3. *Complexes Formed by α-Hydroxy-amidines with Transition-metal Ions. Part II.*[1] *Complexes with Copper*(II).

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The formation of strong, uncharged complexes of copper(II) with some α-hydroxy-amidines has been demonstrated. The stability constants for these complexes in aqueous solution at 25° have been measured and a study of their optical and magnetic properties is reported. The visible-region spectra of square-planar copper(II) complexes is discussed briefly with reference to those of the α-hydroxy-amidine–copper(II) compounds. The relationship between the α-hydroxy-amidine complexes and those formed with α-amino-acids is noted and the function of the α-hydroxy-groups in complex formation is discussed.

THE formation of transition-metal complexes by α-hydroxy-amidines is of interest, because they are the formal analogues of the α-amino-acids (the O and NH functions having been interchanged) whose transition-metal complexes have received much attention, and because they provide further information on the role of aliphatic hydroxyl groups in chelate formation. The dissociation of the α-hydroxy-α-phenylamidinium ions, $HO{\cdot}CPhR{\cdot}C({\cdot}NH_2){:}NH_2^+$ as weak dibasic acids has been established for R = H (mandelamidinium ion, abbreviated to mdH_2^+), Me (atrolactamidinium ion, alH_2^+) and Et (α-hydroxy-α-phenylbutyramidinium ion, hbH_2^+). All of these amidines react with cupric ions in aqueous solution if the pH is relatively high (*ca.* 10), giving deep, reddish-blue solutions which, in the case of the two higher amidines, slowly deposit crystals of the complex. The complexes can be extracted from aqueous solution by pentanol, but not by less polar solvents such as carbon tetrachloride or ether.

RESULTS

Formation and Stoicheiometry of the Complexes.—The stoicheiometry of the complexes in aqueous solution was readily demonstrated by Job's method of continuous variations. At the wavelength of maximum absorption of visible light (580 mμ for the mandelamidine complex and 570 mμ for the others), alkaline solutions with a high amidine : copper ratio give good agreement with Beer's law over a ten-fold dilution. The optical density of a solution containing a constant (copper + amidine) concentration increases linearly with copper concentration until a copper : amidine ratio of 1 : 2 is reached. At higher copper : amidine ratios, precipitation of copper hydroxide occurs, but, providing that the total concentration of sodium hydroxide is kept to about twice that of the total (copper + amidine) concentration, the removal of this precipitate results in a linear decrease in absorption.

The amount of hydroxide ion consumed in complex formation was found by pH titrations of various solutions of copper and amidinium ions; these are discussed below under the determination of the stabilities of the complexes. In all cases, a sharp break occurred in the pH titration curve when a quantity of sodium hydroxide equivalent to four times the total copper present had been added.

[1] Part I, *J.*, 1962, 296.

That the complexes are uncharged in aqueous solution was demonstrated by the fact that they failed to migrate when a concentrated solution was subjected to electrophoresis, and that they were readily extracted from aqueous solution by immiscible alcohols, pentanol being especially suitable. The solution of the mandelamidine complex in pentanol deposited plate-like crystals which rapidly lost solvent to give a powder having the approximate formula Cu md_2. None of the complexes was soluble in ether, dioxan, benzene, nitrobenzene, acetone, chloroform, or ethyl acetate, but all were very slightly soluble in pyridine and readily soluble in alcohols, formamide, and piperidine.

