Inorganica Chimica Acta, 11 (1974) 137–142

Metal Complexes of Some Asymmetric Diaminodiamide Ligands. Complexes of Copper(II) in Aqueous Solution[1]

M. M. MUIR* and P. R. RECHANI[2]
Department of Chemistry, University of Puerto Rico, Rio Piedras, Puerto Rico 00931
Received March 29, 1974

The aqueous solution equilibria between Cu(II) and a series of asymmetric diaminodiamides have been studied by potentiometric and spectrophotometric methods. The ligands used were R- and S-N,N'-diglycylpropylenediamine, S,S-N,N'-dialanylethylenediamine, and S,R,S- and S,S,S-N,N'-dialanylpropylenediamine. The copper(II) chelate, CuL^{2+}, lost the amide protons in two steps as the pH was increased to give the dimer, $(CuH_{-1}L)_2^{2+}$, and $CuH_{-2}L$. Some stereoselectivity was observed for the diastereoisomers of dialanylpropylenediamine.

Introduction

Metal complexes of aminoamides, among which are included amino acid peptides, are known[3–21] to undergo displacement of the amide protons at acidic or near neutral pH. Several studies have been made[5, 6, 22–24] of the complexes of a diaminodiamide, N,N'-diglycylethylenediamine (DGEN), in which the presence of two amino groups can provide additional stabilization for the complex. The complexes of DGEN with Cu(II) were observed[6] to undergo not only amide deprotonation but also a polynuclear–mononuclear chelate equilibrium for which the mononuclear complex is favored with increasing pH.

It seemed of interest to observe the effects of substituents on DGEN on the equilibria, in particular on the amide deprotonation and the polynuclear–mononuclear equilibrium. This paper reports the equilibria observed in aqueous solution between Cu(II) and a series of asymmetric diaminodiamides. These were selected so as to permit the observation of any stereoselectivity in the system. The ligands used were R- and S-N,N'-diglycylpropylenediamine (DGPN), S,S-N,N'-dialanylethylenediamine (DAEN), and the diastereoisomers S,R,S- and S,S,S-N,N'-dialanylpropylenediamine (DAPN). Together with DGEN these formulas are shown in Table I.

TABLE I. Melting Points and Specific Rotations for Derivatives of the Diaminodiamides, $H_2N–CHR–CO–NH–CHR'–CH_2–NH–CO–CHR–NH_2$.

Ligand	R	R'	Mp (°C) of Picrate Derivative	Specific Rotation (°) for Dihydrochloride Salt[a]
DGEN	H	H		
R–DGPN	H	CH_3	239–240	+9.8
S–DGPN	H	CH_3	241	−8.1
SS–DAEN	CH_3	H	253–255	+2.0
SRS–DAPN	CH_3	CH_3	253–254	+21.3
SSS–DAPN	CH_3	CH_3	260–261	+1.12

[a] Values for $[\alpha]_D^{20}$ were obtained for 1.00 per cent aqueous solutions.

Experimental

Materials

Pure samples of the dihydrochloride salts of the ligands were available from another study[25] and the syntheses and characterizations will be described elsewhere.[26] The melting points for the picrate derivatives and the specific rotations, $[\alpha]_D^{20}$, for one per cent aqueous solutions of the dihydrochloride salts are given in Table I. The samples used in the study of equilibria were shown by titration with standard NaOH to be at least 99.5 per cent pure, based on the endpoint for titration of two protons per ligand. All other chemicals were reagent grade. Copper(II) solutions were standardized by an iodometric method.[27]

Potentiometric Titrations

All the potentiometric titrations were done with a Corning model 10 pH meter equipped with micro glass and calomel electrodes. Aliquots of solutions of the dihydrochloride salts of the different ligands were titrated with standard NaOH in the absence and in the presence of $Cu(NO_3)_2$. The ionic strength was

maintained relatively constant at 0.1*M* by the addition of appropriate amounts of KNO_3. During the titrations nitrogen gas was bubbled through the reaction mixture. The reaction vessel, a 30 to 50 ml beaker, was fitted with a rubber stopper with holes for the electrodes, buret tip, and nitrogen inlet and outlet. The solution was maintained at 24.6 ± 0.1° by suspending the beaker in a constant temperature bath. An air-driven magnetic stirrer was mounted in the bath below the beaker.

