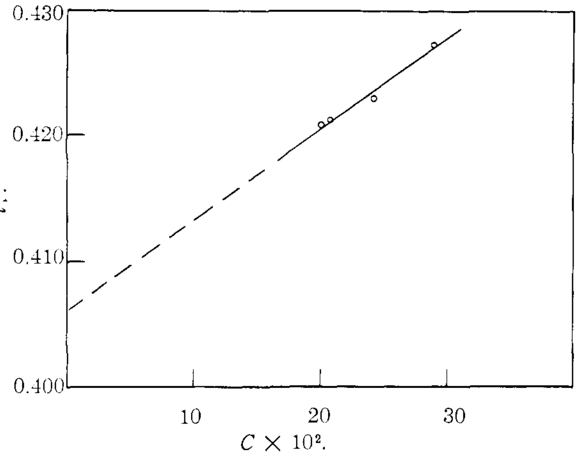

Fig. 1.—The concentration dependence of the Longsworth function for potassium chloride in formamide.

ductances become $\lambda^0_{K^+} = 12.1$, and $\lambda^0_{Cl^-} = 17.6$. Similarly from a value of 27.9 ohms^{-1} cm.$^{-2}$ equiv.$^{-1}$ for the limiting equivalent conductance of hydrogen chloride in formamide at 25°, and $\lambda^0_{Cl^-} = 17.6$, the calculated λ^0 value for the solvated hydrogen ion is 10.3 and its transference number is 0.37.

In passing from water ($t^0_{K^+}$ in KCl = 0.49) to formamide solutions the limiting transference number of the potassium ion in potassium chloride is decreased 17%. The relatively larger solute–solvent interaction with the potassium ion in the latter solvent probably is an ion–dipole effect resulting from the greater dipole moment of the formamide.[7] Evidence that the large dipole moment of formamide produces strong ion–dipole forces appears also in the decrease in transference numbers of the solvated proton from 0.82 in water to 0.37 in formamide. In formamide dissociated protons are held by the solvent molecules with sufficient force to prevent easy transfer from molecule to molecule as occurs in aqueous solutions.

The limiting equivalent ionic conductance–viscosity products for the potassium ion at 25°, in ohm^{-1} cm.^{2} equiv.$^{-1}$ poise, in methanol, ethanol, formamide and water are 0.283, 0.255, 0.400 and 0.656. A complete explanation of the relative magnitudes of these values would involve not only direct ion–solvent interactions but also short-range viscosity effects resulting from the influence of the ions in modifying the normal solvent structure.

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The Copper(II)–Pyridine Complexes and their Reaction with Hydroxide Ions

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The formation constants have been evaluated at an ionic strength of 1.0 and 25.0° for the reactions: $Cu^{++} + py \rightleftarrows Cupy^{++}$, $Cu^{++} + 2py \rightleftarrows Cupy_2^{++}$, . . ., $Cu^{++} + 5py \rightleftarrows Cupy_5^{++}$. The values found are 3.92×10^2, 2.14×10^4, 8.5×10^5, 3.5×10^6 and $1.0_6 \times 10^7$, respectively. Mixtures of these complexes react with hydroxide to form a dimer: $py_2Cu(OH)_2Cupy_2^{++}$. The constant for the reaction $2Cu^{++} + 2OH^- + 4py \rightleftarrows py_2Cu(OH)_2Cupy_2^{++}$ is $5.1 \times 10^{+24}$. The absorption spectra of each of the complexes were determined and the spectral behavior of the solutions was found to be in accordance with the interpretation based upon equilibrium concentration measurements.

Recent publications have described the formation of mixed hydroxy complexes of copper(II) with ethylenediaminetetraacetate,[2] ethylenediamine,[3] 1,10-phenanthroline,[4] α,α'-dipyridyl[5] and ammonia.[6] The hydroxide was shown to occupy a fifth or sixth coördination position on the copper in the case with bis-ethylenediamine and ethylenediaminetetraacetate. However, with 1,10-phenanthroline and α,α'-dipyridyl the coördination of copper is lower (excluding water) as only one molecule of the bidentate ligand per copper was observed in the mixed complexes. The existence of the hydroxy ammonia complex[6] was inferred from spectral evidence and its composition was assumed to be $Cu(NH_3)_3OH^+$. Only in the case of ethylenediaminetetraacetate was the constant for the formation of the mixed complex evaluated. This was found to have a pK of 11.3 for the reaction

