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[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Metal–Amine Coördination Compounds. I. Copper(II) Complexes

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A study of the nature of some of the amine complexes of the copper(II) ion was carried out. Absorptimetric data were compiled for a series of polyamine coördination compounds. The effects of *p*H, non-aqueous solvents and reductants on the coördinated metal amines were determined. Formulas for the complexes of copper with 1,10-phenanthroline, 2,2′-bipyridine and 2,2′,2″-terpyridine were determined together with the changes in coördination with variations in the *p*H of the systems. A value for the stability constant for the copper(II)–1,10-phenanthroline complex was calculated from potentiometric data. A correlation of the nature and behavior of the metal amines studied was made on the basis of variations in the coördinating reagents.

Introduction

The copper(II) coördination compounds under consideration can be divided into two groups on the basis of the type of ligand involved in the coördination. The compounds formed with saturated amines, ammonia, ethylenediamine, diethylenetriamine and triethylenetetramine comprise one group whereas the compounds formed with unsaturated amines, pyridine, 2,2′-bipyridine, 2,2′,2″-terpyridine and 1,10-phenanthroline comprise the other. The complexes of both groups are colored and exhibit such a high degree of stability that they have long been of interest. The present investigation was undertaken in order to obtain data on these compounds and to correlate the results with those in the literature on similar compounds.

A considerable amount of work has been done in the past on the first group of compounds described above. Absorption characteristics, formulas, and stabilities have been studied by many investigators.[2-8] The results obtained by all of these workers indicate a maximum coördination number of five for the copper ion. The compounds of the second group have been investigated along similar lines, but to a lesser degree.[9-13] The results obtained, with the exception of the data on the 2,2′,2″-terpyridine complex,[13] indicate a maximum coördination number of six for the metal ion. The variance of these findings clearly reveals the necessity for further investigation.

The work cited above has been concerned only with certain phases of the chemistry of the copper(II)–amine coördination compounds. Little attention has been focused on the effects of strong bases and non-aqueous solvents upon these substances. In view of the extraction of the copper–pyridine complex into chloroform[14] and the extraction of certain of the copper(I) polyamine compounds into water immiscible alcohols,[15] this phase of the chemistry also warranted consideration. This investigation was concerned with these aspects of the problem, together with a study of the absorption characteristics of the complexes in the presence of high concentrations of hydroxyl ion and in the presence of reductants. Inasmuch as the compounds are colored, a spectrophotometric study in the visible region of the spectrum proved to be appropriate for the major portions of the experimentation.

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(1) An abstract of a thesis submitted by Ronald T. Pflaum to the Graduate School of Purdue University, 1953, in partial fulfillment of the requirements for the Degree of Doctor of Philosophy. Present address, Dept. of Chem., State University of Iowa.

(2) J. Bjerrum, *Kgl. Danske Videnskab. Selbskab. Math-fys. Medd.*, **11**, 3 (1932).

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

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

(5) J. Bjerrum and E. J. Nielsen, *Acta Chim. Scand.*, **2**, 297 (1948).

(6) H. M. Haendler, THIS JOURNAL, **64**, 686 (1942).

(7) H. B. Jonassen, R. B. LeBlanc and Ruth M. Rogan, *ibid.*, **72**, 4969 (1950).

(8) H. B. Jonassen and A. W. Meibohm, *J. Phys. Colloid Chem.*, **55**, 726 (1951).

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

(10) F. M. Jaeger and J. A. van Dijk, *Z. anorg. allgem. Chem.*, **227**, 273 (1936).

(11) P. Pfeiffer and B. Werdelmann, *ibid.*, **261**, 197 (1950).

(12) E. I. Onstott and H. A. Laitinen, THIS JOURNAL, **72**, 4724 (1950).

(13) G. Morgan and F. H. Burstall, *J. Chem. Soc.*, 1649 (1937).

(14) J. M. Kruse and M. G. Mellon, *Anal. Chem.*, **25**, 446 (1953).

(15) G. F. Smith and W. H. McCurdy, *ibid.*, **24**, 371 (1952).

