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Spectral and thermal characterization with antimicrobial activity on Cr(III) and Sn(II) Complexes containing N,O Donor novel schiff base ligand

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Abstract

Metal complexes of Cr(III) and Sn(II) ions with Schiff base ligand 4-((pyridin-2-ylimino)methyl)phenol derived from condensation of 2-amino pyridine with 4-hydroxybenzaldehyde was prepared. The ligand and complexes were isolated from the reaction in the solid form and characterized by conductivity, magnetic moment, TLC, IR, UV-Visible, Thermal analysis and some physical measurements. During complexation reaction with transition metal ions Schiff base act as a deprotonated tridentate ligand and IR spectra showed that N and O atoms are coordinated to the central metal atom. The observed values confirmed that the complexes have octahedral geometry. The Schiff base and its metal complexes have been found to have moderate to strong antibacterial activity.

Keywords: Schiff base, Transition metal complex, IR, UV-Visible spectral analysis, TGA, DTG and antimicrobial activity.

1. Introduction

Schiff base are the compounds containing azomethine group (-HC=N-) formed by the condensation reaction of any primary amine with aldehyde or ketone under specific condition^[1]. These bases can be effective chelating agents either the carbonyl compound as the amine or both contain potentially coordinating functional groups near the site of condensation. Schiff base constitute a very important group of N,O donor chelating ligands^[2]. Schiff bases are some of most widely used organic compounds. They are used as pigments and dyes, catalysts, intermediate in organic synthesis, and as a polymer stabilizer^[3]. On the other hand Inorganic elements play crucial role in biological and biological medical processes, and it is evident that many organic compound used in medicine do not have a purely organic mode of action, some of are activated or bio transformed by metal ions metabolism. Many drugs possess modified toxicological and pharmacological properties in the form of metal complex and probably Schiff base are versatile C=N (Imine) containing compounds possessing broad spectrum of biological activity and incorporation of metals in the form of complexes showed some degree of antibacterial, antifungal, antitumor, anticancer and anti-inflammatory activity^[4, 8]. In vivo studies have indicated that some biologically active compounds may become more carcinostatic and bacteriostatic upon chelation^[9, 12]. Such interaction with transition metal ions with amino acids, peptides and nucleic acids, are of immense biological importance^[13, 14]. Several reviews^[15, 17] showed that the metallo-organic chemistry of such compounds greatly influence their biological action highlighting the catalytic function metals^[18, 19] in many biological processes. Recently, Co(II), Cu(II), and Mn(II) metal complexes of Schiff base ligand derived from cinnamaldehyde and ethylenediamine^[20], also mixed ligand coordinating Co(II) Complex with phthalic acid and heterocyclic amines^[21] were reported from our laboratory. Keeping these facts in view the significance of metal in biology, we here in report the synthesis and characterization of a novel Schiff base ligand derived from 2-amino Pyridine with 4-Hydroxy Benzaldehyde and its Cr(III), and Sn(II) complexes.

2. Experimental

2.1 Materials and Methods

All chemicals and solvents used were of Analar grade.

All metal(II) salts were used as chloride and sulphate. The solvents such as ethanol, methanol, chloroform, diethyl ether, petroleum ether, DMSO (dimethyl sulfoxide) and acetonitrile were purified by standard procedure. The melting point or the decomposition temperature of all the prepared ligand and metal complexes were observed in an electro thermal melting point apparatus model No. AZ6512. Vibrational spectra (IR) were recorded with a NICOLET 310, FTIR spectrophotometer, Belgium, in the range $4000-225\text{ cm}^{-1}$ with a KBr disc as reference. UV-Visible spectra of the complexes in DMSO ($0.5 \times 10^{-3}\text{ M}$) were recorded in the region $200-800\text{ nm}$ on a Thermolectron Nicolet evolution 300 UV-Visible spectrophotometer. The SHERWOOD SCIENTIFIC Magnetic Susceptibility Balance that following the Gouy Method were used to measure the magnetic moment of the solid complexes. The electrical conductance measurements were made at room temperature in freshly prepared aqueous solution (10^{-3} M) and in DMSO using a WPACM35 conductivity meter and a dip-cell with a platinum electrode. Some conductivity were also measured in PTI-18 Digital conductivity meter. The purity of the ligand and metal complexes were tested by Thin Layer Chromatography (TLC).

