with kinetic studies on other complex ions. Taube and Posey[12] present both spectral and kinetic evidence for ion pairs between $[Co(NH_3)_5H_2O]^{3+}$ and $SO_4^=$, a system where ion pairs would be expected. Garrick[13] measured the hydrolysis of $[Co(NH_3)_5Cl]^{2+}$ in the presence of $SO_4^=$ and NO_3^-. The Bjerrum criterion would predict ion pairs with $SO_4^=$, but not with NO_3^-. The observed kinetic results are consistent with this; 0.1 M $SO_4^=$ approximately doubles the rate, 0.1 M NO_3^- increases the rate by approximately 4%.

Acknowledgment.—Helpful suggestions regarding the Bjerrum criterion were made by Dr. Ralph G. Pearson, and the authors wish to acknowledge this assistance.

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(12) H. Taube and F. A. Posey, THIS JOURNAL, **75**, 1463 (1953).

(13) F. J. Garrick, *Trans. Faraday Soc.*, **34**, 1088 (1938).

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

Stepwise Mixed Complex Formation

BY WILLIAM E. BENNETT

RECEIVED SEPTEMBER 6, 1956

The formation constants for a mixed complex composed of copper(II) ion, the negative ion of iminodiacetic acid ($I^=$) and ethylenediamine (en) are determined. The reactions studies were CuI + en = CuIen, $Cuen^{++}$ + $I^=$ = CuIen and 2CuIen = $Cu(en)_2^{++}$ + $CuI_2^=$. The log K values for these reactions are 8.8, 8.2 and −2.0, respectively. The conditions are 30° and an ionic strength of 0.1.

Introduction

Previous work on the formation of mixed complexes of the type MAB, where M is a metal ion and A and B are ligands, has been carried out by Watters and co-workers.[1] These workers have determined the constants for the reaction

$$MA_2 + MB_2 = 2MAB \qquad (1)$$

utilizing such ligands as oxalate and ethylenediamine. One cannot determine from such a constant the constants for reactions such as

$$MA + B = MAB \qquad (2)$$

and

$$MB + A = MAB$$

These reactions are of interest because one can determine the influence one bound ligand has upon the ability of metal ion to combine with another.

The purpose of this work is to determine constants for reactions of type 2.

Experimental

An apparatus was designed such that potentiometric titrations and spectrophotometric studies could be made on the same solutions. This apparatus consisted in part of a titration vessel in a constant temperature-bath. This vessel contained a glass electrode, calomel electrode, stirring apparatus and a nitrogen inlet tube. The titrated solution was continuously pumped through a 10 cm. absorption cell in a Cary recording spectrophotometer. For maintaining a near constant temperature, the tubes leading to and from the absorption cell were jacketed and constant temperature fluid was pumped between the inner and outer tubes. A peristaltic pump, in which liquid is forced through a Tygon tube, was used to circulate the titrated solution.

The *p*H was measured with a modified design of a Beckman GS meter which was standardized before each titration with buffers at *p*H 4.01 and 9.14. The *p*H readings were reproducible to within 0.01 *p*H unit.

In all solutions constant ionic strength was maintained at 0.1 with the use of KCl. During titrations the ionic strength was maintained constant to within ±0.002 unit. Carbonate-free potassium hydroxide was prepared by the method of Schwarzenbach and Biedermann.[2] A nitrogen atmosphere was maintained over the titrated solutions.

Copper solutions were standardized by electro-deposition. Ligand solutions were prepared from commercially available iminodiacetic acid and ethylenediamine which were purified by recrystallization. The ethylenediamine was recrystallized as the dihydrochloride.

Calculations

The constants for the combination of protons with ethylenediamine and the iminodiacetic acid anion are expressed in terms of hydrogen ion activity and of the concentrations of other species. The metal complex formation constants are in terms of concentrations of species.

In the calculation of the constants there occurs a charge balance relationship. In some cases the hydrogen ion concentration is appreciable as compared to other species and so, in order to obtain consistent K values, a relation between *p*H and hydrogen ion concentration is necessary. To determine concentration of hydrogen ion a value of 0.8 for its activity coefficient is used.

