

Metal Ammine Formation in Solution

XIV. Spectrophotometric Studies of the Complex Formation of Bis(diamine)copper(II) Ions with Ammonia, Butylamine and Pyridine

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Bis(diamine)copper(II) ions possess a weak tendency to bind one more amine molecule. In continuation of studies in this field the formation constants of bis(ethylenediamine)copper(II) ions with ammonia, butylamine, and pyridine were determined. It was found that the absorption bands of the bis(diamine)amine complexes all had a maximum at the same wavelength $\sim 600 \text{ m}\mu$ as those of the tris(ethylenediamine) and tris(propylenediamine) complexes. This and the fact that ethylenediamine is bound to the bis(diamine)copper(II) ion with about the same affinity as butylamine support the authors' opinion that the copper(II) ion in solution cannot exceed the coordination number 5, and that in case of the tris(diamine) complex the 3rd diamine is coordinated with only one of its amino groups.

One of the authors^{1,2} studied in 1931-32 the stepwise formation of the copper(II)ammine complexes in aqueous solution and found that the rather stable tetrammine copper(II) complex ($\beta_4 = 10^{12.3}$) possesses a weak tendency to bind one more ammonia molecule ($K_5 \sim 1/3$). Rosenblatt³ found that also the bis(ethylenediamine)copper(II) complex possesses some tendency to bind an ammonia molecule, and Bjerrum and Nielsen⁴ showed that the bis(ethylenediamine) complex with a corresponding shift of the absorption band binds a 3rd ethylenediamine molecule, but less strongly ($K_3 \sim 0.1$) than it binds an ammonia molecule. These facts give some evidence that the tris(ethylenediamine) complex instead of having a Jahn-Teller distorted octahedral configuration has the 3rd ethylenediamine molecule monodentate bound to the planar bis(ethylenediamine) complex. The spectral changes when Cu en_2^{2+} combines with ammonia, butylamine, and pyridine, and the circular dichroism spectra of the bis(*l*-propylenediamine)copper(II) complex in water, butylamine, and *l*-propylenediamine are reported in this paper and were measured in order to obtain more facts to elucidate this problem.

EXPERIMENTAL

Materials. All reagents were of good commercial quality. The butylamine (bu) was carefully dried over KOH and distilled through a column. The fraction boiling at 77.6°C was collected. The equivalent weight determined by titration with HCl was found to be 74.0. The theoretical value is 73.2. The pyridine (py) was treated in a similar way, and the fraction boiling at 115.4°C was used. The commercially available anhydrous ethylenediamine (en) was dried by double distillation over sodium, and the fraction boiling at 117.0–117.3°C was collected. The propylenediamine (pn) used in the circular dichroism experiments was partially resolved by repeated recrystallizations of the salt with D-tartaric acid.⁵ The specific rotation $[\alpha]_D^{25}$ of the base obtained by this treatment was -25.6° compared to Delépine's value for the pure enantiomer -29.7° . The boiling point of the product was 120.5–120.9°C, and the equivalent weight 73.8 (theoretical value 74.1).

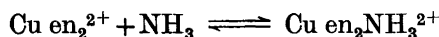
$\text{Cu en}_2(\text{ClO}_4)_2$ was prepared by mixing $\text{Cu}(\text{ClO}_4)_2$ and the base in methanolic solution in the ratio 1:2. The salt was recrystallized twice from water containing a small amount of free ethylenediamine. It was washed with acetone and kept over silicagel, and analyzed for copper by electrolysis. (Found: Cu 16.7. Calc. for $\text{Cu en}_2(\text{ClO}_4)_2$: Cu 16.6). $\text{Cu}(l\text{-pn})_2(\text{ClO}_4)_2$ was prepared in a similar way and recrystallized from alcohol. (Found: Cu 15.2. Calc. for $\text{Cu pn}_2(\text{ClO}_4)_2$: Cu 15.5).

Solutions. The copper(II)bis(diamine)-amine solutions were prepared in measuring flasks from analyzed amounts of $\text{Cu}(\text{ClO}_4)_2$ and the amines, or especially in case of the nonaqueous solutions by dissolution of weighed amounts of the bis(diamine) salt in the pure amines. The copper(II) perchlorate was prepared from copper(II)oxide and 70 % perchloric acid, and recrystallized three times from water. A stock solution of the salt as analyzed for copper by electrolysis and for perchlorate by titration of the perchloric acid after cation exchange with Amberlite IR 120, showed complete equivalence between copper and perchlorate ions. Stock solutions of ammonia were prepared carbon dioxide-free from a cylinder, and redistilled water was used in all experiments.

