Studies on the Complex Formation of N,N-Diethylglycine with Copper(II) in Acetonitrile

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The formation of copper(II) complexes with N,N-diethylglycine in acetonitrile has been investigated by visible, infrared as well as NMR spectral techniques. It has been found that 1:1 and 1:2 complexes are formed. In both compounds nitrogen and carboxyl oxygen of ligand molecules are involved in coordination. The stability constants are reported.

Untersuchungen von Kupfer(II)-Komplexen mit N,N-Diethylglycin in Acetonitril

Die Bildung von Kupfer(II)-Komplexen mit N,N-Diethylglycin in Acetonitril wurde mit Hilfe von UV-VIS, IR- und NMR-Spektroskopie untersucht. Es wurde festgestellt, daß sich Komplexe der Zusammensetzung 1:1 und 1:2 bilden. In beiden Verbindungen koordinieren Stickstoff und Carboxylsauerstoff der Liganden. Die Stabilitätskonstanten wurden bestimmt.

Introduction

A number of papers on the copper complexes of amino acids have appeared in the literature in recent years. The complexes of transition metals with amino acids are of interest because of the biological importance of this family of compounds and the presence of potential coordinating amino and carbonyl groups. But only a few copper(II) complexes of the amino acids derivatives such as N,N-dimethylglycine and N,N-diethylglycine have been reported[1-8] (mainly for N,N-dimethylglycine). Moreover, as far as we know, no attempt has been made to study their chemistry of complex equilibria in nonaqueous solvents exept for water-organic solvent mixtures[4,5].

In order to explain the nature (mode of coordination, stability, and

composition) of the copper(II) complexes with N,N-diethylglycine sodium salt (*DEG*) in acetonitrile, the investigation by visible, infrared and NMR spectral techniques has been carried out.

Experimental

Acetonitrile (Mallinckrodt AR) was refluxed over sodium hydride and then distilled. The distillate was treated with P_2O_5 and again distilled. The product was next refluxed over calcium hydride and also distilled. The first 10% and last 10% of each distillate volume was rejected.

Hexaaquocopper(II) perchlorate was recrystallized from water and then dried under vacuum condition at about 70 °C for 24 h. The content of water in this salt was determined by means of indirect titration with *EDTA* using murexide as an indicator[18]. The result of titration indicates that $Cu(ClO_4)_2 \cdot 3 H_2O$ was obtained.

Lithium perchlorate (G. Frederick Smith Chemical Co.) was recrystallized once from water, then dried in a vacuum drier at about 70 °C for one day.

N,N-diethylglycine sodium salt (Eastman Organic Chemicals) was re-crystallized from the water-acetonitrile mixture. 1 ml of water was added to about 0.2 g of the compound in a seperatory funnel. Then 50 ml of acetonitrile were added to the above solution and the slightly yellow water phase was separated. It was made immediately after the addition of acetonitrile. The fine white crystals of the salt were being formed in the upper acetonitrile phase. The separated crystals of the sodium salt were washed with ether and then dried in vacuo at about 70 °C for one day. This very hydroscopic compound was stored over P_2O_5.

Visible spectra were obtained with a Cary Model 14 spectrophotometer. For all measurements at a chosen wavelength a Beckman DB (manual) spectropho-tometer was used. Infrared spectra were recorded with a Perkin-Elmer Model 421 spectrophotometer. Ligand and complexes were examined in solution using calcium fluoride cells.

The NMR measurements were made with Varian EM 360 60 MHz spectro-meter using CD_3CN as solvent.

Complexes are prepared by mixing of the proper volumes of the ligand and $Cu(ClO_4)_2$ solutions. The ion strength for all samples was 0.1. It was kept by adding the calculated amount of $LiClO_4$ in acetonitrile.

Results and Discussion

The N,N-diethylglycine sodium salt is practically insoluble in acetonitrile, but when some lithium perchlorate is added to the solvent, the solution up to 0.1 *M* can be obtained, if the concentration of $LiClO_4$ is high enough. According to literature data a complex between Li^{+} and solvent is formed[15] by polarization of the nitrile bond. Therefore, the solvation properties of the system are changed. Lithium forms the complex with acetonitrile interacting with nitrogen of solvent molecule at which a free electron pair is located. This causes shifts of ^{1}H and ^{14}N signals of acetonitrile. The formation of the compound
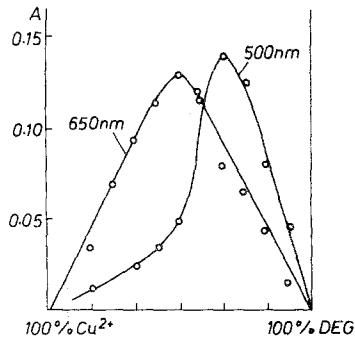
Fig. 1. *Job*'s method of continuous variations for the Cu^{2+}/DEG system; $[Cu^{2+}] + [DEG] = 0.6 \cdot 10^{-2} M$
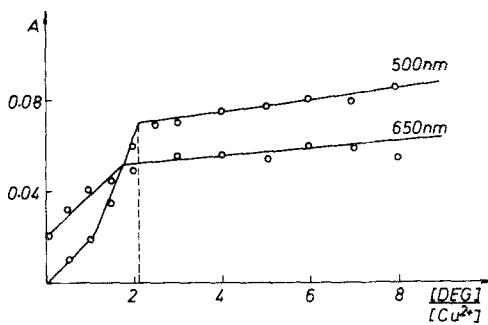