Spectrophotometric Titrations

Spectra were taken with a Perkin Elmer model 202 double beam spectrophotometer and the location of the isosbestic points was checked with a Hitachi–Perkin Elmer model 139 single beam spectrophotometer. An initial volume of 2 ml of the solution containing the ligand hydrochloride and copper nitrate was placed in a 1 cm stoppered quartz cell equipped with a $^3/_8$ in long magnetic stirring bar. After each addition of base the solution was stirred for 1 or 2 minutes before the spectrum was taken. Longer periods of stirring produced no change in the spectrum.

Results and Calculations

Constants and Corrections

A correction was made to all pH values using the mean activity coefficient, 0.796, for HCl at the ionic strength, 0.1*M*, and temperature used.[28] The corresponding value[29] used for K_w, the ionization constant of water, was 1.604×10^{-14}. The analytical concentrations of ligand, metal, and base, C_L, C_M, and C_B, respectively, were corrected for dilution at each titration point. The standard NaOH solution was 0.0925*M*.

Potentiometric Titrations of the Diaminodiamides

Typical curves from the potentiometric titrations of the dihydrochloride salts of the diaminodiamides with sodium hydroxide are shown in Figures 1 and 2. In each figure, curve A is for $10^{-2}M$ ligand and curve B for $10^{-3}M$ ligand. At least two titrations were done at each of the two concentration levels for each ligand. It is apparent from all these curves that the two ammonium protons dissociate from the ligand salt, H_2L^{2+}, in overlapping steps, since only one break in the curve is observed, at a ratio, *a* (number of moles of NaOH added per mole of ligand), of 2 moles of base to 1 mole of ligand.

The values of the acid protonation constants, K_1^H and K_2^H,

$$K_1^H = \frac{[HL^+]}{[H^+][L]} \quad (1)$$

$$K_2^H = \frac{[H_2L^{2+}]}{[H^+][HL^+]} \quad (2)$$

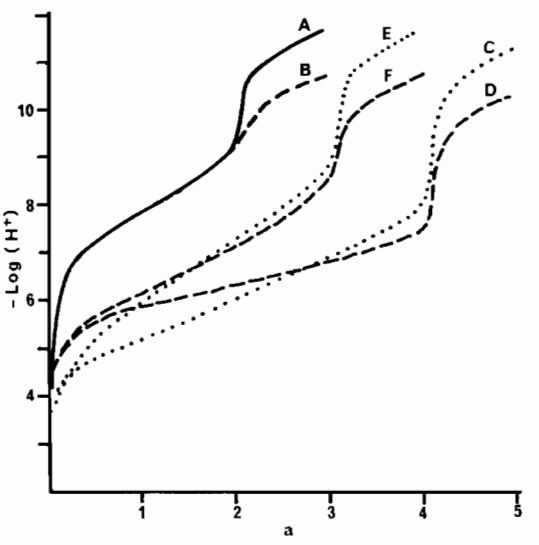


Figure 1. Potentiometric titration curves for S,S-DAEN and its copper(II) complexes. Solution concentrations: (A), $1.0 \times 10^{-2}M$ DAEN; (B), $1.0 \times 10^{-3}M$ DAEN; (C), $5.0 \times 10^{-3}M$ DAEN and $Cu(NO_3)_2$; (D), $5.0 \times 10^{-4}M$ DAEN and $Cu(NO_3)_2$; (E), $5.0 \times 10^{-3}M$ $Cu(NO_3)_2$ and $1.0 \times 10^{-2}M$ DAEN; (F), $5.0 \times 10^{-4}M$ $Cu(NO_3)_2$ and $1.0 \times 10^{-3}M$ DAEN. All solutions were 0.10*M* in KNO_3.

