

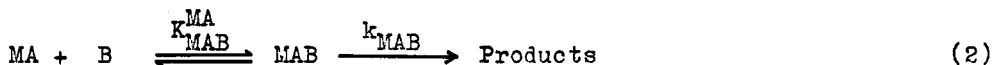
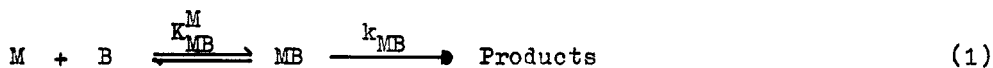
## Dynamics of ternary complex formation and dissociation

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**Abstract** - Using recent experimental results, dynamics of formation and dissociation of ternary complexes and their relevance in understanding thermodynamic stabilities of such species as also factors causing labilization of a ligand by another auxiliary ligand in a metal complex are discussed.

Metal ions are well-known Lewis acids and the *in vivo* catalytic activity of metal ions as metalloenzymes in biological systems generally involves the formation of ternary complexes by the metal ion, M, of the type MAB, where A represents the protein part of the metalloenzyme and B the substrate the reaction of which is catalyzed by the metalloenzyme, MA. The free metal ion often exhibits similar catalytic activity but in combination with A its activity is often increased enormously and further a certain degree of selectivity is imparted. Schematically we may say



Hence, it follows that the specific rate constants for these catalyzed reactions under the conditions that concentrations of MB and MAB are negligible compared to the total concentration of the metal in the system (present virtually as M or MA) will be

$$k_M = K_{MB}^M \cdot k_{MB} \quad (3)$$

$$k_{MA} = K_{MAB}^{MA} \cdot k_{MAB} \quad (4)$$

Now  $k_{MA} \gg k_M$  and this may be due to either  $K_{MAB}^{MA} \gg K_{MB}^M$  or  $k_{MAB} \gg k_{MB}$  or both. Again, a higher stability of the ternary complex MAB compared to that of the binary complex MB may be due to either a higher rate of formation of MAB from MA and B compared to that of MB from M and B, or due to a lower rate of dissociation of MAB into MA and B, or both factors may be responsible. Hence, studies on the dynamics of formation and dissociation of ternary complexes are of much relevance in understanding the thermodynamic stabilities of such species.

The stability of a ternary complex MAB compared to that of the binary complex MA or MB can be expressed as follows (ref. 1,2) :

$$\Delta \log K = \log K_{MAB}^{MA} - \log K_{MB}^M = \log K_{MAB}^{MB} - \log K_{MA}^M \quad (5)$$

where K is the equilibrium constant for the reaction



On statistical considerations a negative value is expected for  $\Delta \log K$  and ternary complexes are expected to be less stable than the corresponding binary complexes. This is often the case, but in some situations a ternary complex may be more stable and this leads to positive values of  $\Delta \log K$ . This generally happens when a metal binds to a strong sigma and

$\pi$  donor ligand (such as having oxygen donors) and another  $\pi$  acceptor ligand such as pyridine, imidazole, 2,2'-bipyridyl, 1,10-phenanthroline, etc. and many examples are well-known (ref. 3,4). Intramolecular stacking interaction also enhances stability in suitable cases (ref. 5) such as  $\text{Cu}(\text{amp})(\text{bipy})$  ( $\text{amp}^{2-}$  = adenosine-monophosphate) for which  $\Delta \log K$  value (ref. 4) is +0.5 at 25°. It is remarkable that while  $\text{HPO}_4^{2-}$  forms much more stable complexes with  $\text{M}^{2+}$  ions ( $\text{M} = \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$ ) than pyridine, the reverse is more significantly true for complexation of  $\text{M}(\text{nta})^-$  with these ligands (ref. 6). Examples are numerous that an aqua ligand bound to a metal ion is significantly labilized by a strong sigma donor ligand (see Table 1).

Table 1. Rate constants for some ligand replacement processes in chromium(III) complexes (25°, I = 1 M).