Fig. 2. Curves of the molar ratio method for the Cu^{2+}/DEG system; $[Cu^{2+}] = 1.0 \cdot 10^{-3} M$

Table 1. *Visible spectral data of* Cu^{2+} *and its complexes with N,N-diethylglycine in acetonitrile*

Concentration of Cu^{2+} (M)	$\dfrac{[DEG]}{[Cu^{2+}]}$	λ_{max} (nm)
$2.5 \cdot 10^{-3}$	without ligand	760
$2.5 \cdot 10^{-3}$	1:1	660-670
$2.5 \cdot 10^{-3}$	2:1	560-570
$2.5 \cdot 10^{-3}$	3:1	550 560
$1.25 \cdot 10^{-3}$	4:1	550-560
$1.25 \cdot 10^{-3}$	6:1	550-560
$1.25 \cdot 10^{-3}$	8:1	550-560
$1.25 \cdot 10^{-3}$	10:1	550-560

CH_3—$C \equiv N^{\delta-} \cdots Li^+$ is similar to that described by *V. Gutmann* and *R. Schmid*[16]. There is a posibility of complex formation between Li^+ and amino acid but no evidence has been found that such a complex exists in this system.

The copper(II) ion forms with N,N-diethylglycine a stable deep blue-coloured complex in acetonitrile. The results of visible spectra measurements are given in Table 1. Very broad bands are formed.
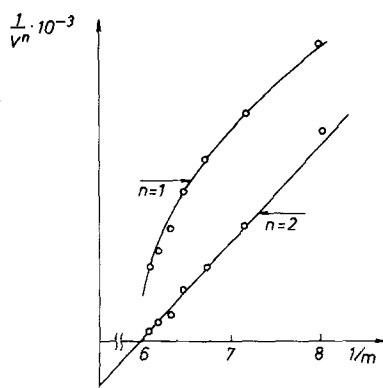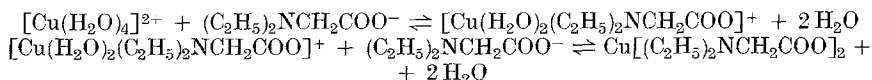

Fig. 3. *Asmus* method for the Cu^{2+}/DEG system; $V = 10^{-2}\,dm^3$, $v_0 = 0.5\,cm^3$, $a_0 = 2.5 \cdot 10^{-2}\,M$, $\lambda = 550\,nm$

The maxima of adsorption are shifted from 760 nm in the case of $[Cu(H_2O)_4]^{2+}$ ion to about 550-560 nm in the case of the solution of complex with large excess of the ligand.

Considering the shape of the curves and the change in positions of the absorption maxima the conclusion may be drawn that several species exist simultaneously in the system. The results presented in Table 1 indicate that the highest complex in the system is a 2:1 one. This conclusion is in good agreement with results obtained from the study of composition using *Job's*, the molar ratio and *Asmus* methods[9]. From the results of composition study presented in Figures 1, 2 and 3 one can conclude that the complexes of molar ratio 1:1 and 2:1 exist simultaneously in the system. The shapes of the molar ratio and *Job's* methods curves taken at 500 nm also confirm that there are two complex species.

The following succesive equilibria may be proposed for the system:

$$[Cu(H_2O)_4]^{2+} + (C_2H_5)_2NCH_2COO^- \rightleftharpoons [Cu(H_2O)_2(C_2H_5)_2NCH_2COO]^+ + 2\,H_2O$$
$$[Cu(H_2O)_2(C_2H_5)_2NCH_2COO]^+ + (C_2H_5)_2NCH_2COO^- \rightleftharpoons Cu[(C_2H_5)_2NCH_2COO]_2 + 2\,H_2O$$

It is assumed that acetonitrile does not exchange water because of the higher donors number of the latter[17].

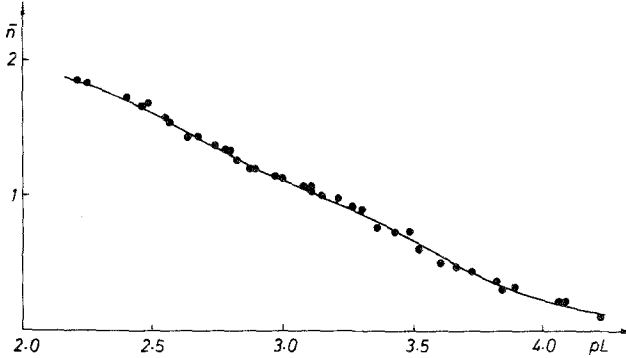*Bjerrum's* corresponding solution method has been applied to determine the consecutive formation constants[10,11].