The crystals deposited from aqueous solution by atrolactamidinium and α-hydroxy-α-phenylbutyramidinium ion in the presence of cupric ion and an excess of alkali gave good analyses as dihydrates, the *complex* with the latter giving: C, 52·2; H, 6·2; N, 12·4; ash, 17·5% (Cu $hb_2,2H_2O$ requires C, 52·9; H, 6·7; N, 12·3; CuO, 17·6%). The atrolactamidine *complex* gave: C, 51·3; H, 6·3; N, 13·2; ash, 18·8% (Cu $al_2,2H_2O$ requires C, 50·8; H, 6·2; N, 13·2; CuO, 18·7%). While the former crystals are dehydrated only under a vacuum at high temperatures, where they decompose further, the latter are readily dehydrated at 100° to a deliquescent powder (Found: H_2O, 8·0. Cu $al_2,2H_2O$ requires H_2O, 8·4%). The crystals of the hydroxyphenylbutyramidine complex were sufficiently discrete for application of *X*-ray crystallography. They were shown to belong to space group $P2_1$, and to have a molecular weight of 454·8 (calc. for Cu $hb_2,2H_2O$: 454). Further work is being undertaken on the structural parameters of the molecule.[2] Solutions of the mandelamidine complex did not yield crystalline products, and the amidine decomposes fairly rapidly in alkaline solution.[1]

Stability Constants of the Complexes.—Decomposition studies similar to those reported earlier for the amidinium ions [1] were undertaken in the presence of cupric ions, but, for pH values less than about 9, there was no significant decomposition. Since there was no need to measure solutions of such high pH in order to prepare the formation curves for the complexes, batch methods were deemed unnecessary, and direct titrations were performed as follows:

Solutions were made up, in an ionic medium kept constant at 0·1M with potassium chloride, in such a way that, at the midpoint of the titration, the volume of the solution would be 50 ml., and the total concentrations of copper 0·0004, 0·001, and 0·002M, and of amidine between 0·004 and 0·04M. Since free acid was added with the copper solution, two breaks were observed in the titration curves, the distance between them corresponding quantitatively to the addition of four hydroxyl ions per cupric ion. When the amidine : copper ratio was greater than 10 : 1, the solution remained clear throughout the titration. At lower ratios, however, precipitation occurred in the middle portion of the titrations, and was evident before it was clearly visible by a fall-off in pH as more sodium hydroxide was added. Since the precipitate coagulated and did not readily return to solution even when more than enough sodium hydroxide was added to effect complete complex-formation, a back-titration method was devised whereby an excess of sodium hydroxide was run rapidly into the mixture, and the resulting clear solution was titrated with hydrochloric acid until precipitation occurred. In this manner, a considerable portion of curves could be obtained, and, in order to check the validity of the method, it was also applied to some of the solutions with a higher proportion of amidine. The complete curve thus obtained could be superimposed on that obtained by the direct titration, as is shown in Fig. 1.

Calculation of the Stability Constants.—No intermediate break corresponding to the addition of two hydroxyl ions per copper ion was detectable, suggesting that the two stability constants for the attachment of amidine groups must be of comparable magnitude, and the fact that the attachment of a chelating group does not occur as a discrete step before the loss of the second proton from the ligand was indicated by the observation that titrations of samples of identical copper : amidine ratios, but differing in total concentration by a factor of two, gave curves evenly separated throughout by a distance of about 0·16 pH unit ($\approx \frac{1}{2}$ log 2).[3]

On these assumptions, and because of the apparently great stability of the complexes, two simplifications are possible in Bjerrum's general formula for the calculation of stability constants from pH data: [4] First, the degree of formation, $\bar{n}$, may be assumed to be proportional to the amount of sodium hydroxide added over the part of the titration curve between the

[2] Iball and Morgan, personal communication.

[3] Van Uitert and Fernelius, *J. Amer. Chem. Soc.*, 1954, **76**, 375.

[4] Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

breaks; and, secondly, the concentration of the species H_2L^+, for all values of pH less than 8, may be assumed to be equal to $[L]_t - \bar{n}[Cu]_t$, since, below that pH, the concentrations of the species HL and L^- cannot be greater than 0·001 of the concentration of H_2L^+. The pH titration curves for a representative number of concentrations of hbH_2Cl and a single concentration of copper are given in Fig. 1; the effect of formation of precipitate in the central region can here be seen. The formation curves, or plots of $\bar{n}$ as a function of pL ($= pk_1 + pk_2 - 2pH - \log[H_2L^+]$),* can thus be readily prepared. Theoretical curves, corresponding to the constants given in Table 1 were fitted to the experimental points by the projection-strip method [5] employed in Part I. The calculated values of the stability constants for the copper complexes of the three amidines are thus based on the acid dissociation constants reported previously,[1] and are given in Table 1.