2.2 Preparation of Schiff base

4-hydroxy Benzaldehyde (1.2 g, 10 mmol) dissolved in absolute ethanol (20 mL) was added drop wise to a constant stirring solution of 2-amino Pyridine (0.941 g, 10 mmol) in 30 mL ethanol with 2 mL of conc. H_2SO_4 and the mixture was refluxed for 4h. On cooling, a solid white product was formed which was filtered, washed with ethanol, acetone and diethyl ether and dried in vacuum over anhydrous CaCl_2 . The reaction of monitored by TLC using petroleum ether, ethyl acetate, toluene and methanol solvents. The product was found to be soluble in methanol, chloroform and DMSO and insoluble in Ethanol, acetone, diethyl ether, Petroleum ether and Isopropanol. It provided 72% yield at $36\text{ }^\circ\text{C}$ temperature. The structure of Schiff base was shown in fig-1.

2.3 Synthesis of Cr(III) and Sn(II) complexes

All metal complexes were prepared in 1:2 molar ratio (metal: ligand). Ethanolic solution (20 mL) of Chromium (III) nitrate nonahydrate (0.400 g, 1 mmol)/ Tin(II) chloride dihydrate (0.266 g, 1 mmol) was taken in a two necked round bottom flask and kept on magnetic stirring. A warm ethanolic solution (20 mL) of prepared Schiff base ligand (0.396 g, 2 mmol) was added drop wise and stirred with heating for 4h. On cooling, precipitates were formed which were filtered, washed with ethanol, acetone, and diethyl ether and dried in vacuum desiccators over anhydrous CaCl_2 . The purity of each

complexes were tested by TLC using different solvents. The complexes were soluble in water, methanol, DMSO and DMF. The structure of metal complexes was shown in fig-2.

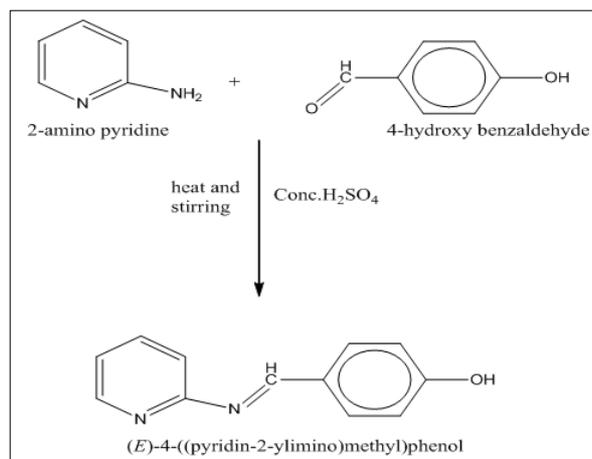


Fig 1: Structure of Schiff base L= $[\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}]$

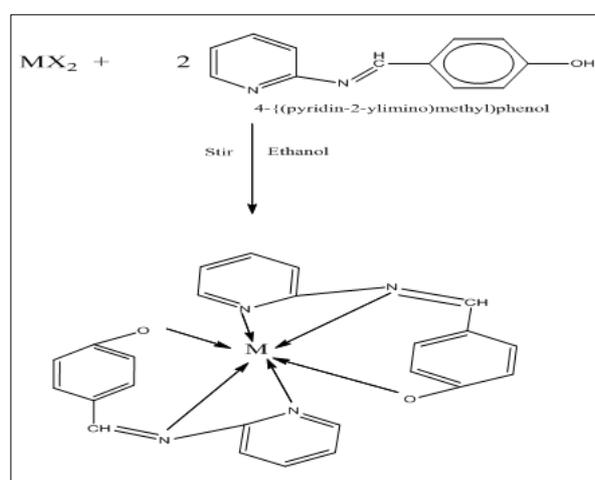


Fig 2: Structure of Metal complexes
Where M= Cr(III), Sn(II) and X= Cl^- ions.

3. Result and discussion

3.1 Physical properties

All of the synthesized ligand and metal complexes were air and moisture stable. The complexes are intensely colored, powdered solids, which decomposes above $300\text{ }^\circ\text{C}$. Molar conductance values of the in aqueous solution and in DMSO (10^{-3} M) showed low values (32-63 $\mu\text{S}/\text{cm}$) indicating them to be non-electrolyte.

Table1: Physical and analytical data of the Schiff base and metal complexes.