Experimental

Materials Used.—Ethylenediamine, diethylenetriamine and triethylenetetramine were obtained from the Carbon and Carbide Chemical Company. The 2,2′-bipyridine, 2,2′,2″-terpyridine, 1,10-phenanthroline and substituted 1,10-phenanthroline reagents were obtained from the G. Frederick Smith Chemical Company.

Standard solutions of copper(II) sulfate were prepared from the recrystallized salt and standardized by electrodeposition. All other inorganic chemicals used were reagent grade quality.

Technical grade solvents were redistilled before use.

Spectrophotometric Data.—A General Electric automatic recording spectrophotometer and a Beckman Model B spectrophotometer were used to obtain absorptimetric data. All measurements were made in matched 1.0-cm. cells. Molar absorptivities for the various complexes were calculated on the basis of the copper ion present.

Determination of Formulas.—Formulas for the various species in solution were determined by the method of continuous variations.[16] Stock solutions of 3×10^{-2} *M* copper(II) sulfate and the reagents were prepared and aliquots mixed in the appropriate ratios. Adjustments in *p*H were made with dilute sulfuric acid and dilute sodium hydroxide. Absorption measurements were made at selected wave lengths. Absorbance values were obtained by subtracting the absorbance for zero complexation from the observed readings. Formulas were determined from a plot of absorbance against the mole fraction of copper(II) ion.

Determination of the Effect of *p*H.—The effect of *p*H was determined on solutions containing copper ion and the complexing agent. Measurements of *p*H were made on a Beckman Model H-2 *p*H meter. The effects of changes in *p*H were determined spectrophotometrically in all cases in which the reacting species were soluble over the *p*H range studied.

Stability Measurements.—A value for the stability constant of the copper(II)-1,10-phenanthroline complex was calculated according to the method described by Carlson, McReynolds and Verhoek.[17] The *p*H values of solutions containing 2.5×10^{-2} *M* copper(II) nitrate, 4×10^{-1} *M* sodium nitrate, nitric acid and varying concentrations of 1,10-phenanthroline were measured on a Leeds and Northrup *p*H indicator. A plot of the formation curve was made and equilibrium constants evaluated according to reported procedure.[4,17]

Effects of Non-aqueous Solvents.—The effects of miscible organic solvents on the various complexes were studied on solutions containing 50% by volume of the non-aqueous solvent. Spectrophotometric curves were obtained on those mixtures that did not result in precipitation. In general, miscible alcohols, acetone, dioxane and methylcarbitol were studied.

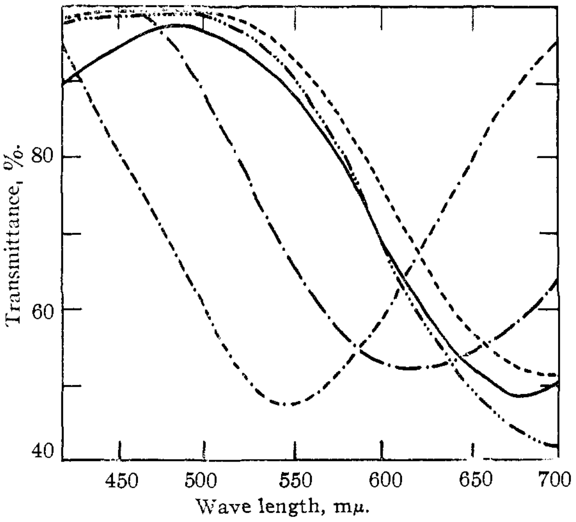

Fig. 1.—Comparison of spectra of Cu(II) complexes: --·--, ethylenediamine, *p*H 10; —·—, diethylenetriamine, *p*H 6; ----, 1,10-phenanthroline, *p*H 4; —···—, 2,2′-bipyridine, *p*H 4; ——, 2,2′,2″-terpyridine, *p*H 4.