A. Water exchange (ref. 7)		B. Anation by oxalate (ref. 8,9)	
Complex	$10^5 k_{\text{ex}}, \text{s}^{-1}$	Complex	$10^5 k_{\text{ox}}, \text{M}^{-1} \text{s}^{-1}$
$\text{Cr}(\text{H}_2\text{O})_6^{3+}$	0.25	$\text{Cr}(\text{H}_2\text{O})_6^{3+}$	4
$\text{Cr}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$	5.8	$\text{Cr}(\text{ox})(\text{H}_2\text{O})_4^+$	53
<u>cis</u> - $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+}$	5.9	<u>cis</u> - $\text{Cr}(\text{ox})_2(\text{H}_2\text{O})_2^-$	14
<u>trans</u> - $\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{3+}$	1.2	<u>cis</u> - $\text{Cr}(\text{bigH})_2(\text{H}_2\text{O})_2^{3+}$	660
<u>fac</u> - $\text{Cr}(\text{NH}_3)_3(\text{H}_2\text{O})_3^{3+}$	5.8	(bigH = biguanide) (ref.9)	
<u>trans</u> - $\text{Cr}(\text{NH}_3)_2(\text{H}_2\text{O})_4^{3+}$	1.0		

The data in Table 1(A) indicate that the strong sigma donor  $\text{NH}_3$  causes significant labilization of  $\text{H}_2\text{O}$  in trans position to  $\text{NH}_3$ ; while data in Table 1(B) indicate that the strong ligand bigH causes considerable labilization of aqua ligands essentially by bond weakening and as such the  $\Delta H^\ddagger$  value for the oxalate anation of the bis-biguanide complex is  $84.5 \text{ kJ M}^{-1}$  as against a value of  $111.3 \text{ kJ M}^{-1}$  for the corresponding reaction of  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ . In fact, the former reacts by an  $I_d$  process (ref. 9) in contrast to  $I_a$  process in the latter. Also of significance to note in this connection the rate of acid catalyzed dissociation of a bigH ligand from the complexes cis- $\text{Cr}(\text{bigH})_2(\text{H}_2\text{O})_2^{3+}$  (I) (ref. 10),  $\text{Cr}(\text{bigH})_2(\text{ox})^+$  (II) (ref. 9) and  $\text{Cr}(\text{bigH})(\text{H}_2\text{O})_2(\text{ox})^+$  (III) (ref. 9). At 25° under comparable conditions the  $10^5 k_{\text{H}}, \text{M}^{-1} \text{s}^{-1}$ , values are 3.53, 296 and 1.01 respectively for the three species, i.e. in the ratio of 1: 84 : 0.29; most significant being almost 300 fold decrease in rate for the species III compared to that of species II having identical charge.

Labilization of an aqua ligand due to a ligand L in  $\text{ML}(\text{H}_2\text{O})_5$  is reported (ref. 11) to be related to the electron donating ability of L as measured by the  $E_n$  value in the Edwards' nucleophilicity scale :

$$\log(k_{\text{ex}}^{\text{ML-OH}_2} / k_{\text{ex}}^{\text{M-OH}_2}) = \gamma E_n \quad (7)$$

where the  $k$ -s are the specific rate constants for the exchange of the bound aqua ligand in  $\text{ML}(\text{H}_2\text{O})_5^{n+}$  and  $\text{M}(\text{H}_2\text{O})_6^{m+}$  complexes with solvent water, and  $\gamma$  is a constant which has been evaluated using eq. (7) for Fe(III), Cr(III), Co(II), Ni(II) and  $\text{O}=\text{V}(\text{IV})$  and shown to be related to the "softness parameter"  $\sigma$  (ref.12) :

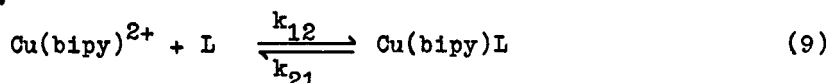
$$\gamma = -5.5\sigma + 5.5 \quad (8)$$

$\sigma$  values for twenty-six metal ions have been evaluated and hence corresponding  $\gamma$  values can be calculated using eq. (8). Hence, it is possible to

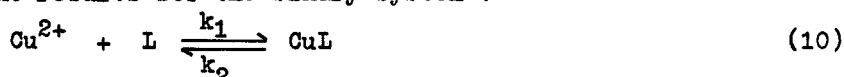
predict the value of  $k_{\text{ex}}^{\text{ML-OH}_2}$  for these metal ions once  $k_{\text{ex}}^{\text{M-OH}_2}$  is determined experimentally.