$$CuY^= + OH^- \rightleftarrows CuYOH^\equiv$$

The reactions of the copper–pyridine complexes were investigated in order to throw more light on the nature of the reactions of the copper ammines with hydroxide. Pyridine was chosen because it is a monodentate ligand and its activity in aqueous solutions can be determined very easily by measuring the distribution into toluene. The conventional pH method of Bjerrum[7] cannot be used in the present case to determine the nature and stability of the mixed complexes because the pyridinium ion does not exist in appreciable quantities at the pH values optimum for the reaction with hydroxide. In Bjerrum's method the concentration of

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[3] H. B. Jonassen, R. E. Reeves and L. Segal, THIS JOURNAL, **77**, 2748 (1955).

[4] R. T. Pflaum and W. W. Brandt, *ibid.*, **76**, 6215 (1954).

[5] T. Wagner-Jauregg, B. E. Hackley, Jr., T. A. Lies, O. O. Owens and R. Proper, *ibid.*, **77**, 922 (1955).

[6] J. Bjerrum, C. J. Ballhausen and C. K. Jorgensen, *Acta Chem. Scand.*, **8**, 1275 (1954).

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

the pyridinium ions in the solution must be known so that the concentration of free pyridine can be determined using the measured *p*H.

It is necessary to know the stabilities of the copper–pyridine complexes before their reaction with hydroxide can be assessed. Bruehlman and Verhoek[8] report values of 2.52, 1.86, 1.31 and 0.85 for the logarithms of the successive stepwise formation constant in 0.50 *M* potassium nitrate, 0.100 *M* nitric acid and 0.0300 *M* cupric nitrate at 25°. Bjerrum and Nielsen[9] report corresponding values of 2.41, 1.88, 1.14 and 0.60 in 0.50 *M* pyridinium nitrate at 25°. However, because of a change in the experimental conditions in the present work it was deemed necessary to redetermine these constants. Distribution and *p*H measurements both were used to evaluate the formation constants in 0.99 *M* potassium nitrate, 0.030 *M* cupric nitrate and 0.0110 *M* pyridinium nitrate at 25°. The small amount of pyridinium nitrate was used so that the formation of any hydroxy complexes through reactions such as

$$\mathrm{Cupy}_n{}^{++} + \mathrm{H_2O} \rightleftarrows \mathrm{Cupy}_m\mathrm{OH}^+ + (n - m - 1)\mathrm{py} + \mathrm{pyH}^+$$

could be detected by a discrepancy in the value of the free pyridine concentration as measured by the *p*H and distribution methods.

Experimental

Pyridine, Baker Analyzed Reagent was refluxed over barium oxide for 6 hours and then distilled. The fraction boiling over the range 113–114° at 743 mm. was collected. The redistilled pyridine was stored and transferred under a blanket of nitrogen. Solutions of known concentration were prepared by weight from the reagent.

Copper nitrate, 0.1565 *M*, was prepared from the Mallinckrodt, Reagent Grade, product and standardized electrolytically. The stock solution was made up 0.005 *M* in nitric acid to prevent hydrolysis. The amount of acid present was checked by the method of Blaedel and Panos.[10]

Perchloric acid, anhydrous, 0.500 *M* in glacial acetic acid, was prepared and standardized according to the directions of Kolthoff and Bruckenstein.[11]

Potassium nitrate, 3.05 *M*, was prepared from the Baker and Adamson reagent grade product.

Nitric acid, 0.504 *M* and sodium hydroxide, 0.1025 *M*, were prepared and standardized according to the usual procedures.

The *p*H measurements were made with a Beckman model G *p*H meter using a 1190-80 glass electrode. The instrument was standardized before and checked after a measurement with Beckman buffer at *p*H 7.00.

All solutions were prepared with air-free redistilled water and were equilibrated at 25.0 ± 0.1°.

Absorption spectra were determined using a Cary Model 14 and a Beckman DU spectrophotometer. The Beckman instrument was equipped with a cell compartment thermostated at 25.0 ± 0.2 and the Cary was in a room thermostated at 25°.

