

Kinetics of Complexation of Ni(II) & Cu(II) with L- α -Amino- β -indolepropionic Acid

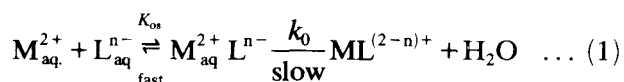
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The kinetics of complexation of Ni(II) and Cu(II) by L- α -amino- β -indolepropionic acid have been investigated at 25, 30, 35 and 40 $\pm$ 0.05°C and at $I = 0.1$ mol dm⁻³ KNO₃ in the pH range 6.08-7.43 in the case of Ni(II) and 2.50-3.31 in the case of Cu(II). Only one reaction has been observed in the case of Ni(II) whereas two reactions take place in the case of Cu(II). The anionic form of the ligand is found to be reactive whereas protonated form is found to be slightly reactive in case of Ni(II) but appreciably reactive in case of Cu(II). For the fast reaction, k_{12} and k_{43} corresponding to the interaction of protonated and deprotonated forms of the ligand with metal ions respectively and the corresponding activation parameters have been calculated.

The rates of complexation reactions of metal ions with a large variety of ligands¹⁻⁴ depend to a large extent on the charge of the reacting ligand. Generally the rates of substitution on metal ion is controlled by the rate of water exchange, and the rate determining step is the loss of water molecule from inner coordination sphere of the metal ion.



L- α -Amino- β -indolepropionic acid (L-tryptophan) is found in human blood plasma. Ultracentrifugation study⁵ using ⁶⁴Cu shows that Cu(II) interacts more rapidly with amino acids than albumin in blood serum. In view of this it was thought of interest to determine the binding steps, rate constants corresponding to the binding steps (see Eq. 1) and activation parameters corresponding to the interaction of protonated and deprotonated forms of the ligand.

Materials and Methods

L- α -Amino- β -indolepropionic acid (L-tryptophan, Loba), 2,6-lutidine (Merck-Schuchardt) and bromothymol blue (BDH) were used as such. Other chemicals used were of AR quality. Solutions of Ni(II) ($\sim 10^{-2}$ mol dm⁻³) and Cu(II) ($\sim 10^{-2}$ mol dm⁻³) were prepared from Ni(NO₃)₂·6H₂O (Merck) and Cu(NO₃)₂·3H₂O (Merck) and standardised by EDTA titration. Doubly distilled water was used for preparing all the solutions. The ionic strength was kept constant at 0.1 mol dm⁻³ (KNO₃). Freshly prepared solutions 1.26×10^{-3} and 3.80×10^{-3} mol dm⁻³ of L- α -amino- β -indolepropionic acid were used for Ni(II) and Cu(II) respectively.

In the case of Ni(II)-L- α -amino- β -indolepropionic

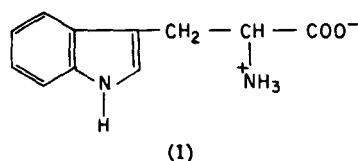
acid reaction, Ni(II) and L- α -amino- β -indolepropionic acid were buffered with 2,6-lutidine (0.052 mol dm⁻³). Bromothymol blue ($\sim 10^{-5}$ mol dm⁻³) was added to L- α -amino- β -indolepropionic acid. The initial pH's of the metal and ligand solutions were made the same. There was, however, slight change in the pH (of the order of 0.05 pH unit) after mixing. The pH's reported in the case of Ni(II) are those of the reaction mixtures. But in the case of Cu(II)-L- α -amino- β -indolepropionic acid, the pH was adjusted by dropwise addition of KOH/or HNO₃. The final pH was adjusted with an accuracy of ± 0.01 unit. Radiometer pH meter (model pH M 26) was used for pH measurements. Kinetic measurements were made on Aminco-Morrow stopped flow spectrophotometer. The driving syringes and reaction chamber were thermostated at 25, 30, 35 and 40 $\pm$ 0.05°C. In the stopped flow reaction chamber, the solution of Ni(II)/Cu(II) ion having ionic strength $I = 0.1$ mol dm⁻³ and at the desired pH (6.08-7.43 for Ni and 2.50-3.31 for Cu) was mixed with a solution of L- α -amino- β -indole propionic acid at the same pH and ionic strength. Changes in transmittance brought about by Ni(II)-L- α -amino- β -indolepropionic acid reaction were monitored at 620 nm using bromothymol blue as an indicator. In case of Cu(II)-L- α -amino- β -indolepropionic acid reaction changes in transmittance were monitored at 600 nm without using any pH indicator since in this case transmittance changes were large enough to be monitored directly.

