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Anti-Bacterial and Anti-Fungal Study of Schiff Bases and their Metal Co (II)& Zn (II) Complexes

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ABSTRACT

Synthesis of Schiff bases from different types of aromatic aldehyde and 3-amino-2- napthol-4-sulphonic acid and then prepared the Co (II), Zn (II) complexes. Metal complexes of Schiff bases have occupied a central role in the development of coordination Chemistry. A number of verities of stable chemical species have been synthesized, containing transition metal and multifarious ligand. Metal complexes of Schiff base shows the strong anti fungicidal, anti bacterial activity, anti viral infection, anticancer, herbicides, plant growth regulators and anti covulsants. Metal complexes also find a wide applications in the field of industrial chemistry, analytical chemistry, pharmaceutical chemistry, agricultural chemistry and bioorganic chemistry. Recently hetrocyclic such as 2 'al' pyrrol, 2 'al' furan, 2 'al' thiophen and aromatic aldehyde, there metal Zn (II), Co (II) complexes have also gained a focal position in bioinorganic field and frequently used as antifungal, plant growth regulators and anticancer.

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 KEY WORDS : Anti-bacterial, Antifungal, Metal complexes, Schiff bases
 Table : 01

Introduction

Coordination Chemistry of transition metals has made tremendous growth in the last half century. This wide field of chemistry has been applied in many useful ways in recent years. The most remarkable applications of coordination compounds are in agriculture chemistry, industrial chemistry, analytical chemistry, clinical and pharmaceutical chemistry^{2,5}. Coordination compounds of Schiff bases have played an important role in the development of coordination chemistry. Considerable interest has been shown in the synthesis of transition metal Schiff base complexes due to their pharmacological and therapeutic applications. Schiff base ligand have nitrogen, oxygen and sulphur as a donor set⁸. These ligands have a great interest due to their activeness against various fungus, bacteria, virus, tumour, cancer, pest and tuberculosis⁴. The role of metal chelats in medicinal chemistry is now well recognized. Biological studies have shown that organic compounds have Coordinating groups like-NH₂, -SH, -COOH, -N- and -OH and do minimum damage in exposed organisms. Ethlene of amino tetra acetic acid may be considered as example of such types of organic compounds¹¹.

Synthesized the various Schiff bases (ligand) by hetrocyclic aldehyde and aromatic aldehyde:

- (i) Ortho hydroxyl benzaldemine–2–N–3–hydroxy–1– sulphonic acid naphthalene.
- (ii) Furan–2–aldimine–2–N–3 hydroxy–1 sulphonic acid naphthalene.
- (iii) Thiophene–2–aldimine–2–N–3 hydroxy–1 sulphonic acid naphthalene.
- (iv) Pyrrole–2–aldimine–2–N–3 hydroxy–1 sulphonic acid naphthalene.
- (v) Benzaldimine-2-aldimine-2-N-3 hydroxy-1 sulphonic acid naphthalene.
- (vi) Ortho nitro benzaldimine–2–N–3–hydroxy–1– sulphonic acid naphthalene.

Experimental Synthesis

Structure of the new Schiff bases was confirmed by elemental analysis and spectral data.

1. Ortho hydroxyl benzaldemine-2-N-3-hydroxy-1-sulphonic acid naphthalene

Salicyladehyde (0.01 mol) and 2-amino-3-napthol-1-sulphonic acid (0.01 mol) were mixed in 50 c.c. of ethyl alcohol. The mixture was refluxed for 4–5 hours on a water bath. The resulting content was filtered to get light brown coloured crystals which were washed with ether and then recrystallized from ethanol. The crystal were then dried under reduced pressure over fused calcium chloride.

Molecular Formula	-	C ₁₇ H ₁₃ NO ₅ S
Melting Point	-	126 ⁰ C

2. Furan-2-aldimine-2-N-3 hydroxy-1 sulphonic acid naphthalene

Furon 2 carboldehyde (0.01 mol) and 3 amino 2 napthol–4–sulphonic acid (0.01 mol) were mixed in 50 c.c. of ethanol. The mixture was refluxed for 5–6 hours on water bath. The resulting content was filtered to get reddish colour crystals. The crystals were washed with ether and recrystallized from ethanol and dried under reduced pressure over fused calcium chloride.

