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NMR Relaxation Studies in Solutions of Transition Metal Complexes. VIII. Equilibrium Dynamics in Aqueous Solution of Copper(II)–N-methylethylenediamine, -N,N'-dimethylethylenediamine and -N-methylglycine Systems

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The equilibrium relations and the dynamics of equilibria have been studied in aqueous solutions of copper(II)–N-methylglycine, -N-methylethylenediamine and -N,N'-dimethylethylenediamine systems in 1 M *KCl at 25 °C. It is shown that CuL_2OH and CuL_3 complexes are also formed in the copper(II)–N-methylglycine system, beside the CuL and CuL_2 parent complexes; their formation constants are given. The paramagnetic relaxation times determined for the different protons in the coordination sphere suggest that the OH^- ligand is axially coordinated to the copper(II) ion.*

The difference in the ligand exchange rate constants of some diamine and aminoacid complexes is interpreted by the formation and dissociation of the tris complexes, with an upper limit of $\sim 10^8$ s^{-1} rate constant for the Jahn–Teller inversion of the complexed copper(II) ion.

Introduction

The results of a comparative study of the dynamics of equilibria in aqueous solutions of some copper(II) complexes, including copper(II)–glycine and copper(II)–ethylenediamine systems, have been reported in the first two parts of this series [1, 2]. The paramagnetic relaxation times for the labile -NH_2 protons of a number of copper(II) complexes, the ligand exchange rate constants and, in some cases, the rate constants of the proton exchanges within the diamagnetic environments, are available from the earlier relaxation studies.

The aim of our present work is to get information on the effect of N-methyl substituent on the parameters representing the dynamics of equilibria in aqueous solution of the copper(II) complexes. Some NMR relaxation measurements have already been carried out by Griffel [3] in the case of the N-methyl substituted ethylenediamines, but this work indicates only qualitatively the exchange rate decreasing effect of the methyl substituents.

The most important condition for studying the dynamics of equilibria is to know exactly the composition and stability of the complexes formed in the system under the same condition which is used for NMR relaxation studies. Thus, beside the kinetic studies, equilibrium measurements have also been carried out pH-metrically and spectrophotometrically. The results of the equilibrium studies are also reported in the present paper.

Experimental

The equilibrium studies have been carried out pH-metrically at 25 °C in 1 *M* KCl using a Radiometer PHM-52 pH-meter with a GK 2301 B combined electrode. The method of Irving *et al.* [4] was adopted to calibrate the electrode system. 2–3 titration curves at different (0.003–0.01 *M*) total ligand concentrations were measured for the calculation of the protonation constants. 4–6 titration curves were measured at different total metal (0.002–0.008 *M*) and total ligand (0.004–0.02) concentrations for the calculation of the formation constants.

The systems have also been studied photometrically to get the

$$K_3 = \frac{[CuL_3]}{[CuL_2][L]}$$

stepwise formation constant. In this case the total copper(II) concentration varied between 0.003–0.01, while the total ligand concentration varied between 0.01–1.5 *M*.

A Newport N-20 type instrument working at 2.5 MHz frequency was used to measure the T_2 relaxation time of water protons by the single echo [5] technique, at 25 °C in 1 *M* KCl.

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TABLE I. Logarithm of the Formation Constants of the Species Formed in the Systems together with Comparable Data from the Literature.

$$\beta_{M_xA_yH_z} = \frac{[M_xA_yH_z]}{[M]^x[A]^y[H]^z}$$

	N-methylglycine				N-methylethylenediamine				N,N'-dimethylethylene-diamine		
	a	b	c	d	a	e	f	g	a	f	g
H A	10.14	10.14	–	–	10.34	10.40	10.14	–	10.32	10.17	–
H_2A	12.42	12.44	–	–	17.79	17.96	17.40	–	17.79	17.47	–
CuA	7.80	–	7.85	7.94	10.56	–	–	10.40	10.27	–	10.10
CuA_2	14.24	–	14.46	14.59	19.38	–	–	19.09	17.58	–	17.26
$Cu_2A_2H_{-2}$	–	–	–	–	–	–	–	–	7.13	–	7.81
CuA_2H_{-1}	2.94	–	–	–	–	–	–	–	–	–	–
$CuAH_{-2}$	–	–	–	–	–	–	–	–	–	–	−9.01
CuA_3	13.78*	–	–	–	–	–	–	–	–	–	–