The distribution measurements were made by shaking an aqueous phase containing an initially known amount of pyridine with 15.0 ml. of toluene. The rate of equilibration was rapid. The equilibrium concentration of pyridine in the toluene phase was determined by titrating an aliquot introduced into acetic acid with the standard solution of perchloric acid. The experiments were designed so that the equilibrium volume of the aqueous phase was 30.0 ml. A preliminary run was made for each experiment to determine approximately the amount of pyridine transferred and in the final run the volume of the aqueous phase was adjusted appropriately. Also, it was necessary to know the final volume of the toluene phase to compute the results. The volume changes of the two phases accompanying pyridine transfer were calculated using values of the apparent molar volume of pyridine which were determined to be 80 ml. per mole in the aqueous phase and 76 ml. per mole in the toluene phase.

The equilibrium distribution of free pyridine between the two phases was determined in experiments in which the copper(II) nitrate was replaced by an equivalent amount of barium nitrate. At a constant ionic strength of 1.0 the distribution of free pyridine was the same within experimental error regardless of whether the solution contained 0.030 *M* barium nitrate or only pyridinium and potassium nitrates. It was found that the equilibrium concentration of free pyridine in the aqueous phase is given by the equation

$$(\mathrm{py})_{\mathrm{w}} = 0.373\ (\mathrm{py})_{\mathrm{tol}} + 0.064\ (\mathrm{py})^2_{\mathrm{tol}}$$

The standard deviation in $(\mathrm{py})_{\mathrm{w}}$ was found to be ±0.002 *M* from the results of 14 experiments throughout the range of $(\mathrm{py})_{\mathrm{tol}}$ from 0.028 *M* to 1.130 *M*.

The value of pK_{a} for the pyridinium ion was found to be 5.51 for solutions in which barium ions replaced copper(II). As above this value was found to be independent of the type of the electrolyte as long as the ionic strength remained constant.

The Copper(II)–Pyridine Complexes.—In solutions containing copper(II) the values of $\bar{n}$, the average number of molecules of pyridine combined with a copper(II) ion, were calculated from the results of the *p*H and distribution measurements using the method outlined by Bjerrum.[7] The conventional *p*H method was used on 13 solutions in which the free pyridine concentration covered the range 1.5×10^{-4} to 0.0694 *M* (values of $\bar{n}$ from 0.057 to 2.82) and the distribution measurements were made on 17 solutions covering the range 0.018 to 0.388 *M* free pyridine ($\bar{n}$ 1.87 to 4.11).[12]

The *p*H of the aqueous phase was also determined in each of the distribution experiments. To determine whether or not significant hydrolysis of the copper(II) occurred in these solutions the values of *p*H calculated assuming no hydrolysis were compared with those observed. If significant formation of hydroxy complexes occurred this would result in an increase in the pyridinium ion concentration and the observed *p*H would be lower than that calculated. The agreement between the calculated and observed values of *p*H was found to be within 0.02–0.03 unit. Positive and negative deviations were scattered randomly. This shows that in 0.030 *M* copper(II) solutions the presence of 0.0110 *M* pyridinium nitrate is sufficient to repress the formation of appreciable amounts of the hydroxy complexes.

The values of $\bar{n}$ could then be calculated directly from the data. These values showed no tendency to level off to a value of $\bar{n}$ equal to four as the pyridine concentration was increased. Plots of the data according to the method of Rossotti and Rossotti[13] indicated the existence of complexes up to $\mathrm{Cupy_5}^{++}$. Letting the symbol β_n represent the over-all formation constant for the reaction: $\mathrm{Cu}^{++} + npy \rightleftarrows \mathrm{Cupy}_n{}^{++}$, values of β_1 and β_2 were evaluated from the plots using the method of least squares to effect the extrapolation. Values of β_3, β_4 and β_5 were obtained by using the method of least squares to obtain three simultaneous equations. The values so calculated are 392, $2.14 \times 10^{+4}$, 8.5×10^5, 3.5×10^6 and $1.0_6 \times 10^7$ for $\beta_1, \ldots \beta_5$, respectively. Values of $\bar{n}$ calculated using these constants agree with those observed with an average deviation of ±2% in the range of $\bar{n}$ from 4.11 to 2.9, ±1.8% in the range 2.6 to 1.0 and ±3% in the range 0.86 to 0.056.