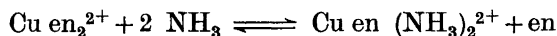
Spectral measurements. The spectrophotometric measurements were performed at 25°C with a Cary 14 and a Beckman DU spectrophotometer. The circular dichroism measurements were made with a Roussel-Jouan dichrograph, and the polarimetric measurements with a Perkin-Elmer spectropolarimeter model 141.

MEASUREMENTS AND RESULTS

The Cu en_2^{2+} , NH_3 system. Rosenblatt³ has spectrophotometrically studied the equilibrium



in strong ammonia solutions without adding a small excess of ethylenediamine to the bis(diamine) salt. For this reason his measurements are disturbed by the equilibrium



In order to examine to what extent this is the case we have studied the constancy of the isobestic point in Cu en_2^{2+} -ammonia solutions with small excess concentrations of ethylenediamine (under these conditions the formation of the tris(ethylenediamine) complex is negligible). Measurements of this kind are shown in Fig. 1, and it will be seen that a concentration of free ethylenediamine of about 0.2 M is necessary in order to have a fairly constant isobestic point for ammonia concentrations up to about 3 M. From the deviations from the isobestic point in Fig. 1 it is possible to make a rough estimate of the disproportionation constant for the mixed complex

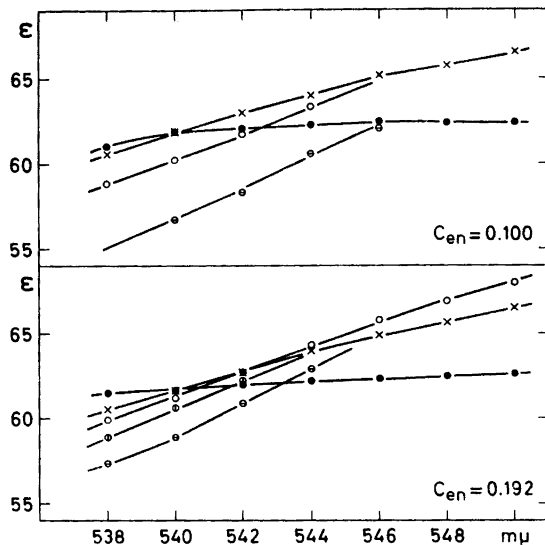


Fig. 1. Molar extinction curves for Cu en_2^{2+} -ammonia solutions in the neighbourhood of the isobestic point. The concentration of Cu en_2^{2+} is 0.0103 M, and the excess concentrations of ethylenediamine are in the upper division of the figure 0.100 M, and in the lower division 0.192 M. The signature of the points corresponds to the following ammonia concentrations: ● 0.00 M, × 1.58 M, ○ 3.43 M, ◻ 4.49 M and ⊙ 6.60 M.

$$K_M = \frac{[\text{Cu en}(\text{NH}_3)_2^{2+}]^2}{[\text{Cu en}_2^{2+}][\text{Cu}(\text{NH}_3)_4^{2+}]}$$

applying the rule of average environment, *i.e.* that the spectrum of the mixed complex is the average of those of Cu en_2^{2+} and $\text{Cu}(\text{NH}_3)_4^{2+}$. This is a reasonable assumption at the wavelength for the isobestic point 541 μ (*cf.* Fig. 2 in Ref. 4). At this wavelength the values of $\epsilon_{\text{Cu en}_2^{2+}}$ and $\epsilon_{\text{Cu}(\text{NH}_3)_4^{2+}}$ are 62 and 38, respectively. Therefore, $\epsilon_{\text{Cu en}(\text{NH}_3)_2^{2+}}$ is probably close to 50. By means of this value the concentration ratio $[\text{Cu en}(\text{NH}_3)_2^{2+}]/[\text{Cu en}_2^{2+}]$ is estimated from the deviations from the isobestic point in Fig. 1 to be ~ 0.56 in the 6.60 M ammonia solution with $C_{\text{en}} = 0.100$ M, and to ~ 0.24 in the same solution with $C_{\text{en}} = 0.192$ M. From the expressions for the stability constants of the complexes $\text{Cu}(\text{NH}_3)_4^{2+}$, Cu en_2^{2+} , and $\text{Cu en}(\text{NH}_3)_2^{2+}$ one derives the following relationship for the concentration ratio