Coetzee and coworkers have determined the ratio  $N$  of the rate constants of the reactions of  $\text{NiXS}_n^+$  and  $\text{NiS}_6^{2+}$  with a ligand  $Y$  ( $X =$  a monoanion,  $S =$  solvent and  $Y =$  a neutral heteroaromatic ligand) in the cases of  $S = \text{CH}_3\text{OH}$  (ref. 13) and  $S = \text{CH}_3\text{CN}$  (ref. 14). The data shown in Table 2 indicate that the labilization varies not only with  $X$ , but for the same  $X$  depends considerably on the nature of the solvent  $S$ .

Pasternack and coworkers (ref. 15) have determined by temperature-jump method the rates of formation and dissociation of ternary complexes in the reaction of  $\text{Cu}(\text{bipy})^{2+}$  with  $L$  ( $L =$  ethylenediamine, glycinate,  $\alpha$ -alaninate,  $\beta$ -alaninate) :



and compared the results for the binary system :



Similar results have been reported (ref. 16) for the  $\text{Cu}(\text{bipy})(\text{acac})^+$  system. The results summarized in Table 3 are significant and indicate that

Table 2. Accelerating effect of anionic inner-sphere substituents ( $X$ ) on rate of reaction of nickel(II) with  $Y$  in methanol and acetonitrile, at 25°.

Y	X	In methanol (ref. 13)		In acetonitrile (ref. 14)	
		$\log k_{\text{NiX}}$	$\log N$ (a)	$\log k_{\text{NiX}}$	$\log N$ (a)
4-Phenylpyridine	Cl	3.9	1.8	-	-
	Br	3.3	1.2	-	-
	I	2.8	0.7	-	-
	SCN	2.9	0.8	-	-
bipy	Cl	3.1	1.1	6.3	2.7
	Br	2.5	0.5	-	-
	I	2.3	0.3	-	-
	SCN	3.0	1.0	-	-
phen	Cl	3.1	0.3	6.6	1.9
terpy	Cl	2.8	1.2	6.3	2.9
	Br	2.2	0.6	5.7	2.3
	I	1.8	0.2	4.8	1.4
	SCN	2.8	1.2	5.5	2.1
	$\text{NO}_3^-$	-	-	4.4	1.0

(a)  $N = k_{\text{NiX}} / k_{\text{Ni}}$

Table 3. Rates of formation and dissociation of some binary  $\text{Cu}L$  and ternary  $\text{Cu}(\text{bipy})L$  complexes of copper(II) and their relative stabilities, at 25° and  $I = 0.1 \text{ M}$  (ref. 15,16)

L	$\Delta \log K$ (a)	$k_1$ (b) $\text{M}^{-1}\text{s}^{-1}$	$k_2$ (b) $\text{s}^{-1}$	$k_{12}$ (c) $\text{M}^{-1}\text{s}^{-1}$	$k_{21}$ (c) $\text{s}^{-1}$	$k_{12}/k_1$	$k_{21}/k_2$
en	-1.29	$3.8 \times 10^9$	0.1	$2.0 \times 10^9$	1.4	0.5	14
gly <sup>-</sup>	-0.35	$4.0 \times 10^9$	22	$1.6 \times 10^9$	19	0.4	0.9
$\alpha$ -ala <sup>-</sup>	-0.26	$1.3 \times 10^9$	12	$1.0 \times 10^9$	10	0.8	0.8
$\beta$ -ala <sup>-</sup>	-0.59	$2.0 \times 10^8$	11	$3.4 \times 10^8$	110	1.7	10
acac <sup>-</sup>	+0.32	$9.0 \times 10^8$	3.2	$1.1 \times 10^9$	1.9	1.2	0.6

