

Synthesis and Characterization with Antimicrobial Activity Studies on some Transition Metal Complexes of N, O Donor Novel Schiff Base Ligand

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Abstract

Metal complexes of Mn(II), Fe(II), Co(II) and Cd(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; Metal complex; Spectral analysis; Antibacterial activity; TGA and DTG.

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1. Introduction

Schiff base named after Hugo Schiff (1864) 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]. Schiff bases are the nitrogen analogue of aldehyde or ketone in which the active carbonyl group (>C=O) is replaced by an imine or azomethine group. 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 constitutes 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 compounds used in medicine do not have a purely organic mode of action, some of them are activated or bio transformed by metal ions metabolism. Many drugs possess modified

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toxicological and pharmacological properties in the form of metal complex and probably Schiff bases 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 [9-13]. Such interaction with transition metal ions with amino acids, peptides and nucleic acids, are of immense biological importance [14-16]. Several reviews [17-20] showed that the metallo-organic chemistry of such compounds greatly influence their biological action highlighting the catalytic function metals [21-23] in many biological processes. H. Chohan *et al.* [24] was reported some substituted pyridine Schiff bases obtained from salicylaldehyde and showed good antibacterial activity. Recently, we have reported some Schiff base metal complexes and their biological application from our laboratory [25,26]. 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 Mn(II), Fe(II), Co(II), and Cd(II) complexes.

2. Experimental

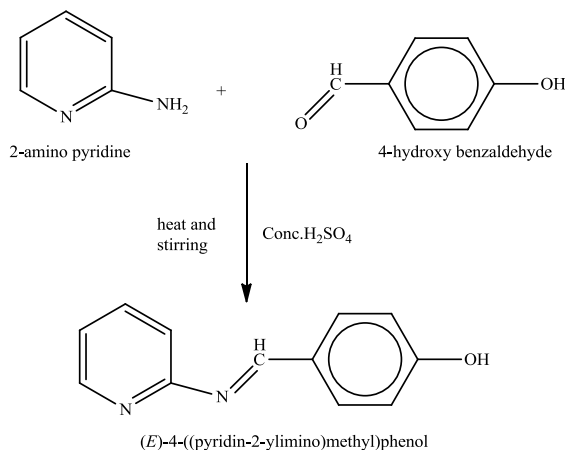
2.1. Materials and instruments

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 and acetonitrile were purified by distillation 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. Infrared spectra were recorded on a FTIR-8400, SHIMADZU, Japan using a KBr disc, in Central Science Lab of Rajshahi University. The thermogravimetric analysis (TGA) was performed on Perkin Elmer Simultaneous Thermal Analyzer, STA-8000. The electronic spectrum of the complex in solution phase (5×10^{-4} M) was recorded on a Shimadzu Double Beam spectrophotometer model UV-1200 and UV-1650PC. 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. 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 was 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°C . The structure of Schiff base was shown in (Scheme 1).



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

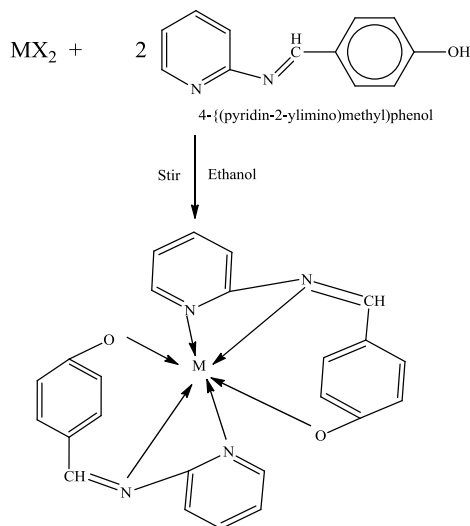
2.3. Synthesis of Mn(II), Fe(II), Co(II) and Cd(II) complexes