In the remainder of the paper the following abbreviations will be used

en = ethylenediamine
$I^=$ = iminodiacetic acid anion
K^{H}_{Hen} = constant for $Hen^+ + H^+ = H_2en^{++}$
K^{H}_{en} = constant for $en + H^+ = Hen^+$
K^{H}_{HI} = constant for $HI^- + H^+ = H_2I$
K^{H}_{I} = constant for $I^= + H^+ = HI^-$
K^{en}_{Cu} = constant for $Cu^{++} + en = Cuen^{++}$
K^{en}_{Cuen} = constant for $Cuen^{++} + en = Cu(en)_2^{++}$
K^{I}_{Cu} = constant for $Cu^{++} + I^= = CuI$
K^{I}_{CuI} = constant for $CuI + I^= = CuI_2^=$
K^{en}_{CuI} = constant for $CuI + en = CuIen$
K^{I}_{Cuen} = constant for $Cuen^{++} + I^= = CuIen$
K^{CuIen}_{CuIen} = constant for $2CuIen = Cu(en)_2^{++} + CuI_2^=$

The absorption spectra of the species $Cuen^{++}$, $Cu(en)_2^{++}$, CuI and $CuI_2^=$ were determined by titration of mixtures of Cu^{++} and the ligand with KOH. From the usual relationships at each point in the titration curve, the concentration of each complex species can be determined. The absorption spectrum of each can then be determined from the composite spectrum of the mixture.

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(1) (a) R. DeWitt and J. I. Watters, THIS JOURNAL, **76**, 3810 (1954); (b) J. I. Watters, J. Mason and A. Aaron, *ibid.*, **75**, 5212 (1953); (c) J. I. Watters and E. D. Loughran, *ibid.*, **75**, 4819 (1953).

(2) G. Schwarzenbach and W. Biedermann, *Helv. Chim. Acta*, **31**, 339 (1948).

To determine the formation constant for the mixed complex CuIen, the procedure was to titrate a 1:1:1 mixture of copper(II) ion, iminodiacetic acid and ethylenediammonium chloride. The formation constants of the species $Cuen^{++}$ and CuI are not much different ($\log K^{en}_{Cu} = 11.12$ and $\log K^{I}_{Cu} = 10.42$). Ethylenediamine is a stronger base than the iminodiacetic acid anion so that at the beginning of the above titration only the species CuI is formed. This is in evidence in Fig. 1. The spectrum of the mixture in the initial part of the titration is that of the complex CuI. As the *p*H reaches the value of 4, a new complex is formed. It appears from the spectrum that the CuI is being converted into a different species. That species is assumed to be CuIen. This will be true if the mixed complex is stable with respect to disproportionation. That is, if it does not undergo the reaction

$$2\mathrm{CuIen} = \mathrm{CuI_2^=} + \mathrm{Cu(en)_2^{++}} \qquad (3)$$

to any extent, the spectrum at the end-point should be that of the mixed complex. Knowing the absorption spectra of CuIen and CuI, the concentration of each can be measured. If one assumes that

$$\text{Total ethylenediamine} = [\mathrm{en}] + [\mathrm{Hen^+}] + [\mathrm{H_2en^{++}}] + [\mathrm{CuIen}] \qquad (4)$$

it follows from the definitions of K^{H}_{Hen} and K^{H}_{en} that

$$\text{Total ethylenediamine} = [\mathrm{en}](1 + K^{H}_{en}[\mathrm{H^+}] + K^{H}_{Hen}K^{H}_{en}[\mathrm{H^+}]^2) + [\mathrm{CuIen}]$$

or

$$[\mathrm{en}] = \frac{(\text{total ethylenediamine}) - (\mathrm{CuIen})}{(1 + K^{H}_{en}[\mathrm{H^+}] + K^{H}_{Hen}K^{H}_{en}[\mathrm{H^+}]^2)} \qquad (5)$$

The constant K^{en}_{CuI} can be evaluated

$$K^{en}_{CuI} = \frac{[\mathrm{CuIen}]}{[\mathrm{CuI}][\mathrm{en}]} \qquad (6)$$

The constant K^{I}_{Cuen} can be obtained as

$$K^{I}_{Cuen} = \frac{K^{en}_{CuI}K^{I}_{Cu}}{K^{en}_{Cu}} \qquad (7)$$

For the above assumptions to be valid, it must be demonstrated that the disproportionation (3) is small. The constant for this disproportionation reaction is

$$K^{CuIen}_{CuIen} = \frac{K^{en}_{Cuen}K^{I}_{CuI}}{K^{en}_{CuI}K^{I}_{Cuen}} \qquad (8)$$

The constant K^{CuIen}_{CuIen} may be measured independently by the spectrophotometric titration of a solution of $CuI_2^=$ with ethylenediamine. Figure 4 illustrates the results of such a titration.

