Inorganica Chimica Acta, 57 (1982) 135–140

NMR Relaxation Studies in Solution of Transition Metal Complexes.
3. Equilibrium Dynamics in Aqueous Solution of Copper(II)–Bipyridyl–Glycine System

F. DEBRECZENI and I. NAGYPÁL

Institute of Inorganic and Analytical Chemistry, L. Kossuth University, H-4010 Debrecen, Hungary

Received February 25, 1981

The rate constants of the ligand exchange processes and the paramagnetic relaxation involving the mixed ligand copper(II)–bipyridyl–glycine complex have been determined by measuring the T_2 *relaxation time of the water protons. It was found that the kinetic activity of the* $CubipyG^+$ *mixed complex against the ligand exchange process is not significantly different from that of the* CuG_2 *parent complex. An extremely high rate constant was found for the*

$$Cubipy_2^{2+} + G^- \underset{k_6}{\overset{k_{-6}}{\rightleftharpoons}} CubipyG^+ + bipy$$

reaction ($k_{-6} = 7.1\ 10^8\ M^{-1}\ sec^{-1}$), i.e. *the kinetic background of the stabilization of the mixed complex is the lability of the cis-octahedral* $Cubipy_2^{2+}$ *complex. The decrease of* T_{2B} *of the mixed complex compared to that of* CuG_2 *shows, that the stabilization is reflected not only in the Cu–O bond, but in the Cu–N bond as well.*

Introduction

It is well known from the systematic work of Sigel *et al.* [1–6] that the mono-bipyridyl copper(II) complex exhibits discriminating behaviour toward the second ligand. It forms relatively stable mixed complexes with ligands containing oxygen donor atom, but there is no significant stabilization in the mixed ligand complexes with ligands containing nitrogen donor atoms [7]. The mixed complex formed with glycine is also significantly stabilized, this effect being attributed to the presence of the carboxylate group.

Pasternack *et al.* [8] studied the kinetic background of the stabilization, by measuring the formation rate constants. They found that the second order rate constant of the $Cubipy^{2+} + G^- \rightleftharpoons CubipyG^+$ mixed complex formation is four times higher than that of the $CuG^+ + G^- \rightleftharpoons CuG_2$ reaction, while the kinetic stability of $CubipyG^+$ against spontaneous dissociation is 2.5-times higher than that of CuG_2. Thus the more favourable formation and the decreased lability of the mixed complex are responsible for the thermodynamic stabilization. One of the aims of the present work was to see how the thermodynamic stabilization is reflected in the kinetic parameters of the exchange reactions taking place in the copper(II)–bipyridyl–glycine system.

In the previous parts of this series [9, 10] the NMR relaxation method was used to study the equilibrium dynamics in aqueous solution of some copper(II) parent complexes. The secondary aim of this work was to see the applicability of the method for studying the ligand exchanges in mixed ligand systems. The copper(II)–bipyridyl–glycine system is especially suitable for this because only the glycine has labile protons in its ligand form: only the glycine is responsible for the transfer of the paramagnetic relaxation to the water protons. The use of this method for the study of mixed complexes has been attempted only in one research group [11–13]. The equilibrium data were not completely available at those experimental conditions which were used in the kinetic studies (1 *M* KCl, 25 °C); thus some pH-potentiometric titrations were also performed to obtain the necessary equilibrium constants.

Experimental

pH-potentiometric measurements were performed for the determination of the formation constant of the $Hbipy^+$ species and the equilibrium constants for the $Cubipy^{2+} + bipy \rightleftharpoons Cubipy_2^{2+}$, $Cubipy_2^{2+} + bipy \rightleftharpoons Cubipy_3^{2+}$ and $Cubipy^{2+} + G^- \rightleftharpoons CubipyG^+$ reactions. The formation constant of $Cubipy^{2+}$ species can not be determined pH-metrically, because the $Cu^{2+} + Hbipy^+ = Cubipy^{2+} + H^+$ reaction is practically stoichiometric even at pH 1–1.5. The other constants necessary to calculate the concentration distribution are known [14]. The pH resulting from the $Cubipy^{2+} + Hbipy^+ = Cubipy_2^{2+} + H^+$ reaction is also near to its stoichiometric value, thus a special titration method was chosen for the determination of the

TABLE I. The Concentrations of Solutions Used for Equilibrium Studies in the Copper(II)–Bipyridyl–Glycine System.

