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NMR Relaxation Studies in Solution of Transition Metal Complexes.
2. Comparative Study of the Dynamics of Equilibrium in Aqueous Solution of Some Copper(II) Complexes

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The equilibrium dynamics in aqueous solution of copper(II)-α-alanine, β-alanine, -ethylenediamine and -1,3-diaminopropane complexes have been studied by measuring the T_2 relaxation time of water protons. It was experimentally verified that the $-NH_2 \rightleftharpoons H_2O$ proton exchange may control the paramagnetic relaxation of water protons in the copper(II)–α-alanine and –ethylenediamine systems. The appropriate proton exchange rate constants are given.

The T_{2B} values of the $-NH_2$ protons in the CuL_2 complexes have been determined. No significant difference was found between the exchange kinetics of Cu(II)–α-alanine and –β-alanine complexes in spite of their basically different formation kinetics. The ligand exchange in the Cu(II)–ethylenediamine system is much slower than in case of aminoacids. Assuming that the ligand exchange takes place through a Jahn–Teller inversion, this can be explained by the difference of the strength of equatorial Cu–O and Cu–N bonds.

Although the exchange kinetics of α-alanine and β-alanine complexes containing five and six-membered chelate rings are similar, there is one order of magnitude difference between the exchange rate constants of the ethylenediamine and 1,3-diaminopropane system containing five and six-membered N,N chelate rings; respectively.

Introduction

In the first part of this series [1], it has been illustrated on the copper(II)–glycine system that the kinetic parameters representing the paramagnetic relaxation, the rate constants of exchange processes between the coordinated and bulk ligands, as well as the $-NH_2 \rightleftharpoons H_2O$ proton exchange processes, could all be determined simultaneously by measuring the T_2 relaxation time of water protons. The mathematical description of the effect of the simultaneous processes on the measured relaxation time has been given by using kinetic [1], kinetic and probability theory [2] considerations, and also by the extension [3] of the matrix formulation [4] of the Bloch equations given by Reeves and Shaw. The interdependence of the parameters representing the coupled paramagnetic sites has also been analyzed. The aim of the present work was the comparative study of the equilibrium dynamics in aqueous solution of copper(II) complexes containing five and six-membered chelate rings, with (N,N) and (N,O) donor atoms. For this, the rate constants of the exchange reactions and the paramagnetic relaxation taking place in the copper(II)–α-alanine, –β-alanine, –ethylenediamine and –1,3-diaminopropane systems have been determined. The ligands are denoted by αA, βA, en and pn, a ligand in general by L.

The most important condition for studying the equilibrium dynamics is to know exactly the composition and stability of the complexes formed. Although a great number of equilibrium data for the systems studied are known, the data concerning the complexes formed in high ligand excess – where the exchange reactions could be studied – are missing. The data for Cu(II)–βA and Cu(II)–pn are not available for the experimental conditions used by us. The earlier results for the Cu(II)–en system can be accepted [5], for which $K_3 = [Cuen_3]/([Cuen_2][en]) = 0.1$, also given by Bjerrum and Nielsen [6]. Thus, beside the kinetic studies, spectrophotometric measurements have also been carried out to determine the K_3 stability constants for the Cu(II)–αA and –βA systems. The total equilibrium analysis of the Cu(II)–βA and Cu(II)–pn systems has been done pH-metrically.

Experimental

The visible spectra of the Cu(II)–αA and –βA solutions containing 0.01 *M* $CuCl_2$, and free ligands

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TABLE I. Concentrations of the Solutions Used for T_2 Measurements in the Case of Cu(II)–α Alanine System.

No.	Constant concentrations		Changing concentrations	No. of exp. points	Sensitive parameters
	$[CuL_2]$	$[HL^{\pm}]$	$[L^-]$		
1.	$1.654\ 10^{-3}$	0.1	0–0.07	18	k_2, k_{-3}
2.	$2.515\ 10^{-3}$	0.1		17	$T_{2B}^{(2)}$
3.	$3.309\ 10^{-3}$	0.1		17	
4.	$7.941\ 10^{-4}$	0.4995	0–0.95	24	k_2, k_{-3}
5.	$1.654\ 10^{-3}$	0.4995		25	$T_{2B}^{(2)}, T_{2B}^{(3)}$
	$[L^-]$	$[HL^{\pm}]$	$[CuL_2]$		
6.	$5.003\ 10^{-3}$	$5.015\ 10^{-3}$	0–0.018	14	k_4, k_5
7.	$7.380\ 10^{-3}$	$2.620\ 10^{-3}$		14	k_5^*
	$[CuL_2]$	$[L^-]$	$[HL^{\pm}]$		
8.	$2.250\ 10^{-2}$	$1.000\ 10^{-3}$	0–0.06	23	k_5, k_5^*

in 0.1–0.9 *M* concentration range have been recorded by a Beckman Acta M4 spectrophotometer. The protonation constants of βA and pn have been determined pH-metrically at the total ligand concentration of 0.005, 0.010 and 0.020 *M*. For the pH-metric study of Cu(II)–βA system, relatively high concentrations had to be used to get reliable data for K_3, thus this system was investigated at 0.1 *M* ligand and at 0.012, 0.020 and 0.028 *M* copper(II) concentration. The Cu(II)–pn system has been studied at 0.001, 0.002 and 0.003 *M* copper(II) concentration, in all cases at the ligand/metal ratio of 3:1, 4:1 and 5:1. The pH-metric titrations have been evaluated by our modified [7] computer program [8].