All metal complexes were prepared in 1:2 molar ratio (metal : ligand). Methanolic solution (20 mL) of manganese (II) chloride tetra hydrate (0.198 g, 1 mmol)/Iron(II) sulphate hexahydrate (0.278 g, 1 mmol)/cobalt(II) chloride hexahydrate (0.24 g, 1 mmol) / cadmium(II) chloride monohydrate (0.201 g, 1 mmol) was taken in a two necked round bottom flask and kept on magnetic stirring. A warm methanolic solution (20 mL) of prepared Schiff base ligand (0.396 g, 2 mol) 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 complex was tested by TLC using different solvents. The complexes were soluble in methanol, DMSO and DMF. The proposed structure of complex was shown in (Scheme 2).

2.4. Antibacterial studies

Any chemical or biological agent that either destroys or inhibits the growth of microorganisms is called antimicrobial agent. The synthesized Schiff base ligand and the metal complexes were screened for their antibacterial activity against pathogenic bacterial

strains, *Escherichia coli*, *Pseudomonas aeruginosa* and *Acetobacter aceti*. The disc diffusion method [25,26] was adopted for the determination of antibacterial activity.



Scheme 2. Structure of metal complexes.

Where M= Mn(II), Fe(II), Co(II) and Cd(II) and X= Cl^- , SO_4^{2-} ions.

3. Results and Discussion

3.1. Physical properties

All of the synthesized ligand and metal complexes were air and moisture stable (Table 1). The complexes are intensely colored, amorphous solids, which decomposes above 200°C. Molar conductance values of the compounds in DMSO (10^{-3} M) showed low values (12-45 μ S/cm) indicating [25] them to be non-electrolyte.

Table 1. Physical and analytical data of the Schiff base and metal complexes.

Compounds/mol. Formula / Mw.	Color	Yield (%)	M.P (°C)/(decomp)	Conductivity (μ S/cm)
Ligand (L) $C_{12}H_{10}N_2O$ [198]	White	72	180-182	12
[Mn(L) ₂] $C_{24}H_{18}MnN_4O_2$ [451]	White	62	>300	16
[Fe(L) ₂]. H ₂ O $C_{24}H_{20}FeN_4O_3$ [470]	Yellowish	58	> 300	19
[Co(L) ₂] $C_{24}H_{18}CoN_4O_2$ [454]	Pink	63	> 300	45

Compounds/mol. Formula / Mw.	Color	Yield (%)	M.P (°C)/(decomp)	Conductivity ($\mu\text{S}/\text{cm}$)
[Cd(L) ₂].2H ₂ O C ₂₄ H ₂₂ CdN ₄ O ₄ [546.41]	White	60	> 300	22

Where, L= Schiff base ligand [C₁₂H₁₀N₂O]

3.2. Infrared spectra

IR spectra of the Schiff base showed a strong bands at 1662 cm⁻¹ assigned [25, 28] 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. It was assumed that amino and aldehyde moieties of the starting reagents were absent and had been converted into the azomethine moiety (Scheme 1). 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 ($>\text{C}=\text{N}$) in a Schiff base was shifted to lower frequency represented [24] 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 [25-27] the metal-oxygen $\nu(\text{M}-\text{O})$ and metal – nitrogen $\nu(\text{M}-\text{N})$ frequency respectively.

Table 2. IR spectral data of the schiff base and meta complexes.

Ligand/complexes	IR (cm ⁻¹)				
	$\nu(\text{OH})$	$\nu(\text{CH}=\text{N})$	$\nu(\text{C}=\text{N})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$
Ligand C ₁₂ H ₁₀ N ₂ O	3388	1662	1635	-	-
[Mn(L) ₂] C ₂₄ H ₁₈ MnN ₄ O ₂	3369	1658	1631	254	519
[Fe(L) ₂].H ₂ O C ₂₄ H ₂₀ FeN ₄ O ₃	3332	1656	1622	294	509
[Co(L) ₂] C ₂₄ H ₁₈ CoN ₄ O ₂	3350	1645	1627	340	606
[Cd(L) ₂].H ₂ O C ₂₄ H ₂₂ CdN ₄ O ₄	3322	1654	1622	243	509

