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KINETICS OF THE COMPLEXATION OF Ni (II) AND Cu(II) WITH *L*-α—AMINOGLUTARIC ACID

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The kinetics of the complexation of Ni(II) and Cu(II) by *L*-α-aminoglutaric acid was studied at 25-40 (± 0.05) °C and at $I = 0.1$ M KNO_3. The study covered the *p*H range 6.46-7.59 for Ni (II) and 2.18-3.70 for Cu(II). Only one reaction was observed for Ni(II) whereas two reactions were found for Cu(II). For the fast reaction, specific rate constants corresponding to the interaction of protonated and deprotonated form of the ligand with metal ions were calculated. The explanation for the slow reaction in the case of Cu(II) has also been given. The values of activation parameters corresponding to specific rate constants have been calculated. Values of K_{os} and k_o have been calculated. The values of k_o was in good agreement with k_o, calculated from NMR study.

Key Words : Kinetics; Ni(II); Cu(II); Complexation; L-α-Aminoglutaric Acid

INTRODUCTION

Complexation of metal ions by a large variety of ligands[1-5] indicate that the complexation reactions are generally controlled by the rate of water exchange and the rate determining step is the loss of water molecule from inner coordination sphere.

$$M^{2+}_{aq} + L^{n-}_{aq} \overset{K_{OS}}{\rightleftharpoons} M^{2+}_{aq}\, L^{n-} \xrightarrow[\text{slow}]{k_o} ML^{(2-n)+} + H_2O \qquad \dots(1)$$

It is seen from the literature[1-5] that not even a single study has been reported on the activation parameters corresponding to the interaction of metal ions with protonated and deprotonated form of the amino acids. In some cases,[3,6] activation parameters for overall reaction were calculated. Review of the literature[1-6] also reveals that no kinetic study on the complexation of metal ions with *L*-α-aminoglutaric acid (*L*-glutamic acid) has been reported. Therefore, a comprehensive kinetic study on the complexation of Ni(II) and Cu(II) with L-α-aminoglutaric acid was carried out.

EXPERIMENTAL

L-α-Aminoglutaric acid (*L*-glutamic acid, E. Merck), 2,6-lutidine (Merck-Schuchardt) and bromothymol blue (BDH) were used. Other chemicals used were KNO_3, KOH, and HNO_3 (analar). Solutions of Ni(II) (~10^{-2} M) and Cu(II)

($\sim 10^{-1}$ M) were prepared from $Ni(NO_3)_2.6H_2O$ (Merck) and $Cu(NO_3)_2.3H_2O$ (BDH) and standardised by EDTA titrations. Doubly distilled water was used in the preparation of all the solutions. The ionic strength of reaction mixtures were kept constant at 0.1 M KNO_3. Freshly prepared solutions of *L*-α-aminoglutaric acid (9.70×10^{-4}M) and (3.33×10^{-2}M) were used for Ni(II) and Cu(II) espectively.

In the case of Ni(II)-*L*-α-aminoglutaric acid reaction, bromothymol blue was added to *L*-α-aminoglutaric acid solution. Both Ni (II) and *L*-α-aminoglutaric acid were buffered with 0.052 M 2,6-lutidine and the initial *p*H of the solution containing Ni(II) and L-α-aminoglutaric acid were kept constant at 6.64, 6.94, 7.12, 7.35 and 7.59. Slight change in the *p*H (of the order of 0.05) was observed after mixing and values of *p*H's given in table are those of reaction mixtures. But in the case of Cu(II)-*L*-α-aminoglutaric acid, the *p*H's of Cu(II) and *L*-α-aminoglutaric acid were adjusted by KOH/or HNO_3. The final *p*H's were taken to be 2.30, 2.84, 3.30, 3.58 and 3.70 ± 0.01 unit on Radiometer *p*H meter (model *p*H M 26 Copenhagen).

Kinetic Measurements

Kinetic measurements were made on stopped flow spectrophotometer (Aminco Morrow, USA). The driving syringes and reaction chamber were thermostated at desired temperature with a circulating type thermostat (German model NBE). In the stopped flow reaction chamber, the solution of Ni(II) ion having ionic strength $I = 0.1$ M and at the desired *p*H was mixed with a solution of *L*-α-aminoglutaric acid with indicator at the same *p*H and same ionic strength as that of Ni(II) ion solution. Similarly, the Cu(II) ion with ionic strength $I = 0.1$ M and at the desired *p*H was mixed with a solution of *L*-α-aminoglutaric acid at the same *p*H as that of Cu(II) ion solution.