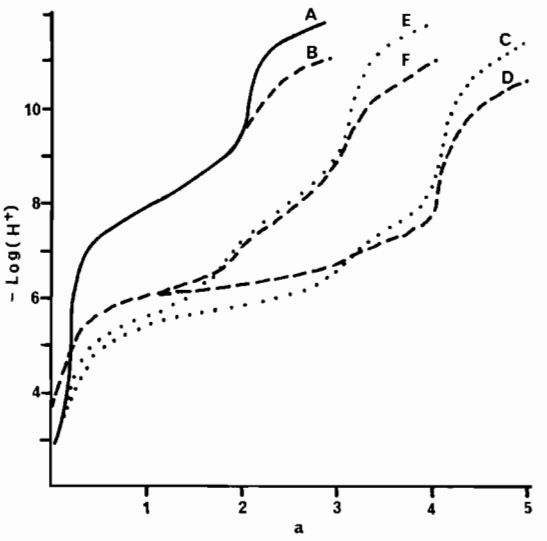


Figure 2. Potentiometric titration curves for R-DGPN and its copper(II) complexes. Solution concentrations: (A), $1.0 \times 10^{-2}M$ DGPN; (B), $1.0 \times 10^{-3}M$ DGPN; (C), $5.0 \times 10^{-3}M$ DGPN and $Cu(NO_3)_2$; (D), $5.0 \times 10^{-4}M$ DGPN and $Cu(NO_3)_2$; (E), $5.0 \times 10^{-3}M$ $Cu(NO_3)_2$ and $1.0 \times 10^{-2}M$ DGPN; (F), $5.0 \times 10^{-4}M$ $Cu(NO_3)_2$ and $1.0 \times 10^{-3}M$ DGPN. All solutions were 0.10*M* in KNO_3.

were obtained by a linear least squares fit of the data to an equation of the form

$$y = x K_1^H + K_1^H K_2^H \quad (3)$$

which was derived[30] from the definitions of the constants and the expressions for ligand balance and electroneutrality. The average values of $\log K_1^H$ and $\log K_2^H$ for the various ligands are listed in Table II. About 20 points in the buffer region were used in each calculation. Only small differences were observed between the values at different concentration levels. For example, for DAEN the average values of $\log K_1^H$ were 8.36 at 0.01 *M* and 8.38 at 0.001 *M* and of $\log K_2^H$ were 7.28 and 7.24, respectively. The values in Table II are the averages for all the titrations at both concentrations. All calculations were performed on an IBM–360 computer.

Potentiometric Titrations of Ligands in the Presence of Cu(II)

Typical curves obtained from the potentiometric titrations with sodium hydroxide of the dihydrochloride salts of the diaminodiamides in the presence of copper(II) are shown in Figures 1 and 2. In each Figure, curves C and D are for titrations with a ligand to copper concentration ratio of 1:1 and curves E and F are for a ratio of 2:1. Curves C and E are for 5×10^{-3} *M* Cu(II) and curves D and F are for 5×10^{-4} *M* Cu(II). The curves for the ligands DGPN and DAPN are all very similar to the curves in Figure 2.

For titrations in which the ligand to metal ratio is 1:1, it can be seen that four protons dissociate, two from the ligand salt and two from complexes formed with the Cu(II). In the case of DAEN, Figure 1 shows that the first three protons dissociate in overlapping steps, since only two definite breaks are seen, at $a = 3$ and $a = 4$. The first three protons are the two ammonium protons and one of the amide protons. The other amide proton apparently dissociates in a separate step, at higher pH. None of the 1:1 titration curves for the remaining ligands, DGPN and DAPN, shows a definite break at $a = 3$, but all show the break at $a = 4$. Thus all four protons dissociate in overlapping steps for the ligands R- and S-DGPN and for S,R,S- and S,S,S-DAPN. Analysis of the 2:1 titration curves shows a similar difference between DAEN and the other ligands.

TABLE II. Acid Protonation Constants for the Diaminodiamides.

Ligand	$\log K_1^H$	$\log K_2^H$
DGEN[a]	8.22	7.48
S,S–DAEN	8.37 ± .03	7.26 ± .04
R–DGPN	8.22 ± .06	7.38 ± .01
S–DGPN	8.37 ± .02	7.33 ± .01
S,R,S–DAPN	8.32 ± .03	7.38 ± .02
S,S,S–DAPN	8.35 ± .03	7.24 ± .04

[a] Values taken from ref. 6.