Immiscible solvents such as benzene, chloroform, carbon tetrachloride, isoamyl alcohol and toluene were studied from the standpoint of the extraction of the copper(II) complexes. Extractions were carried out from both acidic and basic solutions. Equal volumes of the immiscible solvent and the aqueous solution of the complex were mixed in separatory funnels.

An investigation into the extraction of copper(II)-pyridine and pyridine homolog complexes into chloroform in the presence of cyanate and thiocyanate ions was carried out in conjunction with this study. The effects of substitution in the pyridine nucleus on the resulting complexes were studied spectrophotometrically.

Effect of Reductants.—The effects of 0.01-gram quantities of common reducing agents to 10^{-3} *M* solutions of the copper(II) complexes were studied. Hydroxylamine hydrochloride, sodium hyposulfite and sodium sulfite were added to solutions of the complex made basic with ammonium or sodium hydroxide. The changes in color in the resulting mixtures were used as an indication of the reducing action and the nature of the complex in the lower oxidation state.

Discussion

Spectrophotometric Data.—The spectra for certain of the complexes are shown in Fig. 1. The values for the molar absorptivities (a_m) and the wave lengths of maximum absorption for the various metal amines studied are listed in Table I. The data were obtained on solutions containing a known concentration of copper(II) ion and a threefold excess of the reagent over this metal ion concentration. Inasmuch as the spectra for certain of the complexes change with variations in the *p*H of the system, a dual set of values has been included in Table I. The behavior of copper amines toward *p*H changes will be discussed in another section of this work.

TABLE I

ABSORPTIMETRIC DATA ON COPPER(II) COMPLEXES

Reagent	Wave length of max. abs., mμ	a_m
Ammonia	610	56
Ethylenediamine	550	65
Diethylenetriamine	630	82
Triethylenetetramine	580	150
Pyridine	625	60
2,2′-Bipyridine	685[a]	80
	610[b]	50
2,2′,2″-Terpyridine	680[a]	75
1,10-Phenanthroline	700[a]	60
	616[b]	55
5-Chloro-1,10-Phen.	695[a]	35
	610[b]	. .
5-Methyl-1,10-Phen.	690[a]	62
	620[b]	. .
4,7-Dimethyl-1,10-Phen.	700[a]	75
	630[b]	. .
5,6-Dimethyl-1,10-Phen.	700[a]	45
	600[b]	. .

[a] *p*H 4. [b] *p*H 12.

Considering the relative degree of absorptivity of the colored species listed, the variations observed do not follow any particular pattern. The increase in absorptivity of the chelated species over the ammonia or pyridine complexes is so small as to be insignificant. A similar situation exists with satu-

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[16] P. Job, *Compt. rend.*, **180**, 928 (1925).

[17] G. A. Carlson, J. P. McReynolds and F. H. Verhoek, THIS JOURNAL, **67**, 1334 (1945).

rated and unsaturated organic amine reagents. The very small values for the molar absorptivities, resulting from species that are not highly colored, do not allow one to make rigorous comparisons.

In regard to the wave lengths of maximum absorption, however, an entirely different situation presents itself. The variations are significant and of such degree that definite trends are apparent. With the exception of the absorption maximum for ethylenediamine and triethylenetetramine complexes, the values presented in Table I can be divided into two groups.

The ammonia, diethylenetriamine, pyridine, 2,2′-bipyridine 1,10-phenanthroline and substituted 1,10-phenanthroline complexes show absorption maxima in the range of 600–630 mμ in alkaline solution. The variations that exist in the complexes containing 1,10-phenanthroline and substituted 1,10-phenanthroline ligands do not show conformity to any empirical relationship as do the variations in the iron system described by Brandt and Smith.[18] With the iron(II) complexes, variations in absorption maxima were correlated to methyl substitution in the different positions around the phenanthroline nucleus. Any such correlation in the copper system breaks down when applied to the complexes in acidic and in basic solution. This would indicate that the absorption bands of the copper and iron complexes are derived from different phenomena. This is consistent with the fact that with copper the color of the complex is merely an intensified color of the cupric ion itself, whereas with iron the complex has an entirely different spectrum from that of the free ion.

