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NMR Relaxation Studies in Solution of Transition Metal Complexes. XI. Dynamics of Equilibria in Aqueous Solutions of the Copper(II)–Ammonia System

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The T_2 relaxation time of water protons in aqueous solution of copper(II)–ammonia system at 25 °C in 2 M *NH_4Cl were measured as a function of the free ammonia concentration. It is shown that the NMR relaxation rate may be given as a linear combination of the concentration of the species formed in the system. The temperature dependence of the relaxation rate shows that the measured data are governed by the chemical reactions taking place in the equilibrium state in a significant range of the complex formation curve.*

The results are evaluated by assuming that the dissociation and formation of the successive complexes are responsible for the proton exchange between the paramagnetic and diamagnetic environments. With this assumption the following rate constants have been determined for the consecutive stepwise complex formation:

$$Cu^{2+} + NH_3 \underset{2.0 \times 10^4}{\overset{(3 \pm 1) \times 10^8}{\rightleftharpoons}} Cu(NH_3)^{2+}$$

$$Cu(NH_3)^{2+} + NH_3 \underset{8.4 \times 10^4}{\overset{(2.8 \pm 0.3) \times 10^8}{\rightleftharpoons}} Cu(NH_3)_2^{2+}$$

$$Cu(NH_3)_2^{2+} + NH_3 \underset{2.9 \times 10^5}{\overset{(1.7 \pm 0.3) \times 10^8}{\rightleftharpoons}} Cu(NH_3)_3^{2+}$$

$$Cu(NH_3)_3^{2+} + NH_3 \underset{3 \times 10^6}{\overset{(3.5 \pm 1.0) \times 10^8}{\rightleftharpoons}} Cu(NH_3)_4^{2+}$$

Introduction

The solvent and ligand exchange processes taking place in aqueous solutions of paramagnetic transition metal complexes have drawn considerable attention since the foundation of the NMR relaxation method [1] to study these reactions. Recently we have also done some systematic relaxation studies in solutions of a number of copper(II) complexes [2–4]. One of the most important conclusions of our work on the copper(II)–glycine system [2] is that the so called ligand exchange process

$$\mathrm{CuGG} + \overset{*}{\mathrm{G}}^- \overset{k_2}{\rightleftharpoons} \mathrm{CuG}\overset{*}{\mathrm{G}} + \mathrm{G}^-$$

$$v_2 = k_2[\mathrm{CuG_2}][\mathrm{G}^-]$$

without the stabilization of the intermediate state and the

$$\mathrm{CuG_3^-} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{CuG_2} + \mathrm{G}^-$$

$$v_3 = k_3[\mathrm{CuG_3^-}] = k_{-3}[\mathrm{CuG_2}][\mathrm{G}^-]$$

cannot be distinguished, and only a combination of the second order rate constants can be determined:

$$3k_2 + 2k_{-3} = 2.3 \times 10^8\ \mathrm{mol^{-1}\ dm^3\ s^{-1}}$$

A possible way of distinguishing between the exchange and the formation and dissociation of the subsequent complex in the stepwise series was to study the copper(II)–NTA–ammonia mixed ligand system, where the ammonia does not replace NTA, and below $T_{NH_3} : T_{CuNTA^-} = 1:1$ ratio only the formation and dissociation of the mixed ligand complex influences the measured relaxation rate of water protons (NTA stands for nitrilotriacetate). The results of the detailed study on a number of Cu(II)–NTA–B ligand system is given in Part IX [5], only the normalized relaxation rate of water protons up to 1:1 mole ratio is illustrated in Fig. 1.