Several different sets of equilibria were tested by curve fitting and iterative calculations. That which gave consistent values of the constants at all concentrations was the same as the set used by Martell[6] for the Cu(II)–DGEN system.

$$Cu^{2+} + L \overset{K_1}{\rightleftharpoons} CuL^{2+} \qquad K_1 = \frac{[ML^{2+}]}{[M^{2+}][L]} \quad (4)$$

$$2\ CuL^{2+} \overset{K_{1Ad}}{\rightleftharpoons} (CuH_{-1}L)_2^{2+} + 2\ H^+$$

$$K_{1Ad} = \frac{[(MH_{-1}L)_2^{2+}][H^+]^2}{[ML^{2+}]^2} \quad (5)$$

$$(CuH_{-1}L)_2^{2+} \overset{K_{1Bm}}{\rightleftharpoons} 2\ CuH_{-2}L + 2\ H^+$$

$$K_{1Bm} = \frac{[MH_{-2}L]^2[H^+]^2}{[(MH_{-1}L)_2^{2+}]} \quad (6)$$

However, the assumption that K_{1Bm} can be neglected for 1:1 curves in the region from $a = 0$ to $a = 3$, or in other words that no significant amount of monomer $CuH_{-2}L$ is formed below $a = 3$, was not valid for the ligands used in this study. This is consistent with the absence of a sharp break at $a = 3$, which shows that all four protons dissociate in overlapping steps.

The procedure used to obtain the constants was as follows. Initial values of K_{1Ad} and K_{1Bm} were found for the different ligands for the more concentrated 1:1 mixtures using equations (4) to (7) from ref. 6. From these values correction factors β and β' were calculated for each titration point in the range $a = 1.7$ to $a = 2.5$ for 1:1 titrations and $a = 0.8$ to $a = 1.3$ for 2:1 titrations.

$$K_{AB} = \sqrt{K_{1Ad} K_{1Bm}} \quad (7)$$

$$\beta = 1 + K_{AB}/[H^+]^2 \quad (8)$$

$$\beta' = 1 - K_{AB}/[H^+]^2 \quad (9)$$

New values of K_1 and K_{1Ad} were then found from equations (10) and (11).

$$a_2[L]^2 + b_2[L] + c_2 = 0 \quad (10)$$

$$K_{1Ad} = \frac{[H^+]^2\{C_L - [L](\alpha + \beta K_1(C_M - C_L + \alpha[L]))\}}{2 K_1^2[L]^2(\alpha[L] - C_L + C_M)^2} \quad (11)$$

$$a_2 = \alpha\beta' K_1$$
$$b_2 = \alpha' + \alpha + K_1\beta'(C_M - C_L)$$
$$c_2 = [H^+] - [OH^-] + C_B - 3\,C_L$$
$$\alpha = [H^+]^2 K_1^H K_2^H + [H^+]K_1^H + 1$$
$$\alpha' = 2\,[H^+]^2 K_1^H K_2^H + [H^+]K_1^H$$

Similarly, the initial values of K_{1Bm} and [L] from equations (6) and (7) of ref. 6, in which $[M^{2+}]$ and $[ML^{2+}]$ were considered negligible, were used to find

correction term t, which in turn was used in equations (13) and (14) to give new values of K_{1Bm} and [L].

$$t = [M^{2+}] + [ML^{2+}] \quad (12)$$
$$[M^{2+}] = C_M - C_L + \alpha[L]$$
$$[ML^{2+}] = K_1[M^{2+}]\ [L]$$

$$\alpha'^2[L]^2 + \alpha'(2C_M - 2S + 2t + \frac{K_{1Bm}}{2[H^+]^2})\ [L] +$$
$$C_M^2 + S(S - 2C_M - 2t - \frac{K_{1Bm}}{2[H^+]^2}) + t^2 + 2tC_M +$$
$$\frac{t\,K_{1Bm}}{[H^+]^2} = 0 \quad (13)$$

$$\alpha_d^2[L]^2 + (2\alpha_d C_L - 2\alpha_d S + 2\alpha_d t + \frac{\alpha' K_{1Bm}}{2[H^+]^2})\ [L]$$
$$+ C_L + S(S - 2C_L - 2t - \frac{K_{1Bm}}{2[H^+]^2}) + t^2 + 2C_L t$$
$$+ \frac{tK_{1Bm}}{[H^+]^2} = 0 \quad (14)$$

$$\alpha_d = \alpha' - \alpha$$
$$S = 2\,C_L + 2\,C_M - C_B - [H^+] + K_w/[H^+]$$

Two or three cycles of correction of all the constants gave consistent values for each ligand. The average values for all concentration levels are listed in Table III.