[a]Present work. [b]25 °C, 0.5 *M* KCl [8]. [c]25 °C, 0.01 *M* [9]. [d]25 °C, 0.1 *M* $NaClO_4$ [10]. [e]25 °C, 0.5 *M* KNO_3 [11]. [f]25 °C, 0.5 *M* KNO_3 [12]. [g]25 °C, 0.5 *M* KNO_3 [13]. *K_3 = 0.35 ± 0.07 from the photometric measurements.

Our own modified program [6, 7] was used for the evaluation of equilibrium measurements. The evaluation of the NMR measurements was based on the least squares treatment of the logarithm of T_2 data, according to the models described in the following section.

Results and Discussion

Equilibrium Studies

The results of the equilibrium studies are summarized in Table I, together with comparable data from the literature.

The standard deviation of our data for the protonation constants and for the CuL complexes is ~0.01, for the CuL_2 complexes is ~0.02 and for the hydrolized species is ~0.05 log units. The agreement between our data and the data from the literature is in general satisfactory, if the difference in the composition and concentration of the background electrolyte is taken into account. Some differences, however, should be mentioned.

i) There is a definite base-consuming process in the copper(II)–N-methylglycine system in the pH range 10.5–12, *i.e.* the deprotonation of the CuL_2 complex takes place with pK = 11.3. This pH range was not studied earlier in the system.

ii) The formation of CuL_3 could only be detected in the copper(II)–N-methylglycine system in very high ligand excess photometrically.

iii) We could not detect the formation of the $CuLH_{-2}$ complex in the copper(II)–N,N'-dimethylethylenediamine system.

iv) We could not distinguish between the two species $CuLH_{-1}$ and $Cu_2L_2H_{-2}$ in the copper(II)–N,N'-dimethylethylenediamine system, because we have not studied the system at around 1–1 metal ligand concentration ratio. As we shall see later this (these) complex(es) is (are) not important in the interpretation of the NMR relaxation results, thus we accepted the assignment of Barbucci *et al.* [13] (*i.e.* Table I contains the result given by assuming the formation of $Cu_2L_2H_{-2}$). The experimental data could be fitted equally well by assuming the formation of $CuLH_{-1}$ (log β = 2.07), but the change of the other formation constants was less than 0.01 log unit. The assumption of the formation of both species led to an ill-conditioned system of equations in the course of the calculations.

Relaxation studies

Copper(II)–N-methylethylenediamine and -N,N'-dimethylethylenediamine systems

The CuL_2 complex is practically stoichiometrically formed in ligand excess, and this is the only paramagnetic site where the relaxation of the labile -NH protons takes place. This effect is transferred to the water protons through the

$$CuL_2 + \overset{*}{L} \rightleftharpoons CuL\overset{*}{L} + L$$

ligand exchange process and through the very fast mixing of -NH- and H_2O protons. Another reason for the increase of the relaxation rate of water protons is the fast water exchange between the bulk water and the water molecules remaining in the

TABLE II. Concentrations of the Copper(II)–N-methylglycine Solutions Studied by NMR Relaxation.

No	T_{Cu}	T_L	pH Range	Number of exp. points
1	0.0300	0.0600	3.2–10.8	16
2	0.0200	0.0400		19
3	0.0050	0.0100		17
4	0.0025	0.0050		14
5	0.0020	0.0800	7.3–12.1	12
6	0.0181	0.0800	9.0–11.6	12
7	0.0080	0.0800	9.0–12.1	18
8	0.0128	0.120	8.7–12.0	11
9	0.0181	0.120	8.7–11.6	14
10	0.008	0.120	8.8–12.1	13
11	0.003	2.00	8.0–11.2	8
12	0.006	2.00	7.7–11.3	12

first coordination sphere of the CuL_2 complex. This process, however, is relaxation controlled, and thus may be taken into account as the product of a molar relaxation coefficient and the concentration of CuL_2. Because the mixing of -NH- and H_2O protons is very fast compared to that of the ligand exchange in both systems, the following relation may be derived to describe the concentration dependence of the paramagnetic contribution to the measured relaxation rate [1]:

$$\frac{T_{2M}^{-1} - T_{2O}^{-1}}{[CuL_2]} = r_{CuL_2} + \frac{1}{[H_2O]}\,\frac{X\cdot k_2[L]}{2 + k_2T_{2B}[L]} \qquad (1)$$

where:

T_{2M} = the measured relaxation time

T_{2O} = the T_2 relaxation time of water protons in absence of paramagnetic species

r_{CuL_2} = the molar relaxation coefficient of CuL_2

X = the number of labile -NH protons in the ligands

k_2 = the ligand exchange rate constant

T_{2B} = the paramagnetic relaxation time of the labile protons in the CuL_2 complexes.

It follows from eqn. (1) that the paramagnetic contribution to the overall relaxation time, normalized for $[CuL_2]$, may be described as a sum of a constant parameter and a saturation curve, which is a linear function of [L] when $k_2T_{2B}[L] \ll 2$ and reaches a constant value when $k_2T_{2B}[L] \gg 2$. The experimental data transformed according to eqn. (1) for the copper(II)–N-methylethylenediamine system are seen in Fig. 1. It is seen from the Figure that the $k_2T_{2B}[L] \ll 2$ relation is valid up to [L] ~ 0.25 *M*, thus only the k_2 rate constant can be calculated from the data. The numerical value of r_{CuL_2} is 435 M^{-1} s^{-1} for N-methylethylenediamine and 443 M^{-1} s^{-1} for N,N′-dimethylethylenediamine. The k_2 data are found as k_2^{max} in Table IV.

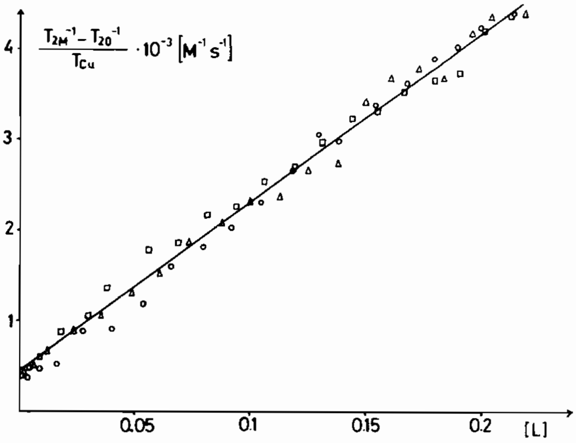


Fig. 1. The relaxation rate, normalized for the total copper(II) concentration as a function of the free ligand concentration in the copper(II)–N-methylethylenediamine system.

Notation	T_{Cu}
o–o–o	0.01 *M*
△–△–△	0.03 *M*
□–□–□	0.05 *M*

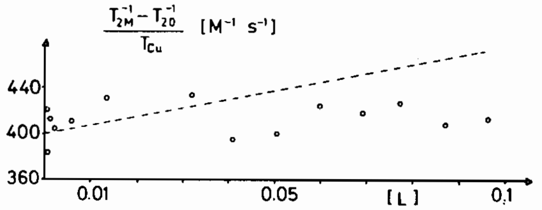


Fig. 2. The relaxation rate, normalized for the total copper(II) concentration as a function of free ligand concentration in the copper(II)–N,N′-dimethylethylenediamine system. T_{Cu} = 0.075 *M*. The dotted line shows the slope of 10^3 M^{-2} s^{-1}.

Figure 2 shows the same relation for the copper(II)–N,N′-dimethylethylenediamine system. It is seen that the normalized relaxation rate is constant up to [L] ~ 0.1 *M*, which means that the ligand exchange rate is much slower than in the case of copper(II)–N-methylethylenediamine. A slope of about 10^3 M^{-2} s^{-1} would be significant (see dotted line), thus an upper limit of $k_2 < 6 \times 10^4$ M^{-1} s^{-1} only may be given from the experimental data (Table IV).

