

Interaction of Ni(II), Co(II) and Cu(II) with DL-aminobutanedioic acid— A kinetic approach

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Received 28 December 1993; revised 14 April 1994; accepted 6 July 1994

Comprehensive kinetic study on the interaction of Ni(II), Co(II) and Cu(II) with DL-aminobutanedioic acid has been carried out in the pH range 6.00-7.13 for Ni(II) and Co(II) and 2.11-3.11 for Cu(II) in 0.1M KNO₃ at different temperatures 25-40 ($\pm 0.05^\circ\text{C}$) using stopped-flow spectrophotometer. The complexation reactions have been discussed in terms of Eigen mechanism in which the loss of water molecule from the metal ion in the ion pair is an important rate determining step. Experimental rate constants have been resolved into stepwise rate constants and the activation parameters corresponding to different binding steps have been evaluated. The determined values of k_0 (the rate constant for exchange of water molecule) compare well with the expected values as determined by NMR studies.

DL-Aminobutanedioic acid (DL-aspartic acid) is an important constituent of a large number of proteins, polypeptides and enzymes and is required for the synthesis of peptides like carnosine, anserine, coenzyme A and pantothenic acid¹. It plays an important role in the excretion of nitrogen waste as urea via urea cycle² and also it is converted by transamination reaction to oxaloacetic acid which plays significant role in Krebs's citric acid cycle³. Thus, it is significant both in carbohydrate catabolism and photosynthesis.

Metal ions like Ni(II), Co(II) and Cu(II) present in body tissues and fluids can interact with DL-aspartic acid present in blood plasma. Thus, comparative knowledge of binding of metal ions by DL-aminobutanedioic acid can help in the preparation of model systems.

Review of the literature reveals that earlier studies^{4,5} on the complexation of DL-aminobutanedioic acid with metal ions were made only at one temperature, taking into consideration only one dissociation constant corresponding to NH₃⁺ groups. Also, activation parameters corresponding to stepwise rate constants have not been determined which are quite important for establishing the mechanism for the complexation reaction.

In the present kinetic study, we have taken into consideration all the three dissociation constants of DL-aminobutanedioic acid to investigate the finer details of the complexation reactions of DL-aminobutanedioic acid with Ni(II), Co(II) and Cu(II). The values of water exchange rate con-

stant (k_0) alongwith the activation parameters corresponding to the stepwise rate constants have also been computed.

Materials and Methods

DL-Aminobutanedioic acid, (BDH, England), Ni(NO₃)₂·6H₂O, Co(NO₃)₂·6H₂O, Cu(NO₃)₂·3H₂O (all Merck), 2,6-lutidine (Merck Schuscharadt), bromothymol blue (BDH), KNO₃, KOH and HNO₃ (all A.R. grade) were used as such. Freshly prepared solution of DL-aminobutanedioic acid was used for all complexation reactions, and triply distilled water was used for the preparation of all solutions. The temperature of the system was maintained using immersion type thermostat (German Model NBE).

Kinetic measurements

The kinetic study was made on Aminco Morrow stopped-flow spectrophotometer under pseudo-first order conditions i.e., $[M(II)] \gg [DL\text{-aminobutanedioic acid}]$ to ensure the formation of mono-complex only. The reactions were investigated at different temperatures 25-40 ($\pm 0.05^\circ\text{C}$) in 0.1M KNO₃. Transmittance changes in the case of complexation reactions of Ni(II) and Co(II) with DL-aminobutanedioic acid were monitored at 620 nm using bromothymol blue as pH indicator and at 600 nm in the case of Cu-DL-aminobutanedioic acid. No indicator was used in the case of Cu(II) since the absorbance changes were large enough to be monitored directly.

In the case of Ni(II) and Co(II), solutions containing metal ion and the ligand were buffered with 2,6-lutidine and HCl to make the initial pH of metal ion solution and ligand solution same and constant. After mixing, slight change in the pH (of the order of 0.05 unit) was observed and the reported values are those of the mixture. In the case of Cu-DL-aminobutanedioic acid reaction, pH was adjusted by dropwise addition of KOH/HNO₃. The final pH was taken on radiometer pH meter (pH M26, Copenhagen).