Blank experiments in which Ni(II) ions were mixed with buffer (2,6-lutidine) and indicator showed no change in the transmittance on mixing. Transmittance changes for each run were traced out

from the oscilloscope. The k'_{obs} were calculated from the semilogarithmic plots of $\log \Delta V$ (change in voltage) versus time.

Results and Discussion

The structure of the protonated form of L- α -amino- β -indolepropionic acid (I) should be able to form three fused rings⁶, viz five-membered, seven-membered and eight-membered on reaction with Ni(II) and Cu(II). But seven- and eight-membered rings are unstable due to large steric strain and this is in conformity with the literature⁷ that indole nitrogen does not take part in complexation. Therefore, it is obvious that reaction of Ni(II) and Cu(II) should lead to the formation of a five-membered ring through α -amino acid moiety.



Ni(II)-L- α -amino- β -indolepropionic acid reaction

The dissociation of L- α -amino- β -indolepropionic acid can be written as:



where $\text{HN}^+ - \text{OH}$, $\text{HN}^+ - \text{O}^-$ and $\text{N} - \text{O}^-$ are diprotonated, monoprotonated and deprotonated forms of the ligand. The overall rate equation for Ni(II)-L- α -amino- β -indolepropionic acid can be represented by Eq. (2).

$$\text{Rate} = k'_{\text{obs}} \{[\text{HN}^+ - \text{OH}] + [\text{HN}^+ - \text{O}^-] + [\text{N} - \text{O}^-]\} \quad \dots (2)$$

where $k'_{\text{obs}} = k_{\text{obs}} [\text{Ni}^{2+}]$. Values of k_{obs} are given in Table 1.

The three forms of amino acid can react with Ni(II) in a stepwise manner as shown in Scheme 1.

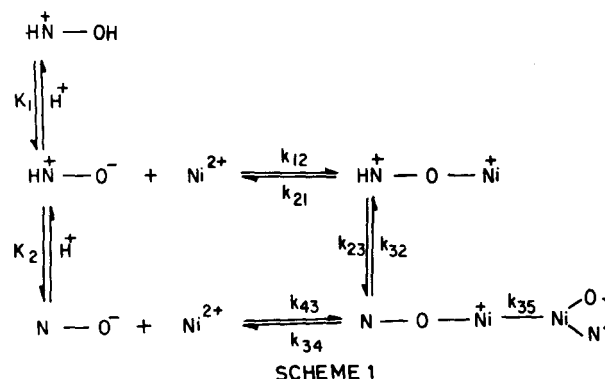


Table 1—Second Order Rate Constants (k_{obs}) for the Reaction of Ni(II) and Cu(II) with L- α -Amino- β -indolepropionic Acid

[L- α -Amino- β -indolepropionic acid] = 1.26×10^{-3} mol dm⁻³ for Ni(II) and 3.80×10^{-3} mol dm⁻³ for Cu(II); $I = 0.1$ (KNO₃) mol dm⁻³