The wave lengths of maximum absorption for the chelate complexes in acidic solution group themselves in the range of 680–700 mμ. The 2,2′-bipyridine and 2,2′,2″-terpyridine complexes show maxima at wave lengths shorter than that of the 1,10-phenanthroline complex. The inverse relationship exists among these complexes in the iron system. In that system, the tris-2,2′-bipyridine–iron(II) ion and the tris-1,10-phenanthroline–iron(II) ion have maxima at 552 and 510 mμ, respectively.[18] The bis-2,2′,2″-terpyridine–iron(II) ion shows a maximum at 552 mμ.[18]

Influence of *p*H and Formulas of Species.—Inasmuch as *p*H exhibits such a great influence on the formulas of the species studied, these two aspects of the chemistry of polyamine complexes will be discussed together. In this regard, the compounds containing benzenoid ligands show a particularly interesting behavior with changes in *p*H. As an example, the changes in the spectrum of the copper–1,10-phenanthroline complex with changes in hydrogen ion concentration are shown in Fig. 2. The absorption maximum is shifted toward shorter wave lengths as the *p*H is increased. In strongly basic solution, the absorption curve closely resembles that of the copper–ammonia complex.

In acidic solutions containing more metal ion than either phenanthroline or bipyridine, a blue precipitate slowly formed. The precipitation was fastest in solutions of highest acidity. Analysis of the phenanthroline compound showed it to be Cu(phen)$SO_4 \cdot 3H_2O$. This salt was completely insoluble in acidic solution, but readily soluble in the presence of excess phenanthroline or in alkaline solution. The nitrate salt is green.

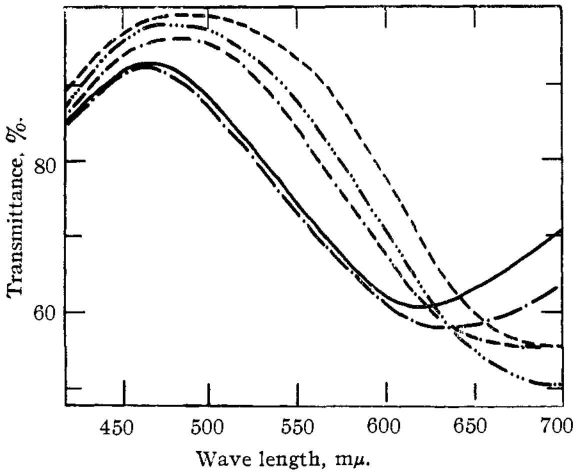

Fig. 2.—Effect of *p*H on phenanthroline–copper(II) system: —··—, *p*H 2; ---, *p*H 4; --·--, *p*H 8; ——, *p*H 13 (1:1 ratio); –·–, *p*H 13.

The results of continuous variations studies on certain of the absorbing species are shown in Fig. 3.

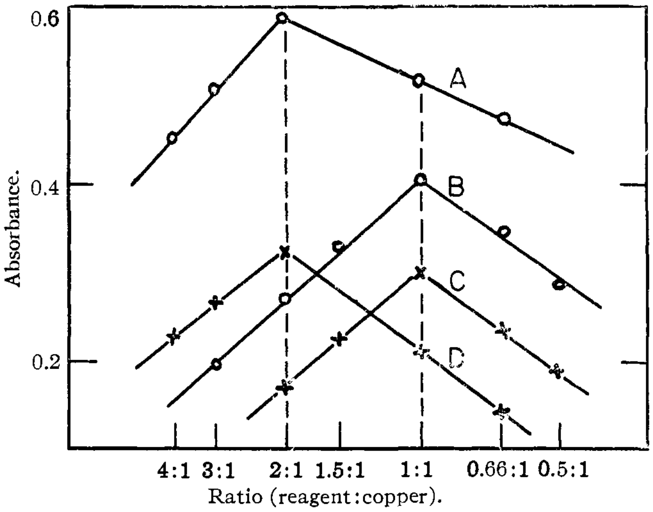

Fig. 3.—Continuous variation studies of copper(II) complexes: A, 1,10-phenanthroline, *p*H 4; B, 1,10-phenanthroline, *p*H 12; C, 2,2′,2″-terpyridine, *p*H 4; D, 2,2′-bipyridine, *p*H 4.