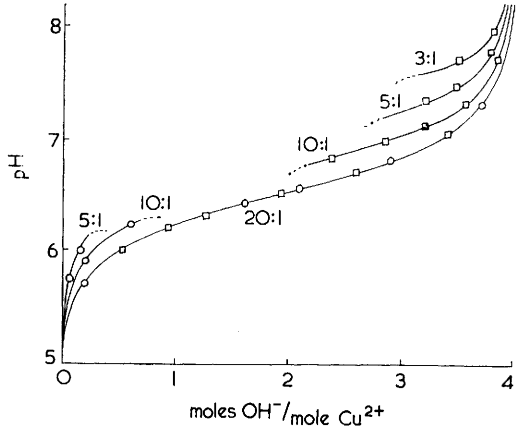

FIG. 1. pH titrations of mixtures of hbH_2^+ and Cu^{2+}, for solutions containing 0·04M-Cu^{2+} and given copper : amidine ratios, showing formation (○) and decomposition (□) of complexes. Broken lines indicate areas of precipitation.

TABLE 1.

Stability constants of copper complexes with some α-hydroxy-amidines at 25° and an ionic strength of 0·1M.

Complex	Cu md_2	Cu al_2	Cu hb_2
log K_1	12·50	12·73	12·86
log K_2	11·30	11·57	11·70

Polarographic Studies.—An attempt to measure the stability constants by the method of Lingane as modified by Keefer [6] for ligands whose effective concentration varies with pH was made under similar conditions to those above (potassium nitrate was used to adjust the ionic strength, and gelatine as a maximum suppressor). The waves obtained, however, were not reversible (the slope of the plot of log $[(i_d - i)/i]$ against E being 0·045 ± 0·005 for solutions containing mandelamidine or atrolactamidine, and 0·060 ± 0·005 for those containing α-hydroxy-α-phenylbutyramidine—a two-electron reduction reported for similar copper complexes [6,7] requires a slope of 0·030) and the method was abandoned. In any case, the pH measurements required for this method enable the direct method of calculation given above to be employed.

Visible Spectra of the Complexes.—Study of the spectra of the complexes was greatly hindered by there being so few solvents in which they were soluble. Since non-polar or weakly polar solvents did not dissolve the complexes, while such strongly polar ones as glacial acetic acid decomposed them, the only solvents available were the aqueous alkali in which they were formed, alcohols, and certain reactive nitrogen-containing compounds, in particular piperidine and formamide. The complexes were almost insoluble in pyridine, and the visible spectrum

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* In this paper, K_n refers to metal stability constants, and k_n to acid dissociation constants.

[5] Rossotti, Rossotti, and Sillén, *Acta Chem. Scand.*, 1956, **10**, 203.

[6] Keefer, *J. Amer. Chem. Soc.*, 1946, **68**, 2329.

[7] Flannery, Ke, Grieb, and Trivich, *J. Amer. Chem. Soc.*, 1955, **77**, 2996.

of the hydroxyphenylbutyramidine complex dissolved in a mixture of one part of pentanol with five parts of pyridine was indistinguishable from one in pure pentanol.

In each of the above solvents, the spectrum was measured over as much of the region between 300 and 2000 mμ as was practicable, and, in all cases, a single broad absorption band with an asymmetric contour was obtained in the visible region. The gaussian analysis of the spectra was done by trial and error, and, in all cases, it was found that two curves could be made to fit the envelopes with a high degree of precision, and that no better agreement could be obtained by postulating three components.[8] The analysed spectrum for solutions of about 0·02M-Cu hb_2 in pentanol is given in Fig. 2 and Table 2. The other amidines and solvents gave closely related spectra, the important features of which are also summarised in Table 2.

