

Stability and Antimicrobial Studies of Some Transition Metal Chelates of N,N'-bis(salicyldehyde)-1,8-Naphthalenediamine

SHEETAL NIKAM, HARDIK AMIN, PULKESHI DESAI and KIRAN MANGAONKAR*

Department of Chemistry, Ramnarain Ruia College, Matunga, Mumbai-400 015, India

E-mail: hardik_amin@rediffmail.com

Stability constant values of metal chelates of the ligand N,N'-bis(salicyldehyde)-1,8-naphthalenediamine with Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) have been determined pH-metrically at $25 \pm 0.5^\circ\text{C}$ and at a constant ionic strength (0.1 M) in 75 : 25 (v/v) dioxane-water medium. The formation constants have been calculated using the Bjerrum half \bar{n} integral method. Antimicrobial studies of the ligand as well as its metal chelates were determined against both the Gram-positive as well as Gram-negative microorganisms by disc diffusion method.

Key Words: Stability constant, Transition metal complexes, N,N'-bis(salicylaldehyde)-1,8-naphthalenediamine, Antimicrobial activity.

INTRODUCTION

Metal complexes of Schiff bases have occupied a central role in the development of coordination chemistry¹. Presence of the metal ions in these complexes plays an important role in their antimicrobial activity^{2, 3}. Many attempts have been made to evaluate different factors affecting the stability of metal chelates along with their stability constants⁴⁻⁸.

1,8-Naphthalenediamine is a class of organic compounds holding two primary amino groups at various positions of the naphthalene moiety. Therefore, synthesis of some compounds of diaminonaphthalene including imino function enables us to study the organic compounds and their ligational behaviour towards metal ions to form new coordination compounds. Our interest is to investigate the nature of these anils, their biological activity and whether chelation with metal ions improves their biological activity. A few complexes of dioxouranium(VI) and thorium(IV) with the Schiff bases derived from 1,8-diaminonaphthalene and aromatic aldehydes have been reported⁹ and these complexes exhibit an octahedral geometry.

With a view to investigate the feasibility of the formation of metal complexes of Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) of N,N'-bis(salicylidene)-1,8-naphthalenediamine in solution state, the formation constants have been determined. Also, antimicrobial studies of the ligand as well as its metal complexes were carried out.

EXPERIMENTAL

The pH titrations were carried out on an expanded scale pH-meter model No. EQ-614 supplied by Equiptronics, a precision research pH-meter with a wide range glass electrode and a reference calomel electrode. The pH-meter has an arrangement for normal and expanded scale. The smallest scale division on the expanded scale is 0.01 pH units. The pH-meter was standardized with potassium hydrogen phthalate and phosphate buffers before performing the titrations.

The solution of the ligand was prepared in dioxane. All the metal solutions were prepared and standardized by conventional procedures mentioned in Vogel¹⁰. A solution of potassium hydroxide was prepared (0.2 M) in double distilled carbonate-free water and standardized with standard solution of succinic acid. 1,8-Naphthalenediamine was of E. Merck grade and all other chemicals used were of analytical reagent grade. The titrations were carried out in an inert atmosphere of nitrogen, which was presaturated with double distilled carbonate-free water. All measurements were carried out at temperature $25 \pm 0.5^\circ\text{C}$. The method of Bjerrum and Calvin as modified by Irving and Rossotti¹¹, was used to determine \bar{n} and pL values.

Synthesis of Schiff base: One mole of respective aldehyde was taken in a round bottom flask, dissolved in minimum quantity of alcohol. Then one mole of respective 1,8-naphthalenediamine was dissolved in the same manner taking alcohol as a solvent. The alcoholic solution of amine was added slowly with constant stirring in the round bottom flask. The resulting mixture was refluxed on a water bath. TLC checks the completion of the reaction. After concentrating the reaction mixture by partial removal of the solvent, a solid Schiff base separated out which was filtered by suction. The Schiff base was crystallized from ethanol.

pH-titration: The following solutions were titrated pH-metrically against standard carbonate-free potassium hydroxide (0.2 M) solution keeping the total volume 40 mL [V_0]. All the titrations were carried out in 75% (v/v) dioxane-water and at 0.1 M KCl ionic strength to determine \bar{n} and pL values of the complexes.

- (i) 4 mL HCl (0.16 M) + 3.68 mL KCl (1 M) + 2.32 mL distilled water + 30 mL dioxane.
- (ii) 4 mL HCl (0.16 M) + 3.68 mL KCl (1 M) + 2.32 mL distilled water + 4 mL ligand (0.05 M) + 26 mL dioxane.
- (iii) Requisite amount of metal chloride solution + 4 mL HCl (0.16 M) + 3.68 mL KCl (1 M) + requisite amount of distilled water + 4 mL ligand (0.05 M) + 26 mL dioxane

The pH-meter readings were plotted against the volume of KOH used for each titration.

Synthesis of metal chelates: The solution of hydrated metal chloride in minimum quantity of water and the alcoholic solution of Schiff base were mixed in 1 : 1 molar proportion and stirred well. Metal chelates completely precipitate on dropwise addition of 0.1 N NaOH till pH became 8.0–8.5. After complete precipitation of metal chelates they were filtered under vacuum, dried and crystallized using chloroform.