Absorption spectra were determined for solutions of the aquo copper(II) ion and eleven solutions covering values of $\bar{n}$ from 0.34 to 4.1. These spectra were resolved into those

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(12) At the higher values of $\bar{n}$, the distribution method was found to be more precise. At a value of $\bar{n}$ equal to four, the error of about 1% in the determination of the free pyridine concentration introduces an error of about 3% into the calculated value of *n*. At this same value of $\bar{n}$, an error of 0.02 *p*H unit in determining the *p*H introduces an error of 13% into $\bar{n}$. On the other hand, at the low values of $\bar{n}$ the *p*H measurements are better because the titration errors in the distribution experiments assume relatively large importance.

(13) F. J. C. Rossotti and H. S. Rossotti, *Acta Chem. Scand.*, **9**, 1166 (1955).

of the complexes. To do this a plot was made at each chosen wave length of the absorbance *vs.* $-\log (\text{py})_w$. A smooth curve was drawn through the points and values from this curve together with the equilibrium constants reported above were used to obtain five simultaneous equations which were solved for the extinction coefficients of the complexes. The resolved spectra are shown in Fig. 1. Values of the absorbance of mixtures of the complexes calculated from the equilibrium constants and the values in Fig. 1 agree with those observed within 1-2%.

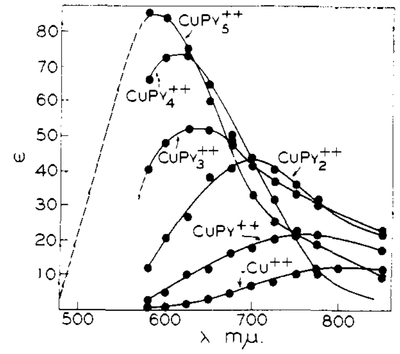

Fig. 1.—The absorption spectra of the copper(II)-pyridine complexes.

The Reaction with Hydroxide.—Most of the solutions for the study of the reaction with hydroxide were prepared in the same manner as those described above except the nitric acid was omitted, varying amounts of standard sodium hydroxide were added and the final solutions were made 1.00 *M* in potassium nitrate. Several additional distribution measurements were made on solutions which were 0.060 *M* in copper nitrate and 0.91 *M* in potassium nitrate.

It was found that the amount of sodium hydroxide taken up by the solution before the appearance of a precipitate (cupric hydroxide or basic nitrates) depends greatly on the concentration of free pyridine in the solution. Only in those solutions in which the concentration of free pyridine was 0.13 *M* or greater was it possible to add sufficient hydroxide without precipitation to obtain interpretable results. The amount of hydroxide that is held in dilute pyridine solutions was found to be less than one mole per mole of copper. However, in 10 *M* pyridine, 0.030 *M* copper nitrate it was found possible to titrate the copper with a solution of sodium hydroxide and obtain no precipitate until the molar ratio of hydroxide to copper reached 1:1.

The details for the experiments carried out in dilute pyridine solutions are given in Table I.

Calculations.—The results of the titration in 10 *M* pyridine show that copper and hydroxide react in the molar ratio of 1:1 to form a soluble complex. This stoichiometry is that most likely to be maintained in the experiments described in Table I as in these solutions there was always an excess of copper over hydroxide. Then analogous to the definition of n, the average composition of the hydroxy complexes present in a solution can be represented by the formula, $\text{Cupy}_{\bar{m}}\text{OH}^+$. The value of $\bar{m}$ can be obtained using the equations

$$(\text{Cupy}_{\bar{m}}\text{OH}^+) = [\text{OH}^-] - [\text{HNO}_3] + (\text{pyH}^+)$$
$$(\text{Cupy}_{\bar{n}}^{++}) = [\text{Cu}^{++}] - (\text{Cupy}_{\bar{m}}\text{OH}^+)$$
$$\bar{m} = \frac{[\text{py}]_w - \bar{n}(\text{Cupy}_{\bar{n}}^{++}) - (\text{py})_w - (\text{pyH}^+)}{(\text{Cupy}_{\bar{m}}\text{OH}^+)}$$

where the quantities in brackets refer to total concentrations and the quantities in parentheses refer to equilibrium concentrations. The pyridinium ion arises from hydrolysis and its concentration was calculated from pK_a and the measured values of pH and concentration of pyridine, $(\text{py})_w$. The nitric acid is from the copper nitrate stock solution. The value of $\bar{n}$ was calculated using the experimental values of $(\text{py})_w$ and the formation constants determined above.

The results of the calculations of $\bar{m}$ are presented in Table I. The deviation is calculated on the basis of an error of ±2% in the value of $\bar{n}$.