The linear portions at the left of each curve represent that region where the concentration of $Cu(en)_2^{++}$ is small compared to CuIen and $CuI_2^=$. If CuIen does not disproportionate this line would continue as illustrated by the dashed line tangent to the 637.5 mμ curve. In this straight line region the following will hold

$$D = \epsilon_{CuIen}[\mathrm{CuIen}] + \epsilon_{CuI_2^=}[\mathrm{CuI_2^=}] \qquad (9)$$

D represents the total absorbance. ϵ_{CuIen} and $\epsilon_{CuI_2^=}$ represent the extinction coefficients of the complexes. Due to the relative magnitudes of the formation constants effectively all ethylenediamine added, will complex to form CuIen or $Cu(en)_2^{++}$ and initially

$$[\mathrm{CuIen}] = T_{en} \text{ and } [\mathrm{CuI_2^=}] = T_{Cu} - T_{en} \qquad (10)$$

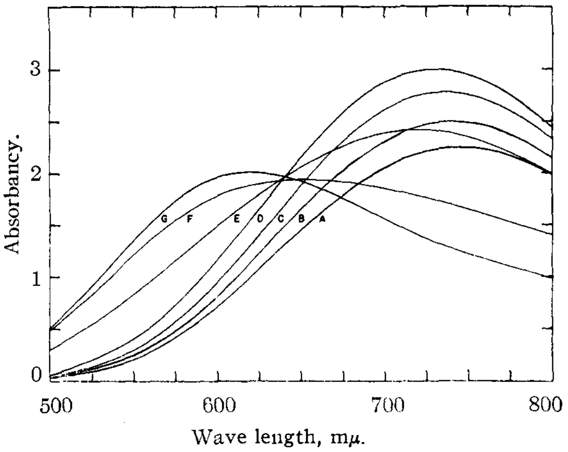

Fig. 1.—Typical curves obtained in the titration of an equimolar solution of copper, iminodiacetic acid and ethylenediammonium chloride. Initial concentration of each was 5×10^{-3} mole per liter, the initial volume of solution was 160 ml. and the concentration of KOH was 0.0941 mole per liter. The curves are those obtained after the addition of the following quantities of KOH: A, 0 ml.; B, 6 ml.; C, 12 ml.; D, 18 ml.; E, 24 ml.; F, 30 ml.; G, 34 ml.

T_{Cu} and T_{en} represent the total concentrations of copper and of ethylenediamine added. Equations 9 and 10 combine to give the form

$$D = \epsilon_{CuIen}T_{en} + \epsilon_{CuI_2^=}(T_{Cu} - T_{en}) \qquad (11)$$

If the extent of dilution is small T_{Cu} is constant and (11) represents a straight line. Both ϵ_{CuIen} and $\epsilon_{CuI_2^=}$ may be determined by the use of (11).

Beyond the straight line region, and where T_{en} is less than T_{Cu} the following will be true

$$2[\mathrm{Cu(en)_2^{++}}] + [\mathrm{CuIen}] = T_{en} \qquad (12)$$

$$[\mathrm{Cu(en)_2^{++}}] + [\mathrm{CuIen}] + [\mathrm{CuI_2^=}] = T_{Cu} \qquad (13)$$

$$D = \epsilon_{Cu(en)_2^{++}}[\mathrm{Cu(en)_2^{++}}] + \epsilon_{CuIen}[\mathrm{CuIen}] + \epsilon_{CuI_2^=}[\mathrm{CuI_2-}] \qquad (14)$$

Combining (12), (13) and (14) one obtains

$$[\mathrm{CuIen}] = \frac{D - \epsilon_{CuI_2^=}T_{Cu} - {}^1/_2(\epsilon_{Cu(en)_2^{++}} - \epsilon_{CuI_2^=})T_{en}}{\epsilon_{CuIen} - {}^1/_2(\epsilon_{Cu(en)_2^{++}} + \epsilon_{CuI_2^=})} \qquad (15)$$

From these one may evaluate [CuIen], $[Cu(en)_2^{++}]$ and $[CuI_2^=]$. These values define K^{CuIen}_{CuIen}.