A Radiometer PHM 52 type pH-meter with GK-2301 B type combined electrode was used for the pH-titrations, calibrated for $-\lg[H^+]$ according to Irving *et al.* [9]. The end points of the acid-base titrations to standardize the stock solutions were determined according to Gran [10].

The T_2 relaxation times have been measured by a Newport N20 NMR spectrometer working at 2.5 MHz frequency, and – in some cases – by measuring the NMR linewidth of the water protons on a JEOL JNM MH 100 type instrument. The NMR measurements have been arranged as 'titrations', with KOH solution. A sample for measurement was taken for each titration point; afterwards it was quantitatively returned to the titration vessel, before the next addition of titrant. The concentrations for the individual systems were different; these will be given in the following section. The measurements have been carried out at 25 ± 0.5 °C; all of the solutions studied were 1 *M* in KCl.

Results and Discussion

Copper(II)–α-alanine System

The spectra recorded showed unambiguously the CuL_3^- type complex formation in ligand excess. The K_3 value calculated by using the least squares method at five different wavelengths varied between 0.52 and 0.65 without trend; its average is 0.57.

For studying the exchange processes involving the different environments, stock solution-pairs were prepared in which the concentration of two species altered significantly. The relaxation time measurements have been carried out on solutions made by appropriate mixing. The two constant concentrations, the concentration range of the third species, the number of experimental points and the parameters sensitive to the given titration are given in Table I. Titrations on the $\bar{n} < 2$ range of formation function have also been carried out to determine the r_i (defined by eqn. (11) of Part 1.) for $Cu\alpha A_2$; this was found to be 440 M^{-1} sec^{-1}. The $(T_{2P}T_{Cu})^{-1}$ values – where T_{Cu} denotes the total copper(II) concentration – calculated from the directly measured data of titrations No. 1–5 as a function of free alaninate concentration, are represented by completely coincident saturation curves, independent of the total copper(II) concentration and the frequency of measurements. The agreement of these data at different frequencies clearly indicates that T_{2B} is a frequency-independent quantity in this case.

Titrations 6–8 were carried out to study the effect of $-NH_2 \rightleftharpoons H_2O$ proton exchange on the T_2 relaxation time of water protons. Figure 1 shows the change of relaxation rate as a function of CuL_2

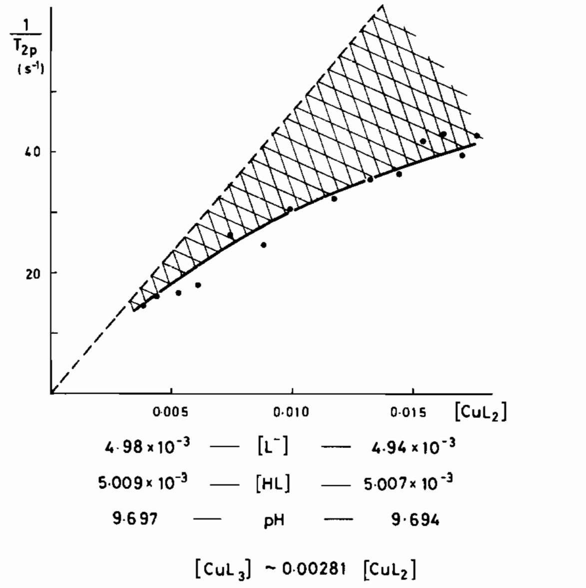


Fig. 1. T_{2P}^{-1} as a function of CuL$_2$ concentration; titration No. 6 in Table I. The changes of [L$^-$], [HL$^\pm$] and pH between the first and last points are also given.

TABLE II. Concentrations of the Solutions Used for T_2 Measurements in the Case of Cu(II)–β Alanine System.[a]

No.	T^o_{Cu}	T^o_L	C_{KOH}	No. of exp. points[b]	pH_{max}
1.	0.03	0.100	0.958	8	10.28
2.	0.02	0.070	0.383	8	10.28
3.	0.04	0.150	0.958	4	9.32
4.	0.02	0.120	0.958	8	10.10
5.	0.01	0.060	0.958	16	10.82
6.	0.01	0.035	0.383	8	10.22
7.	0.008	0.100	0.958	17	11.06
8.	0.004	0.025	0.383	9	11.43
9.	0.004	0.050	0.383	21	10.95
10.	0.004	0.100	0.958	18	11.14
11.	0.002	1.000	4.534	19	11.08
12.	0.0014	1.000	4.534	19	11.08
13.	0.0008	1.000	4.534	20	11.08

[a] Initial concentrations of ligand and proton are equal in all cases. [b] At pH > 8.0, *i.e.* in ligand excess.

concentration. The interpretation of the phenomenon illustrated in Fig. 1 is the same as given in part 1.