Molecular Formula- $C_{15}H_{11}NO_5S$ Melting Point- $113^{0}C$

3. Thiophene-2-aldimine-2-N-3 hydroxy-1 sulphonic acid naphthalene

Thiophene 2 carboldehyde (0.01 mol) and 3 amino 2 napthol–4–sulphonic acid (0.01 mol) were mixed in 50 c.c. of ethanol. The mixture was refluxed for 4–5 hours on water bath. The resulting content was filtered to get reddish colour crystals. The crystals were washed with ether and recrystallized from ethanol and dried under reduced pressure over fused calcium chloride.

Molecular Formula	-	$C_{15}H_{11}NO_4S_2$
Melting Point	-	103 ⁰ C

4. Pyrrole-2-aldimine-2-N-3 hydroxy-1 sulphonic acid naphthalene

Pyrole 2 carboldehyde (0.01 mol) and 3 amino 2 napthol–4–sulphonic acid (0.01 mol) were mixed in 50 c.c. of ethanol. The mixture was refluxed for 5–6 hours on water bath. The resulting content was filtered to get reddish colour crystals. The crystals were washed with ether and recrystallized from ethanol and dried under reduced pressure over fused calcium chloride.

Molecular Formula- $C_{15}H_{12}N_2O_4S$ Melting Point- 114^0C

5. Benzaldimine-2-aldimine-2-N-3 hydroxy-1 sulphonic acid naphthalene

Benzaldehyde (0.01 mol) and 2–amino–3–napthol–1– sulphonic acid (0.01 mol) were mixed in 50 c.c. of ethyl alcohol. The mixture was refluxed for 4–5 hours on a water bath. The resulting content was filtered to get light yellow coloured crystals which were washed with ether and then recrystallized from ethanol. The crystal were then dried under reduced pressure over fused calcium chloride.

Molecular Formula	-	C ₁₇ H ₁₃ NO ₄ S
Melting Point	-	120 ⁰ C

6. Ortho nitro benzaldimine-2-N-3-hydroxy-1sulphonic acid naphthalene

Ortho nitro benzaldehyde (0.01 mol) and 2–amino–3– napthol–1–sulphonic acid (0.01 mol) were mixed in 50 c.c. of ethyl alcohol. The mixture was refluxed for 6–7 hours on a water bath. The resulting content was filtered to get shiny yellow coloured crystals which were washed with ether and then recrystallized from ethanol. The crystal were then dried under reduced pressure over fused calcium chloride.

Synthesis of Co (II) Complexes

1. Ortho hydroxyl benzaldemine-2-N-3-hydroxy-1-sulphonic acid naphthalene Co (II) complex :

Salicyladehyde (0.01 mol) dissolved in 20 ml of ethanol, 3–amino–2–napthol–4–sulphonic acid (0.01 mol) in 20 ml of ethanol and cobalt nitrate (0.01 mol) in 10 ml of water and ethanol were taken together in a flask. The contents were then refluxed for 7–8 hours on a water bath and the solution was reduced to 1/3 volume. Crystalline solid so obtained was filtered, washed with ether and then recrystallized from ethanol and dried in desiccators over fused calcium chloride.

Molecular Formula $-Co(C_{17}H_{11}NO_5S).3H_2O$ Melting Point -211^0C

2. Furan-2-aldimine-2-N-3 hydroxy-1 sulphonic acid naphthalene Co (II) complex :

Furan–2–carbaldehyde (0.01 mol) dissolved in 20 ml of ethanol, 3–amino–2–napthol–4–sulphonic acid (0.01 mol) in 20 ml of ethanol and cobalt nitrate (0.01 mol) in 10 ml of water and ethanol were taken together in a flask. The contents were then refluxed for 7–8 hours on a water bath and the solution was reduced to 1/3 volume. Crystalline solid so obtained was filtered, washed with ether and then recrystallized from ethanol and dried in desiccators over fused calcium chloride.

3. Thiophene-2-aldimine-2-N-3 hydroxy-1 sulphonic acid naphthalene Co (II) complex:

This complex was prepared above similar procedure.