In solutions 0.030 *M* in copper(II) the value of $\bar{m}$ comes close to 2 within the experimental error.[14] Also, the values of $\bar{m}$ show no trend with increasing concentration of pyridine. Therefore, only one mixed complex of the general formula Cupy_2OH^+ appears to be formed under the present experimental conditions.

Apparent equilibrium constants, K_m and K_d, were calculated assuming monomer and dimer formation for the equilibria

$$\text{Cupy}_3^{++} + \text{OH}^- \rightleftarrows \text{Cupy}_2\text{OH}^+ + \text{py}$$

and

$$\text{Cupy}_3^{++} + \text{OH}^- \rightleftarrows {}^1\!/_2\text{py}_2\text{Cu(OH)}_2\text{Cupy}_2^{++} + \text{py}$$

These "constants" are also reported in Table I. Concentration units were used except for the hydroxide ion which is in terms of activity. The values of K_d show less relative deviation than do those of K_m. Also, better agreement is observed with the K_d values when comparing the 0.030 and 0.060 *M* copper(II) solutions. The most convincing evidence favoring the dimer formulation lies in the agreement discussed above between the calculated and observed values of pH in the distribution determination of n. The magnitude of K_m is such that the experimental values of pH should have been appreciably lower than those calculated. The value of K_d is of the correct order to agree with the observations. The difference lies in the fact that the dimer concentration varies inversely as the square of the hydrogen ion concentration and, therefore, the change of about one pH unit in the experimental conditions exerts considerable effect on the dimer concentration.

Absorption spectra were determined for solutions 5, 6 and 10 of Table I and for a solution containing 0.0313 *M* copper nitrate, 0.496 *M* pyridine and 0.0205 *M* NaOH in 1.0 *M* KNO_3. For each solution the absorbance due to py_2Cu-

TABLE I

THE REACTION OF HYDROXIDE WITH COPPER(II) IN SOLUTIONS CONTAINING PYRIDINE

Exp.	$(\text{py})_w$, moles l.$^{-1}$	$[\text{py}]_w$, moles l.$^{-1}$	pH	(pyH^+), moles l.$^{-1}$ × 10^{-3}	$(\text{Cupy}_{\bar{m}}\text{OH}^+)x$, moles Cu l.$^{-1}$	$(\text{Cupy}_{\bar{n}}^{++})$, moles l.$^{-1}$	$\bar{n}$	α_3	$\bar{m}$	K_m × 10^{-5}	K_d × 10^{-6}
1	0.135	0.228	7.39	1.77	0.0076	0.0224	3.39	0.51	2.0 ± 0.2	3.7	3.0
2	.217	.321	7.68	1.46	.0073	.0227	3.74	.38	2.4 ± .2	3.9	3.2
3	.220	.317	7.71	1.39	.01068	.0193	3.76	.38	2.2 ± .1	6.2	4.3
4	.223	.314	7.95	0.80	.0135	.0165	3.76	.38	2.1 ± .1	5.4	3.3
5	.310	.407	8.02	0.95	.0102	.0198	4.00	.28	1.7 ± .2	5.4	3.8
6	.311	.406	8.18	0.66	.0134	.0166	4.00	.28	2.1 ± .1	5.9	3.6
7	.400	.506	8.19	0.83	.0101	.0199	4.18	.21	2.2 ± .2	6.3	4.4
8	.341	.577	7.73	1.76	.0101	.0499	4.06	.24	(3.1)	5.3	3.8
9	.345	.573	7.80	1.76	.0135	.0465	4.08	.25	(2.7)	6.4	3.9
10	.348	.569	7.89	1.45	.0166	.0434	4.08	.25	(2.6)	6.9	3.8
									Av.	5.5	3.7

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[14] In the solutions containing 0.060 *M* copper(II) the values of $\bar{m}$ are slightly higher. These latter values are not as reliable because only slight changes in the distribution coefficient of pyridine or in the equilibrium constants with the slightly different conditions would bring about appreciable changes in $\bar{m}$. The equilibrium constants calculated from the results in 0.060 *M* solutions reflect these slight changes much less and can be compared directly with those calculated for the 0.030 *M* copper(II) solutions.