It follows from the above that the same model could be used for the computation of the kinetic parameters, described in detail in part 1 for the copper(II)–glycine system. The k_5 and k_5^* could not be calculated from these experiments so that the same datum ($k_5 + k_5^* = 3.8 \times 10^8$ M^{-1} sec^{-1}) as that given for glycine [11] was used. This selection is justified by the lack of a more appropriate value for α-alanine. It is reassuring however that the change of this datum by half an order of magnitude in both directions has no significant effect on parameters calculated and on the fit of the experimental data. The numerical values of the parameters are given in Tables VII–IX.

Copper(II)–β-alanine System

Four features of the recorded spectra indicated that from an equilibrium point of view this system is more complicated than the copper(II)–glycine or copper(II)–α-alanine:

i. There is no isosbestic point in the spectra.

ii. The spectra do not exhibit any approach to each other at higher ligand concentrations.

iii. The spectra are also dependent on the [HL$^\pm$] concentration, at constant [L$^-$].

iv. The change of the spectra is much greater than in the case of Cu(II)–glycine or –α-alanine.

These features – especially iii. – indicate the formation of an OH$^-$ containing species beside CuL$_3^-$. The trial and error evaluation of the pH-metric data unequivocally indicated that this species is CuL(OH), which is formed in significant concentration (~10% of the total copper(II)) between pH 7–9. It is interesting to note that in spite of the formation of this species, the formation functions up to $\bar{n} = 2$, calculated by assuming the formation of CuL and CuL$_2$ only, agree with each other at the different metal ion concentrations. This phenomenon could be explained by the fact that the formation of both CuL(OH) and CuL$_2$ is accompanied by a release of two protons, thus their pH effect is nearly the same. This may explain why the earlier studies did not indicate the formation of CuL(OH). The formation functions deviate from each other in the $\bar{n} > 2$ range. The only indication of a 'third' complex is the T-jump studies of Makinen *et al.* [12], who measured three-component T-jump relaxation spectra. The interpretation with the formation of CuL$_3^-$ was attempted, but led to unacceptable results. In the light of the above, the reason for the contradiction may be that the species formed was CuL(OH) in the pH range used (pH < 5.26). The formation of CuL$_3^-$ was detected by us only in the higher pH range.

The NMR titrations could not be done by a similar procedure as that used for copper(II)–glycine and –α-alanine system, because of the precipitate formation in the absence of a significant ligand excess. Thus the concentration of the reacting species was altered by KOH-titrations at different total copper(II) and –β-alanine concentrations (see Table II).

From the first part of the titrations, where there was no free ligand in significant concentration ($\bar{n} <$ 2, pH < 7), the r_i values (defined in part 1.) were calculated and were found to be 1120 ± 20 M^{-1}

TABLE III. Results of Curve-Fitting for Copper(II)–β-alanine System (see text).

$3k_2 + 2k_{-3}$ (M^{-1} sec^{-1})	$k_3^{-1} + T_{2B}^{(3)}$ (sec)	$T_{2B}^{(2)}$ (sec)	$CuL(OH) + \overset{*}{O}H^- \overset{k}{\rightleftharpoons} CuL(\overset{*}{O}H) + OH^-$ (M^{-1} sec^{-1})	q
1.88 10^8	3.22 10^{-5}	12.2 10^{-7}	9.3 10^8	0.0279
1.86 10^8	2.86 10^{-5}	10.6 10^{-7}	–	0.0427

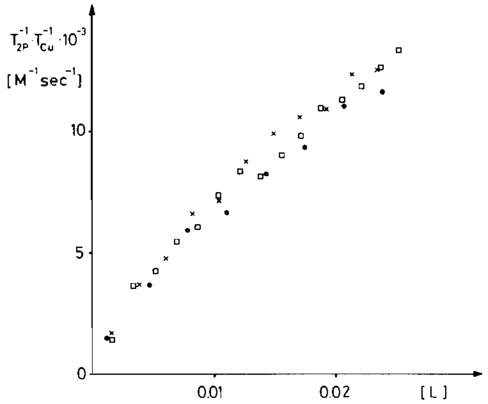


Fig. 2. $(T_2PT_{Cu})^{-1}$ as a function of free β-alaninate concentration. ●, titration No. 1 in Table II. X, titration No. 5 in Table II. □, titration No. 9 in Table II.

sec^{-1} for CuL, 460 ± 30 M^{-1} sec^{-1} for CuL_2 and 900 ± 250 M^{-1} sec^{-1} for CuL(OH). The relatively large error for $r_{CuL(OH)}$ is the consequence of its low concentration. The r_i for CuL_3 cannot be determined, however, it was assumed to be half of r_i for CuL_2. The correction of the relaxation rates in that part of the titrations where the exchange processes take place remained below 10% for 90% of the experimental points.