S.	Name of Ligand /Complex	Conc. in	Antifungal		Antibacterial		
NO.		ppm	A. flaves	A. niger	E. coli	S. aureus	B. subtillis
1	Ortho hydroxyl benzaldemine	250	_	_	_	_	_
	-2-N-3-hydroxy-1-sulphonic	500	_	-	_	_	_
	acid naphthalene	750	++	-	_	_	++
		1000	+++	++	-	++	++
2	Ortho hydroxyl benzaldemine-2-N-3-	250	-	_	-	-	_
	hydroxy–1–sulphonic acid naphthalene	500	-	-	_	_	_
	Co (II) complex :	750	++	++	_	-	++
		1000	+++	+++	-	-	++
3	Ortho hydroxyl benzaldemine-2-N-3-	250	-	_	_	_	_
	hydroxy–1–sulphonic acid naphthalene	500	++	++	_	_	++
	Zn (II) complex :	750	+++	++++	-	++	+++
		1000	++++	++++	-	+++	+++
4	Furan–2–aldimine–2–N–3 hydroxy–1 .	250	_	_	_	_	-
	sulphonic acid naphthalene	500	_	_	_	_	_
		750	_	-	_	_	_
		1000	++	+	_	++	+
5	Furan–2–aldimine–2–N–3 hydroxy–1	250	_	_	_	_	_
	sulphonic acid naphthalene Co (II)	500	-	-	_	-	_
	complex :	750	-	-	_	_	_
		1000	+++	++	-	++	+
6	Furan-2-aldimine-2-N-3 hydroxy-1	250	-	-	_	-	-
	sulphonic acid naphthalene Zn (II)	500	-	-	_	-	_
	complex :	750	+++	++	_	+++	++
		1000	+++	++++	-	++++	+++
7	Thiophene-2-aldimine-2-N-3	250	_	-	_	-	_
	hydroxy–1 sulphonic acid	500	+	-	_	_	++
	naphthalene.	750	++	++	_	+++	++
	naphthalene.	1000	+++	+++	_	++++	++++
8	Thiophene–2–aldimine–2–N–3 :	250	+	_	_	_	
	hydroxy–1 sulphonic acid	500	++	-	_	++	++
	naphthalene Co (II) complex	750	++	++	_	++	++
		1000	+++	++++	_	+++	+++

9	Thiophene-2-aldimine-2-N-3	250	_	_	_	_	_
	hydroxy–1 sulphonic acid	500	_	-	_	_	_
	naphthalene Zn (II) complex:	750	++	-	_	_	++
		1000	+++	++	-	++	++
10	Pyrrole–2–aldimine–2–N–3	250	_	-	_	_	_
	hydroxy–1 sulphonic acid	500	_	-	_	_	_
	naphthalene.	750	-	_	-	_	_
		1000	++	+++	_	_	_
11	Pyrrole-2-aldimine-2-N-3	250	-	-	_	-	-
	hydroxy–1 sulphonic acid	500	_	_	_	_	_
	naphthalene Co (II) complex :	750	-	_	_	_	_
		1000	+++	++	_	++	++
12	Pyrrole-2-aldimine-2-N-3	250	_	-	_	_	_
	hydroxy–1 sulphonic acid	500	++	_	-	_	
	naphthalene Zn (II) complex :	750	++++	++	_	+++	++
		1000	+++++	++++	_	+++	+++
13	Benzaldimine-2-aldimine-2-N-3	250	-	-	-	-	_
	hydroxy–1 sulphonic acid naphthalene.	500	_	_	_	_	_
		750	_	-	_	_	-
		1000	-	+	-	++	+
14	Benzaldimine2–N–3 hydroxy–1	250	_	_	_	_	-
	sulphonic acid naphthalene	500	-	-	_	_	_
	Co (II) complex :	750	_	-	_	_	-
		1000	+	+	-	+	+
15	Benzaldimine2–N–3 hydroxy–1	250	-	-	_	-	_
	sulphonic acid naphthalene Zn	500	-	-	-	-	-
	(II) complex :	750	++	-	-	-	-
		1000	+++	++	-	+	+++
16	Ortho nitro benzaldimine–2–N–3–	250	_	-	_	_	_
	hydroxy–1–sulphonic acid	500	-	-	-	-	-
	naphthalene:	750	_	_	_	_	_
		1000	_	++	_	+	+
17	Ortho nitro benzaldimine–2–N–3–	250	_	-	_	-	-
	hydroxy–1–sulphonic acid	500	_	_	_	_	_
	naphthalene Co (II) complex :	750	_	_	_	_	_
		1000	++	+	_	+	+++
18	Ortho nitro benzaldimine-2-N-3-	250	_	_		_	_
	hydroxy–1–sulphonic acid	500	_	-	_	-	_
	naphthalene Zn (II) complex :	750	++	_	_	_	_
		1000	+++	+++	_	++++	++++

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4. Pyrrole–2–aldimine–2–N–3 hydroxy–1 sulphonic acid naphthalene Co (II) complex :

This complex was prepared by similar procedure. **Molecular Formula** – Co(C30H22N4O8S2).2H2O

Melting Point –209°C

5. Benzaldimine2–N–3 hydroxy–1 sulphonic acid naphthalene Co (II) complex :

This complex was prepared by above similar procedure.