Figure 1 shows—for comparison—the same data in the copper(II)–NTA–glycinate system. The relaxation rate should decrease as the second ligand is coordinated to the CuNTA⁻ complex, because of the decrease of the number of water molecules remaining in the first coordination sphere. This expectation is fulfilled when the second ligand is glycine. If, however, the second ligand is ammonia, then the relaxation rate increases, indicating a fast dissociation and formation of the mixed ligand complex even if there is no excess free ammonia in the solution. Thus the

$$\mathrm{CuNTA(NH_3)} + \overset{*}{\mathrm{N}}\mathrm{H_3} \rightleftharpoons \mathrm{CuNTA(}\overset{*}{\mathrm{N}}\mathrm{H_3)} + \mathrm{NH_3}$$

process may not be responsible for increase of the relaxation rate (the parabolic change of the curve

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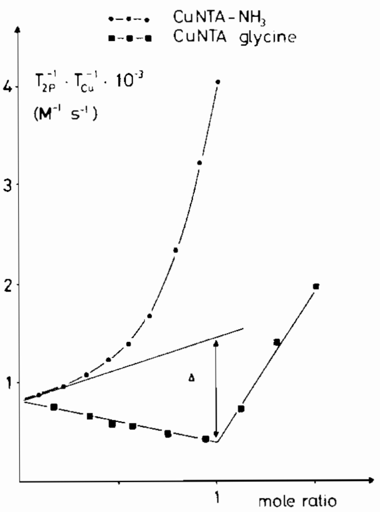

Fig. 1. The paramagnetic contribution to the relaxation rate of water protons normalized for the total copper(II) concentration as a function of the mole ratio in the copper(II)–NTA–glycine and in the copper(II)–NTA–ammonia systems. The arrow indicates the difference between the limiting slopes at 1:1 mole ratio.

may be interpreted by the above exchange process, which, however, cannot be distinguished from the formation and dissociation of the mixed complex containing two ammonia molecules).

From the difference of the limiting slopes at 1:1 mole ratio, the formation and dissociation rate constants could be calculated: $k_b = 3.6 \cdot 10^4\ s^{-1}$, $k_f = 2.1 \cdot 10^8\ mol^{-1}\ dm^3\ s^{-1}$ (log K for the $CuNTA^- + NH_3 \rightleftharpoons CuNTA(NH_3)$ equilibrium is 3.74, determined pH-metrically).

The formation rate constant seems acceptable, although no directly comparable data are available in the literature. The difference in the relaxation behaviour of the $CuNTA–NH_3$ and CuNTA–glycinate systems is evidently the consequence of the difference in their formation constants (log K for the $CuNTA^- + gly^- \rightleftharpoons CuNTAgly^{2-}$ process is 5.39, thus the dissociation rate is much smaller).

The stepwise formation constants for the well known copper(II)–ammonia system, however, are near to or less than the equilibrium constant for the $CuNTA(NH_3)$ complex, thus it seemed to be a reasonable assumption that the proton relaxation studies might give information on the stepwise dissociation and formation rate constants of the different Cu(II)–ammonia complexes. The results of these relaxation studies are reported in the present paper.

Experimental

The T_2 relaxation time of the water protons were measured at 25 ± 1 °C by a NEWPORT N20 instrument at 2.5 MHz frequency, using the single echo [6] technique. 220 experimental points were taken by titration of an initial solution of 2 mol dm^{-3} NH_4Cl, containing $CuCl_2$ at seven different concentrations, with KOH solutions. The temperature dependence of the relaxation time between 0–70 °C has been measured in 14 separate samples at different $\bar{n}$ values.

The comparative study of the copper(II)–ethylenediamine system was necessary for the interpretation of the relaxation results. The molar relaxation coefficients (r_i) describing the relaxation time of water protons in the copper(II)–ethylenediamine system between $\bar{n} = 0–2$,

$$T_2^{-1} - T_{20}^{-1} = r_0[Cu^{2+}] + r_1[Cuen^{2+}] + r_2[Cuen_2^{2+}]$$

have also been determined by measuring T_2 as a function of $\bar{n}$ in 10 different samples in 2 mol dm^{-3} KCl solution, where T_2 = the measured relaxation time, T_{20} = the relaxation time in the absence of paramagnetic species, r_i = the molar relaxation coefficient of the i-th complex.