Figure 2 shows the $(T_{2p}T_{Cu})^{-1}$ values as a function of [L] at different total copper(II) concentrations. It is seen in Fig. 2 that *at this experimental arrangement,* there is no appreciable systematic deviation between the curves; the $-NH_2 \rightleftharpoons H_2O$ proton exchange does not influence the measured relaxation rates, its rate constant can not be calculated. This in turn means that the 'Z/W' part of the equation derived in part 1 can be used to evaluate the experimental data. The results of the evaluation is included in Table III, together with the

$$q = \left(\sum_{1}^{p} (\log T_{2p}^{calc} - \log T_{2p}^{meas})^2/p\right)^{1/2}$$

(p = 175; the number of the experimental points) values which represent the goodness of the fit.

The q value for the 'Z/W' model means more than 10% average deviation between the measured and calculated data, somewhat higher than acceptable. This is probably the consequence of the presence of the CuL(OH) species, which may also take part in exchange processes with either OH^- or L^-. A systematic search for the side-reactions influencing the measured data indicated that the

$$CuL(OH) + \overset{*}{O}H^- \rightleftharpoons CuL(\overset{*}{O}H) + OH^-$$

$$v = k[CuL(OH)][OH^-]$$

exchange process is the most probable with a rate constant of 9 X 10^8 M^{-1} sec^{-1}. The average fit with this assumption is 6.6%. The other parameters calculated are not very sensitive for the assumption of this exchange process; its contribution to the overall relaxation rate exceeds 15% only for 19 experimental points. Thus the parameters included in the first row of Table III are accepted for the copper(II)–β-alanine system; the above considerations for the OH^-–exchange reaction is rather indicative than decisive.

Copper(II)–ethylenediamine System

The composition of initial solutions studied by NMR titrations with KOH are given in Table IV. Although it is generally accepted that the protonated forms of the ligands are kinetically inactive [13], there are results for the ethylenediamine indicating that the Hen^+ also takes part in the formation processes [14, 15]. To decide whether the Hen^+ takes part in exchange reactions or does not, the relaxation times have been measured in the pH range 5–11 in some separate samples. The result of a titration is illustrated on Fig. 3. It can be seen in Fig. 3, that in the range of pH 6–8 where the $Cuen_2$ is already completely formed, but where there is no free ethylenediamine in solution, the relaxation rate is constant indicating that the Hen^+ is inactive in the exchange reactions. The r_i for $Cuen_2$ was calculated from these points, and was found to be 360 M^{-1} sec^{-1}. Some of the results of the measurements carried out in ligand excess at low Cu(II) concentration are illustrated in Fig. 4. The experimental points on a T_{2P}^{-1} scale would be represented by a saturation curve, *i.e.* at low [en] the ligands exchange, while at high [en] the paramagnetic relaxation controls the

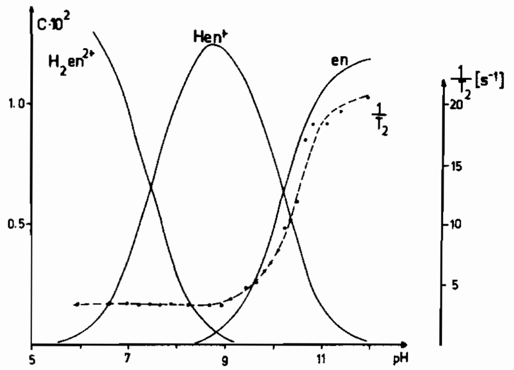


Fig. 3. The relaxation rate and the concentration distribution of ligand and its protonated forms, as a function of pH in the copper(II)–ethylenediamine system. T^0_{Cu} = 0.00582 *M*, T^0_{en} = 0.02910 *M*.

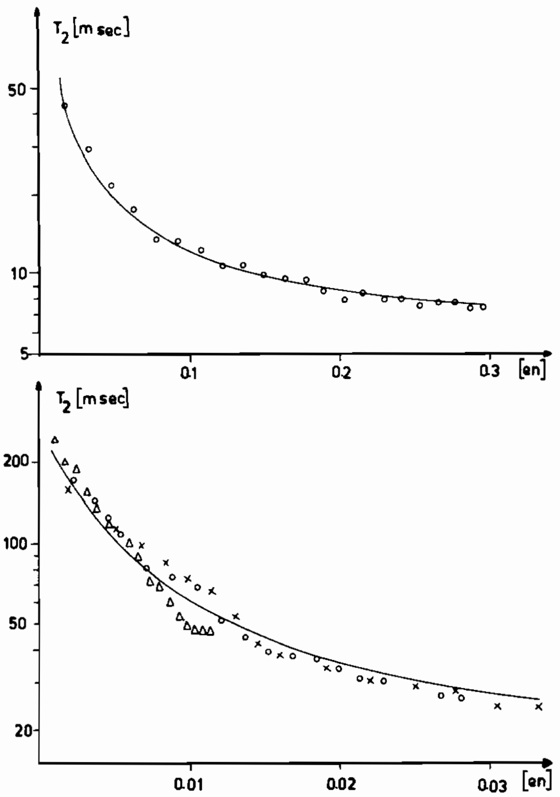


Fig. 4. The relaxation time as a function of free ethylenediamine concentration along the titration curves. Upper part: titration No. 10 in Table II. Lower part: △, titration No. 1 in Table IV. ○ titration No. 2 in Table IV. ×, titration No. 3 in Table IV.

measured relaxation time. The preliminary calculations based on the linearized form of the saturation curve showed that the ligand exchange is much slower than in case of the aminoacids. Thus the $-NH_2 \rightleftharpoons H_2O$ proton exchange may be the rate determining step only at high $Cuen_2$ concentration and at small ligand excess. It is difficult to carry out precise experiments in this concentration range by the use of $CuCl_2$ and H_2en^{2+} stock solutions.

