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Nmr Relaxation Studies in Solution of Transition Metal Complexes.
I. Exchange Reactions in Aqueous Solution of Copper(II)–Glycine System

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The equilibrium dynamics in aqueous solutions of copper(II)–glycine system have been investigated by measuring the transverse relaxation time of water protons in a wide concentration range. The use of a general method is illustrated to represent the paramagnetic contribution of the multi-site exchange processes involving paramagnetic site(s) to the measured relaxation time of water protons. It has been experimentally verified that the $-NH_2 \rightleftharpoons H_2O$ *proton exchange may be the rate determining step in transferring the effect of paramagnetic relaxation to the measured relaxation time of water protons. The rate constants for the* $G^- + H_2O \rightleftharpoons HG^\pm + OH^-$ *and for the* $\overset{o}{G}{}^- + HG^\pm \rightleftharpoons H\overset{o}{G}{}^\pm + G^-$ *proton exchanges are determined.*

It is shown that the rate constants of the

$$CuG_2 + \overset{o}{G}{}^- \xrightleftharpoons{k_2} CuG\overset{o}{G} + G^-$$

and

$$CuG_3^- \xrightleftharpoons[k_{-3}]{k_3} CuG_2 + G^-$$

processes could not be determined individually; only their combination of $3k_2 + 2k_{-3}$ *can be given. A suggestion for the mechanism of the ligand exchange is put forward.*

Introduction

The equilibrium dynamics in aqueous solution of transition metal complexes have been dealt with by a number of authors. Systematic comparative studies have been carried out however, in only a few laboratories [1–5].

One of the most important conditions for the study of exchange processes is to know the composition and stability of the complexes formed, frequently at such a ligand excess which is out of the usual concentration range used in the equilibrium analysis [6, 7]. The experimental and computational methods capable for the determination of the composition and stability of the complexes formed in complicated equilibrium systems have been developed during the last fifteen years [8–13]. The knowledge of equilibrium relations justifies the reinvestigation of the exchange processes and the reinterpretation of the data. It is shown in this paper that the models used for the interpretation of relaxation studies are not complete, even in such a simple system like the copper(II)–glycine.

The proton relaxation studies in aqueous solution of paramagnetic complexes give the possibility of determining the paramagnetic relaxation time (T_{2B}) and average lifetime (τ_B) of the water protons bound in the coordination sphere of the transition metal ions. The comparison of the T_{2B} data may give valuable information on the metal ion–donor atom interaction in the complexes, while τ_B is determined by the kinetics of exchange processes. It has been shown in our previous work [14] that the measured T_2 relaxation time of water protons is influenced by the $-NH_2 \rightleftharpoons H_2O$ proton exchange as well, thus the rate constants of these processes could be determined.

Having elaborated a method capable of taking into account all of the exchange processes which are influencing the measured relaxation time, our aim is to carry out systematic comparative studies of the exchange processes and paramagnetic relaxation in solution of transition metal complexes. The present paper deals with the basis of the method and the results of the reinvestigation of the copper(II)–glycine system. The aim of the reinvestigation was to get direct experimental evidence on the $-NH_2 \rightleftharpoons H_2O$ proton exchange as a limit of paramagnetic line broadening, and to get a deeper insight into the inter-dependence of the parameters representing the CuG_2 and CuG_3^- complexes.

Mathematical Considerations

It is known from the study of Beattie *et al.* [7], that at high ligand excess CuG_3^- complex is also formed beside CuG_2 in the system, thus the labile protons may be found in five different chemical environments: CuG_2, CuG_3^-, $HG^\pm$, G^- and H_2O. In the pH range 8–11 the following exchange processes are to be taken into account [7, 15,16]:

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

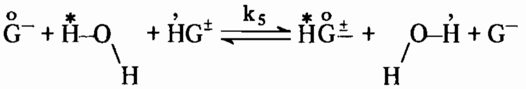
$$v_2 = k_2[CuG_2][G^-] \qquad (1)$$

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

$$v_3 = k_3[CuG_3^-] = k_{-3}[CuG_2][G^-] \qquad (2)$$

$$G^- + \overset{*}{H}OH \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \overset{*}{H}G^\pm + OH^-$$