Spectrophotometric Titrations of Ligands in the Presence of Copper(II)

The absorption spectra obtained during titrations of the various 1:1 Cu(II)–diaminodiamide systems with base were all similar to those shown in ref. 6. In every case an isosbestic point was obtained at values of a greater than 3.34 for the 1:1 titration mixtures. Addition of excess base, a greater than 4.00, produced no further changes in the spectra, except for the predicted dilution effects.

The concentrations of all species present for each spectral curve were calculated using the equilibrium constants. Using these concentrations, the extinction coefficients of each species present were calculated.

TABLE III. Equilibrium Constants for the Interaction of Copper(II) and Diaminodiamides.

Ligand	LogK_1	LogK_{1Ad}	LogK_{1Bm}
DGEN[a]	7.50	− 9.2	−18.40
S,S–DAEN	7.40 ± .10	− 9.03 ± .11	−17.15 ± .16
R–DGPN	7.76 ± .13	−10.05 ± .24	−16.71 ± .08
S–DGPN	8.14 ± .15	− 9.89 ± .23	−16.64 ± .08
S,R,S–DAPN	7.28 ± .11	−10.06 ± .23	−16.23 ± .06
S,S,S–DAPN	7.35 ± .2	− 9.45 ± .12	−16.73 ± .07

[a] Data taken from ref. 6.

These are summarized in Table IV. Figure 3 shows the spectra for the S-DGPN system. The others were all very similar in appearance.

Discussion

The values of the acid dissociation constants for the ligand salts, LH_2^+, in Table II compare reasonably with those for DGEN,[6] although the difference between K_1^H and K_2^H is a little larger for the ligands in this study. The spectra summarized in Table IV for the various Cu(II) complexes in solution are all nearly identical and resemble those reported for the DGEN complexes,[6] which confirms that the same species are present in all the systems. This is in agreement with the fact that other sets of equilibria proposed by other workers[23,24] failed to give consistent values of constants for the ligands in this study.

Although the complexes present, CuL^{2+}, $(CuH_{-1}L)_2^{2+}$, and $CuH_{-2}L$, are the same for all the ligands studied, some of the equilibrium constants, shown in Table III, show significant differences for different ligands. The rather large deviations shown in Table III might have been reduced with additional cycles of corrections to the calculations, but the computing time needed did not seem justified. Any further corrections in the constants would be small, so the conclusions below would not be changed.

TABLE IV. Molar Extinction Coefficients for Complexes Present in the Copper(II) – Diaminodiamide Systems.

	CuL^{2+}		$(CuH_{-1}L)_2^{2+}$		$CuH_{-2}L$	
Ligand, L	λ_{max}, nm	ε, l/mol cm	λ_{max}, nm	ε, l/mol cm	λ_{max}, nm	ε, l/mol cm
DGEN[a]	685	60	590	108	518	166
S-DGPN	690	77	590	107	520	154
R-DGPN	690	60	588	97	520	171
S,S-DAEN	690	74	590	104	510	171
S,S,S-DAPN	690	65	585	107	510	153
S,R,S-DAPN	690	54	585	93	510	150

[a] Data taken from ref. 6. The values for Cu^{2+} are 820 nm and 14 l/mol cm.