TABLE IV. The Composition of the Initial Solutions of Copper(II)–ethylenediamine System Studied by NMR.

No.	T^0_{Cu}	T^0_{en}	T^0_H	Number of titr. points
1.	0.005	0.025	0.0525	16
2.	0.005	0.050	0.1050	17
3.	0.005	0.075	0.1575	15
4.	0.010	0.050	0.1050	17
5.	0.010	0.100	0.2100	20
6.	0.015	0.075	0.1575	22
7.	0.002	0.480	1.008	22
8.	0.003	0.480	1.008	22
9.	0.004	0.480	1.008	22
10.	0.005	0.480	1.008	22
	$T^0_{Cuen_2}$	$(T^{excess}_{en})^0$	T^0_H	
11.	0.1788	0.0088	0.0216	16
12.	0.1788	0.0176	0.0433	14
13.	0.1788	0.0266	0.0656	10
14.	0.2234	0.0111	0.0274	16
15.	0.2234	0.0222	0.0548	12
16.	0.2234	0.0333	0.0822	9

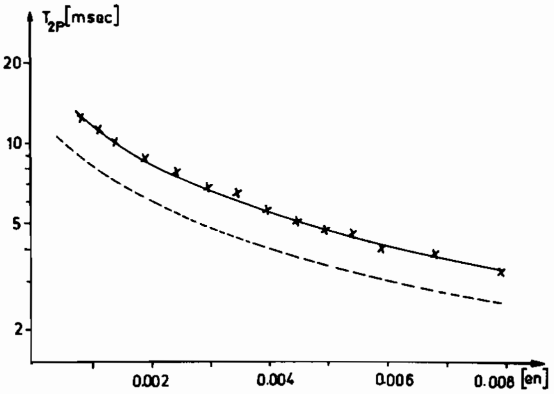


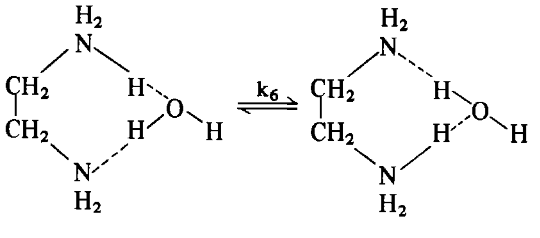
Fig. 5. The relaxation time as a function of free ethylenediamine concentration along the titration No. 12 (in Table IV). The dotted line represents the expected T_{2P}, ignoring the $-NH_2 \rightleftharpoons H_2O$ proton exchange.

To avoid the possible source of increased error originating from the experimental error in the standardization of the stock solutions, a ~ 0.4 *M* $Cuen_2$ solution was prepared by reaction of aqueous $CuCl_2$ and free en base with pH-control, until the predetermined pH of the inflection point was reached. The solutions to be studied were prepared from this; thus the titrations (numbers 11–16 in Table IV) were beginning just at that point, where the $Cuen_2$ is already completely formed, but where there is no free ligand excess at all. Some of the results of these titrations are shown in Fig. 5.

The dotted line in the Figure shows the expected relaxation times calculated from the preliminary k_2 and T_{2B} values, without taking into account the effect of $-NH_2 \rightleftharpoons H_2O$ proton exchanges. The deviation of the experimental points from the dotted line clearly indicates that the measurements are sensitive to the $-NH_2 \rightleftharpoons H_2O$ proton exchange as well.

During the evaluation of the results, the following considerations have been taken into account. The low K_3 value for $Cuen_3$ means that $Cuen_3$ is formed at most only as 3% of the total copper(II) concentration. Therefore the use of the same model which is valid for the aminoacid systems would not yield an acceptable result; these data are insensitive to the parameters representing the $Cuen_3$ site. Therefore its role has been omitted during the calculations. It should be stressed however that this omission does not necessarily mean that the processes denoted by k_3 and $T_{2B}^{(3)}$ are not important in determining the measured data. Rather that the $k_3^{-1} + T_{2B}^{(3)}$ cannot be calculated. The k_2 value determined by using the simplified model is in fact the possible maximum value; its real meaning is the same as in the case of the aminoacids, *i.e.* $3k_2^{calc} = 3k_2 + 2k_{-3}$.

The effect of the different possible proton exchanges have been assumed during the evaluation. Beside the proton exchanges denoted by k_4, k_5 and k_5^* in Part 1, the following proton exchange has also been assumed:



$$v_6 = k_6[Hen^+]$$

No sensitivity of fit of the experimental data for the processes denoted by k_5, k_5^* and k_6 was observed; the data are sensitive for only the

$$en + HOH \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} enH^+ + OH^-$$

process; only the k_4 proton exchange rate constant could be calculated. This result is in agreement with the ultrasonic results of Emara *et al.* [16].