$$\frac{[\text{Cu en}(\text{NH}_3)_2^{2+}]}{[\text{Cu en}_2^{2+}]} = \frac{K_M^{1/2} \cdot \beta_4(\text{NH}_3)^{1/2}}{\beta_2(\text{en})^{1/2}} \cdot \frac{a_{\text{NH}_3}}{[\text{en}]}$$

when $a_{\text{NH}_3} = f_{\text{NH}_3}[\text{NH}_3]$, the activity of ammonia is substituted for the ammonia concentration. $\beta_4(\text{NH}_3)$ is known to be $10^{12.3}$, and $\beta_2(\text{en})$ to be $10^{19.7}$ (in dilute solution at 25°C) and f_{NH_3} is 1.46 in 6.60 M ammonia solution (estimated from Perman's ammonia tension measurements⁶). Inserting these values

and the estimated values for the concentration ratio $[\text{Cu en}(\text{NH}_3)_2]^{2+}/[\text{Cu en}_2]^{2+}$ at the two ethylenediamine concentrations, K_M is calculated to be ~ 9 with $C_{\text{en}} = 0.100$ M, and to be ~ 6 with $C_{\text{en}} = 0.192$ M. This is to be compared with

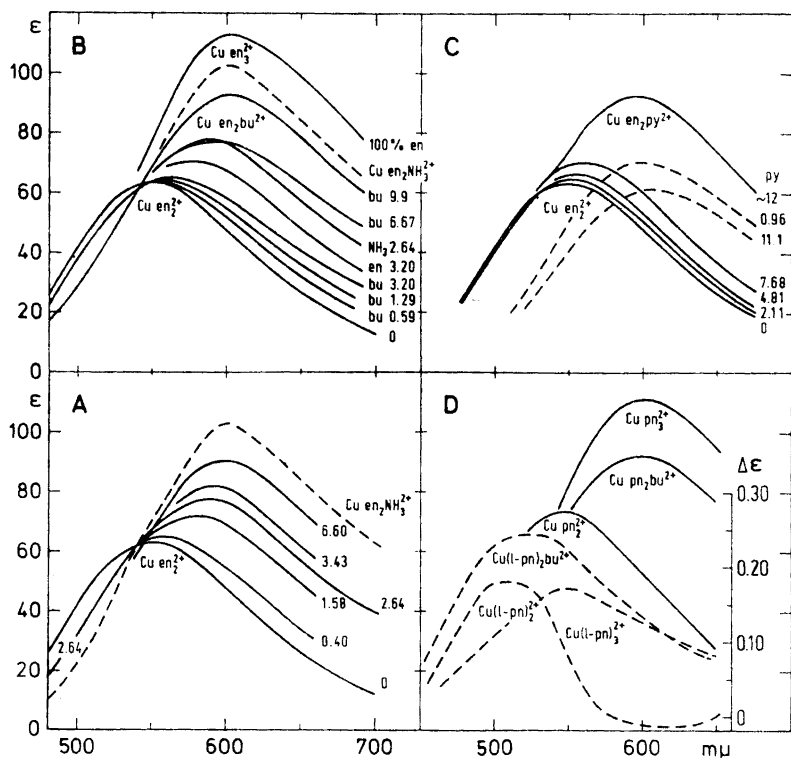


Fig. 2. Spectra of copper(II)-amine complexes at 25°C.

Part A: Molar extinction curves for $\text{Cu en}_2(\text{Cu en}_3)_2$ -ammonia solutions with $C_{\text{Cu en}_2^{2+}} = 0.0103$ M, $C_{\text{en}} = 0.0192$ M, and the following ammonia concentrations 0, 0.40, 1.58, 2.64, 3.43, and 6.60 M. The dotted curve represents the calculated absorption curve for the pentamine complex $\text{Cu en}_5\text{NH}_3^{2+}$.