$$v_4 = k_4[G^-] = k_{-4}[HG^\pm][OH^-] \qquad (3)$$



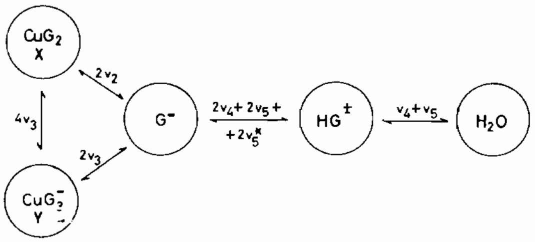
$$\overset{o}{G}^- + \overset{*}{H}\text{–}O(H) + \overset{,}{H}G^\pm \overset{k_5}{\rightleftharpoons} \overset{*}{H}\overset{o}{G}^\pm + (H)O\text{–}\overset{,}{H} + G^-$$

$$v_5 = k_5[G^-][HG^\pm] \qquad (4)$$

$$\overset{o}{G}^- + \overset{*}{H}G^\pm \overset{k_5^*}{\rightleftharpoons} \overset{*}{H}\overset{o}{G}^\pm + G^-$$

$$v_5^* = k_5^*[HG^\pm][G^-] \qquad (5)$$

The different chemical environments and the rate of the exchange processes taking place between them are illustrated on the following scheme:



The coefficients in front of the rates denote the number of protons changing their environment when the exchange process takes place. The rates of the paramagnetic relaxations are also denoted on the scheme by X and Y. These may be expressed with the help of the paramagnetic relaxation times according to the following:

$$X = \frac{4[CuG_2]}{T_{2B}^{(2)}}, \quad Y = \frac{6[CuG_3^-]}{T_{2B}^{(3)}} \qquad (6)$$

It is seen on the scheme that the rate of some of the exchange processes may be regulated independently of each other. If the concentrations of CuG_2 and CuG_3^- are small compared to that of G^-, making $v_2 + v_3 \ll v_4 + v_5$, then the exchange processes within the diamagnetic environments do not influence the measured relaxation time of the water protons. In this case, at low $[G^-]$ the v_2 and v_3 ligand exchange rates, while at higher $[G^-]$ the X and Y relaxation rates, control the measured relaxation times. It is seen moreover that by increasing the v_2 and v_3 rates at low $[G^-]$, *i.e.* by increasing the CuG_2 and CuG_3 concentrations, the v_4 and v_5 exchange rates will determine the measured relaxation time. The concentration-dependence of v_2 and v_3 are the same, therefore these cannot be regulated independently. The ratio of the effect of the paramagnetic relaxation rates (X and Y) is determined by $[G^-]$, because it controls the $[CuG_3^-]/[CuG_2]$ ratio through the equilibrium process $CuG_2 + G^- \rightleftharpoons CuG_3^-$.

The mathematical relation between the rate constants and the measured relaxation time may be derived in three different ways. One of these is based on the matrix formulation of the Bloch equations by Reeves and Shaw [17]. Their considerations may be extended to get an explicit expression for the measured relaxation time; a brief account of the extension is given elsewhere [18]. The second method – based on probability theory considerations – was elaborated in our earlier paper [14]. This approach is rather complicated and difficult to generalize. In this paper a third method is used [19], because this seems to be the most compact and may be applied to all of the systems studied by us so far.

Let us introduce the following notations: $a = [H_2O]$, $b = [HG^\pm]$, $c = [G^-]$, $d = [CuG_2]$, $e = [CuG_3^-]$. f_i stands for the fraction of unrelaxed protons in the i-th chemical environment. Its change in the H_2O environment is detected, the f_i-s for the other sites are unaltered, *i.e.*:

$$-\frac{d(2a \cdot f_a)}{dt} = (v_4 + v_5)(f_a - f_b) = \frac{2a \cdot f_a}{T_{2P}}$$

$$\frac{d(3b \cdot f_b)}{dt} = (v_4 + v_5)f_a + (2v_4 + 2v_5 + 2v_5^*)f_c - $$
$$- (3v_4 + 3v_5 + 2v_5^*)f_b = 0$$

$$\frac{d(2c \cdot f_c)}{dt} = (2v_4 + 2v_5 + 2v_5^*)f_b + 2v_2 f_d + 2v_3 f_e - $$
$$- (2v_2 + 2v_3 + 2v_4 + 2v_5 + 2v_5^*)f_c = 0$$

$$\frac{d(4d \cdot f_d)}{dt} = 2v_2 f_c + 4v_3 f_e - (2v_2 + 4v_3)f_d - \frac{4d \cdot f_d}{T_{2B}^{(2)}} = 0$$

TABLE I. Concentrations of the Solutions Used for T_2 Measurements.