The absence of $Cuen_3$ and the effect of only one proton exchange process result in a much simpler relation to describe the paramagnetic contribution to the measured relaxation time than eqn. (10) of Part 1:

$$\frac{T_{2P}}{2[H_2O]} = \frac{2 + k_2T_{2B}^{(2)}[en]}{8k_2[Cuen_2][en]} + \frac{5}{4k_4[en]} \qquad (1)$$

The results of the calculation are included in Tables VII–X.

TABLE V. The Composition of the Initial Solutions of Copper(II)–1,3-diaminopropane System Studied by NMR Titration.[a]

No.	$T^o_{Cu}\cdot 10^3$	$T^o_L:T^o_{Cu}$	Number of titr. points
1.	3.92	20:1	32
2.	3.92	10:1	29
3.	3.92	5:1	27
4.	3.92	3:1	23
5.	5.88	10:1	26
6.	5.88	5:1	25
7.	5.88	3:1	24
8.	9.80	5:1	37
9.	9.80	3:1	27
10.	19.61	3:1	26
11.	19.61	5:1	23
12.	29.41	3:1	28

[a] $T^o_H/T^o_L = 2.51$ in all samples.

Copper(II)–1,3-diaminopropane System

The trial and error analysis of pH-metric titration curves indicated that the species formed in the presence of ligand excess are the hydrolysed products of CuL and CuL_2. The CuL(OH) formation and its dimerization has also been noted by other authors [5]. In the concentration range studied by us it was not possible to decide whether the dimerization did or did not take place, because CuL(OH) or $Cu_2L_2(OH)_2$ formed only in low concentration, so that the dimerization has only an undetectable pH-effect. The $CuL_2(OH)$ formation at high pH however was unambiguously detected. The data are given in Table VI.

The concentrations of the initial solutions used for NMR titrations are listed in Table V. To decide on the kinetic activity of the Hpn^+ species, all titrations were carried out in the pH range 8–12. The result of one of these (No. 8 in Table V) is illustrated in Fig. 6.

It is seen in Fig. 6, that a considerable increase of the relaxation rate takes place only between pH 11–12. Some measurements at higher ligand concentrations showed that a saturation limit due to the paramagnetic relaxation could not be achieved even at [pn] = 0.3 *M* concentration. Thus, only the titrations included in Table V were used to evaluate the

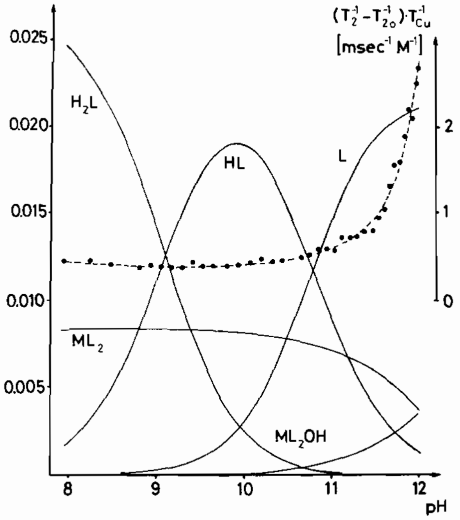


Fig. 6. The relaxation rate and the concentration distribution as a function of pH in the Cu(II)–1,3-diaminopropane system. Titration No. 8 in Table V.

TABLE VI. Formation Constants of the Species Formed in the Systems Studied.

$\lg\beta$	αA	βA[a]	en	pn[a]
$\lg\beta_{HL}$	9.70[b]	10.10	10.18[c]	10.80
$\lg\beta_{H_2L}$	12.03[b]	13.76	17.63[c]	19.91
$\lg\beta_{CuL}$	7.98[b]	6.65	10.82[c]	9.97
$\lg\beta_{CuL_2}$	14.60[b]	11.85	20.20[c]	17.28
$\lg\beta_{CuL(OH)}$	–	13.07	–	15.73
$\lg\beta_{CuL_2(OH)}$	–	–	–	18.95
K_3[e]	0.57[a]	3.0	0.1 [d]	–

[a] This work. [b] Ref. 17. [c] Ref. 5. [d] Ref. 6. [e] Equilibrium constant of $CuL_2 + L \rightleftharpoons CuL_3$ process.

data. The evaluation of the experimental data in this case was much simpler than in the case of previous systems. The absence of the paramagnetic relaxation limit means that only the r_i values for the complexes and the possible exchanges between the para and diamagnetic species have to be considered. In the pH range where the considerable increase of the relaxation rate takes place, there are three paramagnetic [CuL(OH), CuL_2, $CuL_2(OH)$] and two diamagnetic [pn, OH^-] sites for the labile protons which may change their environment. This – in principle – means that six different exchange reactions may be responsible for the measured effects. None of the exchanges couples the paramagnetic sites directly. Let us denote the concentration of paramagnetic species by c_i, that of the diamagnetic species c_j, and let us suppose second order reactions between them. In this case, the following linear equation can be used to represent the measured relaxation time:

$$T_2^{-1} - T_{20}^{-1} = \sum_{i=1}^{3} r_i c_i + \sum_{i=1}^{3} \sum_{j=1}^{2} \chi_{ij} c_i c_j \tag{2}$$