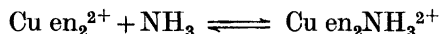
Part B: Molar extinction curves for $\text{Cu en}_2(\text{Cu en}_3)_2$ -butylamine solutions with $C_{\text{Cu en}_2^{2+}} = 0.0103$ M, $C_{\text{en}} = 0.192$ M, and the following butylamine concentrations 0, 0.59, 1.29, 3.20, 6.67, and 9.9 M (=100% butylamine). Further curves are given for Cu en_2^{2+} in 3.20 M ethylenediamine (from Ref. 4), and for 0.0089 M $\text{Cu en}_2(\text{Cu en}_3)_2$ in 100% ethylenediamine. For comparison two of the curves from part A are also repeated.

Part C: Molar extinction curves for $\text{Cu en}_2(\text{Cu en}_3)_2$ -pyridine solutions with $C_{\text{Cu en}_2^{2+}} \sim 0.01$ M, $C_{\text{en}} = 0.192$ M, and the following pyridine concentrations 0, 2.11, 4.81, 7.68, and ~ 12 M ($\sim 100\%$ pyridine). For comparison curves for 0.01 M $\text{Cu}(\text{NO}_3)_2$ in 0.96 and 11.1 M pyridine (from Ref. 9) are given.

Part D: The full-drawn curves represent the spectra of 0.01 M $\text{Cu pn}_3(\text{Cu pn}_2)_2$ in 0.2 M propylenediamine (Cu pn_3^{2+}), of the same solution in 100% butylamine ($\text{Cu pn}_2\text{bu}^{2+}$), and in 100% propylenediamine (Cu pn_3^{2+}). The dotted curves represent the circular dichroism spectra of $\text{Cu}(l\text{-pn})_3^{2+}$, $\text{Cu}(l\text{-pn})_2\text{bu}^{2+}$ and $\text{Cu}(l\text{-pn})_3^{2+}$ of the same solutions prepared from 86% resolved *l*-propylenediamine.

the statistical value of the constant, $K_M=8$. Using the statistical value, one finds that the solution of the bis(ethylenediamine) complex with $C_{\text{NH}_3}=3.43$ M and $C_{\text{en}}=0.192$ M, which shows no observable deviation from the isobestic point, contains about 4 % of the mixed complex.

In Fig. 2 A is given a family of absorption curves corresponding to the equilibrium:



Introducing the ammonia activity instead of the ammonia concentration, one gets for the formation constant of the mixed pentamine complex

$$K_{\text{NH}_3} = \frac{[\text{Cu en}_2(\text{NH}_3)^{2+}]}{[\text{Cu en}_2^{2+}] a_{\text{NH}_3}} = \frac{\varepsilon - \varepsilon_0}{\varepsilon_1 - \varepsilon} \cdot \frac{1}{a_{\text{NH}_3}}$$

ε is the extinction coefficient at the wavelength in question, ε_1 of the mixed complex and ε_0 of the bis(ethylenediamine) complex. The extinction coefficient expression for K_{NH_3} can be transformed into the form:

$$\frac{a_{\text{NH}_3}}{\varepsilon - \varepsilon_0} = \frac{1}{\varepsilon_1 - \varepsilon_0} \cdot a_{\text{NH}_3} + \frac{1}{K_{\text{NH}_3}(\varepsilon_1 - \varepsilon_0)}$$

which is a special form of the Benesi-Hildebrand equation.⁷ In Fig. 3 $a_{\text{NH}_3}/(\varepsilon - \varepsilon_0)$ is plotted *versus* a_{NH_3} for the wavelengths 600, 620 and 650 m μ , and from the slopes and the values of $a_{\text{NH}_3}/(\varepsilon - \varepsilon_0)$ for $C_{\text{NH}_3}=0$ the values for K_{NH_3} and ε_1 given in Table 1 are estimated. The data corresponding to the points in Fig. 3 are given in Table 2. It will be seen that there is some deviation from the straight lines in the Benesi-Hildebrand plots in Fig. 3 only at the smallest ammonia concentration 0.40 where $\varepsilon - \varepsilon_0$ has the relatively