Constant concentrations		Changing concentrations	Number of exp. points	Sensitive parameters
$[CuG_2]$	$[HG^{\pm}]$	$[G^-]$		
0.002	0.001			
0.003	0.005	0–0.05	126	k_2, k_{-3}, $T_{2B}^{(2)}$
0.004	0.010			
0.0004				
0.0009	0.60	0–1.2	173	k_2, k_{-3} $T_{2B}^{(2)}, T_{2B}^{(3)}$
0.0020				
0.0030				
$[G^-]$	$[HG^{\pm}]$	$[CuG_2]$		
0.003				
0.004	0.001 0.010	0–0.02	107	k_4, k_5, k_5^*
0.005				
$[CuG_2]$	$[G^-]$	$[HG^{\pm}]$		
0.002	0.001			
0.004	0.002	0–0.06	72	k_5, k_5^*
0.006	0.003			

$$\frac{d(6e \cdot f_e)}{dt} = 2v_3 f_c + 4v_3 f_d - 6v_3 f_e - \frac{6e \cdot f_e}{T_{2B}^{(3)}} = 0$$

where T_{2P} denotes the contribution of the exchange reactions (1)–(5) to the measured relaxation time. The first equation may be rearranged to get an explicit expression for T_{2P}^{-1}:

$$T_{2P}^{-1} = \frac{1}{2a}(v_4 + v_5)\left(1 - \frac{f_b}{f_a}\right) \tag{8}$$

For the sake of expressing the ratio f_b/f_a, the remaining four equations are divided by f_a, and the $A = 2v_2$, $B = 2v_3$, $C = v_4 + v_5$ and $D = 2v_4 + 2v_5 + 2v_5^*$ notations are introduced:

$$\begin{aligned}
&(C + D)\frac{f_b}{f_a} - D\frac{f_c}{f_a} = C \\
&-D\frac{f_b}{f_a} + (A + B + D)\frac{f_c}{f_a} - A\frac{f_d}{f_a} - B\frac{f_e}{f_a} = 0 \\
&-A\frac{f_c}{f_a} + (A + 2B + X)\frac{f_d}{f_a} - 2B\frac{f_e}{f_a} = 0 \\
&-B\frac{f_c}{f_a} - 2B\frac{f_d}{f_a} + (3B + Y)\frac{f_e}{f_a} = 0
\end{aligned} \tag{9}$$

f_b/f_a may be given by the appropriate determinants of these linear equations. Substituting f_b/f_a into eqn. (8), after the possible simplification the following relation is given:

$$T_{2P}^{-1} = \frac{1}{2[H_2O]}\,\frac{Z}{W}\,\frac{\dfrac{CD}{C + D}}{\dfrac{Z}{W} + \dfrac{CD}{C + D}} \tag{10}$$

where:

$$Z = 3AB(X + Y) + (A + B)XY + 2B^2(X + Y)$$

$$W = (A + 2B + X)(3B + Y) - 4B^2$$

The detailed interpretation of the rather complicated eqn. (10) is given in our previous paper [14].

Experimental

It has been shown above that the effect of the individual exchange processes on the measured

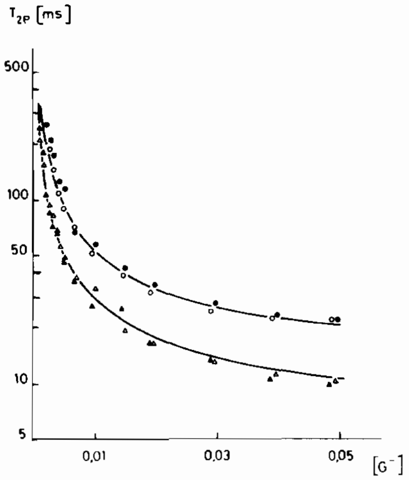


Fig. 1. T_2 relaxation time as a function of free glycinate concentration.

	$[CuG_2]$	$[HG^\pm]$
○——○——○	0.002	0.001
●——●——●	0.002	0.010
▲——▲——▲	0.004	0.001
△——△——△	0.004	0.010

(The $[CuG_2]$ changes along the function, because of CuG_3^- formation. $[CuG_2]$ stands for the total copper concentration in Table I and in the Figures).

