

NOTE

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

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The successive stability constants of the complexes of 2-amino-5-methoxybenzene thiol with various bivalent transition metal cations have been determined in (60% V/V) acetone-water mixture at $25 \pm 0.1^\circ\text{C}$ and constant ionic strength $\mu = 0.1 \text{ M}$ (NaCl) by adopting the pH titration technique of Irving and Rossotti.

Key Words: 2-Amino-5-methoxybenzene thiol, Metal complexes, Stability constant.

In the past a number of workers have reported the stability constants of metal complexes of organic ligands. In the present investigation physico-chemical studies of substituted-2-aminobenzene thiols with various transition metal cations have been carried out in acetone-water mixture (60%) in order to obtain their stepwise stability constants.

Synthesis of the Ligand

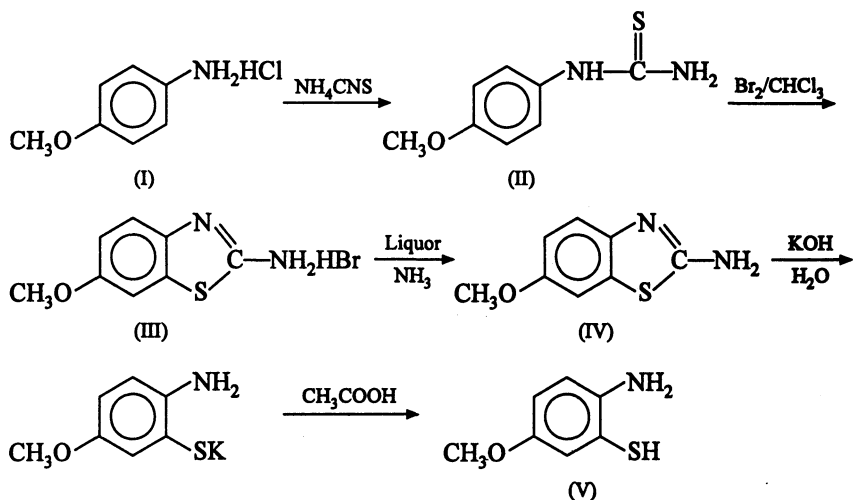
Synthesis of 4-methoxy phenyl thiourea: The mixture of *p*-anisidine (0.1 mol), concentrated HCl (9 mL) and water (25 mL) were heated till aniline hydrochloride was formed. It was then cooled at room temperature and ammonium thiocyanate (0.1 mole) was added to it and finally refluxed for 4 h on a water bath yielded 4-methoxy phenyl thiourea.

Synthesis of substituted 2-amino benzothiazole: Substituted 2-amino benzothiazole was synthesized by cyclization of 4-methoxy phenyl thiourea by bromine in chloroform. The contents were refluxed for about 4 h. Chloroform was removed by distillation and the resulting solid material was treated with aqueous SO_2 solution and filtered. The filtrate was then neutralized with aqueous ammonia and recrystallized from ethanol.

Synthesis of 2-amino-5-methoxy benzenethiol: Substituted 2-amino benzothiazole, KOH and water were then refluxed until the evolution of ammonia gas ceased and finally neutralized with 5 N acetic acid recrystallized with ethanol.

All the chemicals used were of AR and GR grade. Acetone was purified by standard procedure. Solutions of metal salts, ligand and NaCl were prepared by dissolving their requisite amounts in acetone-water (60% v/v). Similarly one

molar solution of NaOH was prepared in conductivity water in order to obtain (0.5 M) and (0.1 M) solutions respectively.



Potentiometric Titration

Potentiometric titrations were performed in a titration cell maintained at $25 \pm 0.1^\circ\text{C}$ and pH values were recorded by employing a Systronics PP-335 digital pH-meter using a glass electrode and a saturated calomel electrode. 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) 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 Irving-Rossotti¹ technique.

To calculate the stepwise stability constants of metal-ligand $\log k_1$ and $\log k_2$, three methods were used:

- (1) Interpolation at half \bar{n} -value method,
- (2) Least Square method, and
- (3) Correction term method.

The values are in good agreement with each other and the average values are reported in Table-1.

TABLE-1
STEPWISE STABILITY OF VARIOUS COMPLEXES

Temp. = $25 \pm 0.1^\circ\text{C}$, M = 0.1 M (NaCl)

Constants	Cu ²⁺	Ni ²⁺	Co ²⁺	Fe ²⁺	Mn ²⁺
Interpolation at half n value					
log k ₁	12.88	12.85	12.84	12.83	12.83
log k ₂	8.62	8.56	8.54	8.50	8.44
log β ₂	21.50	21.41	21.38	21.33	21.27
Least square method					
log k ₁	12.88	12.82	12.81	12.78	12.77
log k ₂	8.61	8.59	8.56	8.54	8.49
log β ₂	21.45	21.41	21.37	21.32	21.26
Correction term method					
log k ₁	12.89	12.86	12.86	12.84	12.82
log k ₂	8.59	8.56	8.53	8.48	8.44
log β ₂	21.48	21.42	21.39	21.32	21.26

An inspection of the above table shows that there is a gradual decrease in the magnitude of both log k₁ and log k₂ as we move from Cu²⁺ to Mn²⁺ complexes. Thus the stabilities of the manganese complexes are the weakest in the series whereas the copper complexes are the strongest.

In the pH region between 1.5 and 2.0 the maximum values of n were obtained, where hydrolysis of metal ion was negligible. This reveals that the metal-ligand ratio in these complexes is 1 : 2. A comparison of log β₂ reveals the following order of metal chelate stabilities.



This is in good agreement with Irving-Williams order⁷.

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