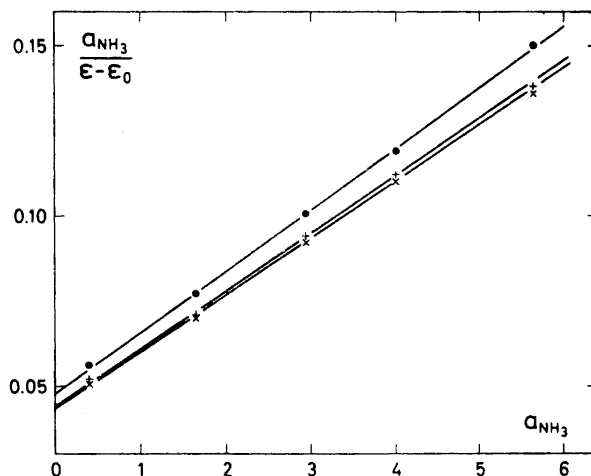


Fig. 3. Benesi-Hildebrand plots for the $\text{Cu en}_2^{2+}, \text{NH}_3$ -system at the wavelengths: 600 m μ ●, 620 m μ ×, and 650 m μ +.

Table 1.

$\lambda(\text{m}\mu)$	K_{NH_3}	ϵ_1
600	0.39	102.4
620	0.38	98.7
650	0.38	85.3

Table 2. Molar extinction coefficients of Cu en₂²⁺-ammonia solutions. Cu en₂²⁺ = 0.0103 M, C_{en} = 0.192 M, t = 25°C.

C _{NH₃}	f _{NH₃}	a _{NH₃}	540	550	580	600	620	650 mμ
0.000	1	0.000	61.6	62.6	56.1	47.4	38.5	26.1
0.396	1	0.396	61.8	63.9	61.0	54.4	46.1	33.9
1.58	1.04	1.645	61.6	66.5	72.5	68.8	61.7	49.2
2.64	1.11	2.93	61.6	67.8	78.3	76.6	70.1	57.3
3.43	1.17	4.01	61.2	68.0	80.2	81.2	74.8	61.9
4.49	1.26	5.65	60.6	68.8	83.5	85.1	80.2	67.1
6.60	1.46	9.64	58.9	67.8	87.0	89.9	86.2	73.6

highest uncertainty, and for the point corresponding to $a_{\text{NH}_3} = 5.65$ where the deviation from the isobestic point cannot be completely neglected. By the procedure described K_{NH_3} is determined under the assumption that both of the complex ions have the same activity coefficient. It is not taken into consideration that the uptake of the ammonia molecule probably is followed by a displacement of a water molecule. However, there is little reason to introduce a correction for the change in the water activity as it would only increase the constant very little (*cf.* Ref. 2, p. 14). The absorption curve for the pure pentamine complex is given in Fig. 2. The values for ϵ_1 in Table 1 are supplemented by means of the data for the solution with $C_{\text{NH}_3} = 2.64$, which, using $K_{\text{NH}_3} = 0.38$, contains 52 % Cu en₂ NH₃²⁺.

The Cu en₂²⁺, butylamine system. Fig. 2 B shows how the absorption of the Cu en₂²⁺ complex is influenced by butylamine in increasing concentrations. Up to about 4 M the absorption curves have an isobestic point at 548 mμ for $\epsilon = 63.0$. The absorption curve of Cu en₂²⁺ in pure butylamine ($C_{\text{bu}} \sim 9.9$ M) is similar to those of Cu en₂ NH₃²⁺ and Cu en₃²⁺ (in 100 % en), and deviates from that of copper(II) ions in pure butylamine which according to Bjerrum and Lamm⁸ has $\epsilon_{\text{max}} = 134$ at 630 mμ. This solution probably contains Cu bu₅²⁺. However, the three adducts of Cu en₂²⁺ all have maxima at 600 mμ, and it is therefore reasonable to assume that the curve for Cu en₂²⁺ in 100 % butylamine represents very closely the spectrum of Cu en₂bu²⁺, and that the influence of Cu en bu₃²⁺ is negligible. Under this assumption K_{bu} is estimated by means of the data in Table 3 and the relationship

$$K_{\text{bu}} = \frac{\epsilon - \epsilon_0}{\epsilon_1 - \epsilon} \cdot \frac{1}{C_{\text{bu}}} = \frac{\alpha}{1 - \alpha} \cdot \frac{1}{C_{\text{bu}}}$$

Table 3. Estimation of K_{bu} from the extinction coefficients of $Cu en_2^{2+}$ (ϵ_0), $Cu en_2bu^{2+}$ (ϵ_1) and of $Cu en_2^{2+}$ in 0.59, 1.29 and 3.20 M butylamine solutions. $C_{Cu en_2^{2+}} = 0.0103 M$, $C_{en} = 0.192 M$, $t = 25^\circ C$.