The species distribution in the copper(II)–ammonia and copper(II)–ethylenediamine systems, under the same conditions, was necessary for the evaluation of the results of the relaxation measurements. Thus pH-metric measurements were also carried out to obtain the protonation and stepwise stability constants of the copper(II)–ammonia system in 2 mol dm^{-3} NH_4Cl and of the copper(II)–ethylenediamine system in 2 mol dm^{-3} KCl. A radiometer PHM-52 pH-meter with GK-2301 electrode, calibrated for –log $[H^+]$ according to [7] was used for the pH-metric titrations. The stability constants and the necessary concentration distributions were calculated using the program PSEQUAD [8].

Results and Discussion

The results of the pH-metric equilibrium studies are collected in Table I. The Table contains the –ΔH values taken from the literature. These data were used to calculate the equilibrium constants at different temperatures for the calculation of the species distribution.

The paramagnetic contribution to the relaxation rate, normalized for the total copper(II) concentration as a function of –log $[NH_3]$, are illustrated in Fig. 2 together with the concentration distribution of the complexes.

It is seen on the Figure that the normalized relaxation rate depends only on the free ligand concentration, which suggests that the relaxation rate may be given as a linear combination of the concentration of the species formed in the system:

$$T_2^{-1} - T_{20}^{-1} = \sum_0^5 r_i[Cu(NH_3)_i]^{2+}$$

TABLE I. Logarithm of the Formation Constants of the Complexes Formed in the Copper(II)–Ammonia (I = 2 *M* NH_4Cl) and in the Copper(II)–Ethylenediamine (I = 2 *M* KCl) System at 25 °C.

Species	Ammonia		Ethylenediamine
	log β	$-\Delta H$ kJ/mole	log β
HA	9.53	51.96[b]	10.30
H_2A	–	–	18.01
CuA	4.18	23.4[c]	10.84
CuA_2	7.70	46.4[c]	20.08
CuA_3	10.46	67.3[c]	–
CuA_4	12.52	92.0[c]	–
CuA_5	11.92[a]	113.3[c]	–

[a] log K_5 = –0.60, 25 °C [14]. [b] 25 °C, 0.1 *M* KCl [15]. [c] 26.8 °C, 2 *M* NH_4NO_3 [16].

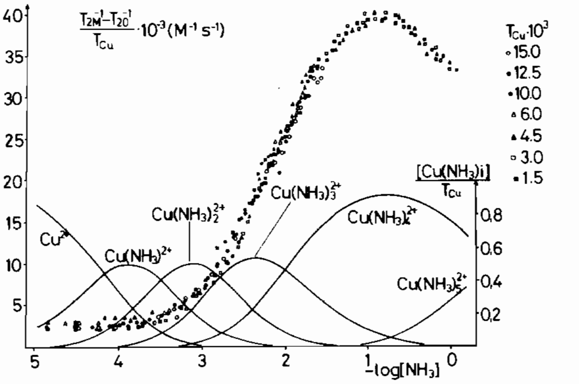

Fig. 2. The paramagnetic contribution to the relaxation rate of water protons normalized for total copper(II) concentrations as a function of the free ligand concentration, together with the concentration distribution of the complexes.

The linear least squares treatment of the data supported this expectation, the average deviation between the experimental and calculated values being less than 4%. The r_i values calculated are found in the left hand side column of Table II. For the interpretation of the results it should be taken into account that the effect of three processes are reflected in these data:

i. The fast exchange of water molecules remaining in the first coordination sphere of the complexes. The effect is, however, relaxation controlled at 25 °C [1], and so this should decrease with the number of water molecules.

ii. The formation and dissociation of the stepwise complexes

$$Cu(NH_3)_{i-1} + NH_3 \underset{k_i^b}{\overset{k_i^f}{\rightleftharpoons}} Cu(NH_3)_i$$

TABLE II. The Molar Relaxation Coefficients of the Complexes Formed in the Copper(II)–Ammonia System.