Fig. 4. Formation curve of the complex of Cu^{2+} with *DEG* obtained applying *Bjerrum's* "corresponding solutions" method; $c_M = 1.0 \cdot 10^{-3} M$, $c_M = 4.0 \cdot 10^{-3} M$, $\lambda = 600\,nm$
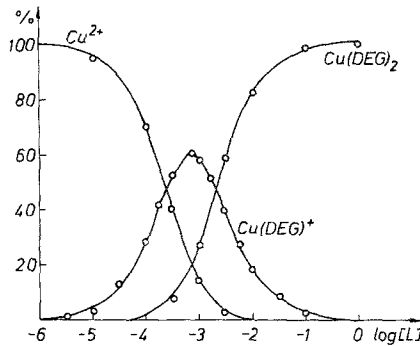

Fig. 5. Percentage composition of various species for the Cu^{2+}/DEG system

The formation curve is shown in Fig. 4.

Curves obtained for different concentration of metal are very close indicating that no polynuclear complexes are formed in the system (within the concentration range under study). The formation constants have been found applying a so-called "correction-term"[12]. The average values of constants are:

$$k_1 = 3.98 \cdot 10^3 \text{ and } k_2 = 4.60 \cdot 10^2$$

Using *Rossotti*'s graphical approximation function[13], the value of k_1 has been also found. Plotting $\dfrac{\bar{n}}{(1-\bar{n})[L]}$ against $\dfrac{(2-\bar{n})[L]}{1-\bar{n}}$ the sector x gives the value of k_1. The average value of the above constant is $3.88 \cdot 10^3$. All data needed for calculation were taken from *Bjerrum*'s formation curves. It should be noted that k_1 and k_2 are the apparent constants.
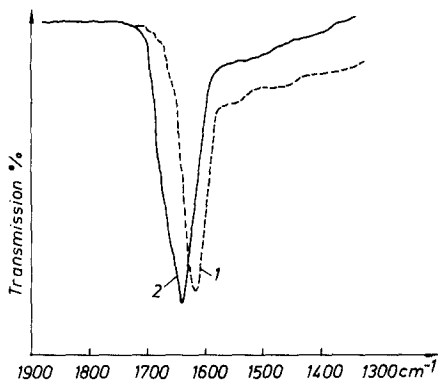

Fig. 6. Infrared absorption spectra of: 1 = *DEG*, 2 = Cu²⁻ with *DEG* complex in acetonitrile

The distribution of Cu²⁺ between particular complexes has been calculated from *Schwarzenbach*'s equations

$$\alpha = \frac{[M]}{[M]} + \frac{[ML]}{[M]} + \frac{[ML_2]}{[M]} = \frac{c_M}{[M]}$$

c_M = total concentration of metal

$$\alpha = 1 + k_1[L] + k_1 k_2 [L]^2$$

Results are presented in Fig. 5.

The site of coordination of Cu(II) ion to N,N-diethylglycine has been determined by infrared as well as by NMR spectral studies.

In the infrared region the free ligand shows a strong absorption bond at $1{,}615 \text{ cm}^{-1}$ which can be assigned to the carboxylate group[14]. For the both complex species (1:1 and 2:1), the bond is shifted to $1{,}640 \text{ cm}^{-1}$ (Fig. 6).

Some structural information has been also obtained from NMR investigation. The coordination sites have been determined on the ground of selective broadening of signals occuring when complexes are

formed[19-21]. Although a definite conclusion cannot be drawn from the line-broadening[22,23] out NMR investigations support previous absorption spectral studies that nitrogen and oxygen as well, are involved in coordination. When small amounts of copper(II) ion are gradually added to a solution containing $0.1 \, mol/dm^3$ of the ligand, the signals (singlet at 3.08 ppm and quartet at 2.63 ppm $J = 6.8 \, c/s$) originating
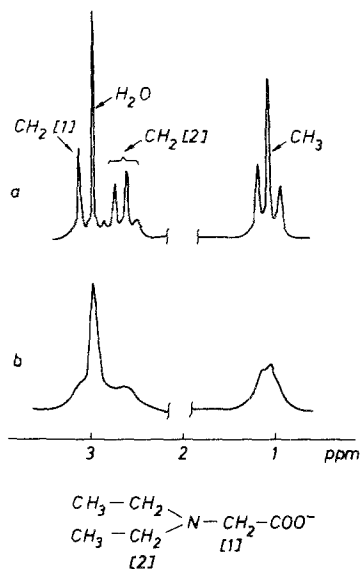
Fig. 7. The NMR spectra of $0.1 \, M \, DEG$ solution in CD_3CN (a) and of $0.1 \, M$ DEG solution in the presence of $0.003 \, M$ of $Cu(II)$ (b)

from protons of the different methylene groups as well as from the methyl group protons (triplet at 1.02 ppm $J = 7.2 \, c/s$) are broadened (Fig. 7) and finally disappear. First the signals coming from methylene groups decay, as it could be expected on the ground of their distance from the site of coordination.

On the basis of investigation described above and consideration of molecular models, it has been found that "*trans*" complexes are formed.
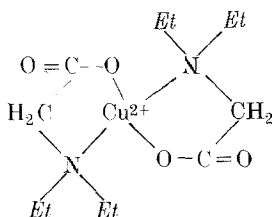
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