Compounds/mol. Formula/Mw.	Color	Yield (%)	M.P ($^\circ\text{C}$)/(decomp)	Conductivity ($\mu\text{S}/\text{cm}$)
Ligand (L) $\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}$	White	72	180-182	32
$[\text{Cr}(\text{L})_2]$ $[\text{C}_{24}\text{H}_{18}\text{CrN}_4\text{O}_2]$	Greenish	62	>300	42
$[\text{Sn}(\text{L})_2]$ $[\text{C}_{24}\text{H}_{20}\text{SnN}_4\text{O}_2]$	Yellowish	58	> 300	63

Where, L= Schiff base ligand $[\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}]$

3.2 IR and UV-Visible Spectral Analysis

IR spectra of the Schiff base showed a strong bands at 1662 cm^{-1} assigned to the azomethine $\nu(\text{HC}=\text{N})$ linkage, the bands at 1735 and 3420 cm^{-1} were absent in Schiff base which are due to carbonyl $\nu(\text{C}=\text{O})$ and $\nu(\text{NH}_2)$ stretching vibration. In

comparison of the spectra of Schiff base and its metal complexes (Table-2) suggested that each Schiff base coordinated to metal ions using three donors, indicated that the ligand acted as a tridentate ligand. The band appearing at 1666 cm^{-1} and 1635 cm^{-1} due to azomethine ($\text{CH}=\text{N}$) and heterocyclic

ring (C=N) in a Schiff base was shifted to lower frequency represented the azomethine and heterocyclic ring nitrogen in complexation. Further conclusive evidence of the coordination of Schiff base with metals was shown by appearance of weak

low frequency new absorption bands at 509 – 606 cm^{-1} and 243 – 340 cm^{-1} that assigned ^[22] the metal-oxygen $\nu(\text{M-O})$ and metal – nitrogen $\nu(\text{M-N})$ frequency respectively.

Table 2: Selected IR and UV-Visible spectral data of the Schiff base and Meta complexes.

Ligand/complexes	IR (cm^{-1})					$d \rightarrow d$
	$\nu(\text{OH})$	$\nu(\text{CH=N})$	$\nu(\text{C=N})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$	$\lambda(\text{nm})$
Ligand $\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}$	3388	1662	1635	-	-	-
$[\text{Cr}(\text{L})_2] [\text{C}_{24}\text{H}_{18}\text{CrN}_4\text{O}_2]$	3363	1652	1627	254	519	380
$[\text{Sn}(\text{L})_2] [\text{C}_{24}\text{H}_{20}\text{SnN}_4\text{O}_2]$	3342	1646	1632	294	509	420

Where L= Schiff base ligand $[\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}]$

3.3 Thermal analysis of $[\text{C}_{24}\text{H}_{20}\text{SnN}_4\text{O}_2]$

The TGA/DTG curve from (fig-3) proposed that Sn(II) complex was thermally highly stable as it didn't break down up to temperature 410 $^{\circ}\text{C}$, hence there was no water molecule linked to the complex. The Sn(II) complex was decomposed into main three steps where the part of ligand- $\text{C}_7\text{H}_5\text{O}$ -were decomposed at temperature 410-505 $^{\circ}\text{C}$ (calculated 41.33%, experimental 40.21%) at first stage. In 2nd steps of

decomposition at temperature 590-720 $^{\circ}\text{C}$ the other part of ligand- $\text{C}_5\text{H}_4\text{N}_2$ -(calculated 36.22%, experimental 33.15%) were break down. Finally the complex was completely decomposed at above 730 $^{\circ}\text{C}$ and removed as Sn/SnO. The TGA and DTG curve of Sn(II) complex was shown in fig-3. The possible degradation pathway ^[24] of $[\text{C}_{24}\text{H}_{20}\text{SnN}_4\text{O}_2]$ complex that was supported by the TGA and DTG curve was shown in fig-4.