In acidic solution (*p*H 4), copper appears to coördinate with two molecules of 1,10-phenanthroline and 2,2′-bipyridine, but with only one molecule of 2,2′,2″-terpyridine. As a consequence, coördination numbers greater than four, postulated by Bjerrum[2] and Mellor[9] were not observed. In basic solution (*p*H 12), the phenanthroline and the bipyridine complexes each lose all but one molecule of coördinated ligand. The resulting species probably exist as hydroxyl complexes with one molecule of ligand per copper ion. This type of compound was observed by Prue and Schwarzen-

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(18) W. W. Brandt and G. F. Smith, *Anal. Chem.*, **21**, 1313 (1949).

bach[19] in their study of ethylenediamine complexes.

Stability Constants.—A value for the stability constant for the copper(II)–1,10-phenanthroline system was calculated from data obtained according to the method of Bjerrum.[4] Experimental data are presented in Table II. Certain factors in the mathematical expressions presented by Carlson, McReynolds and Verhoek[17] have been rearranged for simplicity. Thus, the equation

$$\bar{n} = C_A - \frac{[AH^+]/\bar{n}A}{C_M}$$

has been converted to

$$n = \frac{C_A - (C_H - [H^+])\left(1 + \frac{K_a}{[H^+]}\right)}{C_M}$$

The expression for $[A] = \alpha[AH^+]/\bar{n}A$ has been converted to

$$[A] = K_a \frac{C_H - [H^+]}{[H^+]}$$

n = av. no. of ligand molecules chelated to metal ion
C_A = total concn. of ligand
C_H = total concn. of acid
C_M = total concn. of metal ion
$[H^+]$ = concn. of measured hydrogen ion in soln.
K_a = acid dissociation constant of ligand
$\bar{n}A$ = mean no. of protons bound to non-complex bound amine
$[A]$ = concn. of free ligand
α = fraction of amine not complex bound
$[AH^+]$ = concn. of protonated ligand

TABLE II

DATA ON THE COPPER(II) NITRATE SYSTEM WITH 1,10-PHENANTHROLINE

2.5×10^{-2} *M* $Cu(NO_3)_2$, 0.4 *M* $NaNO_3$, 25°

$C_A \times 10^2$	$[H^+] \times 10^5$	$C_H - [H^+] \times 10^5$	$[A] \times 10^7$
0.6	95.5	4.5	5.17
1.0	103.0	5.0	5.33
1.2	100.0	5.0	5.48
1.8	100.0	5.5	6.05
2.5	89.0	6.5	8.04
4.0	93.4	6.6	7.78
4.5	87.1	12.9	16.3
5.0	85.2	8.2	10.6
6.0	66.0	34.0	56.6
7.0	33.0	46.3	154

The acid dissociation constant for 1,10-phenanthroline, evaluated by Lee, Kolthoff and Leussing,[20] is 1.1×10^{-5}.

Values for the individual equilibrium constants, determined at half $\bar{n}$ values, are $k_1 = 6.30$, $k_2 = 6.15$, $k_3 = 5.50$. The over-all stability constant is 17.9. This value, based upon the coördination of three molecules of phenanthroline, is similar to the value obtained by Onstott and Laitinen[12] for the copper bipyridine complex. Three molecules of reagent were coördinated in their complex also.

These results put considerable question upon the interpretation of the continuous variation studies discussed earlier. The latter indicate clearly a 2:1 species. The plot is good and would seem highly dependable. The potentiometric results, however, show that considerable amounts of a 3:1 species must exist under the conditions used for the continuous variations study. This would seem to require that the 3:1 complex have a molar absorptivity markedly less than the 2:1. This fact is not consistent with behavior of copper(II) upon the addition of reagent. A smooth progression to a maximum is noticed. Suitable explanation of both points requires a peculiarly fortuitous relationship of stability and color intensity of the species involved. This may be in keeping with the fact that marked changes in absorptivity with complexing are not noticed in the copper amine systems. Spectrophotometric evidence in such systems must thus be viewed with caution.