Results

Titrations were carried out for the purpose of obtaining the absorption spectra of each species involving copper(II) and either ethylenediamine or iminodiacetic acid. Figure 2 shows the absorption spectra of all species $Cuen^{++}$, $Cu(en)_2^{++}$, CuI and $CuI_2^=$. The spectra obtained for the ethylenediamine complexes are similar to those obtained by Jonassen[3] and by Bjerrum[4] under slightly different conditions.

Table I gives the values obtained for the formation constants of the simple complexes which were found in these studies. The acid formation constants are also given. Chaberek and Martell[5] determined the same constants for iminodiacetic acid. Their results are similar to these.

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(3) H. B. Jonassen and T. H. Dexter, THIS JOURNAL, **71**, 1553 (1949).

(4) J. Bjerrum and E. Nielsen, *Acta Chem. Scand.*, **2**, 297 (1948).

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

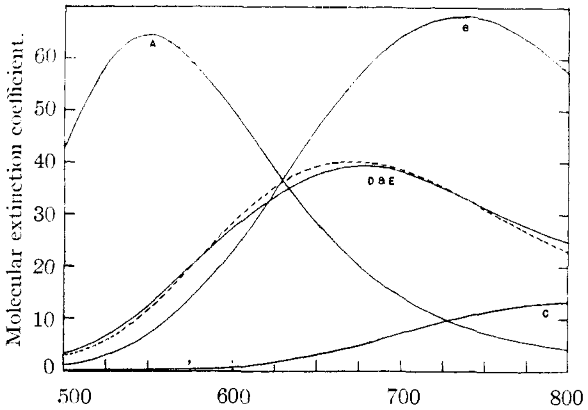


Fig. 2.—The absorption spectra of the following: A, $Cu(en)_2^{++}$; B, $CuI^=$; C, Cu^{++}; D (solid line), $Cuen^{++}$; E (dashed line), $CuI_2^=$.

Figure 1 shows a few of the absorption curves obtained in the titration of the 1:1:1 mixture of cupric ion, iminodiacetic acid and ethylenediammonium chloride. The absorption curve of the final complex is not the same as any other species studied nor is it an equimolar mixture of $Cu(en)_2^{++}$ and $CuI_2^=$.

TABLE I

VALUES OF CONSTANTS

Ionic strength 0.1, temperature 30°

$\log K_{en}^{H} = 10.18$
$\log K_{Hen}^{H} = 7.47$
$\log K_{I}^{H} = 9.46$
$\log K_{HI}^{H} = 2.60$
$\log K_{Cu}^{en} = 11.12$
$\log K_{Cuen}^{en} = 9.61$
$\log K_{Cu}^{I} = 10.52$
$\log K_{CuI}^{I} = 5.49$

Figure 3 shows the curve of *p*H *vs.* ml. KOH. The end-point is at 34 ml. of KOH. Interpretation of these results, as indicated in the Experimental section, gives the values of the concentrations of the species and of the K_{CuI}^{en} which are listed in Table II. Initial concentrations of copper and of ligands were each 5.64×10^{-3} *M*. The titrant was 0.0941 *M* KOH.

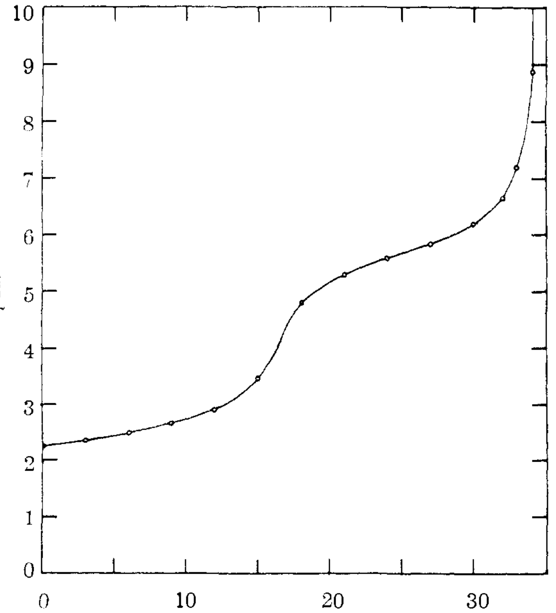


Fig. 3.—The *p*H *vs.* ml. of KOH curve obtained in the titration of the equimolar mixture of copper, iminodiacetic acid and ethylenediammonium chloride.

