

Equilibrium Study of Complex formation of Bivalent Metal ions with Schiff's Bases

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Received: 10th Feb 2020, Revised and Accepted: 15th Feb 2020

ABSTRACT

The present article deals with synthesis of heteroaryl thiazole Schiff bases derived from 4-phenyl 2 amino thiazole and 2- hydroxy 1- naphthaldehyde. Stability constant of complexes have been studied in ethanol –water medium and their pH metric data was employed for proton ligand and metal ligand stability constants.

Keywords: Thiazole, Schiff's Base complexes, Stability constant, biological activity.

1. INTRODUCTION

Schiff bases are the compound containing azomethine (-HC=N-). A Schiff base behaves as flexidentate ligand and commonly coordinated through O atom of the deprotonated phenolic group and the N atom of azomethine group. There are wide applications of Schiff bases and their chelates in biological systems¹⁻² catalysis³⁻⁴ dying process⁵⁻⁶ and analytical applications. Today Schiff bases are used as intermediates for the synthesis of amino acids or as a ligands for preparation of metal complexes having a series of different structures.

Thiazole derivatives are known to exhibit various pharmacological properties⁷, Many commercial available drugs are derived from thiazole entities.

Since the past few decades, the literature has been enriched with progressive finding about the cytotoxic activities of various substituted thiazole derivatives. Keeping the view of these observations, we here in report the synthesis and physicochemical study of Schiff base.

Complexation studies are very important from the point of view of analytical and biochemical researchers. Therefore, this study has received much attention of many researchers in recent years. The extent to which ligand bind to metal ion is expressed in terms of stability constants⁸⁻⁹ they are determined by various methods thus it is useful to carry out research in equilibrium studies, which involves chelation.

The present communication covers experimental details, characterization and study on solution equilibria between ethanol-water media. In

present study pH metric method is used for measurements. These measurements are used for determination of formation curves from which stability constants were determined. These formation curves obtained by Calvin Bjerrum titration technique adopted by Irving and Rosotti.¹⁰

2. EXPERIMENTS

4 Aryl 2 amino thiazole were prepared by using reported method¹¹

Para substituted acetophenone (1a-1d) were synthesized by standard procedure¹². The Schiff bases were synthesized by literature method¹³ Schiff bases were characterized by TLC and IR frequencies.

2.1 Synthesis of para substituted acetophenone

2.2 General procedure for synthesis of thiazole derivatives

A mixture of equimolar concentration of para substituted acetophenone, iodine and thiourea were reflux on water bath for about six hours and were heated again for eight hours after removal of condenser. The crude product was kept in contact with ether with occasional shaking for 48 hours, finally excess iodine was removed by sodium thiosulphate solution.

The resulting product which was nearly colourless and was boiled with water and filtered hot. The filtrate was further treated with concentrated ammonia solution to liberate base. The product was further recrystallised by 50% ethanol, the reaction progress and purity of compound was monitored by TLC.

2.3 General procedure for synthesis of Schiff base (scheme 1)

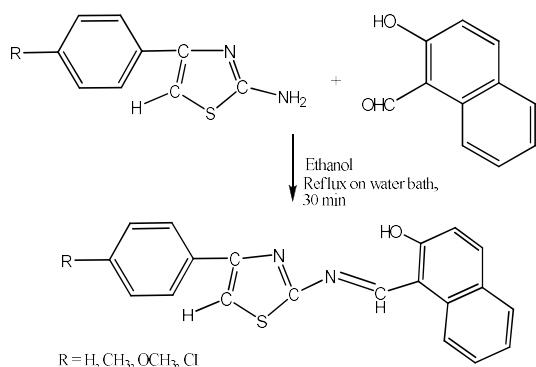
A equimolar solution of 2- hydroxyl 1- naphthaldehyde and 4-aryl -2- amino thiazole in 50 ml of dry ethanol. The mixture was refluxed on water bath for 30 minutes. Then mixture was allowed to cool to obtained crystallized product. The product was filtered, recrystallise from ethanol and dried in vacuo.

Ethanol was dried over freshly calcinated quicklime and distilled twice. Standard carbonate free sodium hydroxide solution was used. The 70% perchloric acid of 2M was used, which was further diluted to 0.2M. 2 hydroxy 1 naphthaldehyde (Fluka) was used directly. Potentiometric titrations were carried out by using Elico digital pH meter model LT - 120, with combined glass electrode type CL 51.

Following Schiff bases were synthesized

1. N-(2- Hydroxy 1- Napthalidene) 4 -(Phenyl) - 2-Amino Thiazole (HNPAT)
2. N-(2- Hydroxy 1- Napthalidene) 4 -(P- Methyl Phenyl) - 2-Amino thiazole (HNMPAT)
3. N-(2- Hydroxy 1- Napthalidene) 4 -(P- Methoxy Phenyl) - 2- AminoThiazole (HNMPAT)

4.N-(2- Hydroxy 1- Napthalidene) 4 -(P- Chloro Phenyl) - 2- AminoThiazole (HNCPAT)



Scheme - 1: Synthesis of Schiff base 2.4 Synthesis of metal complexes:

A mixture of 10 ml ethanol solution of appropriate metal salt solution and 20 ml ethanoic 0.01 M solution of respective Schiff base was refluxed for 2 hours. Then the resulting solution was cool, filtered and reduced to nearby half of its volume. The solution was kept overnight at room temperature, the product was washed with ethanol and then with ether. The crude product was dried and recrystallise with ethanol to gave desired metal complex with metal salts.