Transmittance changes for each run were traced out from the oscilloscope. The values of pseudo-first order rate constants (k'_{obs}) were calculated from the linear plots of $\log \Delta V$ versus time. Second order rate constants, k_{obs} , were evaluated from the relation $k_{\text{obs}} = k'_{\text{obs}} / [M(\text{II})]$.

Blank experiments in which (i) metal ion solution and indicator (solvent in the case of Cu(II)) and (ii) ligand solution and indicator were mixed, showed no transmittance change to interfere with the result.

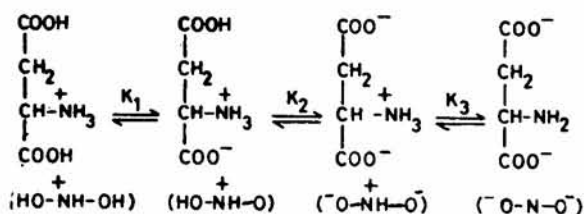
Results and Discussion

Kinetics of the complexation of Ni(II) and Co(II) with DL-aminobutanedioic acid was studied in the pH range 6.00-7.13 in 0.1M KNO₃ at different temperatures 25-40 ($\pm 0.05^\circ\text{C}$). In the case of Cu(II)-DL-aminobutanedioic acid interaction, kinetic investigations were made over the pH range 2.11-3.11 to avoid hydrolysis.

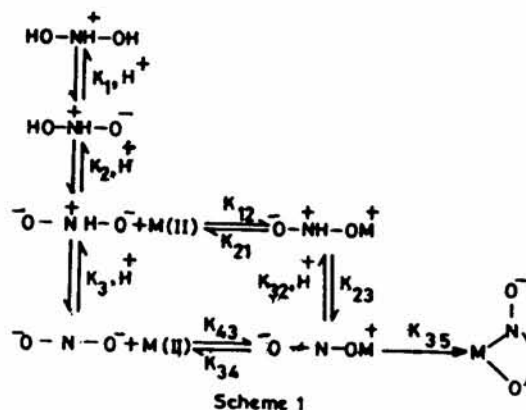
DL-Aminobutanedioic acid has two carboxylic groups and one amino group. Therefore, it is expected that all the three groups should participate in complexation reactions with Ni(II), Co(II) and Cu(II).

In aqueous solution, DL-aminobutanedioic acid may exist as $\text{HOOC}-\text{CH}_2-\text{CH}(\text{NH}_3^+)-\text{COO}^-$ (A), $\text{OOC}-\text{CH}_2-\text{CH}(\text{NH}_3^+)-\text{COOH}$ (B or $\text{HOOC}-\text{CH}_2-\text{CH}(\text{NH}_2)-\text{COOH}$ (C). According to Green and Tong⁶ the ratio of these forms, A:B:C is close to 28000:1600:1. Thus form (A) of DL-aminobutanedioic acid is predominant in aqueous solution.

A dissociation of DL-aminobutanedioic acid can be represented as follows:



These different forms of DL-aminobutanedioic acid (at 25°C , $pK_1 = 1.93$, $pK_2 = 3.7$, $pK_3 = 9.63$)⁷ can react with M(II) in a stepwise manner as shown in Scheme 1.



For the interaction of DL-aminobutanedioic acid with M(II) ions, overall rate of the reaction can be written as

$$\text{Rate} = k_{\text{obs}} [M(\text{II})][\text{DL-aminobutanedioic acid}] \quad \dots (1)$$

$$= k'_{\text{obs}} [\text{DL-aminobutanedioic acid}]_{\text{T}} \quad \dots (2)$$

$$= k'_{\text{obs}} \{ [\text{HO}-\text{NH}-\text{OH}] + [\text{HO}-\text{NH}-\text{O}^-] + [\text{O}-\text{NH}-\text{O}^-] + [\text{O}-\text{N}-\text{O}^-] \} \quad \dots (3)$$

$$\text{where } k'_{\text{obs}} = k_{\text{obs}} [M(\text{II})] \quad \dots (4)$$

$\text{HO}-\text{NH}-\text{OH}$, $\text{HO}-\text{NH}-\text{O}^-$, $\text{O}-\text{NH}-\text{O}^-$ and $\text{O}-\text{N}-\text{O}^-$ are triprotonated, diprotonated, monoprotated and deprotonated forms respectively of the ligand.