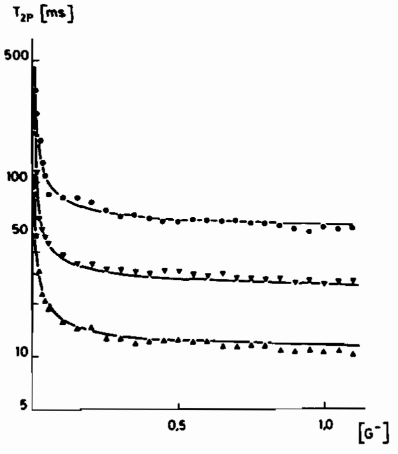


Fig. 2. T_2 relaxation time as a function of free glycinate concentration at high ligand excess. $[HG^\pm] = 0.6$.

	$[CuG_2]$
●——●——●	0.0004
△——△——△	0.0009
▲——▲——▲	0.0020.

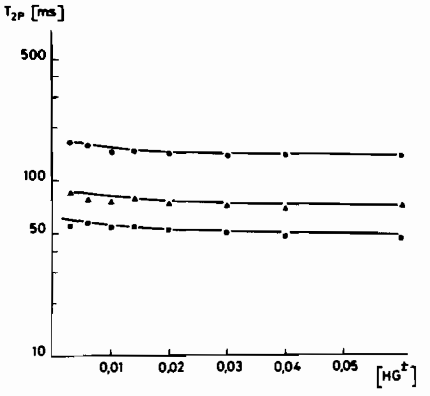


Fig. 3. T_2 relaxation time as a function of $HG^\pm$ concentration. $[CuG_2] = 0.006$.

	$[G^-]$
●——●——●	0.001
▲——▲——▲	0.002
■——■——■	0.003.

relaxation time is determined by the relative concentration of CuG_2, CuG_3^-, G^- and $HG^\pm$. Because of the $CuG_2 + G^- \rightleftharpoons CuG_3^-$ equilibrium, however, the concentration of only three of them could be altered independently.

For studying the individual effect of the exchange processes involving the independent environments, stock solution-pairs were prepared in which the concentration of two species was the same, but the concentration of the third species altered significantly. The relaxation time measurements have been carried out on solutions made from these by appropriate mixing. Thus experimental points on the $(T_2)_{[G^-],[HG^\pm]} = f([CuG_2])$, $(T_2)_{[CuG_2],[HG^\pm]} = f([G^-])$ and $(T_2)_{[CuG_2],[G^-]} = f([HG^\pm])$ functions have been directly measured. The two constant concentrations, the concentration range of the third species, the number of experimental points, and the parameters sensitive to the given experimental arrangement are included in Table I. The two constant concentrations have been used in all combinations. The first part of Table I, for example, indicates nine different series of measurements on the $(T_2)_{[CuG_2],[HG^\pm]} = f([G^-])$ function with 126 experimental points altogether.

The T_2 relaxation times have been measured by a Newport N20 NMR Spectrometer, using a Tektronix 5103 N type memory oscilloscope. This simple instrument is applicable for measuring the T_2 relaxation time of water protons in the 5–500 msec interval with a precision of about 5%. The temperature of the samples was kept constant at 25 ± 0.5 °C; all of the stock solutions were 1 *M* in KCl.

Results and Discussion

Some of the results are illustrated in Figs. 1–5. The lines in the Figures were calculated from the parameters in Table II.

Figure 1 shows that the increase of $[G^-]$ decreases the relaxation time. On a scale which is linear for T_2^{-1}, these points are characterized by saturation

TABLE II. The Exchange Rate Constants and Paramagnetic Relaxation Times in the Copper(II)–Glycine System, together with the Earlier Reported Values.

