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Formation of Low-Valent Metal Templates Using Simple Amino Acids

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Low-valent metal templates of the general formula $[HL]_2$-M_2L' (HL = glycine and alanine; M = univalent metal (Li, Na and K); L′ = de-protonated acid resorcino).have been constructed using glycine and alanine in non-aqueous solvent. The use of this work is to remove univalent metals from their complexes with the help of stem bark of some cultivars of mango containing these free amino acids such as glycine and alanine.

Key Words: Low-valent metal, Amino acids, Templates.

INTRODUCTION

The stem bark of some cultivars of mango contains free amino-acids. The Chausa (an Indian variety of mango) contains the maximum number of amino acids while desi variety does not possess lysine and valine in the free state. Alanine and glycine are present in all stem bark extracts of mango tree.

Chelating resins have become important tools in recent years for removal of metal ions from aqueous solution[1]. Various types of multidentate ligands have thus been introduced into a variety of network polymers[2]. Although these chelating resins take up almost all transition metal ions in high yield, they mostly do not have sufficient selectivity of metal ion.

Now-a-days new ideas are being developed to generate such ligand systems which may be called template polymeric ligand matrices which are employed for ion removing from the complex.

The preparation of ion specific template sites by physical entrapment of oriented dithizone in polymeric matrices has been reported[3].

Thus, in the present work,we selected the glycine and alanine which interact with lithium, sodium and potassium salts of resorcinol, the resin-prone organic compound, in non-aqueous solution where two molecules of glycine and alanine is being attracted towards low-valent metals of resorcinol salts. The interactions of the partners of the reactions are shown as below.

RESULTS AND DISCUSSION

Glycine and alanine when added in metal salts of resorcinol in ethereal medium, the colour of the salt solution goes deeper from red to brown. The pH of the system in solution decreases till we get constant pH. The situation is more

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remarkable with alanine compared to glycine. The colour, pH and infrared bands of the compounds are given in Tables 1 and 2.

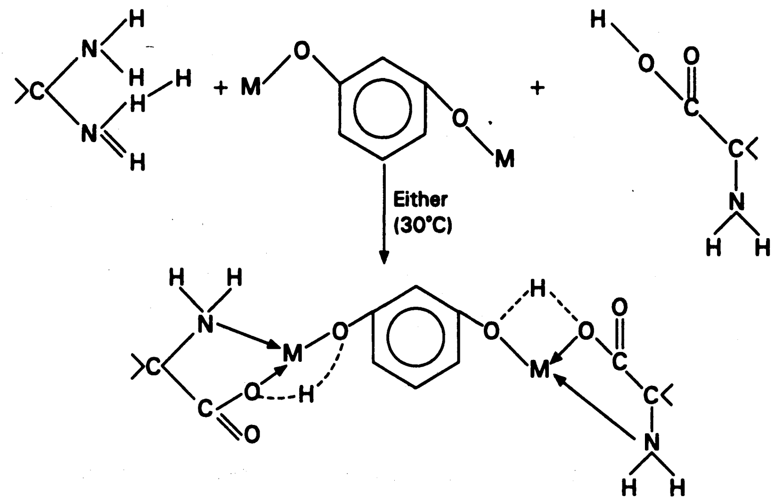

TABLE-1
TEMPLATE FORMATION WITH GLYCINE (L^1 = DEPROTONATED RESORCINOL)

Compounds in solution	Color in solution	pH	IR spectra (cm^{-1})	
			ν(N—H)	ν(COO⁻)
Li_2L^1 (1.25 g) in excess of ether	Deep red	9.5	—	—
Addition of:				
0.50 g glycine (s)	Brown	8.5	3300	1650
1.00 g glycine (s)	Brown	7.5	3280	1630
1.50 g glycine (s)	Dark brown	7.1	3250	1620
Na_2L^1 (1.55 g) in excess of ether	Red	10.1	—	—
Addition of:				
0.50 g glycine (s)	Deep red	8.9	3320	1660
1.00 g glycine (s)	Deep red	7.8	3300	1650
1.50 g glycine (s)	Brown	7.4	3270	1650
K_2L^1 (1.85 g) in excess of ether	Red	10.5	—	—
Addition of:				
0.50 g Glycine (s)	Deep red	9.1	3350	1680
1.00 g glycine (s)	Deep red	8.5	3330	1660
1.50 g glycine (s)	Deep red	7.9	3300	1660