Species	r_i	$r_i^{H_2O}$	$r_i^{NH_3}$
Cu^{2+}	2200	2200	–
$Cu(NH_3)^{2+}$	2020	1485	535
$Cu(NH_3)_2^{2+}$	3240	920	2270
$Cu(NH_3)_3^{2+}$	8340	610	7730
$Cu(NH_3)_4^{2+}$	40900	360	40540
$Cu(NH_3)_5^{2+}$	10400	170	10230

iii. The exchange of the ammonia molecules without the stabilization of the intermediate state:

$$Cu(NH_3)_{i-1} + NH_3 \overset{k_{i-1}^{exc}}{\rightleftharpoons} Cu(NH_3)_{i-1} + NH_3$$

Process iii may not influence the value of r_1. It seems to be a reasonable assumption moreover, that a much more weakly-bound water molecule leaves the coordination sphere when an ammonia is coordinated, thus the role of process ii is dominant over process iii.

The results given in the copper(II)–ethylenediamine system were used to separate the effect of processes i from that of processes ii, because the dissociation rates are much slower than those of the ammonia complexes. The molar relaxation coefficients determined in the copper(II)–ethylenediamine system are seen in Fig. 3, as a function of the water molecules remaining in the first coordination sphere. A third order polinom was fitted to the underlined experimental data, and the intermediate points calculated by interpolation.

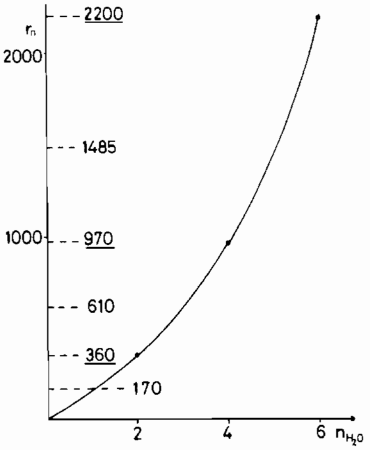

Fig. 3. The molar relaxation coefficients as a function of the number of water molecules remaining in the coordination sphere in the copper(II)–ethylenediamine system. The full line shows a third order polinom fitted to the underlined experimental points.

It is assumed that the relaxation controlled effect of the water exchange in the two systems are the same, thus the r_i values determined in the copper(II)–ammonia system are corrected with these data, to get the effect of the coordinated ammonia separately. The corrections and the molar relaxation coefficients representing the effect of ammonia are found in the middle and right hand side columns of Table II respectively.

It is seen from Table II, that this splitting of the effects may be questionable in the case of the mono complex only, the relative role of the correction is gradual, and sharply decreases with increasing number of ammonia.

The next task was to decide whether the $r_i^{NH_3}$ values are governed by the paramagnetic relaxation times or by the chemical reactions. The temperature dependence of the relaxation times in solutions at different $\bar{n}$ values were studied to answer this question. Some illustrative results are seen on Fig. 4.

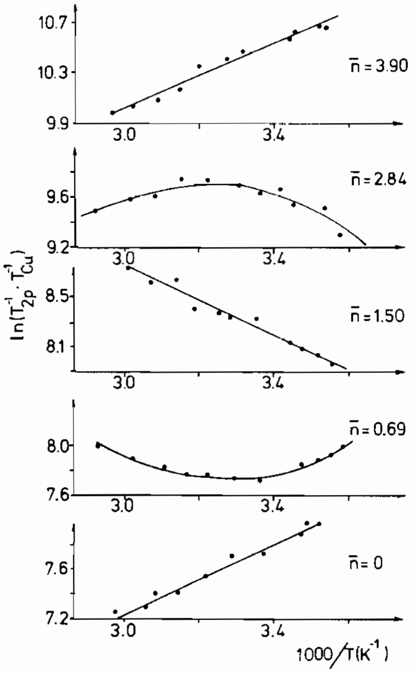

Fig. 4. The temperature dependence of the normalized relaxation rate at different $\bar{n}$ values in the copper(II)–ammonia system.