$(OH)_2Cupy_2^{++}$ was obtained by subtracting the calculated absorbance of the aquopyridino complexes from the observed absorbance. On a molar basis the resulting spectra are identical within the experimental error. In the visible, the curve consists of a single broad peak with a maximum at 625 mμ having an extinction coefficient of 57 ± 2 (mole copper)$^{-1}$ l. cm.$^{-1}$ (the extinction coefficient based on the dimer concentration is twice this value). The resolved absorption spectrum agreed very closely with that obtained directly for a 0.014 *M* solution of the dimer in 10 *M* pyridine. This latter spectrum exhibits a maximum at 625 mμ with an extinction coefficient of 61 (mole copper)$^{-1}$ l. cm.$^{-1}$. Considering the fact that in the former experiments all errors are lumped into the calculated extinction coefficients, the agreement is very good and lends support to the interpretation of the equilibrium data.

In addition, the absorption spectrum of the dimer has a very intense maximum at about 320 mμ. This was not investigated in greater detail, however.

Discussion

It is not surprising that the earlier workers[8,9] did not report the existence of $Cupy_5^{++}$ as this is formed in a region where not much reliance would be placed on the results of ordinary *p*H measurements with the glass electrode. The pyridine system is not unique as the ammonia and ethylenediamine–copper(II) systems also take up a fifth nitrogen[6,7,9,15] but with less ease. For example the value of the stepwise constant, K_5, for the formation of the pentammine from the tetrammine is 0.33 with ammonia[15] but is 30 with pyridine.

The spectral changes accompanying the uptake of the fifth ligand are also different with pyridine than with ammonia and ethylenediamine. These latter systems show a progressive shift of the absorption maximum to the blue with the uptake of successive ligand but with the addition of the fifth group a shift back toward the red is noted.[6,9] With pyridine the shift continues toward the blue with the uptake of the fifth group.

Qualitatively, the difference in the values of K_5 can be correlated with the positions of the absorption maxima of the pentammine on the basis of arguments taken from the crystal field theory.[16,17] The position of the absorption maximum reflects the contribution to the stability of the molecule caused by the splitting of the 3d orbitals of the metal ion by the field of the ligands. This energy is seen to be more favorable with pyridine than ammonia, resulting in a larger value of K_5. On this basis the copper–pyridine system is similar to the copper–dipyridyl and 1,10-phenanthroline systems which have been classified by Bjerrum and Jorgensen[17] as normal octahedral systems of coördination number 6. For the reaction

$$2Cu^{++} + 4py + 2OH^- \rightleftharpoons py_2Cu(OH)_2Cupy_2^{++}$$

the concentration constant is calculated to be $5.1 \times 10^{+24}$. This value was calculated using the values of K_d and β_3 reported herein and a value of 0.59 for the square of the hydroxide ion activity coefficient assuming this to be equal to the quantity $\gamma_H\gamma_{OH}/a_{H_2O}$ as reported by Harned and Owen.[18]

The aquo copper(II) ion also hydrolyzes to form a dimer,[19] the value of *pK* being 10.6 for the reaction

$$2Cu^{++} + 2H_2O \rightleftharpoons Cu(OH)_2Cu^{++} + 2H^+$$

The analogous reaction in the copper–pyridine system is

$$2Cupy_2^{++} + 2H_2O \rightleftharpoons py_2Cu(OH)_2Cupy_2^{++} + 2H^+$$

with a value of *pK* equal to 11.5 calculated using 1.7×10^{-14} as the value of the concentration product of water.[18] Thus, as might be expected the acidity of the dipyridinocopper(II) ion is less than that of the aquo ion.

The spectral changes occurring in the visible region with the formation of the hydroxy complex are similar with pyridine to those reported for 1,10-phenanthroline[4] and ethylenediaminetetraacetate.[2] No great change occurs in the position of the absorption maximum but the height of the maximum decreases with the uptake of the hydroxide ion. The position of the absorption maximum is not different in 10 *M* pyridine. This does not necessarily mean that the hydroxy complex does not take up more pyridine but may indicate that the binding is not strong as is the case with $Cu(NH_3)_6^{++}$.[6] The results with ethylenediamine[3] and ethylenediaminetetraacetate[2] lead one to expect higher complexes with higher pyridine concentration.

The very intense absorption maximum at about 320 mμ exhibited by the hydroxypyridine complex is more likely due to charge transfer.[20] The hydroxy ammonia complex exhibits an intense absorption in this same region. Very likely, the composition of this complex is similar to that of the pyridine complex.

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