No.	Initial solution			Titrant
	T^o_{bipy}	T^o_H		c_{CuCl_2}
1.	0.0200	0.0234		0.1268
2.	0.0200	0.0281		
3.	0.0200	0.0328		
	$T^o_{Cu} = T^o_{bipy} = T^o_G$	T^o_H		c_{KOH}
4.	0.0020	0.00434		0.09643
5.	0.0030	0.00651		
6.	0.0040	0.00868		
	T^o_{Cu}	T^o_{bipy}	T^o_H	c_{KOH}
7.	0.0020	0.020	0.0239	0.3706
8.	0.0020	0.015	0.0179	
9.	0.0040	0.020	0.0239	
10.	0.0040	0.015	0.0179	
	T^o_{bipy}	T^o_H		c_{KOH}
11.	0.0100	0.0120		0.3706
12.	0.0150	0.0179		
13.	0.020	0.0239		

equilibrium constant. Initial solutions containing H^+ and $Hbipy^+$ were titrated by $CuCl_2$, until the T_{Cu}/T_{bipy} ratio reached to 1.2:1.0. The initial concentrations are listed in Table I (upper part).

One of the titration curves – between T_{Cu}/T_{bipy} 0.5–1.0 – is seen in Fig. 1. The dotted line represents the calculated pH limit, which would be measured in completely stoichiometric proton-release. The deviation of the experimental points from this curve is very small, but at this experimental arrangement it is measurable.

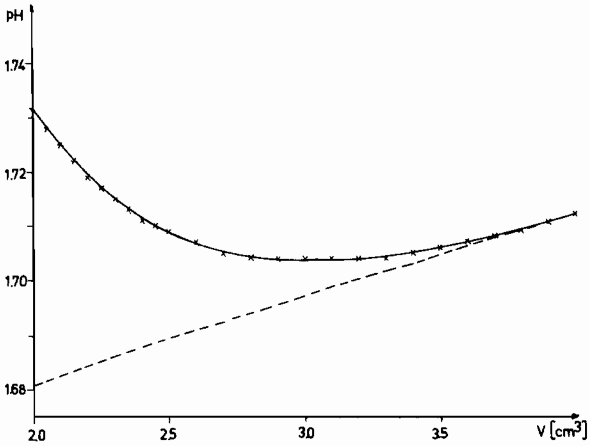


Fig. 1. Titration curve No. 1 in Table I, for the determination of $K^{Cubipy}_{Cubipy_2}$ equilibrium constant. The dotted line shows the theoretically calculated pH, assuming that the $Cubipy^{2+}$ + $Hbipy^+$ = $Cubipy_2^{2+}$ + H^+ reaction is completely stoichiometric.

The calculation of the $1 < \bar{n} < 2$ part of the formation curve is based on such titrations. This part of the formation curve is seen in Fig. 2, indicating that the K_2 equilibrium constant could be safely determined.

The equilibrium constants for the other processes were determined by using the usual pH-titration method. The total concentrations of the components in the initial solutions are given in Table I.