Ni(II)-L- α -Amino- β -indolepropionic acid				Cu(II)-L- α -Amino- β -indolepropionic acid			
[Ni ²⁺] (mol dm ⁻³)	Temp. (°C)	pH	$k_{\text{obs}} \times 10^{-1}$ (dm ³ mol ⁻¹ s ⁻¹)	[Cu ²⁺] (mol dm ⁻³)	Temp. (°C)	pH	$k_{\text{obs}} \times 10^{-3}$ (dm ³ mol ⁻¹ s ⁻¹)
0.012	25	6.21	0.339 ± 0.02	0.0200	25	2.50	0.495 ± 0.05
0.012	25	6.61	0.577 ± 0.04	0.0200	25	2.60	0.577 ± 0.05
0.012	25	6.72	0.825 ± 0.03	0.0200	25	2.78	0.866 ± 0.03
0.012	25	6.89	1.25 ± 0.04	0.0185	25	2.90	1.15 ± 0.06
0.012	25	7.14	2.06 ± 0.04	0.0185	25	2.98	1.39 ± 0.08
0.012	25	7.43	4.12 ± 0.06	0.0220	25	3.00	1.39 ± 0.05
0.012	30	6.16	0.950 ± 0.01	0.0220	25	3.10	1.86 ± 0.04
0.012	30	6.54	1.44 ± 0.03	0.0200	25	3.20	2.37 ± 0.06
0.012	30	6.63	1.99 ± 0.02	0.0200	25	3.31	3.07 ± 0.02
0.015	30	6.81	2.22 ± 0.02	0.0200	30	2.51	0.657 ± 0.03
0.015	30	7.04	3.40 ± 0.04	0.0200	30	2.60	0.820 ± 0.02
0.015	30	7.37	6.42 ± 0.07	0.0200	30	2.84	1.49 ± 0.04
0.012	35	6.10	2.05 ± 0.05	0.0200	30	3.00	2.20 ± 0.07
0.012	35	6.46	2.80 ± 0.03	0.0200	30	3.09	2.65 ± 0.08
0.012	35	6.59	3.61 ± 0.05	0.0200	30	3.19	3.48 ± 0.06
0.015	35	6.79	4.44 ± 0.05	0.0200	35	2.54	1.05 ± 0.04
0.015	35	7.32	11.0 ± 0.06	0.0200	35	2.72	1.65 ± 0.03
0.012	40	6.08	4.25 ± 0.05	0.0200	35	2.87	2.44 ± 0.07
0.012	40	6.54	6.50 ± 0.06	0.0250	35	3.00	3.12 ± 0.08
0.012	40	6.90	9.10 ± 0.03				
0.015	40	7.22	15.4 ± 0.04				
0.015	40	6.44	5.35 ± 0.05				

Scheme 1 is different from the scheme given by Cassatt⁴, Voss and Jordan⁸, who did not take into account the dissociation of $\text{HN}^+ - \text{OH}$. In accordance with Scheme 1, the rate is given by Eq. (3).

$$\text{Rate} = k_{35} [\text{N} - \text{O} - \text{Ni}^+] \quad \dots (3)$$

Using the steady state approximation for $[\text{HN}^+ - \text{O} - \text{Ni}]$ and $[\text{N} - \text{O} - \text{Ni}]$ and applying the approximation $k_{23} > k_{21}$ it can be shown that:

$$\text{Rate} = \frac{k_{12}k_{35}K_1[\text{H}^+] + k_{43}k_{35}K_1K_2}{k_{34} + k_{35}} \cdot \frac{[\text{HN}^+ - \text{OH}][\text{Ni}^{2+}]}{[\text{H}^+]^2} \quad \dots (4)$$

By substituting $[\text{HN}^+ - \text{O}]$ and $[\text{N} - \text{O}^-]$ in terms of $[\text{HN} - \text{OH}]$ in Eq. (2) we get

$$\text{Rate} = \frac{k_{\text{obs}}[\text{Ni}^{2+}][\text{HN} - \text{OH}]}{[\text{H}^+]^2} \{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2\} \quad \dots (5)$$

On comparing Eqs (4) and (5) it can be shown that:

$$k_{\text{obs}} \cdot \frac{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2}{K_1[\text{H}^+]} = \frac{k_{12}k_{35}}{k_{34} + k_{35}} + \frac{k_{43}k_{35}}{k_{34} + k_{35}} \cdot \frac{K_2}{[\text{H}^+]} \quad \dots (6)$$

