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Kinetics and mechanism of complexation of Ni(II) and Co(II) with L-2-Amino 3-mercapto propionic acid

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Abstract
L -2- Amino 3-mercapto propionic acid (Cysteine) is an amino acid with immense biological significance. The kinetic study involving interaction of Ni (II) and Co (II) with L-Cysteine was carried out under first order condition. The concentration values were chosen to be such the only mono-complex formation was possible. The investigations were carried out at 20, 25, 30 and 35 (±0.05) ºC. A scheme consistent with the fact that (-S) atom acts as the bridging ligand even though the deprotonated from of the ligand predominates at pH 7.7 only. The overall rate constant has been resolved into stepwise rate constant.

Keywords: Kinetic, mechanism, complexation, stepwise rate constants, activation parameters

Introduction
L -2- Amino 3-mercapto propionic acid (Cysteine) is an amino acid with an immense biological interest. As a component of tripeptide glutathione, it helps in the formation of conjugated bile acid (Murrag *et al.*, 1990) [1], the form in which bile acids are secreted in bile. The bile is imperative for absorption of fat. Its deficiency results in malabsorption of fat with consequent thinning of the body.

It also has a coenzyme function for cis-trans isomerases. Increase in the number of cis double bonds in a fatty acid leads to a variety of possible spatial configurations of the molecule. This may have profound significance on molecule packing in membranes.

In addition, via the mercapto group, L-2 Amino 3-mercaptopropionic acid participates in both redox and acid base reactions occurring in biological system. The main difficulty in the study of the complexes of L-2-Amino 3-mercdpto propionic acid lies in the possible redox reaction of the mercapto group. Since the -SH and –NH$_2$ groups have relatively high pK values and -S atom may further behave as bridging ligand, there are many possibilities of formation of protonated and polynuclear complexes with metal ions. Formation of poly nuclear complexes (Perrin *et al.*, 1968) [2] of composition M$_3$A$_4^{2-}$is primarily characteristic of Ni (II)-L-2 Amino 3-mercapto propionic acid (Fig. a)
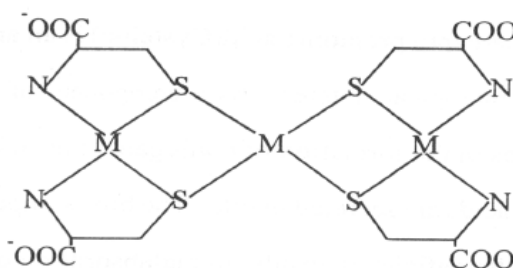

Fig a

Keeping this in view, a comprehensive kinetic study on interaction of Ni (lI) and Co (ll) with L-2-Amino 3-metcapto propionic acid was carried out.

L-2-Amino 3-mercapto propionic acid has three possible active sites:- (1) carboxyl group (2) amino group (3) mercapto group available for binding with metal ions. Dissociation of the ligand is represented as:-

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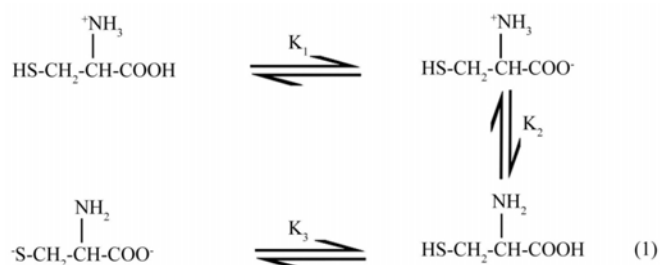
The pK values for COOH, $^+NH_3$ and HS groups at 25 °C are 1.88, 8.15, 10. 29 respectively. These values were corrected for other temperatures of our investigations using equation (2)

$$\text{Log } K_a{}^{T_2} = \log K_a{}^{T_1} + \frac{\Delta H (T_2-T_1)}{4.576 \, T_1 \, T_2}$$

- (2)

These K_a (Martell *et al.*, 1974) values were used subsequently for the evaluation of stepwise rate constants.

Methodology

The kinetics of interaction of Ni(ll) and Co(II) with L-2-Amino 3-mercapto propionic acid was studied in the pH range 5.65 -6.94, using bromothymol blue as an indicator at 620 nm. In this pH range no hydroxy species exist as hydrolysis occurs at higher pH. The ionic strength of the reaction mixture was maintained at 0.1 M using KNO$_3$.