Transmittance changes brought about by Ni(II)-*L*-α-aminoglutaric acid reaction were monitored at 620 nm using bromothymol blue as an indicator. Transmittance changes in the case of Cu(II)-*L*-α-aminoglutaric acid reaction were mentioned at 600nm. No *p*H indicator was used in the case of Cu(II) since transmittance changes were large enough to be monitored directly.

Blank experiments in which Ni(II) ions were mixed with buffer and indicator showed no change in transmittance on mixing. Transmittance changes for each run were traced out from oscilloscope. The k'_{obs} were calculated from the slope of the semilogarithmic plots of ΔV (change in voltage) versus time.

RESULTS AND DISCUSSION

Ni(II)-L-α-Aminoglutaric Acid Reaction

The kinetics of the reaction of Ni(II) with *L*-α-aminoglutaric acid was investigated in the *p*H range 6.46-7.59 and at the ionic strength 0.1 M KNO_3. The temperatures were maintained at 25-40 (± 0.05) °C. Oscilloscope traces of voltage versus time were taken and semilogarithmic plots of ΔV versus time were used to determine the values of k'_{obs}. The second order rate constants were calculated from the relation $k'_{obs}/[Ni^{2+}] = k_{obs} = 0.693/t_{1/2}\,[Ni^{2+}]$. These values are given in Table I.

TABLE I

Second order rate constants (k'_{obs}) for the reaction of Ni (II) and Cu (II) with L-α-aminoglutaric acid

[*L*-α-Aminoglutaric Acid] = 9.70×10^{-4} M for Ni(II)
[*L*-α-Aminoglutaric Acid] = 3.33×10^{-2} M for Cu(II)
$I = 0.1$ M KNO_3

Ni(II)-L-α-Aminoglutaric Acid				Cu(II)-L-α-Aminoglutaric Acid			
$[Ni^{2+}]$ (M)	Temp (° C)	*p*H	$k_{obs} \times 10^{-1}$ ($M^{-1}S^{-1}$)	$[Cu^{2+}]$ (M)	Temp. (° C)	*p*H	$k_{obs} \times 10^{3}$ ($M^{-1}S^{-1}$)
0.012	25	6.64	1.15	0.333	25	2.30	0.68
0.012	25	6.94	1.92	0.333	25	2.84	0.81
0.012	25	7.12	2.89	0.333	25	3.30	1.08
0.008	25	7.35	4.39	0.333	25	3.58	1.51
0.008	25	7.59	7.56	0.333	25	3.70	1.76
0.008	30	6.64	1.44	0.505	30	2.60	0.92
0.008	30	6.83	3.11	0.505	30	3.08	1.21
0.015	30	7.10	4.99	0.505	30	3.36	1.56
0.015	30	7.26	7.70	0.333	30	3.55	1.98
0.015	30	7.51	11.50	0.333	30	3.67	2.35
0.020	35	6.58	3.98	0.333	35	2.18	1.04
0.020	35	6.78	4.81	0.333	35	2.46	1.16
0.020	35	6.99	8.36	0.842	35	3 03	1.40
0.020	35	7.10	9.62	0.842	35	3.22	1.71
0.020	35	7.33	15.28	0.842	35	3.57	2.49
0.012	40	6.46	5.78	0.842	35	2.67	2.97
0.012	40	6.78	8.25	0.333	40	2.30	1.31
0.012	40	7.01	11.55	0.333	40	2.90	1.65
0.012	40	7.43	23.68	0.333	40	3.28	2.20
				0.842	40	3.46	2.81
				0.842	40	3.58	3.23
				0.842	40	3.63	3.55

The overall differential equation for Ni(II)-*L*-α-aminoglutaric acid reaction can be written as follows

$$\text{Rate} = -\frac{d}{dt}[Ni^{2+}] = -\frac{d}{dt}[L\text{-}\alpha\text{-Aminoglutaric Acid}]$$