It is seen in Fig. 4 that the relaxation rate is governed by the paramagnetic relaxation time of water protons ($T_{2B}^{H_2O}$) in the solution of $\bar{n} = 0$, *i.e.* in the slightly acidified (pH ~ 2) solution of $CuCl_2$ in 2 mol dm^{-3} NH_4Cl. With the increase of the $\bar{n}$ values, however, the relaxation rate increases and the slope of the curves gradually changes, indicating that the chemical reactions are governing the measured data at higher temperature. The chemical reactions are governing the measured data at $\bar{n} \sim 1.5$ in the whole temperature range. In the $\bar{n} > 2$ range however, at higher temperature, the paramagnetic relaxation time of the protons in the coordinated ammonia ($T_{2B}^{NH_3}$) becomes the rate controlling factor, *i.e.* a second change of the slope takes place. This change is completed at about $\bar{n} \sim 4$.

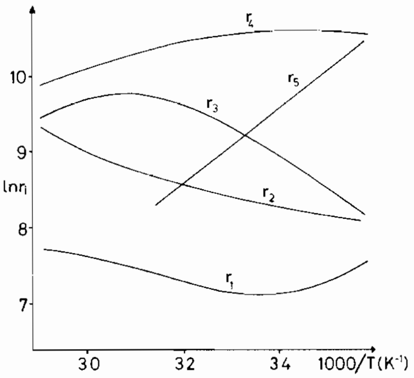

Fig. 5. The temperature dependence of the molar relaxation coefficients in the copper(II)–ammonia system.

The results are summarized in Fig. 5, where the temperature dependences of the molar relaxation coefficients are illustrated.

The complete analysis of these curves would be extremely complicated because of the following:

– The equilibrium data should be known in the whole temperature range studied. The $-\Delta H$ values used in the calculations are valid at 25 °C, thus extrapolation to the higher temperature is questionable.

– The change of the density of the solutions should be taken into account.

– The paramagnetic sites are coupled to each other. In other words, an NH_3 ligand coordinated to the mono complex, for example, might be transferred to the $Cu(NH_3)_2 \ldots Cu(NH_3)_4$ sites before its dissociation from some of these complexes. This means that the paramagnetic relaxation time of the NH_3 protons in each site influences the overall effect of all of the complexes on the measured relaxation time of water protons. The temperature dependence of all of these mutually inter-dependent parameters should also be taken into account for the complete description of the results.

– It is probable that the results at higher temperature cannot be given as a linear combination of the concentrations of the complexes, which was used in the calculation of the curves illustrated on Fig. 5.

Because of these difficulties, the results of the temperature-dependent measurements are used only to help the interpretation of the r_i values at 25 °C.

It is seen in Fig. 5 that the reaction control is valid at 25 °C for r_2 and r_3. The positive slope of r_1 at lower temperature is a straigthforward consequence of the relatively high role of the water molecules remaining in the coordination sphere. From the change of the slope at around 25 °C, however, it may be safely concluded that the $r_1^{NH_3}$ part of the molar relaxation coefficient is chemical reaction controlled.

The r_4 shows its maximum at about 25 °C, thus it may be assumed that the average lifetime ($\tau_B{}^{(4)}$) of ammonia protons in the $Cu(NH_3)_4^{2+}$ environment and their paramagnetic relaxation times ($T_{2B}{}^{(4)}$) have about the same value at this temperature.

The r_5 is controlled by the paramagnetic relaxation time in the whole range. It follows from Fig. 5 moreover, that the T_{2B} for the $Cu(NH_3)_5^{2+}$ is much higher than for the $Cu(NH_3)_4^{2+}$, indicating a change of the geometry around the copper(II) ion when the fifth ligand is coordinated.