2.5 Determination of stability constants:

Proton Ligand stability constants:

The method proposed by Calvin and Bjerrum was adopted for study of formation constants using pH meter which was universal method . the average number of ligands attached per metal ion (n^-) and free ligand exponent (pL)were calculated by titration curves using Irving and Rossotii ¹⁰ , the experimental procedure involves a series of titrations with standard alkali . (i) Perchloric acid ,(ii) perchloric acid + ligand

(iii) perchloric acid + ligand + Metal ion . In all titrations inert electrolye NaClO₄ was used. The constancy of total volume was maintained throughout the present work with 0.1 M ionic strength at 25⁺1 °C

2.6 Free acid titration:

A mixture containing 4 ml of 0.2M HClO₄ , + 0.78 ml 4M NaClO₄ +20 ml ethanol +15.22 ml distilled water was taken in clean and dry beaker and the resulting solution was titrated with standard alkali.

2.7 Schiff base titration:

A mixture containing 4 ml of 0.2M HClO₄ , + 0.78 ml 4M NaClO₄ + 10 ml 0.01M Schiff Base + 10 ml ethanol +15.22 ml distilled water was taken in clean and dry beaker then the resulting solution was titrated with standard alkali.

2.8 Metal titration:

A mixture containing 2 ml of 0.2M HClO₄ , + 2 ml of 0.02M metal perchlorate solution containing 0.02M HClO₄ + 0.78 ml 4M NaClO₄ + 10 ml 0.01M Schiff Base + 10 ml ethanol +15.22 ml distilled water was taken in clean and dry beaker hen the resulting solution was titrated with standard alkali.

Before any titration was performed, the solution concerned was kept in thermostat for half an hour to attained its temperature. Nitrogen gas was then bubbled through it and titration was carried out with standard alkali with constant stirring using calibrated micro burette connected with soda lime guard tube.

Table - 1: Important IR frequencies of Schiff bases (Cm⁻¹)

Schiff Base	v (C-H)	v (C=N)	v (C-O)	v (C-S-C)	v (C=N) Thiazole ring
HNPAT	3305	1628	1250	737	1547
HNMPAT	3307	1631	1251	738	1548

HNMOPT	330	163	125	73	1548
	8	1	1	8	
HNCPT	330	163	125	73	1548
	8	1	1	8	

Table - 2 : Proton Ligand Stability Constants

Ligand	Proton Ligand Stability Constant $\log k_1$	
	Half integral I	Graphical II
HNPAT	11.65	11.64
HNMPAT	11.83	11.89
HNMOPT	11.90	11.94
HNCPT	11.45	11.45

Table - 3: Metal- Ligand Stability Constants

Ligand	Metal ion	Metal- Ligand Constant		Stability	
		Half integral I	Graphical II	Log k1	Log k2
		Log K1	Log K2	Log k1	Log k2
HNPAT	Cu (II)	11.3 4	10.4 8	11.3 4	10.5 0
	Ni (II)	11.1 2	9.98 0	11.1 0	9.96
	Co(II)	10.4 2	9.32 0	10.4 0	9.34
	Zn(II)	10.1 1	8.76 8	10.0 8	8.76
	Mn(II)	9.88	8.20	9.88	8.20
HNMPAT	Cd(II)	9.50	7.32	9.46	7.30
	Cu (II)	10.6 3	9.90 8	10.6 8	9.86
	Ni (II)	10.2 2	8.88 6	10.2 6	8.93
	Co(II)	9.51	7.90	9.46	7.92
	Zn(II)	9.16	7.18	9.12	7.24
HNMOPT	Mn(II)	8.62	6.40	8.64	6.40
	Cd(II)	8.24	5.84	8.24	5.88
	Cu (II)	11.3 4	10.2 1	11.2 4	10.2 2
HNMOPT	Ni (II)	10.2 6	8.92 0	10.4 0	8.96

HNCPT	Co(II)	9.95	8.32	10.0 2	8.28
	Zn(II)	9.64	7.81	9.64	7.78
	Mn(II)	9.35	7.19	9.40	7.22
	Cd(II)	9.04	6.68	9.06	6.74
	Cu (II)	10.9 4	10.3 6	10.8 8	10.4 4
	Ni (II)	10.5 6	9.32	10.5 2	9.36
	Co(II)	10.0 8	8.89	10.1 2	8.92
	Zn(II)	9.06	8.06	9.13	8.10
	Mn(II)	8.80	7.20	8.84	7.22
	Cd(II)	8.40	6.32	8.44	6.42

3. RESULT AND DISCUSSION

3. 1. Proton Ligand stability constant:

Proton ligand stability constant (P^k) values of ligands were calculated by using half integral and graphical method¹⁴⁻¹⁶. Values of ligands contain only one P^{ka} values due to dissociable proton of phenolic OH group. Protonation of imino nitrogen does not take in the p^H range under study. The ligand titration curve, shifted above the acid titration curve due to basic property of ligand that azomethine nitrogen accept proton from strongly acidic medium. In the basic region the curve lies below the acid curve due to release of -OH protons. The P^{ka} values are summarized in table No 2.