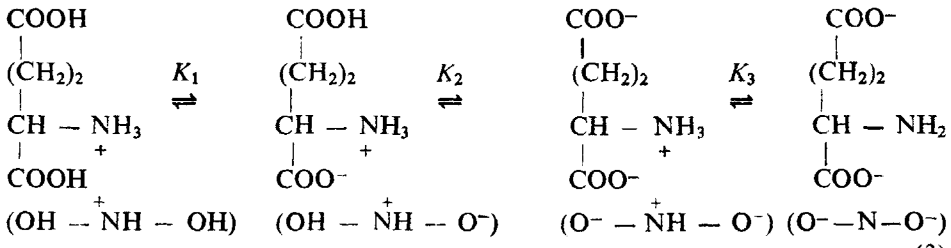
$$= k_{obs}\,[L\text{-}\alpha\text{-Aminoglutaric Acid}]\,[Ni^{2+}]$$

$$\text{or} \quad = k'_{obs}\,[L\text{-}\alpha\text{-Aminoglutaric Acid}]$$

$$= k'_{obs}([HO - \overset{+}{N}H - OH] + [OH - \overset{+}{N}H - O^-] + [O^- - \overset{+}{N}H - O^-] + [O^- - N - O^-]. \quad ...(2)$$

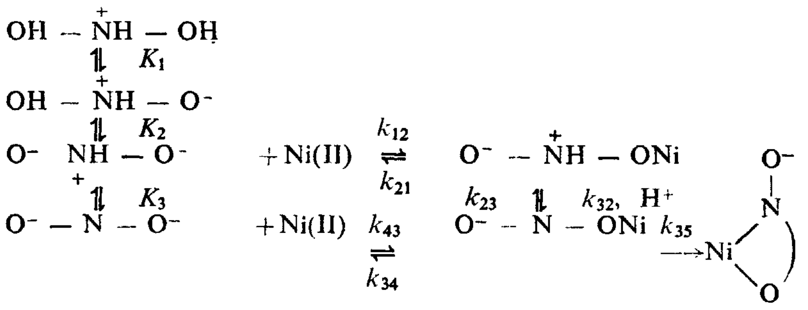
where $k'_{obs} = k_{obs}[Ni^{2+}]$ and $HO - \overset{+}{N}H\text{-}OH$, $OH - \overset{+}{N}H - O^-$, $O^- - \overset{+}{N}H - O^-$ and $O^- - N - O^-$ are triprotonated, diprotonated, protonated and deprotonated form of the ligand respectively.

The dissociation of *L*-α-aminoglutaric acid can be written as :



...(3)

These forms can react with Ni(II) in terms of stepwise scheme I given below :



Scheme I

Scheme I is different from the schemes given by Cassatt[4] and Voss and Jordan,[7] who did not take into account the dissociation of $HO - \overset{+}{N}H - OH$ and $HO - \overset{+}{N}H - \bar{O}$. Rate of formation of complex from the Scheme I can be given as :

$$\text{Rate} = k_{35}[O^- - N - ONi] \quad ...(4)$$

Using the steady state approximation for $[\bar{O} - \overset{+}{N}H - ONi]$ and $[\bar{O} - N - ONi]$ and applying the approximation $k_{23} \gg k_{21}$, it can be shown that

$$\text{Rate} = \frac{k_{12}k_{35}\,K_1K_2\,[\mathrm{H^+}] + k_{43}k_{35}\,K_1K_2K_3}{(k_{34} + k_{35})}\;\frac{[\mathrm{OH} - \overset{+}{\mathrm{N}}\mathrm{H} - \mathrm{OH}]\,[\mathrm{Ni(II)}]}{[\mathrm{H^+}]^3} \qquad \ldots(5)$$

Rate can also be expressed as

$$\text{Rate} = k_{\mathrm{obs}}\,[\mathrm{Ni(II)}]\,([\mathrm{OH} - \overset{+}{\mathrm{N}}\mathrm{H} - \mathrm{OH}] + [\mathrm{OH} - \overset{+}{\mathrm{N}}\mathrm{H} - \mathrm{O^-}] + [\mathrm{O^-} - \overset{+}{\mathrm{N}}\mathrm{H} - \mathrm{O^-}] + [\mathrm{O^-} - \mathrm{N} - \mathrm{O^-}]) \qquad \ldots(6)$$