Antimicrobial Studies: The biological activity of the ligand N,N' -bis(salicyldehyde)-1,8-naphthalenediamine and their Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) chelates in terms of their growth inhibiting property on specific known bacterial culture were evaluated by standard disk diffusion method¹²⁻¹⁴. The bacterial sub-cultures for *E. coli*, *S. aureus*, *B. subtilis*, *C. diphtheriae* and *S. typhi* were used as test organisms and the solutions of all samples (100 mg/mL in DMSO) were prepared in DMSO where DMSO acted as control. All apparatus used were sterilized by heating at 120°C in an oven fully wrapped in inert foil for 6–8 h. Nutrient agar slant used as bacterial culture medium had the composition: peptone (1 g), NaCl (0.5 g), yeast extract (0.3 g), distilled water (100 mL) (pH = 7.4 ± 0.2), agar (2%). The solution of each medium was sterilized by autoclaving at 120°C for 30 min. The petriplates with bacterial culture were kept in an incubator maintained at 37°C for 24 h.

RESULTS AND DISCUSSION

Protonation Constants

The ligand remains in the protonated (or undissociated) form at least up to pH 5.40. The dissociation begins at around pH 5.45 and is completed around pH 7.25. The $\bar{n}A$ values range from 0 to 1 indicating the monobasic nature of the ligand. The pKa value obtained for the ligand by plotting $\bar{n}A$ vs. pH reveals that the ligand is weakly acidic.

Stability Constants of the Metal Complexes

Complexation in all cases of transition metals was uniformly well below the dissociation of the ligand. This means that formation of hydroxides or hydrolysis of metal ions is not interfering in the process of complexation. The observed \bar{n} values which are ranging from 0 to 2 for a bivalent metal ions and greater than 2 for Fe^{3+} reveal the formation of ML_2 and ML_3 complexes respectively for these metal ions (Table-1).

TABLE-1
STABILITY CONSTANTS OF SOME METAL COMPLEXES OF LIGAND
 N,N' -BIS(SALICYLIDEHYDE)-1,8-NAPHTHALENEDIAMINE IN 75% (v/v)
DIOXANE-WATER SOLUTION AT AN IONIC STRENGTH
 $\mu = 0.1$ M KCl AND AT TEMPERATURE = 25 ± 0.5°C

Metal ions	log K_1	log K_2	log K_3	log β_n
H ⁺	9.903	—	—	—
Mn(II)	9.725	8.57	—	18.295
Fe(III)	10.301	0.14	9.475	29.915
Co(II)	9.885	8.69	—	18.575
Ni(II)	10.025	8.58	—	18.605
Cu(II)	9.255	8.27	—	17.495

Antimicrobial Study

The Schiff base and its metal complexes were tested for anti-microbial activity against Gram-negative organism, *viz.*, *E. coli* ATCC 10536 and three Gram-positive organisms, *viz.*, *Corynebacterium diphtheriae*, *Staphylococcus aureus* ATCC 6538 and *Bacillus subtilis*. The Schiff base itself demonstrates strong activity against all these microorganisms. Its Mn(II) complex shows strong activity against all the microorganisms except *E. coli*. The Ni(II) and Co(II) complexes show activity against *Corynebacterium diphtheriae*. The Fe(III) and Cu(II) complexes do not show activity against any of these microorganisms (Table-2).

TABLE-2
ANTIMICROBIAL STUDY OF SOME METAL COMPLEXES

Compound	Test Organism			
	<i>E. coli</i>	<i>S. aureus</i>	<i>C. diphtheriae</i>	<i>B. subtilis</i>
Ligand	++	++	++	++
Mn(II) complex	-	++	++	+
Fe(III) complex	-	-	-	-
Co(II) complex	-	-	+	-
Ni(II) complex	-	-	+	-
Cu(II) complex	-	-	-	-

Note: "+" indicates moderate inhibition of growth; "++" indicates strong inhibition of growth; while "-" indicates no inhibition of growth.

REFERENCES

1. H. Schiff, *Ann. Suppl.*, **3**, 343 (1864).
2. M.N. Rottistrov, G.V. Kulik, E.M. Skrynik, T.V. Garbonos, A.N. Bredikahina and L.A. Taranova, *Fiziol. Aktiv. Veshchestva*, **5**, 123 (1973).
3. N.S. Kozlov, V.D. Pak, V.V. Mashevskii, P.N. Plaksina, *Khim-farm. Zh.*, **7**, 15 (1973).
4. A.E Martell (Ed.), *Stability Constants of Metal-Ion Complexes*, Special Publication No. 17 (1964).
5. M.S. Mayadeo and M.B. Kabadi, *J. Indian Chem. Soc.*, **52**, 993 (1975).
6. M.S. Mayadeo and S.H. Hussain, *J. Indian Chem. Soc.*, **56**, 143 (1979).
7. M.S. Mayadeo and R.L. Ganti, *Curr. Sci.*, **48**, 773 (1979).
8. M.S. Mayadeo and V.P. Dhakappa, *J. Indian Chem. Soc.*, **57**, 849 (1980).
9. T.R. Goudar, G.S. Nadagouda and K.B. Gudasi, *Indian J. Chem.*, **32A**, 1075 (1993).
10. A.I. Vogel, *A Text Book of Quantitative and Qualitative Analysis*, 4th Edn. (1980).
11. H.M. Irving and H.S. Rossotti, *J. Chem. Soc.*, 2904 (1954).
12. G.C. Ainsworth, F.K. Sparrow and A. Sussman, *The Fungi: An Advance Treatise*, Vol. IV AG, Academic Press, London (1973).
13. K. Pytakin, *Microbiology* MIR Publishers, Moscow (1967).
14. P. Bindu, M.R.P. Kurup and Satyakeerty, *Polyhedron*, **18**, 321 (1998).