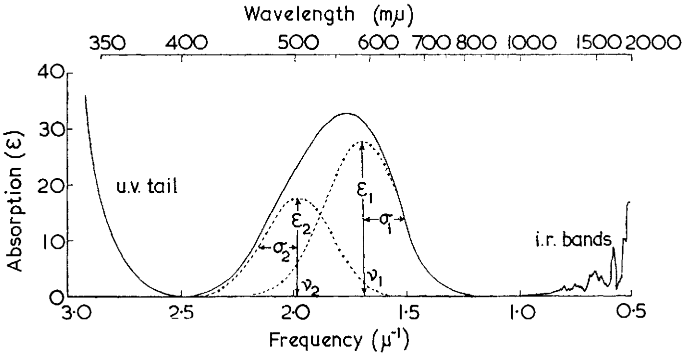

FIG. 2. Visible spectrum of Cu hb_2 solution in pentanol, showing division into gaussian components, with the frequency of maximum absorption, ν, maximum molar absorbance, ε, and half-band width, σ, for each component.

TABLE 2.

Gaussian components of visible spectra of copper(II) complexes with some α-hydroxy-amidines in various solvents; the meaning of the parameters is shown in Fig. 2.

Complex	Solution in	$\nu_1(\mu^{-1})$	ε_1	$\sigma_1(\mu^{-1})$	$\nu_2(\mu^{-1})$	ε_2	$\sigma_2(\mu^{-1})$
Cu md_2	Aq. alkali	1·70	35	0·21	2·00	12·5	0·17
	Pentanol	1·70	27	0·19	1·98	11	0·18
	Formamide	1·64	46	0·19	1·92	17	0·19
Cu al_2	Aq. alkali	1·70	31	0·19	2·00	16·5	0·18
	Pentanol	1·70	26	0·19	1·98	16	0·19
	Formamide	1·64	40	0·21	1·92	21	0·22
Cu hb_2	Aq. alkali	1·70	33	0·20	2·00	16	0·18
	Pentanol	1·70	28	0·19	1·98	18	0·18
	Formamide	1·65	42	0·20	1·92	21	0·23

Magnetic Properties of the Complexes.—The magnetic susceptibilities of the complexes were measured at room temperature by means of a Gouy balance, and the magnetic moments for the copper atoms were calculated by using Pascal's constants [9] for the diamagnetic correction for the ligands. The values found are listed in Table 3.

TABLE 3.

Magnetic susceptibilities of copper complexes with α-hydroxy-amidines and magnetic moments of the copper atoms.

Complex	$10^6\chi_g$ (e.m.u.) (20°)	$\mu_{\text{eff.}}$ (B.M.)
Cu md_2	3·34	1·81
Cu $al_2,2H_2O$	2·84	1·84
Cu $hb_2,2H_2O$	2·82	1·88

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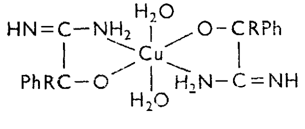
[8] Graddon, *J. Inorg. Nuclear Chem.*, 1960, **14**, 161.

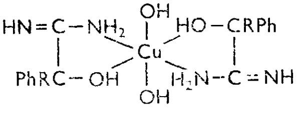
[9] See Selwood, "Magnetochemistry," Interscience Publ., Inc., New York, 1942, p. 52.

Discussion

Formation and Structure of the Complexes.—The studies by the methods of continuous variations and pH measurement show conclusively that complex formation in solution involves four hydroxide ions and two amidinium ions per copper ion, there being no evidence for the formation of higher complexes in a large excess of amidine or of stable 1 : 1 complexes in the absence of a large excess of hydroxide. Since similar complexes are not formed by phenylacetamidine,[10] the formation of a chelate ring involving the hydroxyl group seems certain, and the most probable structures for the crystalline complexes formed by atrolactamidine and α-hydroxy-α-phenylbutyramidine are those given below (co-ordination through the imino-nitrogen seems less likely when the stability of the complexes is taken into account):

(I)





(II)