Since in Scheme 1 the first bond formed will be strong, i.e. $k_{43} > k_{34}$ if reasonable assumption (i.e. $k_{35} \sim k_{43}$) is made, then $k_{35} > k_{34}$ which is the case for normal substitution as reported by Letter and Jordan⁹. Therefore, Eq. (6) becomes Eq. (7).

$$k_{\text{obs}} \cdot \frac{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2}{K_1[\text{H}^+]} = k_{12} + \frac{k_{43}K_2}{[\text{H}^+]} \quad \dots (7)$$

Plots of $k_{\text{obs}} \cdot \{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2\}/K_1[\text{H}^+]$ versus $[\text{H}^+]^{-1}$ were linear at temperatures 25, 30, 35 and 40°C. (The values of K_2 at 25°C was taken from the literature¹⁰ and corrected for temperatures of our investigation). The values of k_{12} and k_{43} obtained from

these linear plots are presented in Table 2. The values of activation parameters corresponding to k_{12} and k_{43} were calculated from the linear plots of $\log k$ and $\log k/T$ versus $1/T$ and these values are given in Table 3.

Finally the rate law in terms of outer sphere complex formation constant (K_{os}) and rate constant of water loss (k_o) (see Eq. 1) is given by

$$\text{Rate} = \frac{d}{dt} [\text{NiL}^+] = K_{\text{os}} k_o [\text{Ni}^{2+}][\text{L}^-] \quad \dots (8)$$

By taking k_{12} and k_{43} steps in Scheme 1, it can be written that

$$\text{Rate} = k_{12} [\text{HN}^+ - \text{O}^-][\text{Ni}^{2+}] + k_{43} [\text{N} - \text{O}^-][\text{Ni}^{2+}] \quad \dots (9)$$

Because $k_{12} \ll k_{43}$, Eq. (9) reduces to

$$\text{Rate} = k_{43} [\text{N} - \text{O}^-][\text{Ni}^{2+}] \quad \dots (10)$$

From Eqs (8) and (10) we get

$$k_{43} = K_{\text{os}} k_o \quad \dots (11)$$

The value of K_{os} at 25°C was calculated to be $2.17 \text{ dm}^3 \text{ mol}^{-1}$. Using these, the value of k_o at 25°C was calculated to be $1.43 \times 10^3 \text{ s}^{-1}$. Swift and Connick¹³ have reported a value of $2.7 \times 10^4 \text{ s}^{-1}$ for the water exchange rate constant of Ni(II) . This difference is due to the formation of stabler outer sphere complex in our case.

Cu(II)-L-α-Amino-β-indolepropionic acid reaction

An oscilloscope trace of voltage versus time

Table 3—Values of Activation Parameters for the Reaction of Ni(II) and Cu(II) with $\text{L-}\alpha\text{-Amino-}\beta\text{-indolepropionic Acid}$

	$\text{Ni(II)-L-}\alpha\text{-Amino-}\beta\text{-indole propionic acid}$	$\text{Cu(II)-L-}\alpha\text{-Amino-}\beta\text{-indole propionic acid}$
$\Delta H_{12}^\ddagger (\text{kJ mol}^{-1}) \times 10^{-2}$	1.32 ± 0.20	0.456 ± 0.30
$\Delta E_{12}^\ddagger (\text{kJ mol}^{-1}) \times 10^{-2}$	1.36 ± 0.24	0.479 ± 0.25
$\Delta S_{12}^\ddagger (\text{JK}^{-1} \text{ mol}^{-1}) \times 10^{-2}$	1.90 ± 0.43	0.425 ± 0.10
$\Delta H_{43}^\ddagger (\text{kJ mol}^{-1}) \times 10^{-1}$	3.59 ± 0.50	1.40 ± 0.25
$\Delta E_{43}^\ddagger (\text{kJ mol}^{-1}) \times 10^{-1}$	3.82 ± 0.65	1.64 ± 0.40
$\Delta S_{43}^\ddagger (\text{JK}^{-1} \text{ mol}^{-1}) \times 10^{-1}$	-7.43 ± 0.55	-1.36 ± 0.35