It is interesting to consider the stability constants for the metal amines of the first transition series of metals. Irving and Williams[21] have stated that, in the first transition series, the stability of complexes increases steadily to a maximum at copper. This situation holds for many systems of complexes, but appears to break down with the coördinated unsaturated benzenoid amines. In these complexes, maximum stability or equivalent stability is exhibited in the iron system. A study of the values in Table III shows this change over to the iron compounds. The values in Table III, except in those cases indicated, have been taken from the compilation of Martell and Calvin.[22] The lack of correlation between the bipyridine and phenanthroline complexes of iron and copper indicates a definite need for further study of these and related species.

TABLE III

STABILITY CONSTANTS OF METAL AMINE COMPLEXES

Ligand	Fe(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)
Ethylenediamine	9.52	13.82	18.61	19.60	12.09
Diethylenetriamine	10.3	14.6	18.9	21.3	14.4
Triethylenetetramine	12.1	14.6	19.9	20.6	11.9
Pyridine[a]	...	...	9.8	10.2	6.05
2,2′-Bipyridine	17.60	...	...	17.85	...
1,10-Phenanthroline	21.3	...	18.3 ± 1.1[c]	17.9[b]	12.2

[a] Reference 7. [b] Calculated value. [c] N. R. Davies and F. P. Dwyer, *Trans. Faraday Soc.*, 49, 180 (1953).

Influence of Organic Solvents.—The influence of organic solvents upon copper(II) complexes is of interest in view of the extraction of copper(I)–1,10-phenanthroline complexes into immiscible solvents.[15] The addition of miscible solvents was shown to cause changes in the absorption spectra of these copper(I) complexes.[23]

The majority of the copper(II) complexes studied do not undergo any change in the presence of organic solvents. The complexes with saturated ligands are precipitated by the addition of miscible solvents. The complexes with unsaturated ligands are unaffected by miscible solvents. Immiscible solvents, other than nitrobenzene,[24] have little effect upon the two classes of compounds.

The behavior of the complex of copper and pyridine toward certain immiscible solvents is of particular interest. In the presence of cyanate or thio-

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[19] J. E. Prue and G. Schwarzenbach, *Helv. Chim. Acta*, **33**, 985 (1950).

[20] T. S. Lee, I. M. Kolthoff and D. L. Leussing, THIS JOURNAL, **70**, 2348 (1938).

[21] H. Irving and R. J. P. Williams, *Nature*, **162**, 746 (1948).

[22] A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952.

[23] M. L. Moss and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **15**, 116 (1943).

[24] D. W. Margerum and C. V. Banks, *Anal. Chem.*, **26**, 200 (1954).

cyanate ions, the complexes of copper and pyridine homologs are extracted into chloroform. It has been reported that copper complexes containing homologs of pyridine are not extracted into chloroform.[14] The colored chloroform extracts show interesting variations as far as absorption maxima are concerned. These maxima are listed in Table IV. This striking anion specificity is also exhibited by the ferrous–phenanthroline system.[24]

TABLE IV

ABSORPTION MAXIMA (mμ) FOR $CHCl_3$ EXTRACTS OF Cu(II) COMPLEXES

Ligand	Cyanate	Thiocyanate
Pyridine	680	410
2-Picoline	640	425
3-Picoline	700	410
4-Picoline	690	400
2,3-Lutidine	640	430
2,4-Lutidine	640	420
2,6-Lutidine	630	425

A study of the data shows that substitution of a methyl group in the alpha position on the pyridine nucleus causes a shift of 40 mμ toward shorter wave lengths for the complexes with cyanate ion. The same substitution causes a shift of 10–20 mμ toward longer wave lengths for complexes with thiocyanate ion. Substitution in the various other positions has little effect upon the absorption maximum of the complex. In multiple substitution, the variations are due almost entirely to the methyl group in the ortho position to the nitrogen atom. The difference in the direction of the wave length shift is quite unexpected since these ions are two of the very few capable of bringing about the extraction. This relationship would have made a close relationship in the changing of the wave length seem more probable. Apparently there is no direct correlation between the two phenomena. The marked effect of the ortho substitution suggests a steric involvement since *para* substitution should produce similar changes in electronic distribution.