		Present work	Ref. 7			Ref. 14
$3k_2 + 2k_{-3}$	$(M^{-1}\ sec^{-1})$	$2.3\ 10^8$				
$T_{2B}^{(2)}$	(sec)	$9.2\ 10^{-7}$	$3.4\ 10^{-6}$ [h]	$7\ 10^{-7}$ [c]	$4\ 10^{-6}$ [d]	$1.4\ 10^{-6}$
$k_3^{-1} + T_{2B}^{(3)}$	(sec)	$1.1\ 10^{-6}$				
k_4	(sec^{-1})	$3.3\ 10^6$		$8\ 10^5$ [e]	$1.6\ 10^6$ [f]	$4.2\ 10^6$
k_5	$(M^{-1}\ sec^{-1})$	$1.3\ 10^8$		$3.4\ 10^6$ [g]	$7.6\ 10^7$ [f]	$4.2\ 10^7$
k_2	$(M^{-1}\ sec^{-1})$	$7.7\ 10^7$ [a]	$1.5\ 10^7$ [h]	$8.2\ 10^6$ [c]	$2.6\ 10^6$ [d]	$1.0\ 10^8$
k_{-3}	$(M^{-1}\ sec^{-1})$	$1.2\ 10^8$ [a]	$1.0\ 10^8$ [b]			
$T_{2B}^{(3)}$	(sec)	$1.1\ 10^{-6}$ [a]	$1.4\ 10^{-6}$ [b]			

[a] The possible maximum value of the parameter. [b] See note 39 in ref. 7. [c] See ref. 5, based on water protons. [d] See ref. 5, based on $-CH_2-$protons. [e] See ref. 21. [f] See ref. 16. [g] See ref. 22. [h] Based on $-CH_2-$protons.

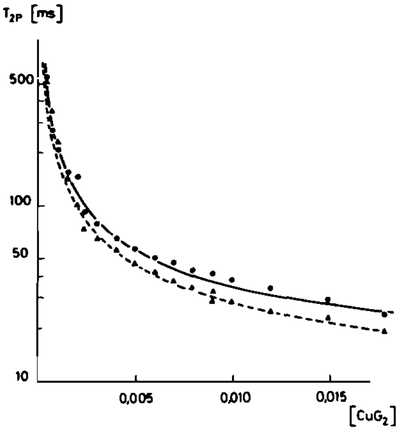


Fig. 4. T_2 relaxation time as a function of CuG_2 concentration. $[Hg^{\pm}] = 0.0012$.

	$[G^-]$
●——●——●	0.004
▲——▲——▲	0.005

curves, indicating that at high $[G^-]$, the measured relaxation rate is determined by the paramagnetic relaxation.

Figure 2 shows the results at higher ligand concentrations. It is seen that there is a small, but continuous decrease of the relaxation time even in the $0.5 < [G^-] < 1.0\ M$ range. This decrease is evidently the consequence of CuG_3^- formation.

Figure 3 illustrates, that the $HG^{\pm}$ concentration has only a minor effect on the measured relaxation rates. This is easily explained because at constant $[CuG_2]$ and $[CuG_3^-]$, the decrease of $[HG^{\pm}]$ is accompanied by the increase of $[OH^-]$, *i.e.* there is no significant change in the v_4 proton exchange rate. The minor, but detectable decrease of the relaxation time indicates the role of v_5 and v_5^* rates in transferring the paramagnetic relaxation to the H_2O environment.

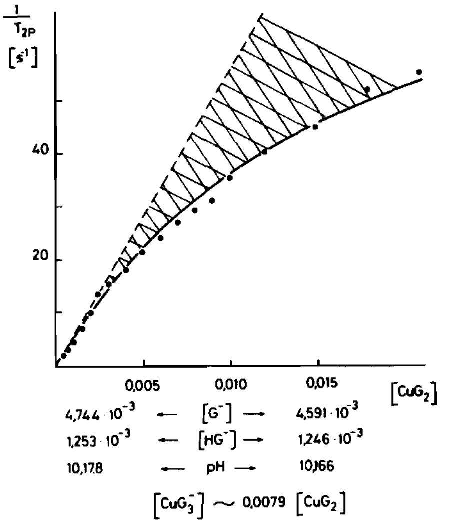


Fig. 5. T_{2P}^{-1} as a function of CuG_2 concentration. The changes of $[G^-]$, $[HG^{\pm}]$ and pH between the first and last points are also given. The ratio of $[CuG_3^-]$ and $[CuG_2]$ is constant along the curve.

Figures 4 and 5 illustrate the $(T_2)_{[G^-],[HG^{\pm}]} = f([CuG_2])$ function on logarithmic and reciprocal T_2 scales. It is seen that the experimental points in Fig. 5 are characterized by a saturation curve. Its deviation from linearity – marked with lines – is direct experimental evidence of the effect of $-NH_2 \rightleftharpoons H_2O$ proton exchange on the paramagnetic relaxation of water protons.

