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pH Metric Study of Ternary Complexes of Co(II) with Mercaptosuccinic Acid, 2-Mercaptopropionyl Glycine and Amino Acids

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The formation and stability constants of ternary complexes of Co(II) with sulphur containing ligands such as 2-mercaptopropionyl glycine, mercaptosuccinic acid (L_1) and glycine (gly), alanine (ala), valine (Val) (L_2) has been investigated potentiometrically. The stability constants are reported at 26 ± 0.5ºC in 0.1 M ($NaClO_4$) ionic strength and compared with stabilities of corresponding Co(II)-amino acids binary complexes. The Δ log K values obtained are positive favoured the formation of ternary complexes.

Key Words: Mercaptosuccinic acid, 2-Mercaptopropionyl glycine, Stability constants.

INTRODUCTION

The coordination chemistry of cobalt is 400 million years old[1]. The (vitamin B_{12}) is nature's famous high tech material prevalent in biological domain. Cobalt corrinoids appeared to have been functionally important even before DNA. Therefore it can be said that cobalt had played key role in the process of evolution[2]. Nair *et. al.*[3] have studied mixed ligand complexes of Ni(II) involving penicillin group drugs and sulphur containing ligands. Patil[4] have studied ternary complexes of sulphur containing ligands with lanthanides. The aim of present investigation is to study the ternary complexes of Co(II) with sulphur containing ligand such as 2-mercaptopropionyl glycine (2-MPG) and mercaptosuccinic acid (MSA) and amino acids. 2-MPG is a radio protective and acts as antidotes against heavy metal ions. It enhances the extraction of mercury, copper and iron[5]. The sulphur of sulphydryl group which is soft in character[6] determines the complex equilibria of sulphur containing ligands. The sulphydryl group of these ligands participate in both redox and acid-base reactions[7].

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EXPERIMENTAL

The ligands MSA, 2-MPG (Sigma) and glycine, alanine and valine used were purified by crystallization and purity was checked by their melting point. The solutions of the ligands were prepared in the glass distilled water and were always a fresh. A stock solution of Co(II) was prepared by dissolving AnalaR grade cobalt nitrate in distilled water and standardized against EDTA[8]. Details regarding other chemicals are described earlier[9]. The pH measurements were carried out with Elico digital pH meter (Model LI-120) and combined glass electrode having pH range 0-14. The titrations were carried out at 26 ± 0.5ºC and an inert atmosphere was maintained by bubbling oxygen free nitrogen gas through the solution throughout the course of titrations.

The Calvin Bjerrum's pH titration technique as modified by Irving and Rossotti[10,11] was applied to determine formation constants. In experimental procedure following thermostated mixtures were titrated with carbonate free 0.20 M sodium hydroxide solution.

1. 2 mL of 0.24 M $HClO_4$
2. 2 mL of 0.24 M $HClO_4$ + 10 mL of 0.01 M ligand L_1
3. 2 mL of 0.24 M $HClO_4$ + 10 mL of 0.01 M ligand L_1 + 2 mL of 0.01 M Co(II) solution
4. 2 mL of 0.24 M $HClO_4$ + 10 mL of 0.01 M ligand L_2
5. 2 mL of 0.24 M $HClO_4$ + 10 mL of 0.01 M ligand L_2 + 2 mL of 0.01 M Co(II) solution
6. 2 mL of 0.24 mL $HClO_4$ + 10 mL of 0.01 M ligand L_1 + 10 mLof 0.01 M ligand L_2 + 2 mL of 0.01 M Co(II)solution

The total volume of above solutions was made 50 mL. The ionic strength was maintained to 0.1 M with the help of sodium perchlorate. The variations of pH *vs.* volume of NaOH are presented graphically in Fig. 1.

RESULTS AND DISCUSSION

The proton-ligand stability constants were determined by Irving Rossotti method[12] and are presented in Table-1. The MSA has three protonation constants. The first protonation constant (10.50) is due to -SH group which is a to one -COOH group and β to another -COOH group while second (8.40) and third (3.20) are due to two -COOH groups. 2-MPG is a novel type of ligand bearing -SH, -CONH and -COOH groups. The two well separated curves are obtained in pH titration curves of this ligand and hence two protonation constants are calculated. The first protonation constant (8.40) is assigned to -SH group while second (3.62) to -COOH group.