Molecular Formula $-Co(C_{34}H_{24}N_2O_8S_2).2H_2O$ Melting Point -255^0C

6. Ortho nitro benzaldimine-2-N-3-hydroxy-1sulphonic acid naphthalene Co (II) complex :

This complex was prepared by above similar procedure.

Synthesis of Zn (II) Complexes

 Ortho hydroxyl benzaldemine-2-N-3-hydroxy-1-sulphonic acid naphthalene Zn (II) complex : Salicyladehyde (0.01 mol) dissolved in 20 ml of ethanol, 3-amino-2-napthol-4-sulphonic acid (0.01 mol) in 20 ml of ethanol and zinc acetate (0.01 mol) in 10 ml of water and ethanol were taken together in a flask. The contents were then refluxed for 6-7 hours on a water bath and the solution was reduced to 1/3 volume. Crystalline solid so obtained was filtered, washed with ether and then recrystallized with ethanol and dried in desiccator over fused calcium chloride.

Molecular Formula	-	Zn(C ₁₇ H ₁₁ NO ₅ S).H ₂ O
Melting Point	-	189 ⁰ C

Zn (II) complexes prepared by approx similar procedure.

2. Furan-2-aldimine-2-N-3 hydroxy-1 sulphonic acid naphthalene Zn (II) complex :

Molecular Formula	-	$Zn(C_{30}H_{20}N_2O_{10}S_2)$
Melting Point	-	163 ⁰ C

3. Thiophene-2-aldimine-2-N-3 hydroxy-1 sulphonic acid naphthalene Ni (II) complex:

Molecular Formula – $Zn(C_{30}H_{20}N_4O_8S_4)$ Melting Point – $162^{\circ}C$

4. Pyrrole–2–aldimine–2–N–3 hydroxy–1 sulphonic acid naphthalene Ni (II) complex :

Molecular FormulaZn(C30H22N4O8S2)Melting Point1710C

5. Benzaldimine2–N–3 hydroxy–1 sulphonic acid naphthalene Ni (II) complex :

Molecular Formula	-	$Zn(C_{34}H_{24}N_2O_8S_2)$
Melting Point	-	172 ⁰ C

6. Ortho nitro benzaldimine-2-N-3-hydroxy-1sulphonic acid naphthalene Ni (II) complex :

Molecular Formula	-	Zn(C ₃₄ H ₂₂ N ₄ O ₁₂ S ₂)
Melting Point	-	169 ⁰ C

Experimental techniques : Techniques *viz.* IR, NMR ESR, Mass, X-ray, Mossbauer, Circular dichroism (CD) spectroscopy and thermogravimetric analysis (TGA) have now become an indispensable tool for deciding the structural aspects of the coordination compounds by spectral and structural coorelationship and are responsible for the advertisement of coordination chemistry. Schiff was the first to report, the condensation reaction between R-NH₂ and the carbonyl compound, but it was only after the remarkable properties of metal-Schiff base complexes. The infrared frequency range of azomethine is mainly 1680–1580cm⁻¹.

We can use various physico-chemical techniques to characterize ligands and complexes. In this work the following techniques have been used for the characterization of the ligands and complexes :-

- (i) Elemental analysis
- (ii) Molar conductance
- (iii) Magnetic susceptibility
- (iv) Infrared spectra
- (v) Electronic spectra

Biological Studies:

Results and Discussion

The antifungal and antibacterial activities of all the synthesized Schiff bases and their metal complexes Co II and Zn II have been determined on *Aspergillus flavous*, *Aspergillus niger* fungi and *Escherichia coli, Staphylococcus aureus* and *Bacillus subtilis* bacteria by cup plate agar diffusion method. The results of these studies have been presented in the Table in terms of their minimum inhibitory concentration. It has been concluded that the general order of the activity for the Schiff bases is as under:

Sulphur containing = o-hydroxyl benzaldimine>pyrrole-2-aldimine = furan-2-aldimine> nitro containing > benzaldimine. The general order of activity of metal complexes is as under:-

Among the metal complexes of these Schiff bases, the Zn (II) metal complexes showed highest activity and Co (II) complexes showed less activity in both antifungal and antibacterial.

The general order of activity of metal complexes is as **Zn (II) > Co (II)**

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