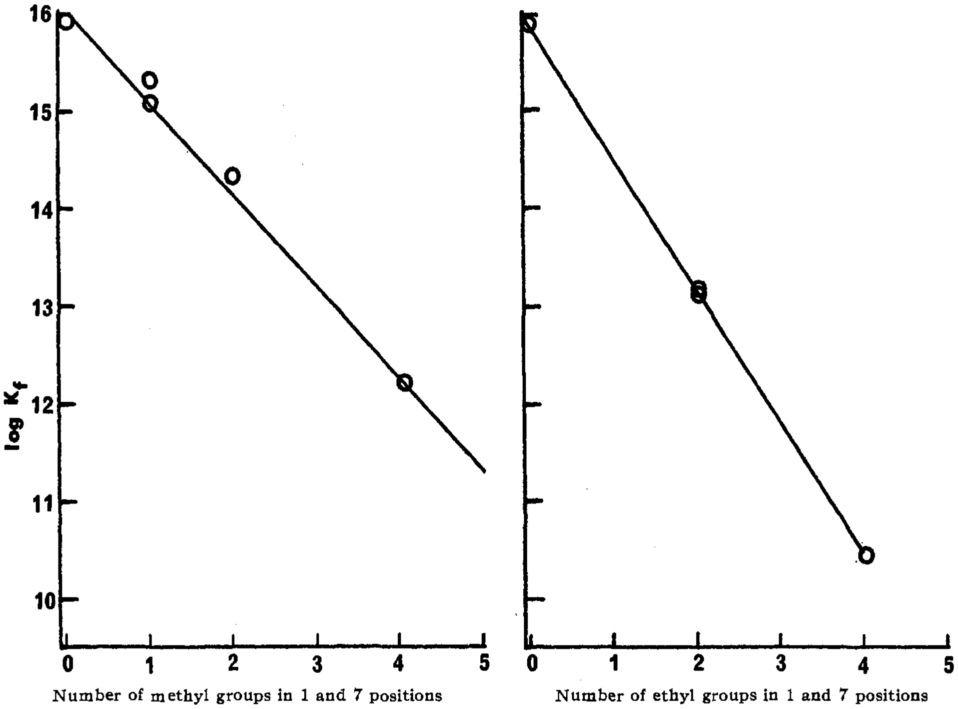

Figure 2.—Correlations of log K_f with the number of methyl (left plot) and ethyl (right plot) groups in the 1 and 7 positions of the Rdien ligands.

ionic strengths. The agreement is not quite as good for the only other reported Rdien, 1,1,7,7-Et_4dien, for which a value of 10.11 has been obtained.[19] This discrepancy is probably related to the difference in K_2 values which was discussed in the previous section.

Since metal complex stability constants for a series of ligands with a given metal have sometimes been correlated with the basicities (pK_a) of the ligands,[23] we examined the relationship between log K_f and the total log K (*i.e.*, log K_1 + log K_2 + log K_3) of the Rdien ligand. A plot of these two functions shows that the methyl- and ethyl-substituted derivatives fall into quite different regions, and even then the ethyl derivatives do not give a simple straight-line correlation.

A better correlation is observed if log K_f is plotted *vs.* the number of methyl groups (or ethyl groups) in the 1 and 7 positions (Figure 2). It appears that methyl or ethyl substitution at the 4 nitrogen does not affect the magnitude of K_f. With increasing substitution at the terminal nitrogens, the stability of the complex decreases regularly. Furthermore, ethyl substitution decreases the stability of the complex much more than does methyl substitution. Similar stability effects have been observed previously[24,25] for Cu(II) complexes of N-substituted ethylenediamine ligands. Since an accurate value of K_f could not be determined for 4-Me-1,1,7,7-Et_4dien, it is not included in Figure 2. An estimated upper limit (9.15), however, is lower than the predicted K_f which should be the same as for 1,1,7,7-Et_4dien. It appears that the methyl group in the 4 position in this ligand does decrease the value of K_f.

Hydroxo Complex Stability Constants, K_{OH}.—The presumed structure of the hydroxo complexes, Cu(Rdien)(OH)$^+$, is one in which the hydroxo and the three nitrogen donor atoms occupy the four positions of a square plane. Such a structure has been suggested for the previously studied Cu(dien)(OH)$^+$ and Cu(1,1,7,7-Et_4dien)(OH)$^+$. These studies yielded values for log K_{OH} of 4.86[10] and 6.04,[19] respectively, which are in fair agreement with 5.17 and 6.18 obtained in the present work.