(a) Ref. 17

(b) See eq. (10)

(c) See eq. (9)

mostly the dissociation rates are primarily responsible for the relative stabilities of the different systems. For  $\text{Co}(\text{bipy})(\text{gly})^+$  also the comparatively high stability compared to that of  $\text{Co}(\text{gly})_2$  can be attributed to a lower dissociation rate for the former ( $k_d$ ,  $55 \text{ s}^{-1}$  at  $25^\circ$ ) than that of the latter ( $330 \text{ s}^{-1}$ ), the formation rate constants being rather similar ( $1.6 \times 10^6$  and  $2.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  respectively) (ref. 18). In contrast, however, the higher stability (ref. 6) of  $\text{Ni}(\text{nta})(\text{im})^-$  compared to that of  $\text{Ni}(\text{nta})(\text{NH}_3)^-$  is primarily due to a much higher formation rate for the imidazole (im) complex as the data (ref. 19) in Table 4 indicate. This higher formation rate is due to a higher value of the association constant for formation of the outer-sphere precursor complex due to hydrogen bonding and pi-bonding interactions of  $\text{Ni}(\text{nta})(\text{H}_2\text{O})_2^-$  with imidazole (ref. 3).

Table 4. Rate constants for formation and dissociation of nickel(II) complexes with ammonia and imidazole, at  $25^\circ$  and  $I = 0.1 \text{ M}$  (ref. 19).

Entering ligand	Substrate				
	$\text{Ni}(\text{H}_2\text{O})_6^{2+}$		$\text{Ni}(\text{nta})(\text{H}_2\text{O})_2^-$		
	$k_f, \text{M}^{-1} \text{s}^{-1}$	$k_d, \text{s}^{-1}$	$k_f, \text{M}^{-1} \text{s}^{-1}$	$k_d, \text{s}^{-1}$	
$\text{NH}_3$	$3.9 \times 10^3$	7.1	$4.6 \times 10^3$	13.3	
im	$4.9 \times 10^3$	4.9	$5.7 \times 10^4$	54.4	
Rate ratio	Substrate		Rate ratio	Ligand	
	$\text{Ni}(\text{H}_2\text{O})_6^{2+}$	$\text{Ni}(\text{nta})(\text{H}_2\text{O})_2^-$		$\text{NH}_3$	im
$k_f^{\text{im}}/k_f^{\text{NH}_3}$	1.3	12.4	$k_f^{\text{Ni}(\text{nta})}/k_f^{\text{Ni}}$	1.2	11.6
$k_d^{\text{im}}/k_d^{\text{NH}_3}$	0.7	4.1	$k_d^{\text{Ni}(\text{nta})}/k_d^{\text{Ni}}$	1.9	11.1

The data in Table 4 also indicate that  $\text{nta}^{3-}$  bound to nickel(II) causes labilization of the other ligands bound to the metal and this is in keeping with the fact that at  $25^\circ$  the rate constants for the water exchange reactions of  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$  and  $\text{Ni}(\text{nta})(\text{H}_2\text{O})_2^-$  are  $2.7 \times 10^4 \text{ s}^{-1}$  (ref. 20) and  $1.4 \times 10^5 \text{ s}^{-1}$  (ref. 21) respectively.

Results of investigations on the kinetics of formation of ternary complexes  $\text{Ni}(\text{A})\text{L}$  in the reactions of  $\text{Ni}(\text{nta})(\text{H}_2\text{O})_2^-$  (ref. 22) and  $\text{Ni}(\text{ada})(\text{H}_2\text{O})_2^-$  (ref. 23), where nta = nitrilotriacetate and ada = anthranilatodiacetate, with amino acids, LH, presented in Table 5 are interesting. The observed values of  $k_f$  are in the following sequence of the amino acids : glycine >  $\alpha$ -alanine > L-phenylalanine > L-valine > L-methionine >  $\beta$ -alanine > sarcosine, which is not quite the sequence of the  $\text{pK}_a$  values of these amino acids.