It follows from the above that the $r_i^{NH_3}$ part of the molar relaxation coefficients for the first three complexes may be transformed to the dissociation rate constants, using the

$$(T_2^{-1} - T_{20}^{-1})^{NH_3} = \sum r_i^{NH_3} [Cu(NH_3)_i] =$$

$$\sum k_i{}^b \frac{3[Cu(NH_3)_i]}{2[H_2O]}$$

i.e.

$$k_i{}^b = 37 r_i{}^{NH_3}$$

equation.

If the $\tau_B{}^{(4)} \sim T_{2B}{}^{(4)}$ relation is accepted for the protons of $Cu(NH_3)_4$ at 25 °C, then

$$1/\tau_B{}^{(4)} = k_4{}^b \sim 74 r_4{}^{NH_3}$$

The formation and dissociation rate constants calculated on this way are collected in Table III, together with the stepwise equilibrium constants.

TABLE III. Stepwise Stability Constants, Dissociation and Formation Rate Constants in the Copper(II)–Ammonia System.

Species	log K_i	k_i^b (s^{-1})	k_i^f (M^{-1} s^{-1})
$Cu(NH_3)^{2+}$	4.18	2×10^4	$(3 \pm 1) \times 10^{8}$ [c]
$Cu(NH_3)_2^{2+}$	3.52	8.4×10^4	$(2.8 \pm 0.3) \times 10^{8}$ [b]
$Cu(NH_3)_3^{2+}$	2.76	2.9×10^5	$(1.7 \pm 0.3) \times 10^{8}$
$Cu(NH_3)_4^{2+}$	2.06	3.0×10^{6} [a]	$(3.5 \pm 1.0) \times 10^{8}$ [a]

[a] Assuming $\tau_B{}^{(4)} \sim T_{2B}{}^{(4)}$ at 25 °C. [b] The standard deviations are calculated values for i = 2 and i = 3. For i = 1 and i = 4, however, they are estimated, including the possible error of the assumptions used in the calculation. [c] Comparable data from T-jump relaxation studies: $k_1^f = 2\ 10^8\ M^{-1}\ s^{-1}$ [12], $k_1^f = 2.3\ 10^8\ M^{-1}\ s^{-1}$ [13].

It is seen in Table III that there is no dramatic change in the forward rate constants of the first four steps, thus the kinetic background of the decreasing thermodynamic stability of the stepwise complexes is the increase of the dissociation rate constants with increasing ammonia. It is interesting to note that a similar relation was found earlier for the formation and dissociation kinetics of copper(II)–ethylenediamine [9], and the opposite relation was found for the copper(II)–glycine and –L-tyrosine complexes [10, 11].

Our data for the first step are rather uncertain. The relatively high standard deviation is an inherent consequence of the fact that the relative role of the remaining water molecules is rather high, *i.e.* $r_1{}^{NH_3}$ is given as a difference of two comparable data. Only the first step of the consecutive processes has been studied earlier [12, 13], results are also given in Table III. Considering the above the agreement is satisfactory, supporting the validity of the assumptions made during the evaluation.

The value of the formation rate constants are roughly the same for all of the four steps, contrary to the usual relation found in ligand substitution reactions of the nickel(II) and cobalt(II) complexes, where the ligand bound to central ion, in general, labilize the remaining water molecules, thus fasten the further ligand substitution processes. The almost constant values of the substitution rates may be interpreted by taking into account that the substitution always occurs at one of the axial positions of the distorted octaeder, and these are occupied by loosely-bound H_2O molecules in the whole $Cu(H_2O)_6^{2+}$–$Cu(NH_3)_4(H_2O)_2^{2+}$ series. It should be taken into account moreover that the role of the neglected exchange reactions (processes iii) may increase with increasing number of water molecules in the complexes.

With the above restriction in mind, the present paper gives the first example for the complete kinetic description of a fast four-step consecutive reaction. T-jump relaxation study of all of four steps, as well as the outlined complete evaluation of the temperature-dependent measurements, would be necessary to get further experimental evidence on the assumptions used in the present work.

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