It is observed (Fig. 1) that the titration curves of amino acid lie before acid curve indicating that in acidic solution the ligand molecule is in association with one equivalent proton. The proton may be attached to the

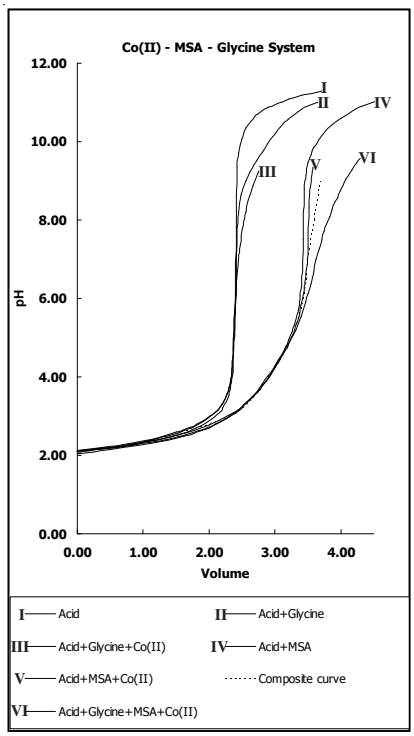

Fig. 1.

TABLE-1
PROTON LIGAND STABILITY CONSTANTS AND METAL LIGAND STABILITY CONSTANTS OF Co(II) ION
Temp. = 26 ± 0.5ºC; μ = 0.1 M ($NaClO_4$)

Stability constant	Ligands				
	MSA	2-MPG	Gly	Ala	Val
log K_1^H	10.50	8.40	9.56	9.63	9.50
log K_2^H	4.70	3.60	2.40	2.40	2.36
log K_3^H	3.20	–	–	–	–
log β_{ML1}	8.36	7.00	4.96	4.26	4.34
log β_{ML2}	12.76	–	8.91	8.01	8.25

nitrogen atom of amino group[10,11] due to lone pair of electrons present on nitrogen. There are two successive deprotonation steps of protonated ligand. The first step is ionization of -COOH group, which takes place in the pH range 2 to 3 and second step is deprotonation of proton attached to nitrogen atom that takes place in the pH range 9 to 11 (Fig. 1). Similar

deprotonation steps are also reported[13-17]. The 2-MPG, MSA and amino acids form 1:1 and 1:2 complexes with Co(II). MSA coordinates metal through sulphur of mercapto and oxygen of carboxylic group while gly, ala and val binds through oxygen of carboxylic and nitrogen of amino group[18]. It is observed that pH of precipitation of ternary titration are higher than individual metal complex titrations leading to the formation of ternary complexes. The formation of mixed ligand chelate was confirmed by comparing mixed ligand curve and composite curve[19]. The horizontal difference between mixed ligand complex curve and composite curve increases. The mixed ligand curve did not coincide with either of the individual metal complex curve, therefore 1:1:1 ternary complex is formed. The simultaneous formation of ternary complex is confirmed from the shape and position of titration curve.

TABLE-2
STABILITY CONSTANTS OF TERNARY COMPLEXES OF Co(II) ION WITH 2-MPG, MSA AND AMINO ACIDS
Temp. = 26 ± 0.5ºC; μ = 0.1 M ($NaClO_4$)

System	log β_{ML1L2}	log $K^{ML1}{}_{ML1L2}$	log $K^{ML2}{}_{ML1L2}$	Δ log K_{ML1L2}
2-MPG-gly	9.99	1.63	5.03	3.33
2-MPG-ala	10.07	1.71	5.81	2.52
2-MPG-val	9.93	1.57	5.59	2.77
MSA-gly	10.96	3.96	6.00	1.00
MSA-ala	11.00	4.00	6.79	0.26
MSA-val	10.92	3.92	6.58	0.42

The stability constants of mixed ligand complexes of cobalt with MSA, 2-MPG and gly, ala and val are presented in Table-2. The log $K^{ML1}{}_{ML1L2}$ (= log βM_{L1L2} - log $K^{M}{}_{ML1}$) values obtained in the present investigation compare favourably with log K_1 of ML_1 binary complexes. In ternary complexes, the MSA binds the metal ion in similar manner as in their binary complexes. Again log $K^{ML2}{}_{ML1L2}$ (= log βM_{L1L2} - log $K^{M}{}_{ML2}$) values obtained in the present investigation compare favourably with log K_1 of ML_2 binary complexes.

The amino acid in M_{L1L2} species binds the metal ion in the same way as in their binary species. The glycine like binding mode[18] results five membered rings which causes less strain to molecules and hence are very stable. Thus, the M_{L1L2} species in all these ternary complex systems would contain two five membered chelate rings. The values of Δ log K_{ML1L2} obtained in these systems are more positive compared to statistical values[20] confirm that MSA, 2-MPG and amino acid preferentially form ternary complexes

to the binary complexes and making extra stabilization of ternary complexes.

In the present investigation, the formation of ternary complex the same coordinating atom oxygen from carboxylic group of both amino acid and mercaptosuccinic acid is involved on both sides of metal ion and also identical size of chelate ring on both sides favors the formation of ternary complex.

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