

Synthesis, Spectral Studies, Antifungal Activity and Biological Study of Bis (2 Hydroxy Benzylidene) Benzidine Titanium (III) Chloride with Schiff Bases Derived from Aromatic Amines

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Abstract- A series of transition metal complexes of Cu(II), Ru(II), Fe(II), Mo(II) with a tetradentate ligand, bis (2-hydroxy benzylidene) benzidine prepared by the condensation of 2-hydroxy benzaldehyde and benzidine. Metal complexes are reported and characterized based on elemental analysis IR, HNMR, Magnetic moment, molar conductance and thermal analysis. The synthesized ligands in comparison to their metal complexes were also screened for their antibacterial activity against bacterial species. The activity data show the metal complexes to be more potent antibacterial than the parent Schiff base ligand against one or more bacterial species.

Keywords: 2-Hydroxy benzaldehyde, Benzidine, Magnetic moment, Transition metal complexes, Molar Conductance, Biological activity, Thermal analysis.

1. INTRODUCTION

Schiff bases complexes with transition metal have played central role in development of co-ordination chemistry. Because Schiff base ligands are potentially capable of forming stable complexes with metal ions. Metal complexes play an important role in agriculture pharmaceutical and industrial chemistry.

By the study of available literatures, it appears that bis (2-hydroxy benzylidene) benzidine and its related compounds have been extensively used as biological screening agents and analytical agents. Considering the above facts, this paper describes the behaviour of the tetradentate aromatic Schiff base ligand with various transition metal ions [1].

The Schiff bases bis (2-hydroxy benzylidene) benzidine were prepared by standard methods and characterized by the determination of melting point and elemental analysis. The complexes of these ligand were prepared with Titanium (III) by standard method and synthesized & characterized by elemental analysis, molar conductance, magnetic susceptibility, IR, Electronic spectral measurement and TGA [2].

1. MATERIALS AND METHODS:

All reagents were used without purification and supplied by Merck. The IR Spectra of the complexes were recorded with Perkin Elmer spectrophotometer model 651 in KBr or nujol phase at RSIC, CDRI Lucknow. The Visible spectra were recorded with Beckmann DU-2 spectrophotometer in the range of 750cm⁻¹ to 300 cm⁻¹ at Department of Chemistry, Bareilly College, Bareilly U.P. (India). The Elemental analyses were carried out at RSIC, CDRI Lucknow, conductivity measurements were carried out at Philips conductivity Bridge model PR 9500 type conductivity cell at department of chemistry, Bareilly College, Bareilly. The conductivity of complexes was measured in methanol, DMF, DMSO, nitrobenzene and acetonitrile. Magnetic Susceptibility of the complexes was determined by department by Gouy method at the Department of Chemistry, Bareilly College, Bareilly With CuSO₄.5H₂O as Calibrate, the diamagnetic corrections were made for the ligand [3].

1.1 Synthesis of Schiff Base:

Methanol solution of N, N'-Bis (2-Hydroxy benzylidene) with methanol solution of benzidine (.01mol) in 2:1 molar ratio is taken. The ligand so formed was filtered and dried. It was purified by recrystallization from methanol. Chemical reaction is represented in Fig. 1 for same.

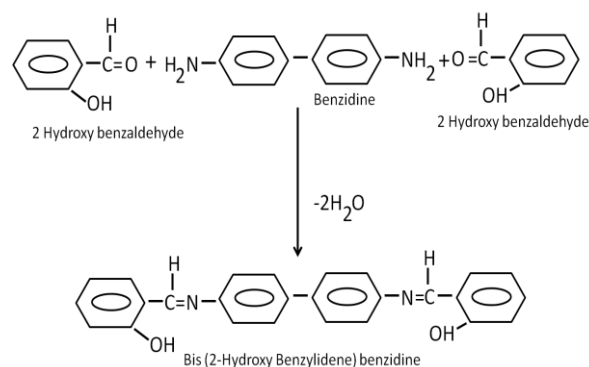


Figure 1: Preparation of Bis (2- Hydroxy Benzylidene) benzidine

1.1 Synthesis of TI (III)

The Solution of the respective ligand was prepared in ethanol. To this solution ethanol is added drop wise to get solution of the respective metal salt. The reaction mixture was refluxed on water bath for about 1h & then cooled to room temperature. The pH was adjusted to 7.5 using 1:1 ammonia solution precipitate solution. Precipitate thus obtained was separated by filtration, washed with distilled water followed by ethanol & then dried in Vacuo [4].

1.2 Physical and characterization of schiff base

The melting point of the ligands is determined. These are characterized by elemental analyses for C, H, N and S. The IR Spectras of the ligand are recorded. The data is given in the Table 1.