Except for Cu(1,1,7,7-Et_4dien)(OH)$^+$ the values of log K_{OH} lie in the very narrow range of 4.8–5.4. Mar-

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gerum and coworkers[19] have attributed the unusually high value for Cu(1,1,7,7-Et$_4$dien)(OH)$^+$ to the displacement of the axial water ligands by the bulky ethyl groups. This allows the copper to coordinate more strongly to the in-plane water ligand making it more acidic. This steric effect seems not to be of such major importance in the other Cu(Rdien)(OH)$^+$ complexes, even in Cu(1,1,4,7,7-Me$_5$dien)(OH)$^+$. The variations in K_{OH} are so small that it is difficult to cite factors which are responsible for them. However, two factors appear to contribute: first the steric effect, as in Cu(1,1-Et$_2$dien) and Cu(1,1-Me$_2$dien), which increases K_{OH}; second, alkyl substitution at the nitrogen trans to the OH group (*i.e.*, the 4 nitrogen). Such substitution appears to decrease K_{OH}, as in Cu(1,4-Me$_2$dien)(OH)$^+$, perhaps as a result of stronger electron donation by the 4 nitrogen thus making the trans H_2O ligand less acidic.[26] The values of K_{OH} for Cu(1,1,4,7,7-Me$_5$dien)(OH)$^+$ and Cu(1,4,7-Et$_3$dien)(OH)$^+$ may be explained by a combination of both effects.

Martell and coworkers[27] had previously determined K_{OH} values for a number of copper(II) complexes of bi- and tridentate ligands. For a variety of ethylenediamines, with widely varying substituents on the carbon and nitrogen atoms, the log K_{OH} values fell within the small range of 6.4–6.8. For tridentate ligands, log K_{OH} was generally smaller; for example, for the iminodiacetate complex, Cu(IMDA)(OH)$^-$, log K_{OH} was found[28] to be 5.7, similar to the values for the Cu(Rdien)(OH)$^-$ complexes. For the nitrilotriacetate complex, Cu(NTA)(OH)$^{2-}$, it was still smaller (4.4).[29] In general,[27] K_{OH} values seem to depend more upon the denticity than on other structural features of the ligand.

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Stability Constants for Amino Acid Coordination by Substituted Diethylenetriamine Complexes of Copper(II) and the Kinetics of Amino Acid Ester Hydrolysis

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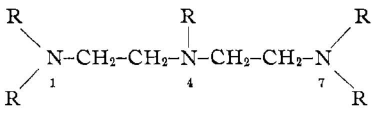
The amino acidates (A$^-$) of glycine, valine, sarcosine, and β-alanine coordinate to Cu(Rdien)$^{2+}$, where Rdien is a substituted diethylenetriamine bearing from one to five methyl or ethyl groups on the nitrogen atoms, to give the complexes Cu(Rdien)(A)$^+$. Stability constants, K_x, depend little on the structure of the Rdien ligand except for sarcosine where the *N*-methyl group of the amino acid significantly decreases K_x when Rdien contains two or more methyl or ethyl groups at the terminal nitrogens. When compared to other copper(II) complexes, Cu(dien)$^{2+}$ forms relatively unstable glycine complexes, as measured by K_x, which decreases as follows: Cu^{2+} > Cu(dipy)$^{2+}$ > Cu(NH$_3$)$_2^{2+}$ > Cu(Gly)$^+$ > Cu(IMDA) > Cu(NTA)$^-$ > Cu(dien)$^{2+}$. The hydrolysis of the amino acid ester methyl glycinate (MeGly) is catalyzed by Cu(dien)$^{2+}$. Kinetic and equilibrium studies suggest that the reaction proceeds by coordination of the ester to form Cu(dien)(MeGly)$^{2+}$ followed by either OH$^-$ or Cu(dien)(OH)$^+$ attack in the rate-determining step. As compared to other copper(II) complexes, Cu(dien)$^{2+}$ is a relatively poor catalyst. Rate constants for the OH$^-$ attack path decrease as follows: Cu^{2+} > Cu(IMDA) > Cu(NTA)$^-$ > Cu(dien)$^{2+}$. Stability constants for the coordination of methyl glycinate by these complexes decrease in the same order.

Introduction

In the preceding paper,[2] we reported proton stability constants, K_1, K_2, and K_3, for a series of *N*-methyl- and *N*-ethyl-substituted diethylenetriamines (Rdien)



as well as stability constants, K_f, for their coordination to Cu^{2+} to form Cu(Rdien)$^{2+}$. The hydroxo stability constants, K_{OH}, for the formation of the Cu(Rdien)(OH)$^+$ complexes were also detailed.

In the present communication, we report equilibrium constants, K_x, for the coordination of amino acids and amino acid esters with the Cu(Rdien)$^{2+}$ complexes

$$\mathrm{Cu(Rdien)}^{2+} + \mathrm{A}^{n-} \rightleftharpoons \mathrm{Cu(Rdien)(A)}^{(2-n)+},\quad K_x = \frac{[\mathrm{Cu(Rdien)(A)}^{(2-n)+}]}{[\mathrm{Cu(Rdien)}^{2+}][\mathrm{A}^{n-}]} \qquad (1)$$

where n is 1 if A is an amino acidate and n is 0 if A is an amino acid ester. These constants were used in interpreting kinetic studies of the hydrolysis of methyl glycinate, as catalyzed by Cu(dien)$^{2+}$.

Experimental Section

Materials.—The amino acids were obtained from commercial sources and used without further purification. They were analyzed for total hydrogen ion content by titration with standard NaOH using a pH meter. To lower the pH at the end points, they were titrated in 10% aqueous formaldehyde solution ac-

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