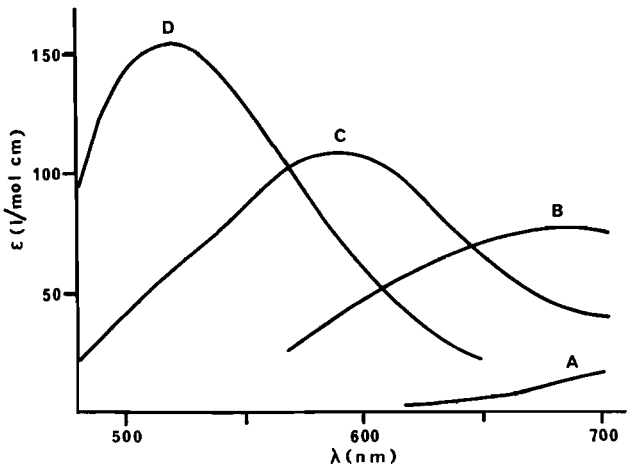


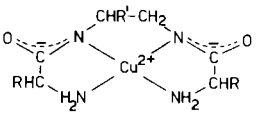
Figure 3. Molar extinction coefficients for complexes in the copper(II)–S-DGPN system. (A), Cu^{2+}; (B), CuL^{2+}; (C), $(CuH_{-1}L)_2^{2+}$; (D), $CuH_{-2}L$.

The values for K_1, for the formation of CuL^{2+}, are all reasonable for formation of a copper(II) peptide complex with extra stabilization due to an extra amine group.[6,10,13] The values for K_{1Ad}, for the formation of the dimer $(CuH_{-1}L)_2^{2+}$, show somewhat greater variation. The value for DAEN is similar to the value for DGEN[6] but the values for DGPN and DAPN are smaller, which implies the formation of dimer at a given pH is less favored when there is a methyl substituent on the central or backbone ethylene group in the ligand. The substituents on the terminal ethylene groups or arms of the ligand have much less effect on the value of K_{1Ad}, which is evident from the similarity of K_{1Ad} for DAPN to the values for DGPN systems, as well as from the similarity noted above for DAEN to DGEN. In other words, the steric effect on formation of the dimer is greater for the backbone than for the arms of the diaminodiamide.

Even larger differences are observed in the values of K_{1Bm} for the different ligands. All of the ligands' in this study have K_{1Bm} values which are significantly larger than that for DGEN. Again it is evident that substituents on the backbone have a greater effect on the constant than do those on the arms of the ligand, although substituents on the arms do have a significant effect on the monomer–dimer equilibrium. This greater steric importance for substituents on the backbone both for the formation and for the disappearance of the dimer can be very useful in deciding which of the many possible structures for the dimer are most probable.

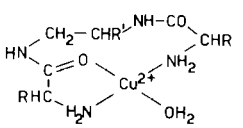
Also of interest are the differences in the values of both K_{1Ad} and K_{1Bm} for the diastereoisomers S,R,S- and S,S,S-DAPN, which show that these ligands are stereoselective with Cu(II). The dimer formed with S,S,S-DAPN is more stable than that with S,R,S-DAPN. This preference for absolute configuration S is particularly significant, since naturally occurring amino acids and peptides have S configuration. Such stereoselectivity can be rationalized by careful examination of Dreiding models of the probable structures of the complexes.

Similarities in the spectra of the complexes imply that the structures, or at least the type of coordination, are the same for all the ligands. $CuH_{-2}L$ almost certainly has the structure **I**. Models of **I** show little difference as the substituents R and R′ are changed from H to CH_3 or as the configuration at the backbone is changed. Any differences in the energies of the complexes should be quite small. This implies that the steric effect for the K_{1Bm} equilibrium is largely due to the dimer.



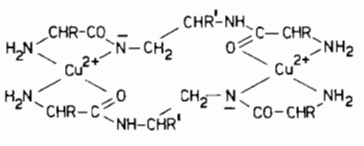
I

Similarly, models of structure **II**, which seems most likely for CuL^{2+} with coordination by the amide oxygen and the amino groups, show only small effects due to substituents at the backbone or the arms, although the S configuration at the backbone might be slightly favored. Calculations of the strain energy rather than qualitative impressions from models would be necessary to confirm this.



II

Of the two structures for the dimer proposed by Martell and Smith,[31] that shown in structure **III** seems preferable and fits well with the steric effects observed in this study. Examination of models suggests that the amide nitrogen which is deprotonated in the formation of the dimer is the one which is farther from the R′ group on the backbone, as indicated in **III**. The observed preference for S configuration for the backbone is in accord with the structure shown. For a planar peptide group with the oxygen *trans* to the amide proton, the R′ group will cause less hindrance and more readily adopt an equatorial position for the isomer of S configuration. For this complex the effect is large enough to be clear from the models, without need for calculations of strain energy. Thus the stereoselectivity of the ligands occurs largely for the dimer.