Substituting the values of $[\overset{+}{\mathrm{O}}\mathrm{H} - \mathrm{NH} - \mathrm{O^-}]$, $[\mathrm{O^-} - \overset{+}{\mathrm{N}}\mathrm{H} - \mathrm{O^-}]$, and $[\mathrm{O^-}\,\mathrm{N} - \mathrm{O^-}]$ in terms of $[\mathrm{OH} - \overset{+}{\mathrm{N}}\mathrm{H} - \mathrm{OH}]$, using equation (3) and after rearrangement, equation (7) is obtained

$$\text{Rate} = k_{\mathrm{obs}}\,\{[\mathrm{H^+}]^3 + K_1\,[\mathrm{H^+}]^2 + K_1K_2\,[\mathrm{H^+}] + K_1K_2K_3\} \times \frac{[\mathrm{OH} - \overset{+}{\mathrm{N}}\mathrm{H} - \mathrm{OH}]\,[\mathrm{Ni(II)}]}{[\mathrm{H^+}]^3} \qquad \ldots(7)$$

By comparing equation (5) and (7) it can be shown that

$$k_{\mathrm{obs}} \cdot \frac{[\mathrm{H^+}]^3 + K_1\,[\mathrm{H^+}]^2 + K_1K_2\,[\mathrm{H^+}] + K_1K_2K_3}{K_1K_2\,[\mathrm{H^+}]} = \frac{k_{12} + k_{35}}{(k_{34}k_{35})} + \frac{k_{43}k_{25}K_3}{(k_{34} + k_{35})[\mathrm{H^+}]} \qquad \ldots(8)$$

Assuming[8] that $k_{35} > k_{34}$, equation (8) becomes

$$k_{\mathrm{obs}} \cdot \frac{[\mathrm{H^+}]^3 + K_1\,[\mathrm{H^+}]^2 + K_1K_2\,[\mathrm{H^+}] + K_1K_2K_3}{K_1K_2\,[\mathrm{H^+}]} = k_{12} + \frac{k_{43}K_3}{[\mathrm{H^+}]} \qquad \ldots(9)$$

Since $[\mathrm{H^+}]^3$ and $\mathrm{K_1}\,[\mathrm{H^+}]^2$ are less as compared to $K_1K_2\,[\mathrm{H^+}]$ and $K_1K_2K_3$ therefore, equation (9) reduces to equation (10).

$$k_{\mathrm{obs}} \cdot \frac{K_1K_2\,[\mathrm{H^+}] + K_1K_2K_3}{K_1K_2\,[\mathrm{H^+}]} = k_{12} + \frac{k_{43}K_3}{[\mathrm{H^+}]} \qquad \ldots(10)$$

Linear plots of $k_{\mathrm{obs}} \cdot \dfrac{K_1K_2\,[\mathrm{H^+}] + K_1K_2K_3}{K_1K_2\,[\mathrm{H^+}]}$ versus

$[\mathrm{H^+}]^{-1}$ at temperature 25, 30, 35 and 40° C are shown in Fig. 1. The values of K_1, K_2 and K_3 at 25° were taken from the literature[9] and corrected for other temperatures using the relation[10].

$$pK_a = \frac{\Delta H_a(T_2 - \mathrm{T}_1)}{4.6\;T_2T_1} + pK_a\;25°\,\mathrm{C} \qquad \ldots(11)$$