Table 1: Details of ligand characterization

Name of the ligands	Bis (2-hydroxy benzylidene) benzidine (HBB)			
Molecular formula	C ₂₆ H ₂₀ N ₂ O ₂			
Colour	Yellow			
M.P./D.T.	152°C			
Percentage Composition	% of C	% of H	% of N	% of Cl
	79.59 (79.26)	5.10 (4.71)	7.14 (7.04)	-

2.4 Preparation of TITANIUM (III) CHLORIDE:

The metal solution of titanous chloride about 200ml (12.5%W/V) containing 12.5% HCl is taken in a conical flask. Dry hydrogen chloride is passed in the flask for ten minutes, to saturate the solution. The flask is then, heated to initiate reaction of metal to produce titanous chloride & evolving hydrogen. This process is repeated several times.

The solution is covered with a layer of toluene in order to avoid oxidation. It is then cooled in freezing mixture & was saturated with HCl till the violet crystal of TiCl₃.6H₂O separated out.

2. SYNTHESIS OF METAL COMPLEXES

The solutions of the respective ligand are prepared with ethanol. To this solution ethanol is added drop wise, the final solution of the respective metal is salt. The reaction mixture is refluxed on water bath for about 1hour and then cooled to room temperature. The pH was adjusted to 7.5 using 1:1 ammonia solution. Precipitate obtained was separated by filtration, washed with distilled water, followed by ethanol & then dried in vacuo [5-6].

2.1 Physical, characterization of metal complexes or analyses

Metal complexes were characterized by elemental analyses for carbon, hydrogen and nitrogen and metal is determine gravimetrically. The colours of the complexes are noted and melting points are determined by open capillary method and are uncorrected. The molar conductance is measured at 10⁻³M dilution at room temperature. Their magnetic properties were also studied by Gouy's method using CuSO₄ .5H₂O as calibrate. The complexes are also subjected to their thermo gravimetric analysis [6-8]. The analytical data indicated that the ligand has reacted with the metal in the molar ratio of 1:1 on this basis the molecular formula of the complex comes out to be in Table 2.

Table 2: Physical, Characteristics and analytical data of the complexes

Name of the ligands	Bis (2-hydroxy benzylidene) benzidine titanium (III) chloride			
Molecular formula	[TiC ₂₆ H ₁₈ N ₂ O ₂ (H ₂ O) ₂]Cl			
Colour	Yellow			
M.P./D.T.	217°C			
Percentage Composition	% of C	% of H	% of N	% of Cl
	61.26 (60.15)	4.35 (4.10)	5.49 (4.99)	6.95 (6.48)
Solubility	DMF, DMSO& Acetonitrile			
Magnetic Moment μ_{eff} (BM)	1.71			

Table 3: Spectroscopic data of complex

Name of complex	Bis (2-hydroxy benzylidene) benzidine titanium (III) chloride		
Important Peaks of IR Spectra	$\nu_{\text{C=O}}$ -ordination water molecule	$\nu_{\text{C=N}}$	$\nu_{\text{C=O}}$
	3200	1595	1285

3. ELEMENTAL ANALYSES

Elemental analyses are performed on a Perkin-Elmer-24°C model at the central drug research Institute (CDRI), LUCKNOW.

3.1 Infra-red studies

The Infra red studies of the complexes are recorded with Perkin Elmer spectrophotometer model 651 in KBr or Nujol Phase from 4000cm⁻¹ to 250cm⁻¹ at R.S.I.C, CRDI, LUCKNOW.

3.2 Conductivity measurements

Conductivity measurements are carried out by Philips conductivity Bridge model PR 9500 with a dip type

conductivity cell at Department of Chemistry, Bareilly College, Bareilly. The conductances of the complex are measured in methanol, DMF, DMSO & nitrobenzene and acetonitrile at room temperature [8-9].

4.3 Magnetic susceptibility

The magnetic susceptibility of the complexes is determined by Gouy's method at the Department of Chemistry, Bareilly College, Bareilly using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as calibrant, the diamagnetic corrections are made for the ligand.

3.3 Thermo gravimetric analysis (TGA)

This analysis is done at the Chemistry Department, GND University, Amritsar.

3.4 Electronic spectra

The electronic spectra of the complexes are recorded by Beckmann-DU spectrometer.

3.5 Visible spectra

Visible spectras are recorded with Beckman DU-2 spectrophotometer in range of 750 cm^{-1} to 300 cm^{-1} at Department of Chemistry, Bareilly College, Bareilly.

4. RESULT & DISCUSSION

The analytical data indicates that the ligand has reacted with the metal in the molar ratio of 1:1. On this basis the molecular formula of the complex comes out to be $[\text{TiC}_{26}\text{H}_{18}\text{N}_2\text{O}_2(\text{H}_2\text{O})_2]\text{Cl}$.

The melting point of the ligand is 95°C and that of the complex is found to be 160°C . This vast difference in the melting points of the ligand and its corresponding complex indicates the formation of the complex. The molar conductance measurement in DMF, DMSO and acetonitrile at 10^{-3} M dilution indicated 1:1 electrolytic nature of the complex [10-11].