From Scheme 1, rate can be written as

$$\text{Rate} = k_{35} [\text{O}-\text{N}-\text{OM}^+] \quad \dots (5)$$

Applying steady state approximation for the intermediates $\text{O}-\text{NH}-\text{OM}^+$ and $\text{O}-\text{N}-\text{OM}^+$, using the value of $[\text{O}-\text{NH}-\text{OM}^+]$ in terms of $[\text{O}-\text{N}-\text{OM}^+]$ and on rearrangement we get

$$\begin{aligned}
 [\text{O}-\text{N}-\text{OM}^+] = & \frac{\{k_{12}k_{23}[\text{O}-\text{NH}-\text{O}^-] + k_{23}k_{43}[\text{O}-\text{N}-\text{O}^-]\}[M(\text{II})]}{k_{21}k_{32}[\text{H}^+] + k_{23}(k_{34} + k_{35})} \\
 & \dots (6)
 \end{aligned}$$

Using this value of $[\text{O}-\text{N}-\text{OM}^+]$ in Eq. (5) we get,

Table 1—Values of k_{12} , k_{43} and k_o for the interaction of Ni(II), Co(II) and Cu(II) with DL-aminobutanedioic acid

Temp.	Ni(II)-DL-Aminobutanedioic acid			Co(II)-DL-Aminobutanedioic acid			Cu(II)-DL-Aminobutanedioic acid		
	$k_{12} \times 10^{-2}$ ($M^{-1} s^{-1}$)	$k_{43} \times 10^{-5}$ ($M^{-1} s^{-1}$)	$k_o \times 10^{-5}$ (s^{-1})	$k_{12} \times 10^{-2}$ ($M^{-1} s^{-1}$)	$k_{43} \times 10^{-5}$ ($M^{-1} s^{-1}$)	$k_o \times 10^{-5}$ (s^{-1})	$k_{12} \times 10^{-2}$ ($M^{-1} s^{-1}$)	$k_{43} \times 10^{-9}$ ($M^{-1} s^{-1}$)	$k_o \times 10^{-9}$ (s^{-1})
25	0.85	2.08	1.05	3.85	2.60	1.31	6.10	3.05	1.54
30	1.05	2.19	1.11	4.5	2.70	1.36	6.60	3.13	1.58
35	1.20	2.30	1.16	5.1	2.79	1.41	7.00	3.20	1.61
40	1.45	2.40	1.21	5.85	2.89	1.46	7.50	3.28	1.65

Rate =

$$\frac{\{k_{12}k_{35}k_{23}[\text{O}^+-\text{NH}-\text{O}^-] + k_{23}k_{35}k_{43}[\text{O}^+-\text{N}-\text{O}^-]\}[\text{M(II)}]}{k_{21}k_{32}[\text{H}^+] + k_{23}(k_{34} + k_{35})} \quad \dots (7)$$

Now, on substituting the values of $[\text{O}^+-\text{NH}-\text{O}^-]$ and $[\text{O}^+-\text{N}-\text{O}^-]$ in terms of $[\text{HO}-\text{NH}-\text{OH}]$ from Scheme 1 in Eq. (7) and on rearrangement, we obtain Eq. (8).

$$\text{Rate} = \left\{ \frac{(k_{12}k_{23}k_{35}K_1K_2[\text{H}^+] + k_{23}k_{43}k_{35}K_1K_2K_3)}{k_{21}k_{32}[\text{H}^+] + k_{23}(k_{34} + k_{35})} \right\} \times \left\{ \frac{[\text{HO}-\text{NH}-\text{OH}][\text{M(II)}]}{[\text{H}^+]^3} \right\} \quad \dots (8)$$