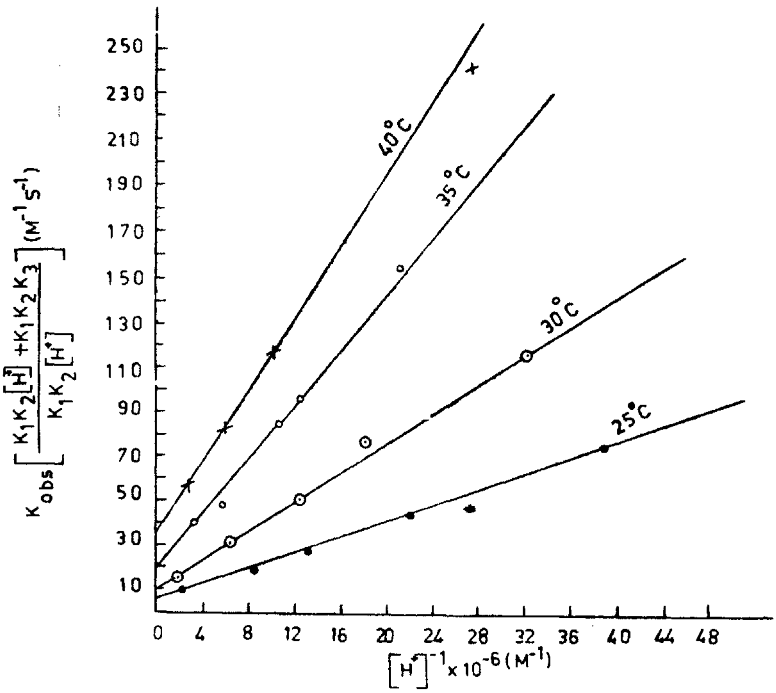


FIG 1 Plot of k_{obs}. $\{K_1K_2[H^+] + K_1K_2K_3\}/K_1K_2[H^+]$ versus $[H^+]^{-1}$ for the Ni (II)-*L*-α-Aminoglutaric Acid Reaction.

The values of specific rate constants k_{12} and k_{43} thus obtained from the Fig 1 have been reported in Table II. The values of activation parameters corresponding to k_{12} and k_{43} were calculated from the linear plots of log k/T and log k versus $1/T$ (Figs. 2 and 3) The values are 22.8, 24.19, 17.4, 11.4, 12.2 and − 6.55 for

$\Delta H^{\neq}_{12}$, $\Delta E^{\neq}_{12}$, $\Delta S^{\neq}_{12}$, $\Delta H^{\neq}_{43}$, $\Delta E^{\neq}_{43}$ and $\Delta S^{\neq}_{43}$ respectively.

Finally the rate law can be reconciled in terms of outer sphere complex formation constant (K_{os}) and rate constant of water loss (k_o), which can be written from equation (1)

TABLE II

Values of k_{12} and k_{43} for the reaction of Ni(II) and Cu(II) with L-α-aminoglutaric acid

Ni(II)-*L*-α-Aminoglutaric Acid			Cu(II)-*L*-α-Aminoglutaric Acid	
Temp. (°C)	k_{12} ($M^{-1}S^{1}$)	$k_{43} \times 10^{-3}$ ($M^{-1}S^{-1}$)	$k_{12} \times 10^{-3}$ ($M^{-1}S^{-1}$)	$k_{43} \times 10^{-8}$ ($M^{-1}S^{-1}$)
25	5	6.85	0.60	8.75
30	10	9.83	0.78	9.09
35	19	14.08	0.96	9.41
40	34	18.74	1.18	9.70

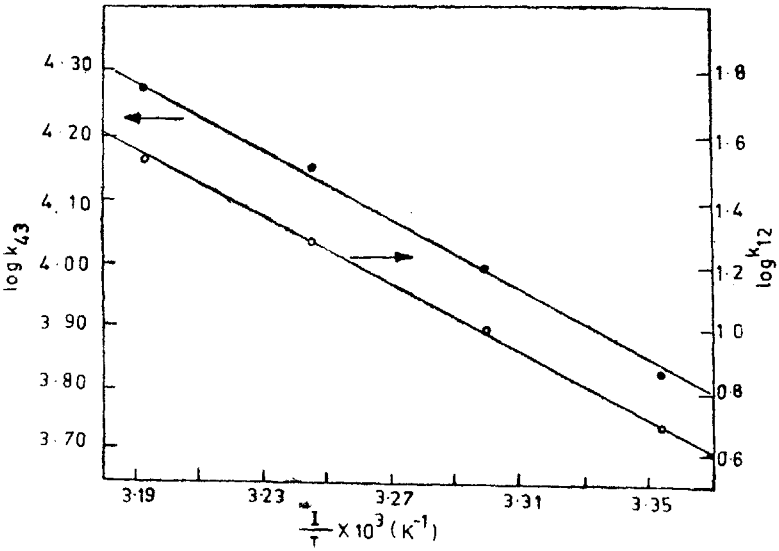


Fig 2 Plot of log k_{12} and log k_{43} versus $1/T$ for the Ni(II)-*L*-α-Aminoglutaric Acid Reaction.