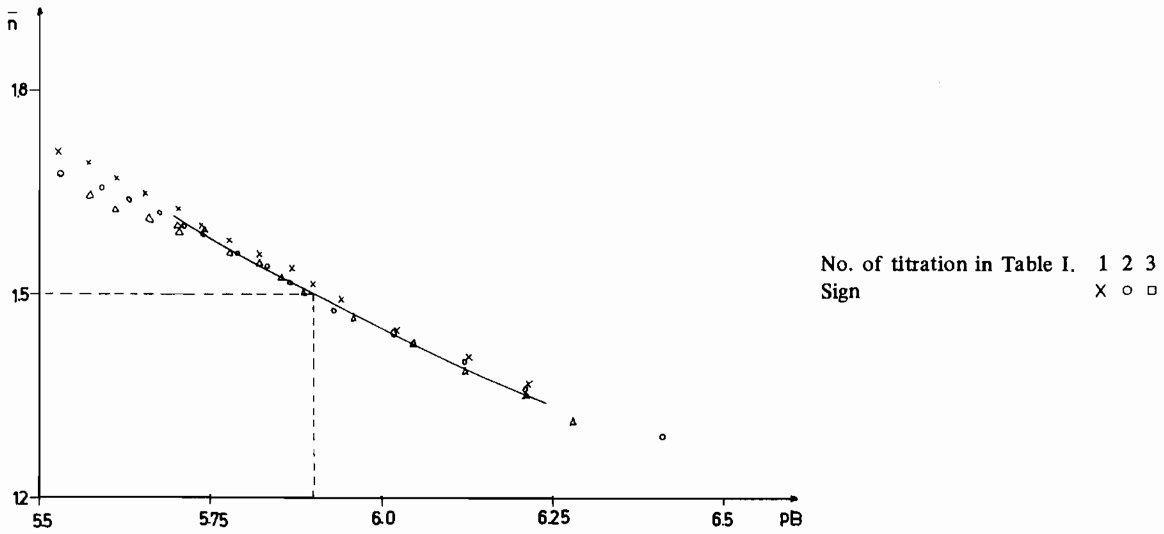


Fig. 2. The $1.2 < \bar{n} < 1.8$ part of the formation curve in the copper(II)–bipyridyl system.

TABLE II. Equilibrium Constants Used for Calculation of the Concentration Distribution (I = 1 *M* KCl, 25 °C).

	L = bipy	L = glycine
$\lg K^{L}_{HL}$	4.63[a]	9.61[c]
$\lg K^{HL}_{H_2L}$	–	2.42[c]
$\lg K^{Cu}_{CuL}$	8.00[b]	7.98[c]
$\lg K^{CuL}_{CuL_2}$	5.90[a]	6.62[c]
$\lg K^{CuL_2}_{CuL_3}$	3.25[a]	0.23[d]
$\lg K^{Cubipy}_{CubipyG}$	7.40[a]	

[a] This work. [b] Ref. 16, I = 0.1 *M* NaClO$_4$, 25 °C, (see text). [c] Ref. 14. [d] Ref. 22.

A Radiometer PHM-52 type pH-meter, with GK-2301B combined electrode calibrated for $-\lg[H^+]$ according to Irving *et al.* [15], was used for the titrations. The formation constant for Cubipy^{2+} is not available at 1 *M* KCl, 25 °C. However, because of the stoichiometric formation, its value does not affect the concentration distribution of the complexes formed in ligand excess, as long as the other equilibrium constants are correct. Thus $\log K_1 = 8.00$ [16] valid for 0.1 *M* NaClO$_4$, 25 °C was used to calculate the concentration distribution. The equilibrium constants used for the calculations are given in Table II.

The T_2 measurements have also been carried out as titrations, in a similar manner as was described in Part 2. The concentrations of the initial solutions are given in Table III.

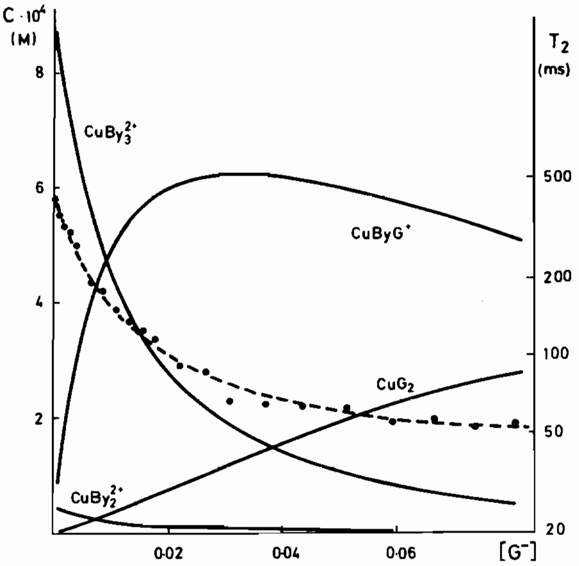


Fig. 3. The T_2 relaxation time and the concentration distribution of the paramagnetic complexes as a function of free glycinate concentration (Titration No. 9 in Table III). The CuG$_3^-$ is only a minor species in this concentration range, and therefore its concentration is not shown.

