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NOTE

Determination of Stability Constants of Some Bivalent Metal Complexes of 2-Amino-5-Methyl-Benzene Thiol

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The successive stability constants of the complexes of 2-amino-5-methyl benzenethiol with various bivalent transition metal cations have been determined in (60% v/v) acetone-water mixture at 25 ± 0.1°C and constant ionic strength $\mu = 0.1$ M (NaCl) by adopting the pH titration technique of Irving and Rossotti[1].

Key Words: Stability constant, Metal-complexes, 2-Amino-5-methyl benzene thiols.

All the chemicals used were of AR and GR grade. 2-Amino-5-methyl benzenethiol **(IV)** was synthesized by the cyclisation of 4-methyl phenyl thiourea **(II)** by bromine in chloroform. Substituted thiourea **(II)** was synthesised from the reaction of 4-methyl aniline hydrochloride with ammonium thiocyanate[1, 2] **(Scheme-1)**. Acetone was purified by standard procedure. Acetone-water (60% v/v) was used as solvent in preparing the solutions of metal salts, ligand and NaCl.

pH values are recorded employing Systronics PP-335 Digital pH-meter using a glass electrode and a saturated calomel electrode. Titrations were carried out in a titration cell maintained at 25 ± 0.1°C. The electrodes were calibrated using potassium hydrogen phthalate for (pH = 4) and checked before and after each titration.

Two sets of titrations were performed, one with the ligand solution and the other with the ligand solution containing bivalent transition metal cations. Changes in pH were recorded as a function of the volume of NaOH added.

The following solutions were used:

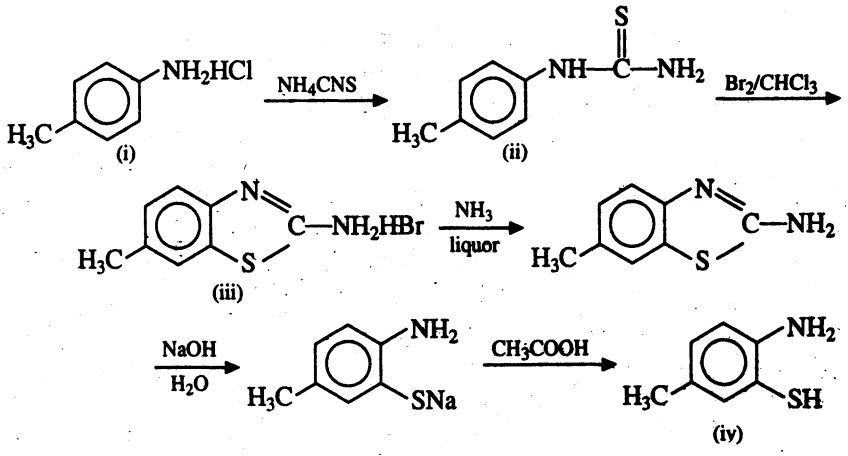
(1) 10 mL (0.05 M) ligand + 20 mL (0.25 M) NaCl + 19.5 mL acetone-water mixture (60% v/v).

(2) 10 mL (0.05 M) ligand + 10 mL (0.0125 M) bivalent transition metal cation + 20 mL (0.25 M) NaCl + 10 mL acetone-water mixture (60% v/v).

In the first titration, the titrant NaOH was of strength 0.5 M, whereas in the second titration the strength of NaOH used was 0.1 M.

From the pH titration curves or formation curves the values of $\bar{n}a$ (the average number of protons attached per ligand molecule), $\bar{n}$ (the average number of ligand ions attached per metal ion) and pL (free ligand exponent) were obtained adopting the Irving-Rossotti technique[3].

The stepwise stability constants of metal-ligand log k_1 and log k_2 were calculated using the half integral method, least square method and correction term method. The values are in good agreement with each other and the average values are reported in Table-1.



Scheme-1

TABLE-1
STEPWISE STABILITY OF VARIOUS COMPLEXES

Temp. = 25 ± 0.1°C μ = 0.1 M (NaCl)

Constants	Cu^{2+}	Ni^{2+}	Co^{2+}	Fe^{2+}	Mn^{2+}
		Interpolation at Half $\bar{n}$ value			
log k_1	13.11	13.06	13.03	13.00	12.93
log k_2	8.62	8.60	8.59	8.56	8.49
log β_2	21.73	21.66	21.62	21.56	21.42
		Least Square Method			
log k_1	13.06	13.01	13.00	12.99	12.93
log k_2	8.67	8.64	8.60	8.57	8.55
log β_2	21.73	21.65	21.60	21.56	21.48
		Correction Term Method			
log k_1	13.11	13.06	13.06	13.03	12.92
log k_2	8.65	8.61	8.54	8.53	8.51
log β_2	21.76	21.67	21.60	21.56	21.43

The maximum values of $\bar{n}$ were obtained in the pH region between 1.5 and 2.0 where hydrolysis of metal ion was negligible. This reveals that the metal-ligand ratio in these complexes is 1 : 2. A comparison of log β_2 reveals the following order of metal chelate stabilities.

$$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+}.$$

This is in good agreement with Irving-Williams order[4].

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