The role of the aliphatic hydroxyl group in chelate systems has been discussed by several workers. Bobtelsky and Bar Gadda [11] state that the 2 : 1 complex of lactic acid with copper is a chelate having un-ionised hydroxyl groups: such a structure is, of course, itself uncharged. While there seems to be no satisfactory evidence for the formation of chelates that involve the loss of the hydroxyl proton between ethanolamine and copper,[7] a 3 : 1 neutral chelate with chromium(III), $Cr(H_2N{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot})_3$, has been prepared.[12] 2-Hydroxyethyl derivatives of ethylenediamine [13] and of glycine [14] have been reported as giving 2 : 1 chelates with copper in which the octahedral positions are occupied by ionised hydroxyl groups at high pH, but, as Courtney *et al.*[15] have pointed out, the pH data could also be interpreted by assuming ionisation of the co-ordinated water molecules in the octahedral positions. In neither of the cases cited was there any evidence of ionisation of the hydroxyl group in the absence of centres for complex-formation.

The structure (I) is nonetheless favoured in the case of the α-hydroxy-amidine complexes for two reasons: the failure of the complexes to dissolve in any but the most polar solvents suggests the need for strong donor molecules to fill the octahedral positions, and the ease with which the hydrated crystals of the atrolactamidine complex lose water is not easily explained by structure (II). On the other hand, strong hydrogen bonding of these water molecules to the adjacent imino-group is possible, and it would be expected to be stronger with the hydroxyphenylbutyramidine complex which is, in fact, less readily dehydrated.

The magnetic properties of the copper atoms approximate to the values expected for a d^9-atom, and are particularly similar to those reported for the 2 : 1 copper complexes of the α-amino-acids.[16]

Stability of the Complexes.—Stability constants have been calculated on the basis of structure (I) and predissociation of the hydroxyl group, and so they are not directly comparable with those reported for a large number of derivatives of ethanolamine by Hall, Dean, and Pacofsky; [17] in any case, the latter all involve co-ordination of polydentate ligands. A more direct comparison is possible with the complexes of the α-amino-acids, but the values reported here for the α-hydroxy-amidine complexes are considerably higher

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[10] Gould, Jameson, and Neilson, *Proc. Chem. Soc.*, 1960, 314.
[11] Bobtelsky and Bar Gadda, *Bull. Soc. chim. France*, 1953, **20**, 276.
[12] Kuntzel and Trabitzsch, *Z. anorg. Chem.*, 1959, **302**, 10.
[13] Hall and Dean, *J. Amer. Chem. Soc.*, 1958, **80**, 4183.
[14] Chabarek, Courtney, and Martell, *J. Amer. Chem. Soc.*, 1953, **75**, 2185.
[15] Courtney, Gustavson, Chabarek, and Martell, *J. Amer. Chem. Soc.*, 1958, **80**, 2121.
[16] Kondo and Kubo, *J. Phys. Chem.*, 1958, **62**, 1558.
[17] Hall, Dean, and Pacofsky, *J. Amer. Chem. Soc.*, 1960, **82**, 3303.

than are those for the 2 : 1 complexes of any simple α-amino-acid.[18] This greater stability is also indicated by a comparison of the continuous variations plot with that measured for the copper–glycine complex,[19] and it indicates a much stronger bond between an alkyloxy-oxygen and a metal ion than between a carboxyl-oxygen and a metal ion.

There is no demonstrable trend in the stabilities of the glycine, alanine, and α-amino-butyric acid chelates with copper as the side-chain length increases.[18] In the case of the α-hydroxy-α-phenylamidines, the increasing stability may be explained by an increase in negative charge on the oxygen atom, together with an apparent increase in hydrogen bonding with the octahedral water molecules. Steric effects would be expected to be small.

