

PHYSICO-CHEMICAL STUDIES OF SCHIFF'S BASE METAL COMPLEXES

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ABSTRACT

Stability constants of iron, nickel, cobalt, zinc, copper and manganese complexes with Schiff's bases derived from salicylaldehyde and the amines *p*-aminophenol and *m*-aminophenol, have been determined in 50% ethanol water mixtures at constant ionic strength. The order of stability constant found is



Values of $-\Delta F$, δH and E_r (Mn – Zn) have been calculated.

SCHIFF'S bases formed by the condensation of an amine with an aldehyde or a ketone have been used for preparing metal complexes. A large variety of such metal complexes has been prepared and their structure determined. Recently some interest has been shown in the metal complex equilibria studies using Schiff's bases as ligands, but in general such studies have been limited to a few metal Schiff's bases and pH titrations are performed to evaluate stabilities of a variety of metal ions with Schiff's bases having oxygen as potential donor. Stability constants of their metal chelates have been determined in 50% alcoholic solutions of ionic strength 0.05 M (KNO_3) at 25°C using Bjerrum calvin pH titration technique¹⁻².

EXPERIMENTAL

Preparation of Schiff's Bases:

Schiff's bases of *m*-aminophenol and *p*-aminophenol with salicylaldehyde were prepared by refluxing equimolar quantities of the amine and the salicylaldehyde and were purified by recrystallization from ethanol³. Ligand solutions (0.01 M) were prepared in absolute alcohol. Solutions of metal ions (0.005 M), were prepared from B.D.H. analar grade reagents and were standardized by conventional methods⁴. Potassium nitrate and nitric acid were used to maintain ionic strength.

Titration Method:

The following solutions were prepared:

- | | | |
|-----|---|-----|
| (A) | 5 ml KNO_3 (0.5 M) + 10 ml HNO_3 (0.01 M) | I |
| (B) | A + 5 ml ligand solution (0.01 M) | II |
| (C) | B + 2 ml metal solution (0.005 M) | III |

The total volume in all the cases was 50 ml, each containing 50% ethanol. The solutions were kept in a thermostat and then titrated separately against standard NaOH solution.

Calculations:

(1) *Protonation constants:* From the titration curves of the solutions (I) and (II) $\bar{n}H$ at different

pH values were calculated using the method of Irving and Rossotti⁵. Protonation constants were evaluated using Bjerrum's half \bar{n} method and Speakman's method⁶. The values of the protonation constants obtained are given in Table I.

TABLE I

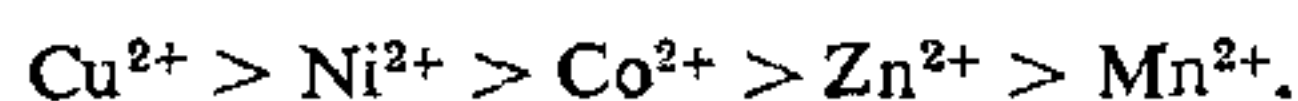
Schiff's base of Salicylaldehyde with	Yield %	Protonation constants of Ligand at 0.05 M ionic strength		
		Log K_1	Log K_2	Log K_3
1. <i>m</i> -aminophenol	72	9.90	8.05	4.65
2. <i>p</i> -aminophenol	78	10.10	8.16	5.00

Metal Ligand System:

The values of \bar{n} and pL were calculated from the titration curves of the solutions (II) and (III). From the formation curves the values of stepwise stability constants were evaluated using the method of interpolation of $\bar{n} = 0.5$. The δH values were calculated according to the method described by George and McClure⁷. The values of step stability constants of metal chelates and δH are given in Tables II and III.

RESULTS AND DISCUSSION

From the results, it is seen that the order of stability of first row of transition metal complexes (d^5 – d^{10}) with Schiff's bases is as follows:



Except for the Fe (II) complexes, this sequence is in agreement with the Mellor and Maley⁸⁻⁹ order. The abnormally high stabilities of Fe (II) complexes can be attributed to the resonance stabilization energy of Fe (II) complexes upon co-ordination with a ligand having aromatic ring systems¹⁰. The values of δH observed for Co (II), Ni (II) and Cu (II) complexes are also of the same order as for other ligands co-ordinating through

TABLE II

Ligand cations	Schiff's base of salicylaldehyde with <i>m</i> -aminophenol			— ΔF KCal/mole	Schiff's base of salicylaldehyde with <i>p</i> -aminophenol			— ΔF KCal/mole
	Log K_1	Log K_2	Log β_2		Log K_1	Log K_2	Log β_2	
Mn ²⁺	4.70	4.4	9.10	12.41	4.15	—	4.15	5.65
Fe ²⁺	7.15	5.7	12.85	17.53	7.40	—	7.40	10.09
Co ²⁺	6.15	4.8	10.95	14.94	4.35	—	4.35	5.93
Ni ²⁺	6.40	4.9	11.30	15.41	4.45	—	4.45	6.07
Cu ²⁺	10.30	6.8	17.10	23.32	9.20	—	9.20	12.55
Zn ²⁺	5.3	5.1	10.40	14.19	5.50	—	5.50	7.50

TABLE III

Calculations of E_r (Mn–Zn) and of δH values for complexes of Schiff's base from salicylaldehyde and *m*-aminophenol

Cations	Mn ²⁺	Fe ²⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Zn ²⁺
Log K_1	4.7	7.15	6.15	6.4	10.3	5.3
ΔG K Cal/mole	6.41	9.752	8.389	8.73	14.05	7.23
ΔH_c (i.e., ΔG relative to Mn ²⁺ value)		3	2	2	8	1
ΔH_H (relative to Mn ²⁺ value)		26	43	62	63	47
ΔH_L (relative to Mn ²⁺ value)		29	45	64	71	48
$[(n-5)/5] E_r$		10	20	30	40	—
δH		19	25	34	31	—

ΔG —Free energy change = $2.303 RT \log K$ (where RT and K have the usual significance; $T = 300^\circ K$).

ΔH_c —Change in heat content for the formation of the complex in solution.

ΔH_H —Heat of hydration of metal ion.

ΔH_L —Heat of complexation referred to metal ion in gaseous and ligand in solution state.

n —Number of electrons in 3rd orbital.

E_r —Lattice energy difference for Zn²⁺ and Mn²⁺ complexes.

δH —Thermodynamic stabilization energy.

one nitrogen atom. This confirms that the metal ions are bonded through one nitrogen and one oxygen atom to the ligand molecule.

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