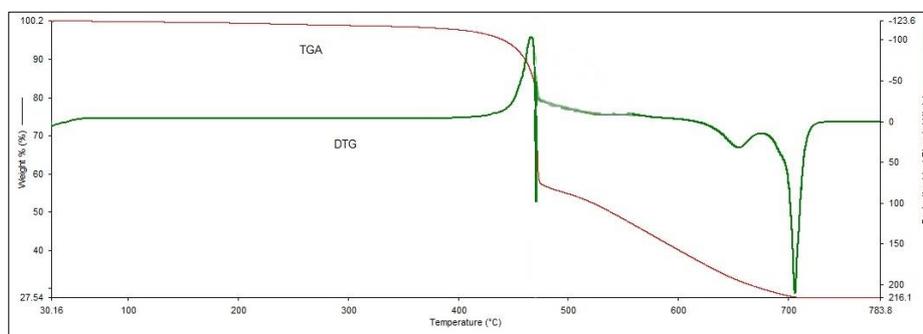


Fig3: TGA and DTG curve of $[\text{C}_{24}\text{H}_{20}\text{SnN}_4\text{O}_2]$ complex

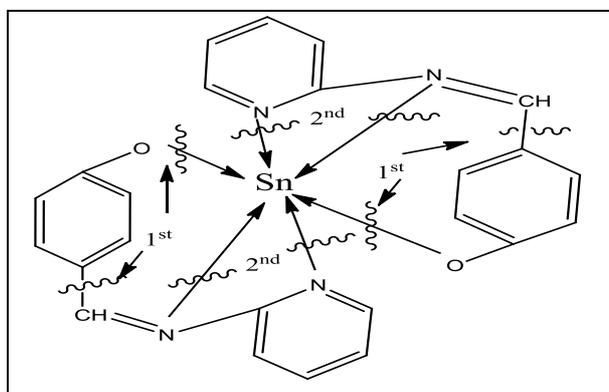


Fig4: Possible degradation pathway of $[\text{C}_{24}\text{H}_{20}\text{SnN}_4\text{O}_2]$ complex

3.4 Antibacterial Properties

The free Schiff base ligand and their metal complexes were screened for their antibacterial activity against the strains the *Escherichia coli*, *Pseudomonas aeruginosa*, *Acetobacter aceti*. The compounds were tested at a concentration of 40 $\mu\text{g}/0.01$ mL in DMSO solution using the paper disc diffusion method. The susceptibility zones were measured in diameter (mm) and the result are listed in table-3. The susceptibility zones were the clear zones around the discs killing the bacteria. All the Schiff base and metal complexes individually exhibited varying degrees of inhibitory effects on the growth of tested bacterial species. Most of the metal complexes showed more antibacterial activity than Schiff base ligand.

Table3: Antibacterial screening activity of Schiff base metal complexes.

Tested Bacteria	Diameter of zone inhibition (mm) of tested compounds			Ampicillin (20 $\mu\text{g}/0.02\text{mL}/\text{disc}$)
	Ligand	$[\text{C}_{24}\text{H}_{18}\text{MnN}_4\text{O}_2]$	$[\text{C}_{24}\text{H}_{20}\text{FeN}_4\text{O}_2]$	
<i>E.coli</i>	11	12	10	17
<i>Acetobacter aceti</i>	10	11	12	16
<i>Pseudomonas Aeruginosa</i>	10	09	10	16

4. Conclusion

In this paper we have explored the synthesis and coordination chemistry of Cr(III) and Sn(II) complexes with new Schiff base ligand derived from the condensation reaction of 2-amino Pyridine with 4-hydroxy Benzaldehyde. The physicochemical analysis indicated the formation of six coordinated metal complexes. IR spectral analysis indicated that N and O atoms are coordinated to central metal atom. Magnetic moment, UV-Visible and Thermo gravimetric analysis confirmed the proposed structure of Metal complexes. TGA analysis Indicated that Sn(II) complex are more stable than that of Cr(III) complex. Biological activity revealed that the ligand

and its metal complexes have good antibacterial activity as compared to the standard antibiotic (Ampicillin).

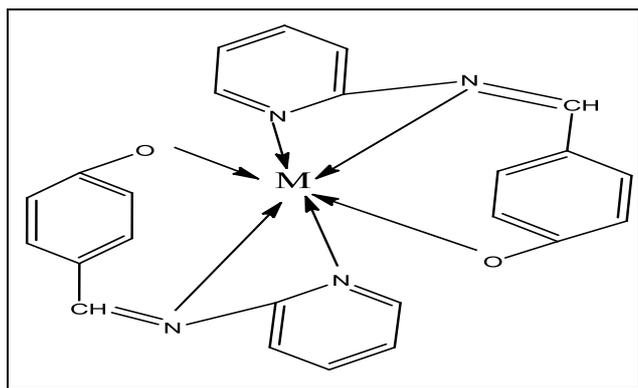


Fig5: Proposed structure of Cr(III) and Sn(II) complexes.

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