Titration No. 1 has been performed to determine the r_i values for Cubipy$_2^{2+}$ and Cubipy$_3^{2+}$. The plot of $(T_2^{-1} - T_{20}^{-1})/[\text{Cubipy}_3^{2+}]$ as a function of $[\text{Cubipy}_2^{2+}]/[\text{Cubipy}_3^{2+}]$ in the $2 < \bar{n} < 3$ range gave a straight line with zero intercept, indicating that no water molecule remains in the first coordination sphere of Cubipy$_3^{2+}$, and that the second sphere relaxation could be neglected. r_i for the Cubipy$_2^{2+}$ complex was found to be 800 M^{-1} sec^{-1}.

TABLE III. Concentration of the Initial Solutions Used for T_2 Relaxation Time Measurements.[a]

No.	Initial solution			Titrant	No. of exp. points
	T^o_{Cu}	T^o_{bipy}	T^o_{H}	c_{KOH}	
1.	0.002	0.02	0.0239	0.3706	25
	T^o_{Cu}		T^o_{bipy}	glycine	
2.	0.002		0.005	0.5 *M* G$^-$ +0.2 *M* HG$^\pm$	25
3.	0.002		0.010		25
4.	0.002		0.015		21
5.	0.002		0.020		24
6.	0.002		0.025		17
7.	0.001		0.005		21
8.	0.001		0.010		19
9.	0.001		0.015		21
10.	0.001		0.020		22
11.	0.001		0.025		20

[a] Before titration of No. 2–11, the titratable proton concentration had been neutralized, *i.e.* $T^o_H = 0$.

The $[G^-]/[HG^\pm]$ ratio during an NMR titration did not change very much; the pH range of the study of the exchange processes remained between 9.6 and 10.0, including all of the experimental points. As an example, the result of titration No. 9 is illustrated in Fig. 3, together with the concentration distribution of the species. The concentration distribution was calculated by a subroutine based on the SCOGS [17] principle.

Results and Discussion

The kinetic parameters of the exchange processes taking place in the copper(II)–glycine system are known from previous work [9]. Thus, for the evaluation of the relaxation time measurements only those processes which involve the mixed complex $\mathrm{CubipyG}^+$ had to be taken into account. The possible second order ligand exchange processes responsible for the transfer of G^- between the mixed complex and the bulk ligands are as follows:

$$\mathrm{Cubipy}\overset{*}{\mathrm{G}}{}^{+} + \mathrm{G}^- \overset{k_1}{\rightleftharpoons} \mathrm{CubipyG}^+ + \overset{*}{\mathrm{G}}{}^-$$

$$L = 2k_1[\mathrm{CubipyG}^+][G^-] \tag{1}$$

$$\mathrm{CubipyG}^+ + \mathrm{G}^- \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} \mathrm{CuG_2} + \mathrm{bipy}$$

$$N = 2\,k_7[\mathrm{CubipyG}^+][G^-] \tag{2}$$

$$\mathrm{CubipyG}^+ + \mathrm{bipy} \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} \mathrm{Cubipy}_2^{2+} + \mathrm{G}^-$$

$$M = 2k_6[\mathrm{CubipyG}^+][\mathrm{bipy}] \tag{3}$$

The relaxation rate in the $\mathrm{CubipyG}^+$ complex is denoted by Q:

$$Q = \frac{2[\mathrm{CubipyG}^+]}{T_{2B}^{(1,1)}} \tag{4}$$

Beside these, the exchange processes and paramagnetic relaxations denoted by A, B, C, D, X and Y in part 1 [9] have to be considered to describe the measured data. Thus, the scheme below represents the system studied.

The methods used to derive the measured T_2 as a function of the rates denoted on the scheme are given elsewhere [9, 18]. The same method could be used for this model, but the result is much more complicated than in the case of the copper(II)–glycine system. The exact mathematical analysis of the function to determine the inter-dependence of the parameters would be extremely difficult. Thus the evaluation was carried out in the following way:

The rate constants determined for the processes C, D and X have been accepted:

$$C = 3.3\ 10^6[G^-] + 1.3\ 10^8[G^-][HG^\pm]$$

$$D = 7.6\ 10^8[G^-][HG^\pm] + 6.6\ 10^6[G^-]$$

$$X = 4[\mathrm{CuG_2}]/9.2\ 10^{-7}$$

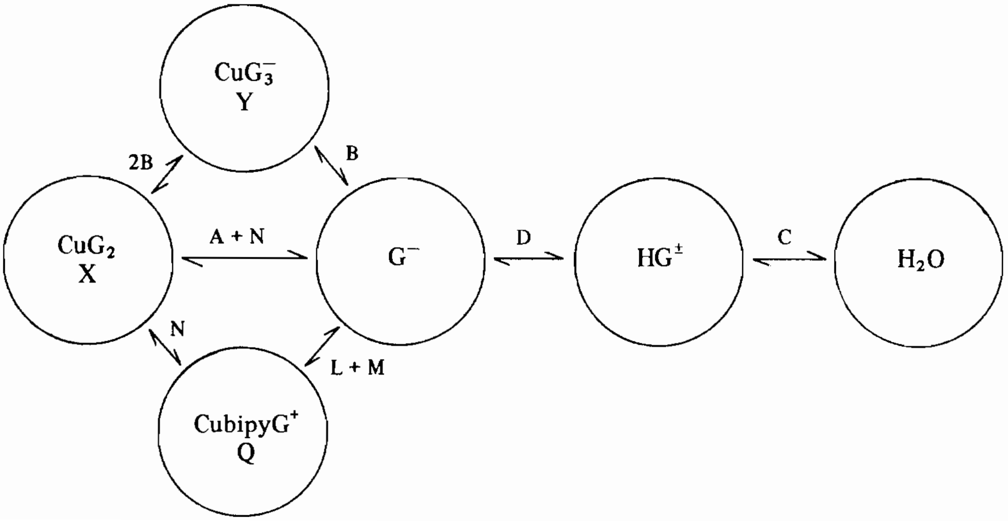
As was seen in part 1, the parameters of the processes denoted by A, B and Y are inter-related. Thus a combination of them, which fulfills the value determined for $3k_2 + 2k_{-3}$ and $k_3^{-1} + T_{2B}^{(3)}$, was used:

$$A = 0$$

$$B = 2.3\ 10^8[\mathrm{CuG_2}][G^-]$$

$$Y = 6[\mathrm{CuG_3^-}]/1.1\ 10^{-6}$$

Accepting the above values, only four parameters, k_1, k_6 and k_7 as well as $T_{2B}^{(1,1)}$ had to be calculated.



A direct search method has been used to find the minimum of

$$\sum_{i=1}^{p} (\lg T_{2i}^{exp} - \lg T_{2i}^{calc})^2$$

function (p = number of experimental points).

A systematic direct search for the best fit showed that the k_1 and k_7 rate constants could not be calculated individually; only their sum could be given. Although the exact mathematical proof has not been attempted, this is the expected result because the concentration dependence of the processes represented by k_1 and k_7 are the same. The $T_{2B}^{(1,1)}$ and the k_6 parameters were found to be independent.

Stopped-flow experiments were also carried out to determine the k_{-7} and k_{-6} rate constants. It was found that processes

$$CuG_2 + bipy \underset{k_7}{\overset{k_{-7}}{\rightleftharpoons}} CubipyG^+ + G^-$$

and

$$Cubipy_2^{2+} + G^- \underset{k_6}{\overset{k_{-6}}{\rightleftharpoons}} CubipyG^+ + bipy$$

are both too fast for stopped-flow measurements; only the pre-calculated equilibrium transmittancy was observed. From this finding a lower limit could only be given:

$$k_{-6}, k_{-7} > 10^5\ M^{-1}\ sec^{-1}$$

The parameters calculated are collected in Table IV.

From the results given in Table IV and from the comparison of the data of the copper(II)–glycine system, the following conclusions could be drawn:

Although the k_1 and k_7 rate constants cannot be determined independently, their sum shows that the kinetic activity of the mixed complex is not very much different from that of the parent complex CuG_2.