Copper(II)–N-methylglycine system

The compositions of the solutions studied are collected in Table II. The concentration distribution of the complexes, the experimental relaxation data and the back-calculated functions describing the relaxation behaviour of the system, are illustrated in Figs. 3–5.

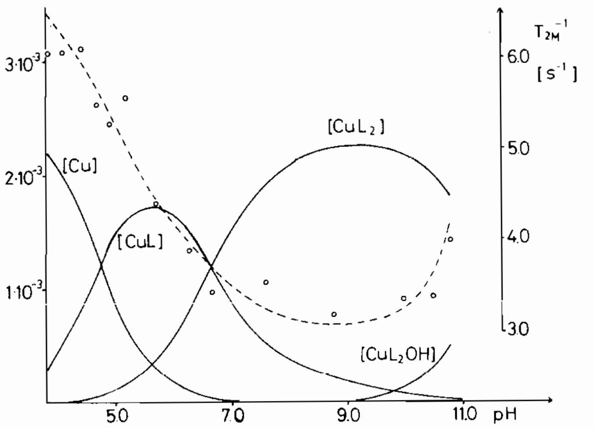


Fig. 3. The change of the normalized relaxation rate and the concentration distribution of the complexes formed in the copper(II)–N-methylglycine system. T_L = 0.005, T_{Cu} = 0.0025 *M*.

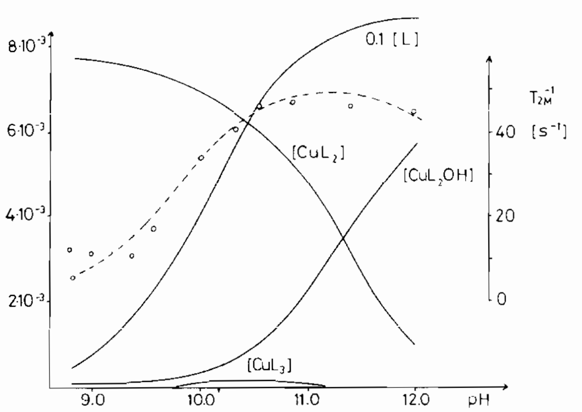


Fig. 4. The change of the normalized relaxation rate and the concentration distribution of the complexes formed in the copper(II)–N-methylglycine system. T_L = 0.12, T_{Cu} = 0.0128 *M*.

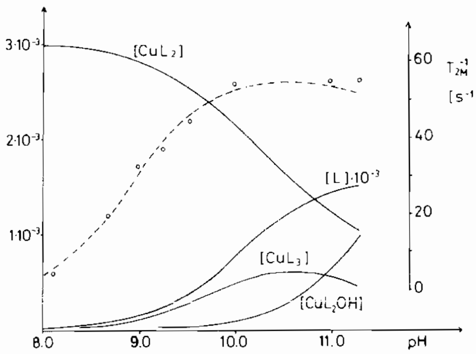


Fig. 5. The change of the normalized relaxation rate and the concentration distribution of the complexes formed in the copper(II)–N-methylglycine system. T_L = 2.0, T_{Cu} = 0.003 *M*.

For the interpretation of the relaxation results, it should be taken into account that there are five paramagnetic species (Cu^{2+}, CuL^+, CuL_2, CuL_3^- and $CuL_2H_{-1}^-$ = [CuL_2OH^-], and there are three species (L^-, H_2O and OH^-), containing labile protons which can be transferred between the paramagnetic and diamagnetic sites.

The paramagnetic effect of the exchange of water protons is relaxation controlled, and thus their role could be taken into account as a product of a molar relaxation coefficient and the concentration of the paramagnetic species in question. This expectation was fulfilled when the titrations at 2:1 ligand to metal concentration ratios (No. 1–4 in Table II) were evaluated. The experimental results of titrations 1–4 could be fitted with the linear combination of the concentration of the complexes formed.