Equation (10) expresses the paramagnetic contribution to the measured relaxation rate. The measured data, however, contain the relaxation of water in the absence of copper(II) containing species and the relaxation rates originating from the exchange of water molecules remaining in the first coordination sphere of the complexes with the bulk water. Therefore the measured data may be given as follows:

$$T_2^{-1} = T_{20}^{-1} + \Sigma r_i [CuL_i] + T_{2P}^{-1} \quad (11)$$

where r_i is the molar relaxation rate effect of the i-th copper(II) containing species. Its value for CuG_2 has been determined by measuring the relaxation time as a function of average number of ligands in the $0.5 < \bar{n} < 1.8$ range (no ligand exchange). r_i for CuG_3^- cannot be determined; it was assumed to be one half of r_i for CuG_2. The numerical values for the parameters of eqn. (11) are as follows: $T_{20}^{-1} = 1.75$ sec^{-1}, $r_{CuG_2} = 440\ M^{-1}$ sec^{-1}, $r_{CuG_3^-} = 220\ M^{-1}$ sec^{-1} (assumed). The contribution of the $\Sigma r_i [CuL_i]$ terms of eqn. (11) to the measured relaxation rate in general remains below 10%. The equilibrium data used for the concentrations of the interacting species are as follows:
$pK = -\lg([H^+][G^-]/[HG^\pm]) = 9.60$ [20],
$K_3 = [CuG_3^-]/([CuG_2][G^-]) = 1.7$ [7], $pK_W = -\lg[H^+][OH^-] = 13.78$ [20]. For the calculation of the rate constants and paramagnetic relaxation times, the $\Sigma(\lg T_{2P}^{exp} - \lg T_{2P}^{calc})^2$ function has been minimized taking into account all of the experimental points.

The results of the computation showed that the k_5 and k_5^* rate constants are insensitive to the experimental data. This is the expected result, taking into account the considerations concerning Fig. 3. Therefore, the earlier result of Scheinblatt and Gutowsky [15] has been accepted: $k_5 + k_5^* = 3.8\ 10^8\ M^{-1}$ sec^{-1}, and only k_4 and k_5 proton exchange rate constants have been calculated.

The calculation of the parameters concerning the paramagnetic environments (k_2, k_3, $T_{2B}^{(2)}$, $T_{2B}^{(3)}$) did not lead to any acceptable result. In our previous paper it was assumed that the computational difficulty is the consequence of the relatively low amount of CuG_3^-. Therefore we have carried out experiments at high $[G^-]$, where more than 50% of the copper(II) is in the CuG_3^- form. In spite of this the four parameters could not be calculated simultaneously; the equations became 'ill-conditioned'. The subsequent mathematical analysis of Z/W showed that the four parameters are not independent of each other; this is in fact a three-parameter function. A rather lengthy, but mathematically simple derivation shows that Z/W may be transformed into the following form:

$$\frac{Z}{W} = \frac{P + R[G^-]}{1 + S[G^-]} [CuG_2][G^-] \quad (12)$$

Then k_2, k_3, $T_{2B}^{(2)}$ and $T_{2B}^{(3)}$ have the following relationships with P, R and S:

$$3k_2 + 2k_{-3} = \frac{R}{4S} + \frac{3P}{4} + \sqrt{\left(\frac{R}{4S} + \frac{3P}{4}\right)^2 - \frac{PR}{S}} \quad (13)$$

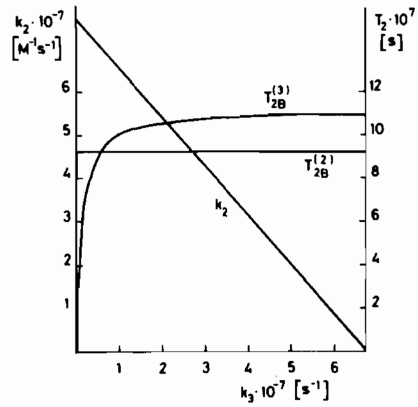


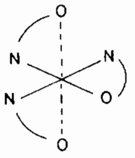
Fig. 6. Inter-dependence of the parameters representing the paramagnetic sites.

$$k_3^{-1} + T_{2B}^{(3)} = K_3/(3P/2 - 3k_2 - 2k_{-3}) \quad (14)$$

$$T_{2B}^{(2)} = \frac{R}{K_3} \frac{k_3^{-1} + T_{2B}^{(3)}}{3k_2 + 2k_{-3}} \quad (15)$$

Equations (13)–(15) show that only the $T_{2B}^{(2)}$ could be determined independently; k_2 and k_{-3} as well as k_3^{-1} and $T_{2B}^{(3)}$ are inter-dependent parameters. Their inter-dependence is illustrated in Fig. 6.