This equation contains nine unknowns, but because of the $[CuL(OH)][L] = K'[CuL_2(OH)] = K''[CuL_2][OH^-]$, only seven are independent from each other (K' and K'' are the appropriate equilibrium constants). The χ_{ij} values are in direct connection with the appropriate second order rate constants. The systematic search for the best fit of the experimental data led to the following results:

– none of the parameters concerning the CuL(OH) could be determined. This does not mean that there is no water exchange from the coordination sphere of CuL(OH), rather that its contribution is negligible. The reason for this may be its low concentration, and/or the dimerization and kinetic inactivity.

– the molar relaxation rate coefficients for CuL_2 and $CuL_2(OH)$ were found to be 350 M^{-1} sec^{-1} and 1100 M^{-1} sec^{-1} respectively. The molar relaxation rate coefficient for $CuL_2(OH)$ is surprisingly large, compared with that of CuL_2. The reason for this is that the effect of the

$$CuL(OH) + \overset{*}{L} \rightleftharpoons Cu\overset{*}{L}(OH) + L$$

and

$$CuL(OH) + L \rightleftharpoons CuL_2(OH) \rightleftharpoons CuL_2 + OH$$

processes are all included into this datum. Thus the $r_{CuL_2(OH)} = 1110\ M^{-1}\ sec^{-1}$ is a linear combination of the rate and equilibrium constants of these processes and the water exchange from $CuL_2(OH)$.

– the assumption of the following three exchanges is justified:

$$CuL_2(OH) + L^* \xrightleftharpoons{k_1} CuLL^*(OH) + L$$

$$CuL_2 + L^* \xrightleftharpoons{k2} CuLL^* + L$$

$$CuL_2(OH) + OH^{-*} \xrightleftharpoons{k_3} CuL_2)OH^*) + OH^-$$

The k_2 and k_3 values are well defined; according to the statistical treatment their relative error is less than 10%. The k_1 however is rather uncertain; only an upper limit of $k_1 < 1.10^6\ M^{-1}\ sec^{-1}$ could be given (see Table VIII.)

Comparison of the Results

The equilibrium data valid for 1 *M* KCl and 25 °C, used for the calculation of the concentration distribution, are given in Table VI.

TABLE VII. $-NH_2 \rightleftharpoons H_2O$ Proton Exchange Rate Constants together with Earlier Reported Data.

Ligand	glycine	α-alanine	ethylenediamine
k_4 10^{-6} [sec^{-1}]	3.3[f] 0.8[b] 1.0[c]	2.1[a] 1.4[d]	14[a] 11[e]
k_5 10^{-7} [M^{-1} sec^{-1}]	13.0[a] 7.9[c]	5.4[a]	–

[a] This work. [b] Ref. 27 (ultrasonic). [c] Ref. 28 (NMR line-shape analysis). [d] Ref. 26 (ultrasonic). [e] Ref. 16 (ultrasonic). [f] Ref. 1 (this method).

TABLE VIII. The $T_{2B}^{(2)}$ Relaxation Time of $-NH_2$ Protons in the CuL_2 Complexes.

L	$T_{2B}^{(2)}$ 10^7 [sec]
glycine	9.2[a] 7.0[b]
α-alanine	7.0
β-alanine	12.2
ethylenediamine	10.8 3.0[b]

[a] Ref. 1. [b] Ref. 20.

The results for the proton exchange processes, together with the earlier reported values, are given in Table VII. The agreement between the ultrasonic results and our data for ethylenediamine and α-alanine is surprisingly good. The k_5 values for α-alanine is not known from earlier report. It should be stressed, however, that our results may only be regarded as an indication of the role of the process represented by k_5; this value is uncertain because of the uncertainty of $k_5 + k_5^*$.

It was shown in part 1 that only the $T_{2B}^{(2)}$ values can be calculated independently from the other parameters. These are given in Table VIII.

The lower $T_{2B}^{(2)}$ may indicate a shorter Cu–N bond length and/or an increased covalency, depending on the relaxation mechanism. It has been proved by Beattie *et al.* [18], as well as by Espersen and Martin [19], that scalar coupling is mainly responsible for the T_2 relaxation of the non-labile protons in copper(II) complexes. Our preliminary T_1 measurements support their finding; $T_{1P}/T_{2P} > 20$ ratio has been found for the labile protons also in all systems. Further studies are in progress in our laboratory to find the correlation between the $T_{2B}^{(2)}$ values and the electron density on the nitrogen donor, as well as the structure of the complexes.

The $T_{2B}^{(2)}$ data reported by us, and the comparable results of Pearson and Lanier [20] are different, especially for en. The difference is probably explained by the fact that the cited authors did not take into account the formation of the CuL_3^- type complex, even though the measurements were carried out in very high ligand excess (12 *M* en) where the formation of this type of complex must be considered.