The paramagnetic effect of the labile -NH- protons is transferred to the water protons through the ligand exchange reactions in ligand excess, where there are CuL_2, CuL_3^-, and CuL_2OH^- species only. The rates of the paramagnetic relaxation in these complexes are as follows:

$$X = \frac{2[CuL_2]}{T_{2B}^{(2)}}\ ;\ Y = \frac{3[CuL_3^-]}{T_{2B}^{(3)}}\ ;\ Q = \frac{2[CuL_2OH]}{T_{2B}^{(4)}}$$

These relaxation rates may be transferred to the water protons through the

$$CuLL + \overset{*}{L} \xrightleftharpoons{k_2} CuL\overset{*}{L} + L$$

$$A = k_2[CuL_2][L]$$

$$CuL_3 \xrightleftharpoons[k_{-3}]{k_3} CuL_2 + L$$

$$B = k_3[CuL_3] = k_{-3}[CuL_2][L]$$

$$CuLLOH + \overset{*}{L} \xrightleftharpoons{k_4} CuL\overset{*}{L}OH + L$$

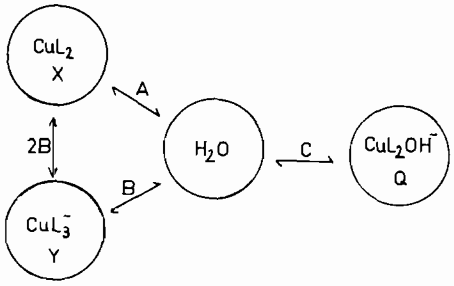
$$C = k_4[CuL_2OH][L]$$

exchange processes, where A, B and C stand for the rate of the exchange of labile protons between the paramagnetic and diamagnetic sites. (Our preliminary experiments showed that the -NH $\rightleftharpoons$ H_2O proton exchanges [1] have no effect on the measured relaxation rate of water protons.)

The above processes are summarized in the following scheme:

TABLE III. Parameters Describing the NMR Relaxation Behaviour of Copper(II)–N-methylglycine System.

r_{Cu}	$1987\,M^{-1}\,s^{-1}$
r_{CuL}	$1130\,M^{-1}\,s^{-1}$
r_{CuL_2}	$448\,M^{-1}\,s^{-1}$
r_{CuL_2OH}	$2660\,M^{-1}\,s^{-1}$
$3k_2 + 2k_{-3}$	$4.44 \times 10^7\ M^{-1}\,s^{-1}$
$k_3^{-1} + T_{2B}^{(3)}$	8.73×10^{-7} s
$T_{2B}^{(2)}$	7.45×10^{-7} s
k_4	$1.1 \times 10^7\ M^{-1}\,s^{-1}$
$T_{2B}^{(4)}$	7.33×10^{-7} s



The mathematical analysis of the above system according to the method given in part I [1] led to the following equation:

$$T_{2M}^{-1} - T_{2O}^{-1} = r_{Cu}[Cu^{2+}] + r_{CuL}[CuL^+] + $$
$$+ r_{CuL_2}[CuL_2] + r_{CuL_2OH}[CuL_2OH] +$$
$$+ \frac{1}{2[H_2O]} \cdot \frac{Z}{W} + \frac{1}{2[H_2O]} \cdot$$
$$\frac{2k_4[L]}{2 + k_4T_{2B}^{(4)}[L]}[CuL_2OH]$$

where:

$$\frac{Z}{W} = \frac{3AB(X + Y) + (A + B)XY + 2B^2(X + Y)}{(A + 2B + X)(3B + Y) - 4B^2}$$

The detailed analysis and meaning of the Z/W part of the equation is found in part I, where it is shown that the four parameters k_2, k_{-3}, $T_{2B}^{(2)}$ and $T_{2B}^{(3)}$ cannot be calculated individually, only the combination of $3k_2 + 2k_{-3}$, $T_{2B}^{(2)}$ and $k_3^{-1} + T_{2B}^{(3)}$ could be given. The results are summarized in Table III.