It is significant that ring size and bulky substituent on the reacting  $\text{NH}_2$  group have a pronounced effect on the  $k_f$  value.

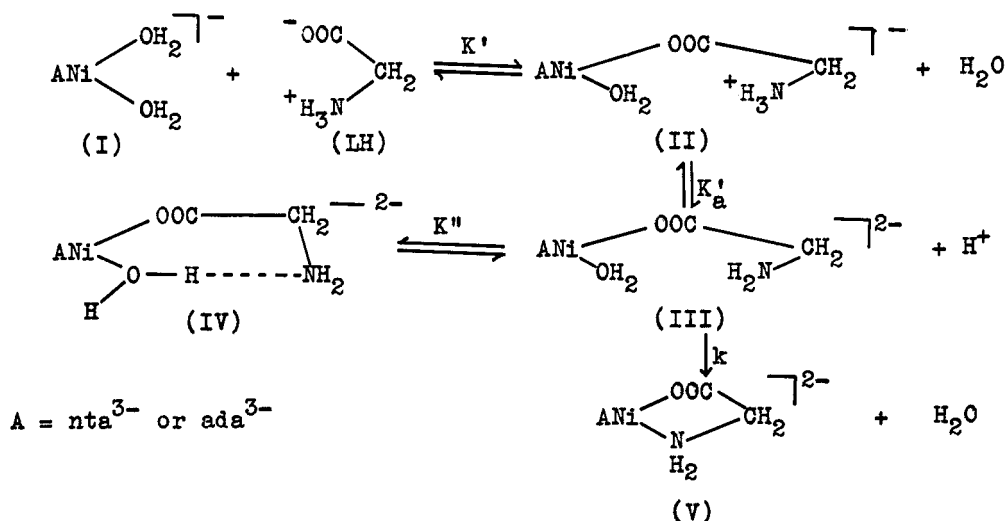
Table 5. Kinetics of formation of some ternary complexes of nickel(II)  $Ni(A)L^{2-}$  in the reaction of  $Ni(A)(H_2O)_2^{2-}$  with amino acids, LH (35°C, I = 0.1 M, pH = 6.0)

LH	$k_f, M^{-1}s^{-1}$	
	A = nta <sup>3-</sup> (ref.22)	A = ada <sup>3-</sup> (ref.23)
$\begin{array}{c} R_1 \quad NH_3^+ \\ \quad \diagdown \quad / \\ \quad \quad C \\ \quad / \quad \diagdown \\ R_2 \quad COO^- \end{array}$		
$R_1 = R_2 = H$	3.86	2.3
$R_1 = H, R_2 = Me$	3.4	1.96
$R_1 = H, R_2 = Ph-CH_2$	3.3	1.84
$R_1 = H, R_2 = Me_2CH$	3.15	1.72
$R_1 = H, R_2 = Me-S-CH_2-CH_2$	3.04(a)	1.68
$\begin{array}{c} H_2C-NH_3^+ \\   \\ H_2C-COO^- \end{array}$	2.43	1.34
$\begin{array}{c} H_2C-NH_2Me^+ \\ \quad \diagdown \quad / \\ \quad \quad C \\ \quad / \quad \diagdown \\ H_2C-COO^- \end{array}$	1.27(a)	0.97

(a) Ref. 23.