λ	ϵ_0	ϵ_1	$\epsilon_{(0.59)}$	$\epsilon_{(1.29)}$	$\epsilon_{(3.20)}$	$\alpha_{(0.59)}$	$\alpha_{(1.29)}$	$\alpha_{(3.20)}$
620	38.0	89.8	43.6	46.8	51.4	0.108	0.170	0.259
650	26.1	78.8	32.2	35.5	40.8	0.115	0.178	0.279
675	19.2	66.9	24.2	28.1	32.5	0.105	0.186	0.279
700	13.0	57.3	18.3	21.7	26.4	0.119	0.196	0.302
					$\alpha_{(bu)} \text{ av.}$	<u>0.112</u>	<u>0.183</u>	<u>0.280</u>
					K_{bu}	0.21	0.17	0.12

The activity coefficients of butylamine in aqueous solution is not known, but must be assumed to decrease with increasing amine concentration, which explains the trend in the estimated values for K_{bu} . Contrary to this the activity coefficient of the more lyophile ethylenediamine increases with increasing concentration of the base. This explains that the concentration constant K_3 in the ethylenediamine system⁴ (0.10 in dilute solution) for $C_{en} = 3.20 M$ is higher (~ 0.20) than $K_{bu} \sim 0.12$ for $C_{bu} = 3.20 M$ (compare the position of the corresponding curves in Fig. 2 B).

The $Cu en_2^{2+}$, pyridine system. Fig. 2 C shows that the absorption band of $Cu en_2^{2+}$ also in the pyridine system is shifted towards the red with increasing concentration of the base as should be expected for a tetramine-pentamine equilibrium. For comparison the absorption curves of 0.01 M $Cu(NO_3)_3$ in 0.96 M and in 11.1 M pyridine are also given. In the first-mentioned solution, according to measurements of one of the authors,⁹ the formation of $Cu py_4^{2+}$ is nearly complete and the fact that the absorption maximum of the band is not shifted towards the red in the concentrated pyridine solution shows that this complex cannot bind a 5th pyridine molecule. This is probably for steric reasons, and the decrease in the absorption maximum of $Cu py_4^{2+}$, when going from water to pyridine, was explained⁹ by ion-pair formation between the pyridinated copper(II) ion and the nitrate ion. The absorption maximum of $Cu en_2^{2+}$ in pure pyridine (with $C_{Cu} = 0.192 M$) is situated at the same wavelength as that for $Cu py_4^{2+}$, but $\epsilon_{max} = 93$ is much higher, and a rough calculation using $\beta_4(py) = 10^{6.03}$, and the activity of pyridine in the pure base ($a_{py} = 3.97$), shows that the relative amount of ethylenediamine displaced from the bis(diamine) complex must be less than 10^{-4} . Therefore, the absorption curve of $Cu en_2^{2+}$ in pyridine must be assumed to represent the curve for $Cu en_2py^{2+}$ possibly somewhat deformed due to ion association with the perchlorate ion. As it will be seen from Fig. 2 C most of the pentamine formation takes place in solutions with a high percentage of pyridine where the water activity decreases strongly for relatively small changes in the pyridine concentration. This gives strong evidence that the uptake of the pyridine molecule is followed by displacement of a water molecule from the aquated bis(diamine) complex. The pentamine constant K_{py} is estimated to be 0.059 from the

knowledge of the extinction coefficients of the pure complexes and of the solution with the lowest concentration of pyridine ($C_{\text{py}} = 2.11 \text{ M}$) by means of the relationship

$$K_{\text{py}} = \frac{\varepsilon - \varepsilon_0}{\varepsilon_1 - \varepsilon} \cdot \frac{1}{a_{\text{py}}} = \frac{\alpha_{(2.11)}}{1 - \alpha_{(2.11)}} \cdot \frac{1}{2.11 \cdot f_{\text{py}}}$$

For the solution in question f_{py} is estimated to be 0.38 from the pyridine tension measurements in Ref. 9, and the water activity is only slightly different from that of pure water. The values of the extinction coefficients for the calculation of K_{py} are given in Table 4.