III

Acknowledgements

The fellowship awarded to P. R. R. by the Bacardi Corporation is gratefully acknowledged. Computing time was provided by the University of Puerto Rico computing center.

References

1 Presented in part at the Caribbean Coordination Chemistry Conference, Mona, Jamaica, December, 1970.
2 Taken from the thesis submitted by P. R. R. to the University of Puerto Rico in partial fulfillment of the requirements for the degree Ph. D., 1972.
3 P.J. Morris and R.B. Martin, *Inorg. Chem., 10,* 964 (1971).
4 E.W. Wilson, Jr. and R.B. Martin, *Inorg. Chem., 9,* 528 (1970).
5 K.S. Bai and A.E. Martell, *Inorg. Chem., 9,* 1126 (1970).
6 K.S. Bai and A.E. Martell, *J. Am. Chem. Soc., 91,* 4412 (1969).
7 J.D. Bell, H.C. Freeman, A.M. Wood, R. Driver and W.R. Walker, *Chem. Commun.,* 1441 (1969).
8 M.S. Michailidis and R.B. Martin, *J. Am. Chem. Soc., 91,* 4683 (1969).
9 M.K. Kim and A.E. Martell, *J. Am. Chem. Soc., 89,* 5138 (1967).
10 M.K. Kim and A.E. Martell, *Biochemistry, 3,* 1169 (1964).
11 W.L. Koltun, R.H. Roth and F.R.N. Gurd, *J. Biol. Chem., 238,* 124 (1963).
12 R.B. Martin, M. Chamberlin and J.T. Edsall, *J. Am. Chem. Soc., 82,* 495 (1960).
13 M.K. Kim and A.E. Martell, *J. Am. Chem. Soc., 88,* 914 (1966).
14 W.L. Koltun, M. Fried and F.R.N. Gurd, *J. Am. Chem. Soc., 82,* 233 (1960).
15 W.L. Koltun and F.R.N. Gurd, *J. Am. Chem. Soc., 81,* 301 (1959).
16 C.B. Murphy and A.E. Martell, *J. Biol. Chem., 226,* 37 (1957).
17 B.R. Rabin, *Trans. Faraday Soc., 52,* 1130 (1956).
18 S.P. Datta and B.R. Rabin, *Trans. Faraday Soc., 52,* 1123 (1956).
19 A.R. Manyak, C.B. Murphy and A.E. Martell, *Arch. Biochem. Biophys., 59,* 373 (1955).
20 H. Dobbie and W.O. Kermack, *Biochem. J., 59,* 257 (1955).
21 H. Dobbie and W.O. Kermack, *Biochem. J. 59,* 246 (1955).
22 P. Pfeiffer and S. Saure, *J. Prakt. Chem., 157,* 97 (1941).
23 A.K. Chakraburtty, N.N. Ghosh, and P. Ray, *J. Indian Chem. Soc., 30,* 185 (1953).
24 A. Zuberbuehler and S. Fallab, *Helv. Chim. Acta, 50,* 889 (1967).
25 P.R. Rechani, *Ph. D. Dissertation,* University of Puerto Rico, 1972.
26 M.M. Muir and P.R. Rechani, to be published.
27 I.M. Kolthoff and E.B. Sandell, 'Textbook of Quantitative Inorganic Analysis', 3rd ed., MacMillan, New York, N.Y., 1952, p. 600.
28 H.S. Harned and B.B. Owen, 'The Physical Chemistry of Electrolyte Solutions', 3rd ed., Reinhold, New York, N.Y., 1958, p. 716.
29 *Ibid.,* pp. 635 and 752.
30 G. Schwarzenbach, A. Willi and R.O. Bach, *Helv. Chim. Acta, 30,* 1303 (1947).
31 T.D. Smith and A.E. Martell, *J. Am. Chem. Soc., 94,* 4123 (1972).