The P^{ka} values follows the trend

HNMOPT > HNMPAT > HNPAT > HNCPT

This is explained on the ground of basic nature of azomethine nitrogen and phenolic oxygen¹⁷⁻¹⁸. The p^k value of HNMPAT is found to be higher than that of HNPAT, the methyl group at para position of aromatic ring increases the electron density on the azomethine nitrogen through hyper conjugation as well as + I effect resulting in stronger chelation. Similarly p^k value of HNMOPT is found to be higher than of HNMPAT, because the methoxy group at para position increases the electron density on azomethine nitrogen due to mesomeric effect of oxygen atom which result stronger chelation. In the case of compound HNCPT the p^k value is found to be lower than HNPAT, this is due to -I effect of chloro substituent at para position.

3.2 Metal ligand stability constants:

The occurrence of metal titration curves below the ligand titration curves at p^H values

much below the pH of metal ion hydrolysis which confirmed the complex formation between the ligand and metal ion. The proton of the phenolic OH group was replaced by metal ion and chelation took place through phenolic oxygen and azomethine nitrogen.

In all system, the highest values of n are more than 1, indicates that 1:1 and 1:2 complexes are formed.

3.3 FT IR of Schiff base complex:

IR spectra of Schiff base showed absence of bands at 1735 cm^{-1} and 3420 cm^{-1} due to carbonyl ν (C=O) and ν (NH₂) stretching vibration, instead the appearance of a strong new band at 1630 cm^{-1} assigned¹⁹⁻²⁰ to the azomethine linkage, this suggests that amino and aldehyde moieties of the starting reagents no more exist and have been converted in to Schiff base linkage.

IR spectra of Schiff bases shows most characteristics bands at 3308 cm^{-1} ν (O-H), 1631 cm^{-1} ν (C=N), azomethine 1548 cm^{-1} , ν (C=N) thiazole, 1251 cm^{-1} ν (C-O) and 738 cm^{-1} ν (C-S-C). All the metal complex shows broad band at $3370\text{--}3410\text{ cm}^{-1}$ which may be due to ν (OH) stretching. The band 1631 cm^{-1} due to azomethine group of Schiff base has shifted to lower frequencies $1599\text{--}1607\text{ cm}^{-1}$ after complex formation, this indicates involvement of azomethine nitrogen to the metal ion, the phenolic (-C-O) stretching vibration that appears at 1251 cm^{-1} in Schiff base shifted toward higher frequencies 39 cm^{-1} in the complexes. This confirms participation of oxygen in the (-C-O-M) bond. In the IR spectrum of complexes the stretching vibration of free ligand ν (O-H) 3308 cm^{-1} is not observed this suggests deprotonation of hydroxyl group and formation of (M-O) bond in the lower frequency region, the band of weak intensities observed for complex in the region $537\text{--}546\text{ cm}^{-1}$ is attributed to (M-O) and in the region $489\text{--}501\text{ cm}^{-1}$ to (M-N), the ν (C=N) at 1548 cm^{-1} and ν (C-S-C) at 738 cm^{-1} of thiazole ring remains unchanged suggest that thiazole group does not participate in coordination to metal ion.

3.4 Biological activities:

The current avenues of development for heterocyclic compounds are many and varied. Among these compounds thiazole compounds have been especially noteworthy in recent years. The thiazole moiety has been incorporated into many different type of chemical structures generating by structure modifications a series of compounds with broad spectrum bioactivity. Thus thiazole compounds have played an increasingly important role in production of highly active pesticides and insecticides.

The insecticides and pesticides activities of Schiff base against some edible plants chilli. (*Capsicum annum* L) Okra (*Abelmoschus esculentus* L Moench) Lay's Finger, Bendi and Tomato. Cu (II) complex shows much more activity²¹⁻²², in present communication Cu (II) and Zn (II) complex shows pesticidal and insecticidal activity. The cytotoxicity, antifungal and antibacterial activity are under study.

4. CONCLUSION

The stability constants were determined by half integral method as well as graphical method, the $\text{p}K$ values for all the systems studied indicates following pattern

HNMOPAT > HNMPAT > HNPAT > HNCPAT

The substituents in the ligand aromatic ring alters electron density at various sites and in turn affect proton ligand and metal ligand stability constants as well as chelation. The $\text{p}K$ values of Schiff base were found higher compare to those aldehyde, which can be attributed to the possibility of formation of H bonding.

Acknowledgement

Author thanks to UGC and Principal of Shri Shivaji College kandhar for providing facilities.

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