The k_{-6} rate constant is extremely high, much higher than any of the ligand substitution processes studied so far. This high value can probably be explained by taking into account the structure of $Cubipy_2^{2+}$ complex. According to a number of authors [19, 20, 21], the $Cubipy_2^{2+}$ is a *cis* octahedral complex, so that two relatively strong coordination sites are available for the incoming glycine ligand. The coordination of the incoming glycine is probably followed by a structural rearrangement; the mixed complex is tetragonally distorted like most of the copper(II) complexes. It may be concluded therefore that the kinetic background of the thermodynamic stabilization is the extremely high kinetic lability of the $Cubipy_2^{2+}$ complex against the

$$Cubipy_2^{2+} + G^- \rightleftharpoons CubipyG^+ + bipy$$

reaction.

TABLE IV. Ligand Exchange Rate Constants and Paramagnetic Relaxation Time in Copper(II)–Bipyridyl–Glycine System.

$k_1 + k_7$	$4.0\ 10^7\ M^{-1}\ sec^{-1}$
k_6	$2.5\ 10^7\ M^{-1}\ sec^{-1}$
k_{-6}	$7.8\ 10^8\ M^{-1}\ sec^{-1}$
$T_{2B}^{(1,1)}$	$7.1\ 10^{-7}$ sec

The $T_{2B}^{(1,1)}$ datum for the mixed complex is lower than for the CuG_2 parent complex, suggesting an increased covalency of the Cu–N bond and/or a shorter bond distance, depending on the mechanism of the paramagnetic relaxation. It follows that although the equilibrium studies indicate the dominance of the oxygen donor in the stabilization of the mixed complex, the increased covalency and/or shorter Cu–N bond also play a role in the stabilization.

Acknowledgement

We are indebted to Professor Robert E. Connick, Department of Chemistry, University of California, for his helpful critical comments.

References

1 H. Sigel. *Chimica, 21,* 389 (1967).
2 P. R. Huber, R. Griesser, B. Prijs and H. Sigel, *Eur. J. Biochem., 10,* 238 (1969).
3 R. Griesser and H. Sigel, *Inorg. Chem., 9,* 1238 (1970).
4 P. R. Huber, R. Griesser and H. Sigel, *Inorg. Chem., 10,* 945 (1971).
5 R. Griesser, B. Prijs, H. Sigel, W. Fory, L. D. Wright and D. B. McCormick, *Biochemistry, 9,* 3285 (1970).
6 H. Sigel, P. R. Huber and R. F. Pasternack, *Inorg. Chem., 10,* 2226 (1971).
7 H. Sigel and D. B. McCormick, *Accounts Chem. Res., 3,* 201 (1970).
8 R. F. Pasternack, P. R. Huber, U. M. Huber and H. Sigel, *Inorg. Chem., 11,* 276 (1972).
9 I. Nagypál, F. Debreczeni and R. E. Connick, *Inorg. Chim. Acta, 48,* 225 (1981).
10 I. Nagypál, F. Debreczeni and F. Erdödi, *Inorg. Chim. Acta, 57,* 125 (1982).
11 A. A. Popel, Magnitno-relaxacionnij metod analiza neorganitscheskih veshestv, Moscow, Himija (1978).
12 A. A. Popel, A. V. Zaharov, K. Kostrova, *Kin. i Katal., (Moscow), 16,* 1326 (1975).
13 M. S. Shapnik, A. N. Gilmanov, V. E. Yermakova and I. H. Muzeyev, *J. Inorg. Chem., (Moscow), 19,* 436 (1974).
14 A. Gergely, I. Nagypál and E. Farkas, *Magyar Kémiai Fi., 80,* 25 (1974).
15 H. M. Irving, M. G. Miles and L. D. Pettit, *Anal. Chim. Acta, 38,* 475 (1974).

16 G. Anderegg, *Helv. Chim. Acta, 46,* 2397 (1963).
17 I. G. Sayce, *Talanta, 15,* 1379 (1968).
18 F. Debreczeni and I. Nagypál, *J. Magn. Res., 37,* 363 (1980).
19 M. Noack and G. Gordon, *J. Chem. Phys., 48,* 2089 (1968).
20 K. Sone, S. Utsuno and T. Ogura, *J. Inorg. Nucl. Chem., 31,* 117 (1969).
21 Yu. I. Skurlatov and A. P. Purmal, *J. Phys. Chem., (Moscow), 43,* 1580 (1969).
22 J. K. Beattie, D. J. Fensom and H. C. Freeman, *J. Am. Chem. Soc., 98,* 500 (1976).