Effect of Reductants.—It was observed that all of the coördination compounds of copper(II) ion reacted with reducing agents to form coördinated compounds of the copper(I) ion. Reduction was effected in basic solution with such reducing agents as hydroxylamine hydrochloride and sodium hyposulfite. Reduction occurred in solutions made basic with either ammonia or an alkali hydroxide. No reaction occurs in acidic solution. This indicates a markedly different relationship between the copper(II) and copper(I) complexes in acidic environment as compared to basic solution. This may be due in part to the effect of the close association of the hydroxyl groups.

The copper(I) complexes of ammonia and the saturated polyamines studied are colorless in alkaline solution. The copper(I) pyridine complex is yellow. The combination of the lower oxidation state of copper and unsaturated polyamine ligands results in highly colored species.[25] These are predominantly yellow or yellow-red. Reduction of the oxidation state of the central metal ion in this group of coördination compounds causes a tremendous change in the absorption spectra with large increases in the color intensity of the species involved.[23] The more highly colored complexes also are the more stable.

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[25] G. Tartarini, *Gazz. chim. ital.*, **63**, 597 (1933).

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUQUESNE UNIVERSITY]

Cadmium and Copper Complexes of Imidazole and 1-Methylimidazole[1a,b]

BY NORMAN C. LI, JAMES M. WHITE AND EDWARD DOODY[1c]

RECEIVED JULY 9, 1954

The over-all formation constants of cadmium complexes of imidazole have been determined in water at 25° and in 18.8% ethanol (by vol.) at 0, 25 and 35°. The values of ΔH° and ΔS° for the reaction $Cd^{++} + 4Im = CdIm_4^{++}$ in 18.8% ethanol are -10.8 ± 0.6 kcal./mole and -2.2 ± 0.1 cal. deg.$^{-1}$ mole^{-1}, respectively. The solvent effect of ethanol on complex formation is negligible. It is shown that the polarographic method gives the formula of the highest order complex with certainty; this is not possible with the Bjerrum *p*H treatment for the cadmium complexes of imidazole. Double waves are obtained for the copper complexes of imidazole: for $CuIm_4^{++}$, $\log k_{f.4} = 12.6$; for $CuIm_2^{+}$, $\log k_{f.2} = 10.8$. The formation constants of 1-methylimidazole complexes of cadmium and copper are of the same order as those of the imidazole complexes. These results indicate that the site of binding on the imidazole molecule is the "pyridine" nitrogen rather than the "pyrrole" nitrogen.

Introduction

Recent work[2] has shown that in the combination of cadmium and copper ion with serum albumin the principal binding sites are the imidazole groups of the histidine residues of the protein molecule. The association of imidazole itself with the ions of cadmium and copper(II) has previously been reported by Tanford and Wagner[3] and by Edsall, *et al.*,[4] respectively. These complexes were investigated by means of the potentiometric *p*H method of Bjerrum only and, at least in the cadmium complexes, the values obtained at high *p*H are so inaccurate that it is not possible to tell what the highest order complex is. For this reason an independent method of investigating complex formation is highly desirable and it will be shown in

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[1] (a) This work has been supported by a grant from the National Science Foundation, Grant No. G510; (b) taken in part from the M.S. thesis of J. M. White, Duquesne University; (c) Christian Brothers College, Memphis, Tenn.

[2] C. Tanford, THIS JOURNAL, **74**, 211 (1952).

[3] C. Tanford and M. L. Wagner, *ibid.*, **75**, 434 (1953).

[4] J. T. Edsall, G. Felsenfeld, D. S. Goodman and F. R. N. Gurd, *ibid.*, **76**, 3054 (1954).