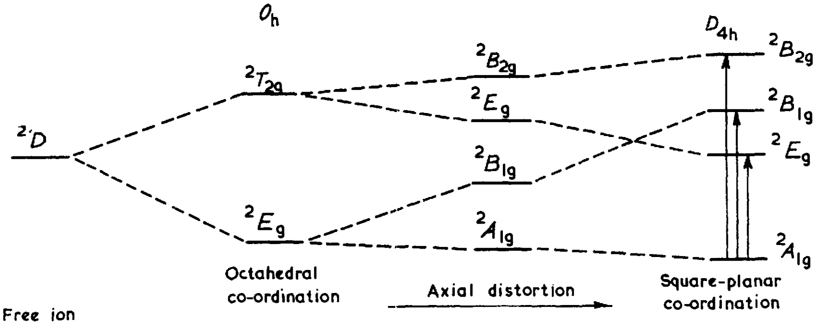

FIG. 3. Ligand-field splitting of the d^9-system in octahedral and square-planar environments.

Spectra of the Complexes.—Recently, the visible spectra of several copper(II) complexes have been interpreted in terms of the ligand-field theory.[8, 20, 21] The Cu^{2+} ion has a d^9-configuration, giving rise to a ^2D-ground state which, if spin–orbit coupling can be ignored, would be split into two terms under the influence of an octahedral field. Since, however, the Jahn–Teller effect leads to considerable tetragonal distortion of copper(II) complexes, they must in practice be regarded as distorted octahedral or approximately square-planar complexes. A representation of this splitting is given in Fig. 3, where the $^2T_{2g}$ term is placed higher than the ^2E_g since the behaviour of a d^9-configuration is conveniently considered as a d^1-hole configuration.

Thus, if there is no further distortion, three transitions will be expected whether the symmetry is essentially square-planar or distorted octahedral. On this basis, therefore, Belford, Calvin, and Belford [20] divided the visible absorption spectra of the acetylacetone and ethyl-acetylacetone chelates of copper in solution in several polar and non-polar solvents into three gaussian components, and assigned them by consideration of the field effects to be expected as the solvent was changed. While this procedure has been adopted by other workers,[21] Graddon [8] pointed out a band of intermediate intensity ($\varepsilon \approx 300$) in the region of $2{\cdot}7\ \mu^{-1}$ in the spectra of the ethyl acetoacetate complexes of copper(II), and showed that the band in the visible region could equally be divided into two components.

Ferguson [22] accepted this assignment of the band at $2{\cdot}7\ \mu^{-1}$, but showed that it is incorrect to treat the ligand field as having the D_{4h} symmetry, which the above argument assumes, but that D_{2h} (or C_{2v}) symmetry is a much better approach. This removes the degeneracy of the doublet level and gives rise to four transitions. While Piper and

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[18] Bjerrum, Schwarzenbach, and Sillén, "Stability Constants," *Chem. Soc. Special Publ. No.* 7 Part I, pp. 8, 15, 25.

[19] Gould and Vosburgh, *J. Amer. Chem. Soc.*, 1942, **64**, 1630.

[20] Belford, Calvin, and Belford, *J. Chem. Phys.*, 1957, **26**, 1165.

[21] Royer, *J. Inorg. Nuclear Chem.*, 1959, **11**, 151.

[22] Ferguson, *J. Chem. Phys.*, 1961, **34**, 1609.

Belford[23] came to a similar conclusion regarding the symmetry of the complex, they questioned the assignment of the high-energy band as a *d–d* transition. They also emphasised that the ground state of these complexes in fact corresponds to a " hole " in the d_{xy}-orbital (*i.e.*, $^2B_{1g}$ symmetry) although the order of the other levels is difficult to ascertain with certainty.

The identification of four *d–d* transitions within the envelope in the visible region had, however, not been possible until the recent low-temperature work of Basu, Belford, and Dickerson.[24] The spectrum of single crystals of di-(3-phenylacetylacetonato)copper(II) at liquid-nitrogen temperatures contains four partially resolved bands in the visible region, which the authors tentatively ascribe to the required *d–d* transitions, and a more intense band corresponding to that observed by Graddon,[8] at 2·3 μ^{-1}. At room temperature, this band persists, but the four former bands are replaced by two broad bands with maxima at 1·6 and 1·9 μ^{-1}.