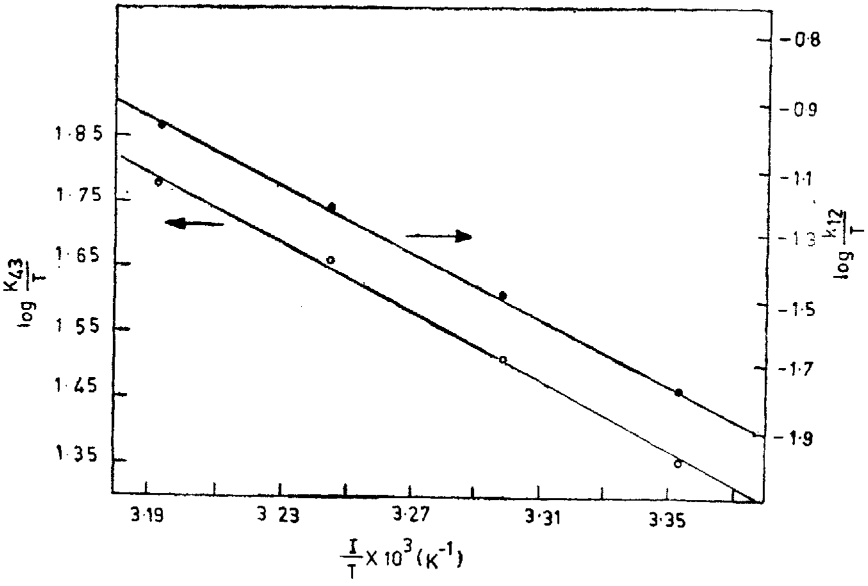


Fig 3 Plot of log $\frac{k_{12}}{T}$ and log $\frac{k_{43}}{T}$ versus $1/T$ for the Ni (II)-*L*-α-Aminoglutaric Acid Reaction.

$$\text{Rate} = \frac{d}{dt}\,[\text{NiL}^+] = K_{os}\,k_o\,[\text{Ni(II)}]\,[L^-] \qquad \ldots(12)$$

Monoprotonated and deprotonated form of the ligand can be considered to react with Ni(II) in the following ways:

$$O^- - \overset{+}{N}H - O^- + Ni(II) \xrightarrow{k_{12}} O - \overset{+}{N}H - ONi \qquad ...(13)$$

$$O^- - N - O^- + Ni\,(II) \xrightarrow{k_{43}} O^- - N - ONi \qquad ...(14)$$

Using equation (13) and (14) rate can be written as

$$\text{Rate} = k_{12}\,[O^- - \overset{+}{N}H - O^-]\,[Ni(II)] + k_{43}\,[O^- - N - O^-]\,[Ni(II)] \qquad ...(15)$$

$\therefore$ $k_{12} \ll k_{43}$, equation (15) reduces to :

$$\text{Rate} = k_{43}\,[O^- - N - O^-]\,[Ni(II)] \qquad ...(16)$$

From (12) and (16), we get

$$k_{43} = K_{os}k_o \qquad ...(17)$$

In order to calculate the value of k_o, we must know the value of K_{os}. The value of K_{os} was calculated using the relation.[11]

$$K_{os} = \frac{4\pi Na^3}{3000}\ \exp\,(-\,u/kT), \qquad ...(18)$$

$$\text{where } U = \frac{Z_1Z_2e_0^2}{aD} - \frac{Z_1Z_2e_0^2\,\chi}{D(1+\chi a)}$$

$$\text{and} \quad \chi^2 = \frac{8\pi Ne_0^2 I}{1000\,DkT}$$

where 'a' is the distance of the closest approach of two ions (often taken 5 Å for reactions of aquo cations with ordinary ligands.)[12] Thus the value of K_{os} at 25° C was found to be 2.17 M^{-1}. Therefore, the value of k_o at 25 °C can be calculated from equation (17) and it was found to be 0.32×10^4 sec^{-1}. This value of k_o is in the same order as experimentally determined by Swift and Connick.[13]