The exceedingly slow rates of reactions of amino acids with these nickel(II) complexes is intriguing, but the results can be explained by the following mechanism of reaction (Scheme I) :

Scheme 1



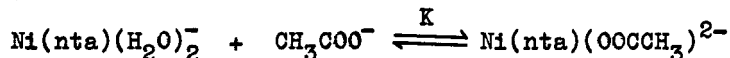
The hydrogen bonded species (IV) in the above scheme is essentially an internal conjugate base and is unreactive; ring closure step involving the species (III) is rate determining. Similar rate determining ring closure has been proposed for the reactions of  $Ni(trien)^{2+}$  with glycine (ref. 24), sarcosine (ref. 25) and ethylenediamine (ref. 25). The above scheme leads to (when  $T_L \gg T_{Ni}$ )

$$1/k_{obs} = [H^+] / T_L k K' K_a + (1 + K'')/k \quad (11)$$

For the  $\text{Ni}(\text{nta})(\text{gly})^{2-}$  the following values were obtained ( $25^\circ$ ,  $I = 0.1 \text{ M}$ ) graphically from eq. (11) :

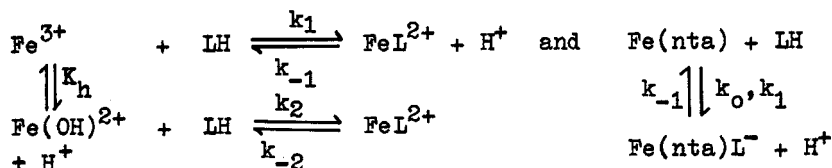
$$kK'K'_a = 3.41 \times 10^{-5} \quad \text{and} \quad k/(1 + K'') = 2.07 \quad (12)$$

For the  $\text{Ni}(\text{nta})^-$  - glycine system the value of  $K'$  may reasonably be expected to be nearly the same as the equilibrium constant for the following reaction :



At  $25^\circ$ ,  $I = 0.1 \text{ M}$ ,  $K = 2.34$  (ref. 6). We may also reasonably assume  $K'_a \approx K_a$  for glycine ( $K_a = 2.45 \times 10^{-10}$  at  $25^\circ$ ,  $I = 0.1 \text{ M}$ ). With these values we get using the relations given in the set of eq. (12) the following approximate values of  $k$  and  $K''$  :  $k = 5.95 \times 10^4 \text{ s}^{-1}$ ,  $K'' = 2.87 \times 10^4$ . This  $k$  value compares well with the reported  $k_f$  value ( $4.1 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$ ) for the reaction of  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$  with glycinate ion (ref. 26) and also agrees with the fact that both  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$  and  $\text{Ni}(\text{nta})(\text{H}_2\text{O})_2^-$  react with  $\text{NH}_3$  at comparable rates (see Table 4).

The kinetics of reactions of  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$  and  $\text{Fe}(\text{nta})(\text{H}_2\text{O})_2$  with benzohydroxamic acid, LH, has recently been investigated (ref. 27). The observed reactions are



$k_0$  is a path independent of LH concentration. The results are summarized in Table 6.

Table 6. Rate constants for reactions of  $\text{Fe}^{3+}$  and  $\text{Fe}(\text{nta})$  with benzohydroxamic acid, LH, at  $25^\circ$ ,  $I = 0.1 \text{ M}$

Values of the constants	$\text{Fe}(\text{H}_2\text{O})_6^{3+}$	$\text{Fe}(\text{nta})(\text{H}_2\text{O})_2$
$k_0, \text{ s}^{-1}$	-	0.18
$k_1, \text{ M}^{-1}\text{s}^{-1}$	4.43	18.3
$k_{-1}, \text{ M}^{-1}\text{s}^{-1}$	$3.33 \times 10^{-2}$	$1.74 \times 10^2$
$k_1/k_{-1}$	133	0.11

The results indicate that  $\text{nta}^{3-}$  bound to  $\text{Fe}(\text{III})$  causes labilization of the other ligand bound to the metal. But the much lower stability of the  $\text{Fe}(\text{nta})(\text{L})^-$  compared to that of  $\text{FeL}^{2+}$  is due to a significant increase in the dissociation rate of the former compared to that of the latter. In keeping with the fact that  $\text{nta}^{3-}$  causes labilization of the other bound ligand by bond weakening it has been observed (ref. 27) that  $\Delta H^\ddagger$  value for the  $k_1$  path for  $\text{Fe}(\text{nta})$  is  $42.3 \text{ kJ M}^{-1}$  as against a value of  $57.8 \text{ kJ M}^{-1}$  for that of  $\text{Fe}^{3+}$ . Again, for the  $k_{-1}$  path the  $\Delta H^\ddagger$  values are 41.2 and  $51.5 \text{ kJ M}^{-1}$  for the reactions of  $\text{Fe}(\text{nta})(\text{L})^-$  and  $\text{FeL}^{2+}$  respectively (LH = benzohydroxamic acid).