Table 2—Values of k_{12} and k_{43} for the Reaction of Ni(II) and Cu(II) with $\text{L-}\alpha\text{-Amino-}\beta\text{-indolepropionic Acid}$

Temp. (°C)	$\text{Ni(II)-L-}\alpha\text{-Amino-}\beta\text{-indolepropionic acid}$		$\text{Cu(II)-L-}\alpha\text{-Amino-}\beta\text{-indolepropionic acid}$	
	$k_{12} \times 10^{-1}$ ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)	$k_{43} \times 10^{-3}$ ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)	$k_{12} \times 10^{-3}$ ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)	$k_{43} \times 10^{-10}$ ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)
25	0.150 ± 0.02	3.08 ± 0.05	2.90 ± 0.08	3.14 ± 0.15
30	0.600 ± 0.02	3.96 ± 0.04	3.95 ± 0.05	3.49 ± 0.15
35	1.50 ± 0.15	5.30 ± 0.05	5.40 ± 0.14	3.90 ± 0.12
40	3.35 ± 0.25	6.54 ± 0.15		

shows that two consecutive reactions are taking place. The fast reaction corresponds to the formation of the mono complex (CuL) and second slow step corresponds to the formation of hydroxy complex. Values of pseudo-first order rate constants (k_{obs}) were calculated using the usual Guggenheim's method. The values of $k_{\text{obs}} = k'_{\text{obs}}/[\text{Cu}^{2+}]$ are given in Table 1.

To avoid hydrolysis, we restricted our investigation to the pH range 2.50-3.31. Rate of the reaction can be given by same equation as described in Ni(II)-L-amino- β -indolepropionic acid reaction.

Plots of $k_{\text{obs}}\{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2\}/K_1[\text{H}^+]$ versus $[\text{H}^+]^{-1}$ were linear and the values of k_{12} and k_{43} and the activation parameters were obtained in a similar way as in the case of Ni(II). These values are given in Tables 2 and 3 respectively. Similarly the value of k_0 was obtained from Eq. (11) as $1.45 \times 10^{10} \text{ s}^{-1}$. Value reported by Swift and Connick¹³ is $2 \times 10^8 \text{ s}^{-1}$. The higher value of k_0 in our case is the direct result of Jahn Teller distortion of Cu(II) ion (i.e. d^9 ion).

The values of k_{43} in the case of Cu(II) is very large as compared to those for Ni(II) (Table 2). This can be explained on the basis of crystal field stabilization energy difference (CFSE). The loss of water molecule from the metal ion changes the geometry from octahedral (O_h) to trigonal bipyramidal (TBP). The CFSE¹⁴ 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 (O_h -TBP) in the case of Ni(II) is 5.73 Dq and for Cu(II) it is 1.09 Dq. The lower value in the case of Cu(II) is responsible for the larger value of k_{43} .

Since the fast reaction was found to be second order and was accompanied by release of a proton, the slower reaction was of little importance. Moreover, the slower reaction has no dependence on $[\text{Cu(II)}]$. This was confirmed by using $[\text{Cu(II)}] = 0.02, 0.04, 0.06$ and 0.08 mol dm^{-3} . In every case $t_{1/2} = 0.15 \text{ s}$ was observed. The slow reaction was also found to be independent of pH (k'_{obs} was found to be $\sim 4.6 \text{ s}^{-1}$ in the pH range 2.50-3.31).

Therefore, it could be assumed that the formation of a small amount of hydroxy complex of the type $\text{Cu(L-}\alpha\text{-amino-}\beta\text{-indolepropionic acid)} \cdot (\text{H}_2\text{O})_3\text{OH}^+$ takes place. This type of hydroxy complex for Ni(II) has been reported in literature⁴.

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