Table 4. Estimation of K_{py} from the extinction coefficients of Cu en_2^{2+} (ε_0), $\text{Cu en}_2\text{py}^{2+}$ (ε_1) and of Cu en_2^{2+} in 2.11 M pyridine solution. $C_{\text{Cu en}_2^{2+}} \sim 0.01 \text{ M}$, $C_{\text{en}} = 0.192 \text{ M}$, $a_{\text{py}} = 0.80$, $t = 25^\circ\text{C}$.

λ	ε_0	ε_1	$\varepsilon_{(2.11)}$	$\alpha_{(2.11)}$
620	38.0	87.8	40.8	0.056
650	26.1	74.1	28.3	0.046
675	19.2	61.0	20.5	0.031
700	13.0	51.5	14.8	0.047
			$\alpha_{(2.11)} \text{ av.}$	0.045
			K_{py}	0.059

Spectra and circular dichroism of copper(II) propylenediamine complexes. Woldbye^{10,11} has shown that complex formation of copper(II) ions with optically active propylenediamine introduces asymmetry to the copper ion, and for both $\text{Cu}(l\text{-pn})(\text{H}_2\text{O})_2^{2+}$ and $\text{Cu}(l\text{-pn})_2^{2+}$ he has recorded the absorption curves and the optical rotatory dispersion curves. In Fig. 2 D the circular dichroism curves of the optically active bis(diamine) complex and of the two "pentammine" complexes $\text{Cu}(l\text{-pn})_3^{2+}$ and $\text{Cu}(l\text{-pn})_2\text{bu}^{2+}$ are compared with the absorption spectra of the same complexes with racemic propylenediamine, which are very similar to those of the ethylenediamine complexes. The CD spectrum found for $\text{Cu}(l\text{-pn})_2^{2+}$ has its maximum at $\sim 510 \text{ m}\mu$ in agreement with the two extrema of the ORD spectrum of the same complex measured by Woldbye^{10,11} being situated at $510 \pm 45 \text{ m}\mu$. It is further noteworthy that the CD band of $\text{Cu}(l\text{-pn})_2^{2+}$ is shifted towards higher wavelengths about as much as the absorption band, and that the shift, as could be expected, is much smaller by the uptake of an inactive butylamine molecule.

DISCUSSION

An important result of this study is that the spectra of $\text{Cu en}_2(\text{ClO}_4)_2$ in anhydrous butylamine, pyridine, ethylenediamine, and propylenediamine have a maximum at the same wavelength as found for $\text{Cu en}_2\text{NH}_3^{2+}$ in ammonia

solutions (see Fig. 2). It should also be mentioned¹² that the reflectance spectra of crystalline $[\text{Cu en}_2\text{NH}_3](\text{BF}_4)_2$ have a maximum at this wavelength ($\sim 600 \text{ m}\mu$). These facts give support to the idea that also the tris(ethylenediamine)- and tris(propylenediamine) copper(II) salts are pentamine complexes in solution with one of the diamine molecules monodentate bound to the copper ion. The formation constants for the uptake of mono- and diamines to the bis(diamine) complex also support this hypothesis. For if the planar bis(diamine) complex by uptake of the 3rd diamine molecule was changed into octahedral configuration, one must expect that the constant in question ($K_3 = 0.10$ for ethylenediamine⁴) would be substantially higher than those for monoamines. The values found for ammonia 0.38, for butylamine 0.17–0.21, and for pyridine 0.06 show that this is far from being the case.

On the other hand there is certain evidence that the solid tris(diamine) copper(II) salts have octahedral configuration. Thus D_3 symmetry has been demonstrated for $\text{Cu en}_3\text{SO}_4$,¹³ and Piper and Karipides¹⁴ have found that Cu en_3^{2+} diluted in hexagonal $\text{Zn en}_3(\text{NO}_3)_2$ has an absorption maximum at a much higher wavelength ($\lambda_{\text{max}} \sim 650 \text{ m}\mu$) and a much lower extinction coefficient ($\varepsilon_{\text{max}} 15-19$) than the pentacoordinated complex in solution. It is also of interest in this connection that Gordon and Birdwhistell from 80 % ethylenediamine have crystallized what they suppose are *d*- and *l*-forms of $\text{Cu en}_3\text{SO}_4$, and from the infrared spectra have proved that all the amino groups are coordinated to copper.