TABLE II

DETERMINATION OF K_{CuI}^{en} FROM 1:1:1 TITRATION

KOH, ml.	*p*H	CuI concn. $\times 10^3$	CuIen concn. $\times 10^3$	en concn. $\times 10^{10}$	$\log K_{CuI}^{en}$
18	4.83	4.23	0.36	0.431	9
21	5.30	3.45	1.05	3.12	8.99
24	5.58	2.62	1.80	8.40	8.91
27	5.85	1.84	2.50	20.0	8.83
30	6.20	0.987	3.25	52.8	>8.8
32	6.65	.452	3.72	178.5	>8.7
33	7.20	.174	3.97	613.0	>8.6

At *p*H values higher than 6.0, the assumption that the complex $Cuen^{++}$ is not present will be wrong. The effect of this assumption would be to make the value of K_{CuI}^{en} appear to be less than the true value. The average of the best values, which are found at 21, 24 and 27 ml. of KOH, is 8.91.

We may now write *preliminary* formation constants for the mixed complexes.

$$CuI + en = CuIen \qquad \log K_{CuI}^{en} = 8.91$$

from (7)

$$Cuen^{++} + I^= = CuIen \qquad \log K_{Cuen}^{I} = 8.31$$

from (8)

$$2CuIen = CuI_2^= + Cu(en)_2^{++} \qquad \log K_{CuIen}^{CuIen} = -2.12$$

Since a small amount of disproportionation does occur, the above values will be in error. An independent determination of K_{CuIen}^{CuIen} was made by the method described using the data illustrated in Fig. 4. The results are given in Table III. These calculations were made using the point (7 ml. of 0.112 *M* ethylenediamine added) where T_{en} is slightly less than T_{Cu}. Other points give the value for K_{CuIen}^{CuIen} which were the same within the limits of error.

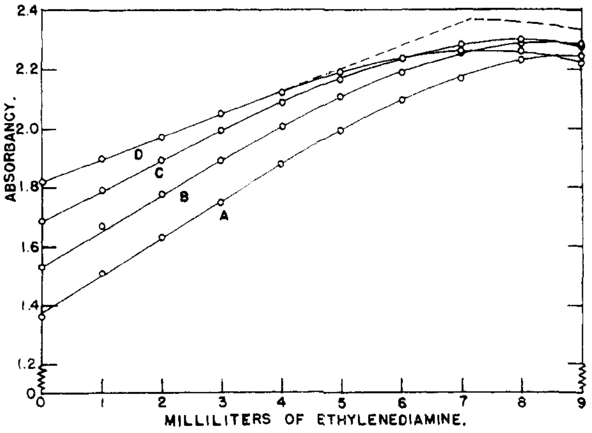


Fig. 4.—Curves obtained in the titration of 160 ml. of 5×10^{-3} *M* $CuI_2^=$ with 10^{-1} *M* ethylenediamine. The curves are at the following wave lengths: A, 600 mμ; B, 612.5 mμ; C, 625 mμ; D, 637.5 mμ.

TABLE III

DETERMINATION OF $K_{\text{CuIen}}^{\text{CuIen}}$ FROM TITRATION OF CuI_2^- WITH ETHYLENEDIAMINE

Wave length, mμ	[CuIen] × 10^3	[Cu(en)_2^{++}] × 10^4	[CuI_2^-] × 10^4	$K_{\text{CuIen}}^{\text{CuIen}}$ × 10^2
600	4.00	3.50	4.45	0.97
612.4	4.00	3.50	4.45	.97
625.0	3.95	3.73	3.67	1.12
637.5	3.99	3.55	4.49	1.00
			Av.	1.02

$$\log K_{\text{CuIen}}^{\text{CuIen}} = -2.0$$

When the value of $K_{\text{CuIen}}^{\text{CuIen}}$ is 1.02×10^{-2} the fraction of CuIen present at the end-point in the titration of the 1:1:1 mixture would be 0.83. The remainder is CuI_2^- and Cu(en)_2^{++}. If the relative concentrations of CuIen, CuI_2^- and Cu(en)_2^{++} remained the same during the titration of the 1:1:1 mixture the correct values of the constants $K_{\text{CuI}}^{\text{en}}$ and $K_{\text{Cuen}}^{\text{I}}$ are simply the preliminary values multiplied by 0.83. This gives for the correct values

$$\log K_{\text{CuI}}^{\text{en}} = 8.8$$
$$\log K_{\text{Cuen}}^{\text{I}} = 8.2$$

From these values and (8) we obtain

$$\log K_{\text{CuIen}}^{\text{CuIen}} = -2.0$$

This value of $\log K_{\text{CuIen}}^{\text{CuIen}}$ is in agreement, within experimental error of that found by independent measurement.