The kinetic study was done under the first order condition i.e. [Ni(II)]$\gg$ [L-2-Amino 3-mercapto propionic acid]. The concentration values were chosen to be such that only mono complex formation was possible. Under our experimental conditions diprotonated and monoprotonated forms of the ligand were expected to be reactive species. But it was proved by spectrophotometric studies (McAulffe *et al.*, 1972) [4] that -S atom acts as the bridging ligand even though deprotonated form of the ligand predominates at pH> 7 only.

The investigations were carried out at 20, 25, 30 and 35 (±0.05)°C. Transmittance changes during the complexation were noted down from the oscilloscope and the plots of concentration change versus time were utilized in evaluating the first order rate constants (k'$_{obs}$) and second order rate constants (k$_{obs}$).

Results and Discussion

The overall differential rate equation for the interaction is given as:

Rate = $\dfrac{-d[\text{Ni(II)}]}{dt}$ -(3)

$= \dfrac{-d[\text{L-2-Amino 3-mercapto propionic acid}]}{dt}$ -(4)

$= k_{obs}[\text{Ni(II)}][\text{L-2-Amino 3-mercapto propionic acid}]_T$ - (5)

$= k_{obs}$ [Ni(ll)] {[HS- $^+NH_3$- COOH] +[HS -$^+NH_3$ - COO$^-$] + [HS - NH$_2$-COO$^-$]+ [$^-$S - NH$_2$-COO$^-$] }   -(6)

Where (HS-$^+NH_3$-COOH),(HS-$^+NH_3$-COO$^-$), (HS-NH$_2$-COO$^-$), ($^-$S-NH$_2$-COO$^-$) are the triprotonated, diprotonated, monoprotonated and deprotonated forms of the ligand. Following Scheme 1 was suggested for the interaction of these forms with M (II) and found to give the best fit with our kinetic data.
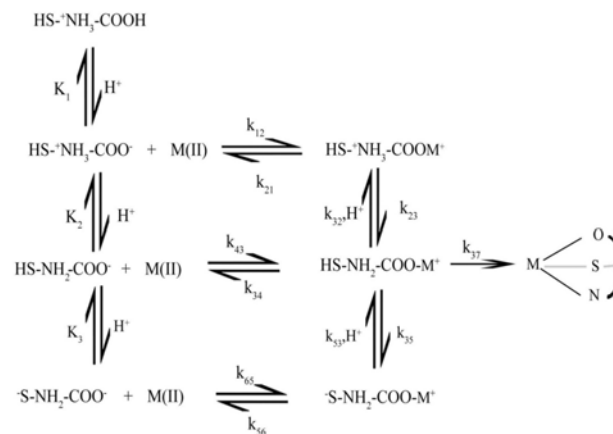
Scheme 1

According to this Scheme, rate of chelate formation is written as:

Rate   = k$_{37}$ [HS-NH$_2$ - COO M$^+$]   - (7)

Applying steady state approximation to intermediate species (HS - $^+NH_3$ - COOM$^+$), (HS-NH$_2$ - COOM$^+$), ($^-$S -NH$_2$ - COOM$^+$), we have:

$$k_{obs} \frac{\{1 + K_3\}}{[H^+]} = k_{43} + \frac{k_{65} \, K_3}{[H^+]}$$

- (8)

The above relation predicts a linear plot for $k_{obs}\{1 + K_3/[H^+]\}$ versus $[H^+]^{-1}$ and that is what was actually observed (Fig.1). Thus, confirming the validity of Scheme 1 for the complexation. The values of specific rate constants k_{43} and k_{65} were obtained from the intercepts and slopes respectively of the linear plots (Fig. 1) and are reported in Table 1. The values of activation parameters corresponding to specific rate constants k_{43} and k_{65} were calculated from the linear plots of log k and log k/T versus 1/T. These values are given inTable 1. The linear plots were also obtained for the complexation of Co (II) with L-2-Amino 3-mercapto propionic acid. The values of specific rate constants and activation parameters are reported in Table 1.
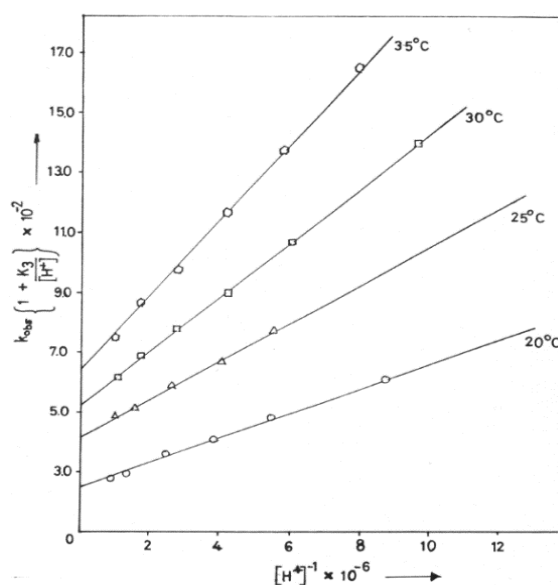