Ternary complex formation in the  $\text{Cu}(\text{bigH})_2^{2+}$  - bipy/phen systems can be represented as in Scheme II. These are typical square-planar complex systems and very few kinetic studies on such systems have been reported so far. For each step the observed pseudo-first order rate constant is  $k_{\text{obs}} = k_0 + k_L [\text{L}]$  (L = bipy or phen). Values of the rate constants are summarized in Table 7.

## Scheme 2

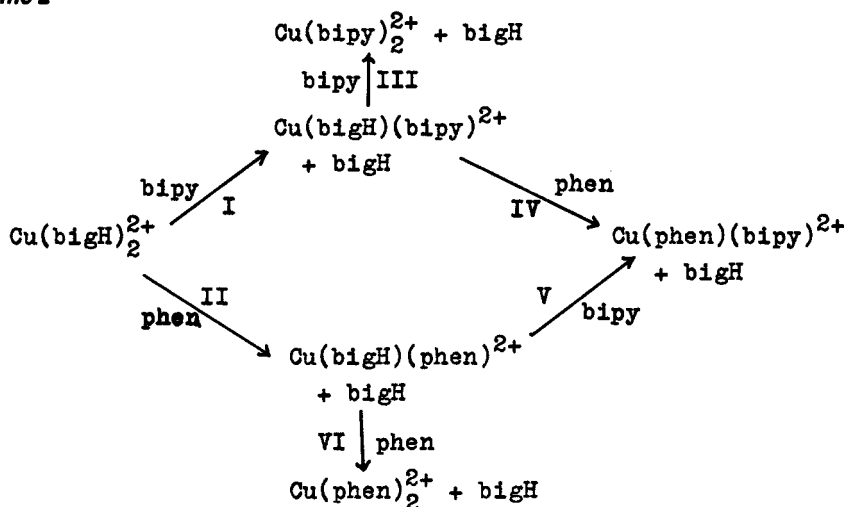


Table 7. Rate constants for the different steps in the reaction in  $\text{Cu}(\text{bigH})_2^{2+}$  - bipy/phen systems, at 25° and I = 0.1 M (ref. 28)

Complex	L	Path	$k_0, \text{s}^{-1}$	$10^{-3} k_L, \text{M}^{-1} \text{s}^{-1}$
$\text{Cu}(\text{bigH})_2^{2+}$	bipy	I	6.1	1.06
	phen	II	6.15	0.74
$\text{Cu}(\text{bigH})(\text{bipy})^{2+}$	bipy	III	0.29	0.32
	phen	IV	0.29	1.65
$\text{Cu}(\text{bigH})(\text{phen})^{2+}$	bipy	V	7.0	0.75
	phen	VI	7.1	0.95

The values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  for the different reactions and paths have also been evaluated. The results indicate  $k_0^{\text{V}} = k_0^{\text{VI}} > k_0^{\text{III}} = k_0^{\text{IV}}$ . Hence, compared to bipy, a greater labilization of the bound bigH is caused by phen in  $\text{Cu}(\text{bigH})(\text{L})^{2+}$ . Also,  $k_L^{\text{IV}} > k_L^{\text{III}}$  and  $k_L^{\text{VI}} > k_L^{\text{V}}$  suggesting associative character for  $k_L$  path. However,  $k_L^{\text{I}} > k_L^{\text{II}}$  presumably due to more favourable stacking interaction of the flexible bipy with  $\text{Cu}(\text{bigH})_2^{2+}$  leading to stronger outer-sphere association in the precursor complex.

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