The studies of magnetic properties give a value of 1.71 B.M to the magnetic moments of the complex. This is very close to the calculated value of 1.73 B.M. for $d1$ system like Ti^{3+} . This value is suggestive of paramagnetic nature and octahedral geometry of the complex [1]. The value also suggests that Ti (III) has not been oxidizing during or after complexation.

The electronic spectra was recorded in nujol phase which had only one band at 20,408 which is due to the transition ${}^2T_{2g} \rightarrow {}^2E_g$ for an Oh symmetry [12].

A careful comparison of the spectra of ligand and complex give information regarding co-ordination through various groups. The IR spectrum of the Schiff base ligand exhibits medium intensity band at 1620 cm^{-1} , which may be assigned to azomethine group. This band shifts downward by 25 cm^{-1} suggesting co-ordination through azomethine nitrogen atom.

A strong band in ligand spectra at 2930 cm^{-1} due to phenolic -OH has been found absent in complex. This indicates the deprotonation of phenolic -OH signal in 1-HNMR spectra of complex [13-14]. The appearance of broad around 3200 cm^{-1} in the spectra of complex has been assigned to associated water molecules. A medium intensity band in the IR spectrum of complex at 745 cm^{-1} , is assignable to rocking mode due to coordinated water molecules. Some new bands in the spectrum of the complex have at 410 cm^{-1} and 550 cm^{-1} which have been assigned to Ti-O and Ti-N bonding [15-17].

5. ANTIBACTERIAL STUDY

The antibacterial screening of the Schiff bases have been carried out against Escherichia coli, aeromonas hydrophila and salmonella typhi using a nutrient agar medium by disc diffusion method [18, 19]. The result showed the schiff bases exhibit moderate activity against the selected bacteria which increase on increasing the concentration [20]. The mode of action of schiff base may involve formation of a hydrogen bond through azomethine ($>\text{C}=\text{N}$) group with the active centres of cell constituent, resulting in the interference to normal cell processes [21, 22]. Though the Schiff bases posses activity they could not reach the effectiveness of the standard drug streptomycin. The variation in the effectiveness of different compounds against different organism depend either on impermeability of cells or the microbe of difference in ribosome of microbial cells [23].

Table-4 Antibacterial activity of ligands & metal complex

Ligand/Complex	Diameter of inhibition Zones (mm)								
	Escherichia cell			Aeromonas hydrophila			Salmonella typhi		
	2.5%	0.5%	1%	0.25%	0.5%	1%	0.25%	0.5%	1%
Bis (2-hydroxybenzylidene) benzidine	9	10	12	10	11	12	8	11	12
$[\text{TiC}_{26}\text{H}_{18}\text{N}_2\text{O}_2(\text{H}_2\text{O})_2]\text{Cl}$	10	12	14	12	16	19	12	15	19

6.1 antifungal activity

Schiff bases are also screened for their antifungal activity by using A. The microbial screening is done by cup diffusion method [24]. The zones of inhibition have been measured and percentage inhibition is calculated for standard griseofulvin, the percentage inhibition is obtained in 83. The formula used calculating percent inhibition is given by Vincent [25].

$$\text{Inhibition \%} = \frac{[(C - T) \times 100]}{C}$$

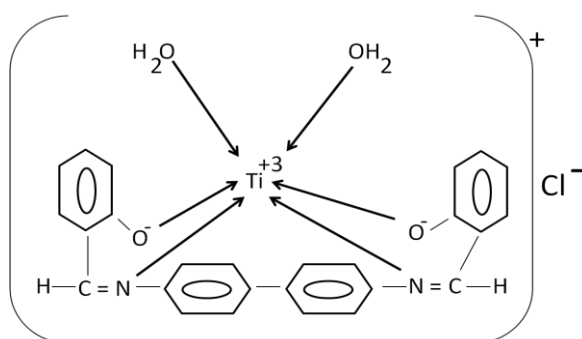
Where, C and T are the growth in mm to control and treatment respectively.

Table-5 Antimicrobial Activity of synthesized Schiff Bases

S.No.	Ligand/Complex	Antifungal activity zone of inhibition(mm) A.awamore
1	Bis(2-hydroxybenzylidene)benzidine	9
2.	[TiC ₂₆ H ₁₈ N ₂ O ₂ (H ₂ O) ₂]Cl	12

6. CONCLUSION

The complex appears with octahedral geometry; four coordination sites are occupied by a tetradentate Schiff base molecule & two by water molecules. This is also supported thermo gram shows the loss of two water molecules at 170°C.



Bis (2-Hydroxy Benzylidene) benzidine Titanium (III) chloride

Figure 2: Structure of Bis (2- Hydroxy Benzylidene) benzidine Titanium (III) chloride

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BIOGRAPHIES



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