Fig 1: Plots of $k_{obs}\{1+K_3/[H^+]\}$ versus $[H^+]^{-1}$ for Ni(II)- L-2-Amino 3-mercapto propionic acid complexation at different temperatures.

Table 1: Values of specific rate constants and their activation parameters for the interaction of Ni(II) and Co(II) with L-2-Amino 3-mercapto propionic acid

Temperature (± 0.05)°C	Ni(II) – Ligand			Co(II) – Ligand		
	$k_{43} \times 10^{-2}$ ($M^{-1}s^{-1}$)	$k_{65} \times 10^{-6}$ ($M^{-1}s^{-1}$)	$k_o \times 10^{-5}$ (s^{-1})	$k_{43} \times 10^{-3}$ ($M^{-1}s^{-1}$)	$k_{65} \times 10^{-7}$ ($M^{-1}s^{-1}$)	$k_o \times 10^{-6}$ (s^{-1})
20	2.50	1.03	5.20	1.90	1.47	7.42
25	4.15	1.25	6.31	2.16	1.70	8.58
30	5.20	1.42	7.17	2.32	1.80	9.09
35	6.40	1.56	7.88	2.61	2.03	10.25
$\Delta H^{\#}$ (kJmol^{-1})	47.14 $\pm$ 5.25	23.57 $\pm$ 1.2	-	13.48 $\pm$ 2.58	11.58 $\pm$ 1.01	-
$\Delta S^{\#}$ (J K^{-1} mol^{-1})	-54.18 $\pm$ 3.24	-66.18 $\pm$ 1.85	-	-152.55 $\pm$ 5.18	-84.30 $\pm$ 3.70	-

Calculation of Water Exchange Rate Constant

The rate law (Eigen et al., 1962) [5] in terms of outer sphere complex formation constant (K_{os}) and rate constant of water exchange (k_o) is given as:

Rate $= \dfrac{d}{dt}[ML^{(2-n)-}] = K_{os}k_o [M_{aq}^{2+}] [L_{aq}^{n-}]$ - (9)

In Scheme 1, water exchange is taking place via steps k_{43} and k_{65}

Rate $= k_{43}[M(II)] [HS\text{-}NH_2\text{-}COO^-] + k_{65}[M(II)] [^-S\text{-}NH_2\text{-}COO^-]$ - (10)

From Table1, it is evident that $k_{43} \ll k_{65}$. Therefore, rate of the reaction is represented as:

Rate $= k_{65} [M(II)] [^-S\text{-}NH_2\text{-}COO^-]$ - (11)

On comparing equation (9) and (11), we get:

$k_{65} = K_{os}k_o$ - (12)

The value of k_{65} and K_{os} is known, thus k_o at different temperatures was calculated and the values are reported in Table 1 (Fuoss, 1958) [6].

Both monoprotonated and deprotonated forms of L-2-Amino 3-mercaptopropionic acid are found to be reactive and the reactivity increases with rise in temperature. At all temperatures of our investigations, deprotonated form of the ligand is found to be more reactive than the monoprotonated form. The proposed mechanism is supported by the obtained values of activation parameters (Table 1). The high value of $\Delta H^{\#}$ corresponding to k_{65} path confirms the greater reactivity of deprotonated form. The negative values of $\Delta S^{\#}$ indicate that the reaction is between oppositely charged ions.

The validity of the proposed mechanism is further confirmed by the calculation of water exchange rate constant (k_o). The value of k_o for Co(II) is found to be 7.42×10^6 s^{-1} at 25°C. The calculated value is comparable to that obtained for Co(II) from NMR studies (Swift et al., 1967) [7], in the absence of ligand, confirming that the reaction proceeds via associative interchange.

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