One of the authors has previously¹⁶⁻¹⁸ been unable to leave out of account the possibility that the copper(II) ion in anhydrous liquid ammonia exists as a hexamine complex irrespective of the fact that the spectrum in this solution deviates little from that of the pentamine complex in aqueous ammonia solutions. However, Tomlinson and Hathaway in a recent paper¹⁹ have given much evidence that hexamine copper(II) salts even in the solid state should be formulated as $[\text{Cu}(\text{NH}_3)_5]\text{X}_2\text{NH}_3$ with a free ammonia molecule in the lattice. Therefore, it must be assumed that copper(II) in solution cannot exceed the coordination number 5. As mentioned in the present paper as well as in earlier publications,^{3,16} there is some evidence that tetrammine ions displace a water molecule by the uptake of an amine molecule, and it is therefore reasonable to conclude that also the aquacopper(II) ion is a pentaqua complex.

In general the trigonal pyramidal is more stable than the square based pyramidal configuration, but it has been shown²⁰ that the last mentioned configuration is stabilized when the central atom is drawn out of the quadratic plane in the direction of the 5th ligand. And such a configuration²¹ with the 5th ligand at a slightly longer distance from the central atom than the four ligand groups in the plane is probably what best explains the chemical and optical properties of the copper(II) amine complexes in solution with the few exceptions where there is steric hindrance for having the four strongly bound amino groups in the same plane, as *e.g.* in case of the dipyridyl and *o*-phenanthroline complexes.^{22,23}

REFERENCES

1. Bjerrum, J. *Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd.* **11** (1931) No. 5.
2. Bjerrum, J. *Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd.* **11** (1932) No. 10.
3. Rosenblatt, F. *Z. anorg. Chem.* **204** (1932) 351.
4. Bjerrum, J. and Nielsen, E. J. *Acta Chem. Scand.* **2** (1948) 297.
5. Delépine, M. and Chéritat, R. *Bull. Soc. Chim. France* [5] **11** (1944) 320.
6. Perman, E. P. *J. Chem. Soc.* **83** (1903) 1168.
7. Benesi, H. A. and Hildebrand, J. H. *J. Am. Chem. Soc.* **71** (1949) 2703.
8. Bjerrum, J. and Lamm, C. G. *Acta Chem. Scand.* **4** (1950) 997.
9. Bjerrum, J. *Acta Chem. Scand.* **18** (1964) 843.
10. Woldbye, F. *Optical Rotatory Dispersion on Transition Metal Complexes*, European Research Office, US Army, Contr. No. DA-91-508-EUC-246, Frankfurt a.M. 1959.
11. Woldbye, F. *Studier over optisk aktivitet*, Dissertation, Polyteknisk Forlag, København 1969.
12. Tomlinson, A. A. G. and Hathaway, B. J. *J. Chem. Soc. A* **1968** 1685.
13. Cola, M., Giuseppetti, G. and Mazzi, F. *Atti Accad. Sci. Torino* **96** (1962) 381.
14. Piper, T. S. and Karipides, A. G. *Inorg. Chem.* **4** (1965) 923.
15. Gordon, G. and Birdwhistell, R. K. *J. Am. Chem. Soc.* **81** (1959) 3567.
16. Bjerrum, J. *Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd.* **12** (1934) No. 15, p. 53.
17. Bjerrum, J. *Metal Ammine Formation in Solution*, P. Haase and Son, Copenhagen 1941, p. 109.
18. Bjerrum, J., Ballhausen, C. J. and Jørgensen, C. K. *Acta Chem. Scand.* **8** (1954) 1275.
19. Tomlinson, A. A. G. and Hathaway, B. J. *J. Chem. Soc. A* **1968** 1905.
20. Zemann, J. *Z. anorg. Chem.* **324** (1963) 241.
21. Jørgensen, C. K. *Biochemistry of Copper*, Academic, London 1966.
22. Jørgensen, C. K. *Acta Chem. Scand.* **9** (1955) 1366.
23. Dwyer, F. P., Goodwin, H. A. and Gyarfas, E. C. *Australian J. Chem.* **16** (1963) 544.

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