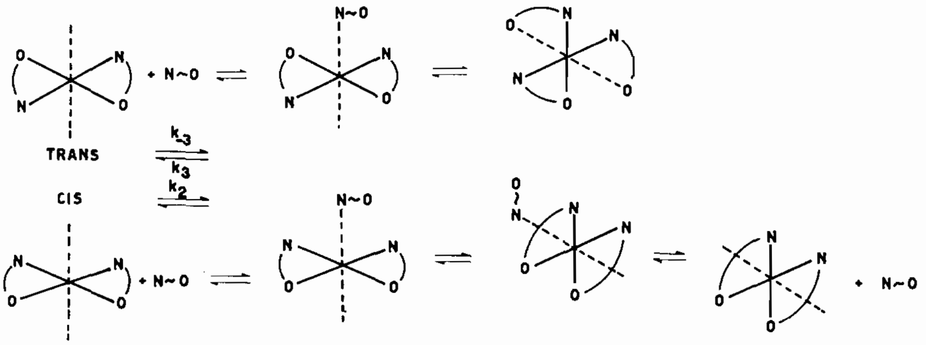
The derived relations show that the assumption of one of the exchange processes denoted by k_2 and k_{-3} would be satisfactory to represent the experimental data. The assumption of both processes however is supported by the following considerations. The CuG_3^- in solution probably contains three equatorial Cu–N bonds, *i.e.* its assumed structure is the following:



It is known that the CuG_2 may occur in *cis* and *trans* form in solution, and the ligand exchange occurs through a Jahn–Teller inversion. Thus the following mechanisms of the ligand exchange are probable (*cf.* Scheme C).

It is seen above that three equatorial Cu–N bonds may be formed only from the *trans* CuG_2 complex, *i.e.* k_2 and k_{-3} may probably be assigned to the *cis* and *trans* CuG_2.

The calculated rate constants and relaxation times are collected in Table II, together with the available literature data. It should be stressed, however, that one relaxation time is calculated for the $-NH_2$ protons of each complexes, although there may be different chemical environments character-



Scheme C

ized by different relaxation times in both CuG_2 and CuG_3^- species.

From the comparison of the data in Table II and taking into account the previous considerations, the following conclusions can be drawn.

The ligand exchange reactions taking place in the system cannot be separated; only their combination could be given. The formulae given by Beattie *et al.* [7] are probably not complete; they have not taken into account the ligand exchange between CuG_2 and CuG_3^- sites when the process denoted by k_3 takes place. This incompleteness may explain that they could give a definite value for k_2, and that they found the $T_{2B}^{(3)} < T_{2B}^{(2)}$ relation, which cannot be easily explained. The $T_{2B}^{(3)} > T_{2B}^{(2)}$ relation is more conceivable because of the presumebly increased Cu–N bond length in CuG_3^- compared to CuG_2. It is interesting, however, that according to their preliminary ultrasonic experiments, $k_{-3} = 1.0\ 10^8$ $M^{-1}\,sec^{-1}$, which agrees well with the maximum value of k_{-3}, at the limiting case of $k_2 = 0$. This agreement suggests that the ligand exchange takes place only through the formation and decomposition of CuG_3^-. The results published in the following parts do not exclude that this is the main reaction pathway, but indicate that the ligand exchange represented by k_2 plays also a role in the overall process.

The surprisingly low values given for k_2 in ref. 5 can probably be explained by the authors not having taken into account CuG_3^- formation.

The deviation of the ligand exchange rate constants and relaxation times given in our previous and present paper is explained in part by the fact that we did not realize the interdependence of the parameters. The aim of the previous paper was first of all the illustration of the effect of $-NH_2 \rightleftharpoons H_2O$ proton exchange on the paramagnetic relaxation of water protons. The present experiments, however, were designed to study the different effects separately, thus to get exact values for all of the parameters.

The proton exchange rate constants determined by us and by Chang and Grunwald [16], taking into account the basically different experimental conditions and methods, are in good agreement.

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