TABLE-2
TEMPLATE FORMATION WITH ALANINE (L^1 = DEPROTONATED RESORCINOL

Compounds in solution	Color in solution	pH	IR spectra (cm^{-1})	
			ν(N—H)	$ν(COO^-)$
Li_2L^1 (1.25 g) in excess of ether	Deep red	9.5	—	—
Addition of:				
0.50 g alanine	Brown	8.2	3250	1650
1.00 g alanine	Brown	7.3	3225	1640
1.50 g alanine	Dark brown	7.0	3200	1620
1.75 g alanine	Dark brown	6.8	3200	1610
Na_2L^1 (1.55 g) in excess of ether	Red	10.1	—	—
Addition of:				
0.50 g alanine	Deep red	8.6	3300	1650
1.00 g alanine	Brown	7.5	3280	1640
1.50 g alanine	Brown	7.2	3250	1620
1.75 g alanine	Dark brown	7.1	3250	1610
K_2L^1 (1.85 g) in excess of ether	Red	10.5	—	—
Addition of:				
0.50 g alanine	Deep red	8.8	3320	1660
1.00 g alanine	Deep red	8.1	3300	1650
1.50 g alanine	Deep red	7.6	3280	1620
1.75 g alanine	Brown	7.2	3280	1610

The idea to fix a metal chelate complex covalently through a functional group in the ligand moiety into a rigid cross linked polymer has been studied[4] so that when the metal ion is removed it leaves the ligand bound to the polymeric matrix in a cavity more compatible to the particular metal ion. This may provide selective absorption independent or less dependent on equilibrium constant. Four template polymers are made with Cu(II), Co(II), Zn(II) and Ni(II) ions and the selectivity of each has been measured.

The investigation by Babu *et al.*[5] is confined to the pH range 6.0–10.0 for the Co(II) and Zn(II) complexes. It has been established that when percentage of species increases, the pH decreases for MLH, ML_2H complexes.

In our work it has been observed that the percentage of attachment ligand available (glycine and alanine) for complexation varies from Li to K. For ethereal solution of Li_2L^1 (L^1 = deprotonated resorcinol), when glycine is added with increasing concentrations, the pH sharply decreases from 9.5 to 7.1. This is the minimum value of pH attainable in this manner. With Na_2L^1 and K_2L^1 compounds, pH also decreases but minimum pH attainable for template formation is 7.4 and 7.9 respectively, higher than the minimum pH value in the case of Li_2L^1 system. It is a remarkable point that when glycine/alanine comes in contact with M_2L^1 in ethereal medium, it is bound to dimerise which are attached at proper sites in template formation.

The data listed in Tables 1 and 2 show that alanine forms stabler template compared with glycine under similar experimental conditions.

In the free interacting partners the shifting of infrared bands for ν(N—H) and $\nu(COO^-)$ to lower wave numbers may suggest the involvement of N and O to the metals of M_2L^1 in the process of template formation. The probability of restraining the attached glycine and alanine for the metals cannot be ruled out due to collapse of the molecule from solution to solid state.

EXPERIMENTAL

The alkali metal salts of resorcinol were prepared by standard methods. The general method for preparing the template compounds was to take weighed amounts of alkali metal salts of resorcinol in excess of ether at 30°C and then add weighed amounts of glycine and alanine, *i.e.*, 0.5 g, 1.0 g, 1.5 g and 1.75 g step by step by heating over a hot plate using magnetic stirrer for 30 min for each step of addition of glycine and alanine. The reaction mixture is allowed to cool at 30°C each time and accordingly measure the pH of each step of resulting solution containing template with the help of pH meter. The IR bands were recorded on Perkin-Elmer.

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