Using the values of $[\text{HO}-\text{NH}-\text{O}^-]$, $[\text{O}^+-\text{NH}-\text{O}^-]$ and $[\text{O}^+-\text{N}-\text{O}^-]$ in terms of $[\text{HO}-\text{NH}-\text{OH}]$ in Eq. (3) and rearranging we get Eq. (9)

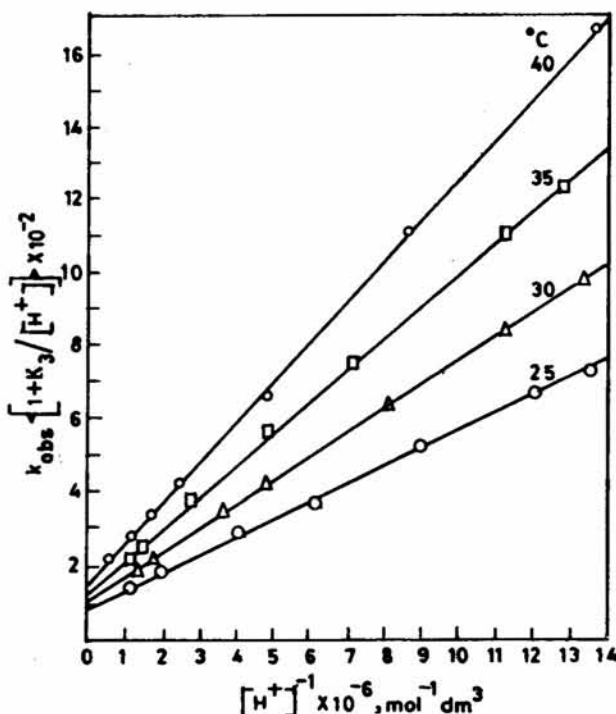
$$\text{Rate} = k_{\text{obs}}[\text{M(II)}][\text{H}^+]^3 + K_1[\text{H}^+]^2 + K_1K_2[\text{H}^+] + K_1K_2K_3 \times \left\{ \frac{[\text{HO}-\text{NH}-\text{OH}]}{[\text{H}^+]^3} \right\} \quad \dots (9)$$

Comparing Eqs (8) and (9) we get

$$k_{\text{obs}}\{[\text{H}^+]^3 + K_1[\text{H}^+]^2 + K_1K_2[\text{H}^+] + K_1K_2K_3\} = \frac{k_{12}k_{23}k_{35}K_1K_2[\text{H}^+] + k_{23}k_{43}k_{35}K_1K_2K_3}{k_{21}k_{32}[\text{H}^+] + k_{23}(k_{34} + k_{35})} \quad \dots (10)$$

Assuming⁸ that $k_{35} \gg k_{34}$ and $k_{21}k_{32}[\text{H}^+] \ll k_{23}(k_{34} + k_{35})$, Eq. (10) becomes

$$k_{\text{obs}} \frac{[\text{H}^+]^3 + K_1[\text{H}^+]^2 + K_1K_2[\text{H}^+] + K_1K_2K_3}{K_1K_2[\text{H}^+]} = k_{12} + \frac{k_{43}K_3}{[\text{H}^+]} \quad \dots (11)$$

Fig. 1—Plots of $k_{\text{obs}}\{1 + K_3/[\text{H}^+]\}$ versus $[\text{H}^+]^{-1}$ for Ni(II)-DL-aminobutanedioic acid interaction at different temperatures

Since under our experimental conditions, $[\text{H}^+]^3$ and $K_1[\text{H}^+]^2$ are negligible as compared to $K_1K_2[\text{H}^+]$ and $K_1K_2K_3$, Eq. (11) can be written as

$$k_{\text{obs}} = \frac{\{K_1K_2[\text{H}^+] + K_1K_2K_3\}}{K_1K_2[\text{H}^+]} = k_{12} + \frac{k_{43}K_3}{[\text{H}^+]} \quad \dots (12)$$

Plots of $k_{\text{obs}}\{1 + K_3/[\text{H}^+]\}$ versus $[\text{H}^+]^{-1}$ for Ni(II)-DL-aminobutanedioic acid interaction are shown in Fig. 1. The values of k_{12} and k_{43} obtained from the intercepts and slopes respectively of these linear plots are reported in Table 1. The values of k_{12} and k_{43} corresponding to Co-DL-aminobutanedioic acid and Cu-DL-aminobutanedioic acid interaction are also reported in Table 1.