From the results summarized in Table III, the following conclusions can be drawn:

– The molar relaxation coefficients for the CuL and CuL_2 complexes are decreasing in accordance with the decreasing number of water molecules in their coordination sphere. The molar relaxation coefficient for the CuL_2OH mixed hydroxo complex in the copper(II)–N-methylglycine system is much higher than could be expected from the effect of one water molecule. Its explanation is that a fast, but relaxation controlled

$$CuL_2OH + \overset{*}{H}OH \rightarrow CuL_2O\overset{*}{H} + HOH$$

proton cxchange takes place in the solution. From the difference of the molar relaxation coefficient and an estimated value assigned to one water molecule ($r_{CuL_2}/2 \sim 224\ M^{-1}\,s^{-1}$) $T_{2B} = 3.7 \times 10^{-6}$ s can be calculated for the paramagnetic relaxation time of the OH proton. This relaxation time is considerably higher than the relaxation time of the OH protons in the $Cu(OH)_4^{2-}$ hydroxo complex (1.4×10^{-6} s), determined in a separate experiment. On the other hand, the $T_{2B}^{(2)}$ and $T_{2B}^{(4)}$ values for the NH protons are almost the same in the CuL_2 and CuL_2OH complexes. This indicates that the uptake of the OH ligand does not significantly influence theCu–N bond, thus the OH ligand is probably coordinated to the axial position.

TABLE IV. The Possible Maximum Values of the Ligand Exchange Rate Constants and the Formation and Dissociation Rate Constant of the CuL_3 Complexes. k_3(glycine) ~ $6 \times 10^7\ s^{-1}$ [14].**

	K_3 M^{-1}	$3k_2 + 2k_{-3}$ $M^{-1}\,s^{-1}$	k_2^{max} $M^{-1}\,s^{-1}$	k_{-3}^{max} $M^{-1}\,s^{-1}$	k_3^{max} s^{-1}	Ref.
glycine	1.7 [14]	2.3×10^8	7.7×10^7	1.2×10^8	6.8×10^7	[1]
α-alanine	0.57	1.5×10^8	5.0×10^7	7.7×10^7	1.3×10^8	[2]
ethylenediamine	0.1 [15]	2.8×10^7	9.4×10^6	1.4×10^7	1.4×10^8	[2]
N-methylglycine	0.35	4.4×10^7	1.5×10^7	2.2×10^7	7.5×10^7	present work
1,3-diaminopropane	0.015*	2.8×10^6	9.4×10^5	1.4×10^6	1.0×10^8***	[2]
N-methylethylenediamine	0.01*	2.1×10^6	6.9×10^5	1.1×10^6		present work
N,N′-dimethylethylenediamine	<0.001*	$<1.8 \times 10^5$	$<6 \times 10^4$	$<9 \times 10^4$		present work

*Estimated values. **See footnote 39. ***See text.

–The $T_{2B}^{(2)}$ for the -NH- proton of N-methylglycine is lower than the $T_{2B}^{(2)}$ for the glycine (9.2×10^{-7} s [1]). This relation is in accordance with our earlier finding that the increasing electron density on the donor N atom (increase of the pK) decreases the paramagnetic relaxation times [2].

– Table IV contains the maximum possible values of the ligand exchange rate constants from the CuL_2 complexes and/or the possible maximum values of the dissociation rate constants of the CuL_3 complexes in those cases where the K_3 stepwise formation constants are known.

It is seen from the Table that the N-methyl-substitution of the ethylenediamine significantly decreases the ligand exchange rate constant. This phenomenon is in qualitative agreement with Griffel's finding [3].

It is seen moreover that there is a surprising agreement between the possible maximum values of the dissociation rate constants of the CuL_3 complexes. They agree well also with the ultrasonic result of Beattie *et al.* [14]. A probable explanation is that the exchange between the dia- and paramagnetic sites takes place mainly through the formation and dissociation of the tris complexes, the effect of the generally accepted ligand exchange reaction without the

$$CuLL + \overset{*}{L} \rightleftharpoons CuL\overset{*}{L} + L$$

stabilization of the intermediate tris complex being negligible. Thus, the $k_3 = (1.0 \pm 0.3) \times 10^8$ s^{-1} dissociation rate constant is in fact the limiting *upper rate* of the Jahn–Teller inversion of the complexed copper(II) ion. If this explanation is accepted then the K_3 formation constants can be estimated for those systems (1,3-diaminopropane, N-methylethylenediamine, N,N′-dimethylethylenediamine) in which the CuL_3 complex is not formed in detectable amounts. The estimated values are also given in Table IV.

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