Cu(II)-L-α-Aminoglutaric Acid Reaction

The kinetics of the reaction of Cu(II) was investigated in the pH range 2.18–3.70 and at ionic strength 0.1 M KNO_3. The temperatures were maintained at 25–40 (± 0.05) °C. An oscilloscope trace of voltage versus time shows that two consecutive reactions are taking place. Therefore, the values of pseudo-first order rate constanst k'_{obs} for the fast reaction were calculated using the usual Guggenheim's method. The values of $k_{obs} = k'_{obs}/[Cu^{2+}]$ are given in Table I.

To avoid the hydrolysis, we restricted our investigation in the above *p*H range. Rate of the reaction can be given by same equation as described for Ni(II)-*L*-α-aminoglutaric acid reaction. The values of k_{12} and k_{43} were obtained in the similar way as in the case of Ni(II). These values are given in Table II. The values of activation parameters corresponding to k_{12}, and k_{43} were obtained from the linear plots of log k/T and log k versus $1/T$. The values are 4.70, 4.36, – 35.83, 0.68, 1.28 and – 19.32 for $\Delta H^{\neq}_{12}$, $\Delta E^{\neq}_{12}$, $\Delta S^{\neq}_{12}$, $\Delta H^{\neq}_{43}$, $\Delta E^{\neq}_{43}$ and $\Delta S^{\neq}_{43}$ respectively.

Similarly, the value of k_0 was obtained from equation (17) and was found to be 4.03×10^8 sec^{-1}. This value was also found to be of the same order as given by Swift and Connick.[13]

The value of k_{43} in the case of Cu(II) is very large as compared to Ni(II) as given in Table II. This discrepancy can be explained on the basis of CFSE (Crystal field stabilization energy) difference. Since the loss of water molecule from the metal ion changes the geometry from octahedral to trigonal bipyramidal. The CFSE[14] of the Ni(II) and Cu(II) for the octahedral geometry can be calculated as 12 Dq (high spin) and 6 Dq (high spin) respectively. For TBP geometry the value of CFSE can be calculated as 6·27 Dq (high spin) and 7.09 Dq (high spin) for Ni(II) and Cu(II) respectively. Therefore, the difference in CFSE (Oh-TBP) in the case of Ni(II) is 5.73 Dq and for Cu(II) is 1.09 Dq. The lower value in the case of Cu(II) is responsible for the larger value of k_{43}. This can be further confirmed from the value of $\Delta E^{\neq}_{43}$ (Table III) which is found to be less in the case of Cu(II) as compared to Ni(II).

TABLE III

Values of activation parameters for the Reaction of Ni (II) and Cu (II) with L-α-Aminoglutaric Acid

	Ni (II)-L-α-Amino-glutaric Acid	Cu (II)-L-α-Amino-glutaric Acid
$\Delta H^{\neq}_{12}$ (kcal mol^{-1})	22.88	4.07
$\Delta E^{\neq}_{12}$ (kcal mol^{-1})	24.15	4.36
$\Delta S^{\neq}_{12}$ (cal K^{-1}mol^{-1})	17.46	– 35.83
$\Delta H^{\neq}_{43}$ (kcal mol^{-1})	11.44	0.68
$\Delta E^{\neq}_{43}$ (kcal mol^{-1})	12.20	1.28
$\Delta S^{\neq}_{43}$ (kcal K^{-1} mol^{-1})	– 6.55	– 19.32

Since the fast reaction was found to be second order and was accompanied by release of a proton, the slow reaction was of little importance. Moreover, the slow reaction has no dependence on Cu(II) ion concentrations. This was confirmed by taking four concentrations (0.012., 0.035, 0.063, 0.075 M) In every case $t_{1/2} \sim 0.12$ sec was observed. The slow reaction was also found to be independent of pH (k'_{obs} was found to be $\sim$ 5.77 sec^{-1} in the pH range 2.18-3.70).

Therefore, it could be said that a small amount of the hydroxy complex of the type Cu(*L*-α-aminoglutaric acid $(H_2O)_3OH^+$ was formed. This type of hydroxy complex for Ni(II) has been reported by Cassatt *et al.*[4]

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