Discussion

It is of interest to compare the two reactions

$$\text{CuI} + \text{I}^- = \text{CuI}_2^- \quad \log K_{\text{CuI}}^{\text{I}} = 5.49$$

and

$$\text{Cuen}^{++} + \text{I}^- = \text{CuIen} \quad \log K_{\text{Cuen}}^{\text{I}} = 8.2$$

Both represent the addition of I^- as a second ligand but show a large difference. The most obvious difference is that the formation of the mixed complex involves neutralization of charge. Charge neutralization, in general, appears to be a type of reaction which is favored probably because of the favorable entropy change in the de-solvation of the charged species. An additional effect may be that the number of coördination positions filled in CuI is greater than in Cuen^{++}.

A second comparison is

$$\text{Cuen}^{++} + \text{en} = \text{Cu(en)}_2^{++} \quad \log K_{\text{Cuen}}^{\text{en}} = 9.61$$
$$\text{CuI} + \text{en} = \text{CuIen} \quad \log K_{\text{CuI}}^{\text{en}} = 8.8$$

There is no charge neutralization in either of these cases and there is only a relatively small difference in log K. We cannot describe with any confidence why this difference exists although here again there is the difference in numbers of coördination positions filled in Cuen^{++} and in CuI.

The constant for the reaction

$$2\text{CuIen} = \text{Cu(en)}_2^{++} + \text{CuI}_2^- \quad \log K_{\text{CuIen}}^{\text{CuIen}} = -2.0$$

may express again the favoring of charge neutralization. On the basis of statistics alone, the mixed complex is favored and $\log K_{\text{CuIen}}^{\text{CuIen}}$ would be -0.6. DeWitt and Watters[1a] found the following for a similar reaction

$$2\text{Cu(ox)en} = \text{Cu(ox)}_2 + \text{Cu(en)}_2^{++} \quad \log K = -0.95$$

It is evident that many more such reactions must be studied in order to increase our understanding of the factors involved.

IOWA CITY, IOWA

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

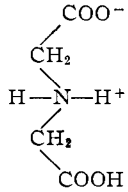
Coördination Compounds of Metal Ions with Derivatives and Analogs of Ammoniadiacetic Acid[1]

BY ROBERT M. TICHANE AND WILLIAM E. BENNETT

RECEIVED SEPTEMBER 6, 1956

To obtain information as to the effect of the structure of a compound on its ability to act as a chelating agent, values for the first and second formation constants of complexes between metal ions and derivatives and analogs of iminodiacetic acid were determined. It was found that definite changes in the chelating ability of ligands could be brought about by structural changes which influence the freedom of motion of the donor groups.

The formation constants of a series of chelates of a given metal ion with ligands of similar structure show a relation with the acid dissociation constants of the ligands. This effect has been noticed in the case of complexes of amines,[2] diketones[3,4] and of compounds related to iminodiacetic acid.[5-9] The general effect observed is that the logarithms of the formation constants of metal complexes of a given type are proportional to the pK values of the complexing agents.



Iminodiacetic acid derivatives are convenient to study since they are generally soluble in water. It was decided that such compounds could be used to study the structural factors which would influence the relationship between the pK of the ligand and its chelating ability. It was of interest to deter-

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[1] From a thesis submitted by Robert M. Tichane to the Graduate College of the State University of Iowa in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1956.

[2] J. Bjerrum, *Chem. Revs.*, **46**, 381 (1950).

[3] M. Calvin and K. W. Wilson, THIS JOURNAL, **67**, 2003 (1945).

[4] L. G. Van Uitert, W. C. Fernelius and B. E. Douglas, *ibid.*, **75**, 457 (1953).

[5] G. Schwarzenbach, H. Ackermann and P. Ruckstuhl, *Helv. Chim. Acta*, **32**, 1175 (1953).

[6] G. Schwarzenbach, A. Willi and R. O. Bach, *ibid.*, **30**, 1303 (1947).

[7] G. Schwarzenbach, G. Anderegg, W. Schneider and H. Senn, *ibid.*, **38**, 1147 (1955).

[8] S. Chaberek and A. E. Martell, THIS JOURNAL, **74**, 5052 (1953).

[9] S. Chaberek and A. E. Martell, *ibid.*, **76**, 215 (1954).