Table 2—Values of activation parameters for the interaction of Ni(II), Co(II) and Cu(II) with DL-aminobutanedioic acid

	Ni(II)-DL-Aminobutanedioic acid	Co(II)-DL-Aminobutanedioic acid	Cu(II)-DL-Aminobutanedioic acid
$\Delta H_{12}^{\ddagger}$ (kJ mol ⁻¹)	25.1	19.3	8.25
$\Delta S_{12}^{\ddagger}$ (JK ⁻¹ mol ⁻¹)	-123	-130	-164
$\Delta H_{43}^{\ddagger}$ (kJ mol ⁻¹)	5.27	2.93	1.79
$\Delta S_{43}^{\ddagger}$ (JK ⁻¹ mol ⁻¹)	-125	-131	-57.4

K_3 at 25°C was taken from the literature⁷ and for other temperatures, K_3 values were calculated using the thermodynamic relation,

$$pK_{T_2} = \Delta H(T_2 - T_1)/4.576 T_1 T_2 + pK_{T_1} \quad \dots (13)$$

The values of enthalpy and entropy of activation were obtained from the linear plots of $\log k/T$ versus $1/T$. These values for the interaction of Ni(II), Co(II) and Cu(II) with DL-aminobutanedioic acid are reported in Table 2.

According to the general mechanism⁹ for complex formation, the rate law in terms of outer sphere complex formation constant (K_{os}) and the rate constant for water loss (k_0) can be written as

$$\text{Rate} = K_{os} \cdot k_0 [M(II)][L] \quad \dots (14)$$

The value of K_{os} can be calculated using the Fuoss equation¹⁰ and is approximated to 1.98 mol⁻¹ dm³ at all temperatures of investigations. From Scheme 1, rate of complex formation involving water exchange can be written as

$$\text{Rate} = k_{12}[-O-NH-O^-][M(II)] + k_{43}[-O-N-O^-][M(II)] \quad \dots (15)$$

From the data in Table 1, it is obvious that

$$k_{12} \ll k_{43}$$

Thus eq. (15) can be written as

$$\text{Rate} = k_{43}[-O-N-O^-][M(II)] \quad \dots (16)$$

Comparing Eqs (14) and (16) we get

$$k_{43} = k_0 K_{os} \quad \dots (17)$$

Knowing the values of k_{43} and K_{os} , the values of k_0 at different temperatures were calculated which compare well with the expected values as calculated on the basis of NMR data¹². These values are reported in Table 1.

The values of k_0 in the case of Ni(II), Co(II) and Cu(II), show the highest rate of complexation

for Cu(II). The decreasing order of water exchange rate constant (k_0), Cu(II) > Co(II) > Ni(II), can be explained on the basis of CFSE values¹¹. The differences in CFSE values (Oh-TBP) for Ni(II), Co(II) and Cu(II) is 5.73 Dq, 2.55 Dq and 1.09 Dq respectively. Thus activation energy barrier is maximum in case of Ni(II) and minimum in case of Cu(II).

In all the cases lower values of $\Delta H_{43}^{\ddagger}$ than $\Delta H_{12}^{\ddagger}$ (Table 2) confirm that the reaction via k_{43} path would be fast as compared to k_{12} path. Also, k_{43} values are much larger than k_{12} values (Table 1). Thus, it can be concluded that zwitterionic form is less reactive than deprotonated form. This may be attributed to the strong electrostatic forces of attraction between positive charge of metal ion and negative charge of carboxylate group.

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