It was shown in part 1 that only the parameter-combination of $3k_2 + 2k_{-3}$ and $k_3^{-1} + T_{2B}^{(3)}$ could be determined. These data – together with the possible maximum values – are given in Table IX. As was seen previously the $k_3^{-1} + T_{2B}^{(3)}$ data could not be determined in the case of the diamines, and the models used in the evaluation of these systems contained only k_2. This is given as the possible maximum

TABLE IX. The Kinetic Parameters and Their Possible Maximum Values in the Systems Studied.

	Cu(II)–gly	Cu(II)–αA	Cu(II)–βA[a]	Cu(II)–en	Cu(II)–pn[b]
$3k_2 + 2k_{-3}$	2.3 10^8	1.5 10^8	1.9 10^8	2.8 10^7	2.8 10^6
$k_3^{-1} + T_{2B}^{(3)}$	1.1 10^{-6}	8.3 10^{-7}	3.2 10^{-5}	–	–
$k_{2(max)}$ [M^{-1} sec^{-1}]	7.7 10^7	5.0 10^7	6.2 10^7	9.4 10^6	9.4 10^5
$k_{3(max)}$ [sec^{-1}]	6.8 10^7	1.3 10^8	3.1 10^7	1.4 10^8	–
$k_{-3(max)}$ [M^{-1} sec^{-1}]	1.2 10^8	7.7 10^7	9.4 10^7	1.4 10^7	1.4 10^6
$T_{2B(max)}^{(3)}$ [sec]	1.1 10^{-6}	8.3 10^{-7}	3.2 10^{-5}	–	–

[a] The second order rate constant for the $CuL(OH) + OH^- \rightleftharpoons CuL(OH) + OH^-$ process is 9.3 10^8 M^{-1} sec^{-1}. [b] The second order rate constant for the $CuL_2(OH) + OH^- \rightleftharpoons CuL_2(OH) + OH^-$ process is 2.7 10^7 M^{-1} sec^{-1}.

TABLE X. The k_2 Ligand Exchange Rate Constants Reported for the Copper(II)–Ethylenediamine System.

k_2 10^{-6} [M^{-1} sec^{-1}]	Reference
9.4	this work
6.0	20
1.8[a]	20
2.6	21
1.2	22
6.8	23

[a]Measured on the $-CH_2-$ protons.

TABLE XI. The Rate Constants of the $CuL + L \overset{k}{\rightleftharpoons} CuL_2$ Processes in the Systems Studied.

L	glycine	α-alanine	β-alanine	ethylene-diamine
k	1.0 10^9	4.2 10^8		1.9 10^9
[M^{-1} sec^{-1}]	[24]	[24]		[15]
	4.0 10^8	1.5 10^8	8.0 10^6	3.6 10^9
	[25]	[12]	[12]	[14]

value, but it must be kept in mind that these may be given as $3k_2 + 2k_{-3}$ as well.

The comparison of kinetic parameters indicates that there is only a slight difference in the second order rate constants for the aminoacids. The parameters for the α-alanine, glycine and β-alanine system are near to each other, in spite of the change of the chelate ring from a five to a six-membered one.

There is almost one order of magnitude decrease of k_2 values for ethylenediamine compared to the aminoacids. Taking into account the suggested mechanism [1] including Jahn–Teller inversion, this is the expected result because two nitrogen donors have to be expelled from the equatorial plane. In the case of aminoacids, two oxygen donors are probably expelled from the equatorial coordination site through the Jahn–Teller inversion of the *trans* forms, and one oxygen and one nitrogen donor atom are expelled when the inversion of the *cis* form takes place.

It is interesting to note that there is one order of magnitude difference between the k_2 values for the five and six-membered diamine complexes, while no significant difference was found between the k_2-s for the five and six-membered amino-acid complexes.

Apart from glycine, these data are not known for the aminoacids from the literature. For ethylenediamine however a number of k_2-s are available from different authors. These are included in Table X. Considering the experimental conditions given in the cited papers, and the fact that some of the authors [21–23] did not take into account even $T_{2B}^{(2)}$ as a limit on paramagnetic relaxation, the considerably lower values given in the literature are understandable. The deviation of the k_2-s determined by Pearson and Lanier [20] and by us may be partially explained in the same way as it was in comparison with the $T_{2B}^{(2)}$ data.

For the comparison of the rate of the coordination of the second and the third ligand, the rate constants available for the $CuL + L \overset{k_2}{\rightleftharpoons} CuL_2$ process are given in Table XI. The maximum possible values of the rate constant of $CuL_2 + L \overset{k_{-3}}{\equiv} CuL_3$ process are listed in Table IX. In the case of glycine, α-alanine and ethylenediamine the $k_{-3} < k_2$ relation is valid, while no firm conclusion could be drawn for β-alanine. The reported data for β-alanine [12] in Table XI probably reflects the uncertainty in the identification of the third complex. It is worth noticing that Pasternack [29] *et al.* have not found a dramatic difference between the rate constants of the $Cubipy + L \rightleftharpoons CubipyL$ process in case of α-alanine and β-alanine (by stands for 2,2'-bipyridyl).

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