In the case of the α-hydroxy-amidine complexes with copper, the asymmetric field would again imply four transitions. The entire envelope is considerably shifted to the violet from that observed by Graddon,[8] and if any *d–d* transition did occur in the near-ultraviolet region, it would be swamped by the tail of a transition, due to the ligand, which occurs in pentanol solution at about 3·7 μ^{-1} ($\varepsilon \approx 37{,}000$). Fig. 3 and Table 2 show clearly that the envelope is consistently divided into two gaussian components, and, while a sub-division of each is, of course, possible, it would not be unique. Similarly, in the spectra studied by Royer,[21] a division into two components is as satisfactory as his adoption of three. One is thus led to the conclusion that examination of spectra obtained at room temperature is of limited value, since the transitions expected are of similar energy, and thermal broadening of the bands makes unambiguous resolution impossible.

It appears, therefore, that the spectra obtained at room temperature of essentially square-planar copper complexes examined so far may be divided empirically into two simple components, and attempts to divide the envelope further cannot be justified at the present stage of theoretical development. Further work on glasses and single crystals at low temperatures must be undertaken to determine whether these bands are a significant combination of the more highly resolved bands found under those conditions.

EXPERIMENTAL

Apparatus.—The apparatus used for the measurement of pH is described in Part I.[1] As the values of pH measured were lower, 0·05M-potassium hydrogen phthalate was used to standardise the meter. A Cambridge pen-recording polarograph with thermostatic control was used for the polarographic measurements. Visible and near-ultraviolet spectra (300—800 mμ) were measured on an Optica CF-4 spectrophotometer, manually operated, and near-infrared spectra (800—2000 mμ) on a Unicam S.P. 700 instrument. Magnetic-susceptibility measurements were made at room temperature with a Gouy balance with a permanent magnet and calibrated with powdered nickel ammonium sulphate hexahydrate.[25]

Preparation and Analysis of Materials.—The preparations of (±)-mandelamidinium, (±)-atrolactamidinium, and (±)-α-hydroxy-α-phenylbutyramidinum chloride and of carbonate-free 0·25M sodium hydroxide are described in Part I.[1] Standard 0·1M-copper(II) solution was prepared by dissolving the appropriate weight of cupric sulphate pentahydrate in ~1·0M-hydrochloric acid. This solution was analysed for copper by using 0·1M-ethylenediaminetetra-acetic acid with PAN indicator, copper foil being used as a primary standard. The acid content was determined by passing the sample through a column of Amberlite 200 on the hydrogen cycle, and titrating the eluate with standard sodium hydroxide.

The aqueous solutions for spectrophotometry were prepared by adding an excess of sodium hydroxide to a 5 : 2 mixture of amidinium and cupric chlorides, the pentanol solutions by extraction from water followed by drying over sodium sulphate, and the methanol, formamide,

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[23] Piper and Belford, *Mol. Phys.*, 1962, **5**, 169.

[24] Basu, Belford, and Dickerson, *Inorg. Chem.*, 1962, **1**, 438.

[25] Cossee, *J. Inorg. Nuclear Chem.*, 1960, **14**, 127.

and piperidine solutions directly from the solid complexes. All solutions were analysed for copper by the method of Callan and Henderson,[26] the absorption of the diethyldithiocarbamate complex being measured at 445 mμ. Solutions in water-miscible solvents (~0·01M in copper) were diluted by a factor of 25, a small amount of dilute sulphuric acid being added to decompose the complex, and aliquot parts (10 ml.) were taken for analysis. Since pentanol is immiscible with water, 50% aqueous methanol was used for its initial dilution. That neither the organic solvents nor the amidines interfered with the analysis was shown by their addition to standard copper(II) solutions, which then gave no appreciable deviation from the calibration curve prepared from solutions free from organic materials.

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[*Received, May* 11*th*, 1962.]

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[26] Callan and Henderson, *Analyst*, 1929, **54**, 650.