Where L= Schiff base ligand [C₁₂H₁₀N₂O]

3.3. Magnetic moment and UV-Visible spectra

The magnetic moment and UV-Visible spectral components are recorded in (Table 3). At room temperature magnetic moment values of Mn(II) complexes was found to 1.93 B. M representing one unpaired electron per Mn(II) ion. The electronic spectra of Mn(II) complex showed absorption bands at 26750 cm⁻¹ which may be assigned to T_{2g} → E_g(D) similarly, Co(II) complexes was found to 4.3 B. M indicative [29-33] of three unpaired

electron per Co(II) ion attaining an octahedral environment. On the other hand, Fe(II) and Cd(II) complex showed zero magnetic moment that correspond to no unpaired electron per metal ion and suggested low spin octahedral geometry of the complexes. The electronic spectra of the Co(II) complex showed three bands observed at 15391–15473 cm^{-1} , 24212–24265 cm^{-1} and 26720–26803 cm^{-1} which may be assigned to $4A_{2g} \longrightarrow 4T_{1g}(F)$, $4A_{2g} \longrightarrow 4T_{2g}(F)$ and $4A_{2g} \longrightarrow 4T_{1g}(P)$ respectively.

Table 3. Magnetic moment and UV-visible spectra of metal complexes.

Complexes	μ_{eff} (B.M)	λ_{max} (cm^{-1})	Assignments
[Mn(L) ₂] C ₂₄ H ₁₈ MnN ₄ O ₂	1.93	26750	$T_{2g} \longrightarrow E_g(D)$
[Fe(L) ₂] C ₂₄ H ₁₈ FeN ₄ O ₂	Diamagnetic	26315	CT
[Co(L) ₂] C ₂₄ H ₁₈ CoN ₄ O ₂	4.3	15380 24275 26740	$4A_{2g} \longrightarrow 4T_{1g}(F)$ $4A_{2g} \longrightarrow 4T_{2g}(F)$ $4A_{2g} \longrightarrow 4T_{1g}(P)$
[Cd(L) ₂] C ₂₄ H ₁₈ CdN ₄ O ₂	Diamagnetic	35842	CT

Where, L= Schiff base ligand [C₁₂H₁₀N₂O]

3.4. Thermogravimetric analysis

TGA was carried out for solid complex [C₂₄H₁₈FeN₄O₂].H₂O, and [C₂₄H₁₈CdN₄O₂].2H₂O under N₂ flow and heating rate was suitably controlled at 30°C min⁻¹ and the weight loss was measured from the ambient temperature up to 800°C. The TGA and DTG curve of the Fe(II) complex is shown in (Fig. 1). The maximum temperature values *T*_{max}/°C, species lost together with the corresponding weight loss for each step of the decomposition reaction was shown in (Table 4). The data obtained strongly supported the proposed formulas of the complex. The data from the TGA, DTA and DTG curve clearly indicated that the decomposition of the Fe(II) complex proceeds in two steps. In the first step of decomposition, one molecule of hydrated water were lost between 62-360°C (calculated 3.83%, experimental 3.75% of weight) [34]. The Fe(II) complex was completely decomposed between temperature range 450-490°C (calculated 84.01% and experimental 82.03%) and above 500°C temperature the complex formed as Fe/FeO. The [C₂₄H₁₈CdN₄O₂].2H₂O was decomposed into 3 or 4 steps process as shown in (Fig. 2). Two hydrated water molecule were removed between temperature ranges 60-140°C (calculated 6.61% experimental 6.10% weight loss). The part of (-2C₆H₅O⁻) of the coordinating Schiff base ligand was gradually decomposed between temperatures 160°C to 290°C (calculated 32.34%, experimental 32.15% of weight) in second step of decomposition. The other part of the ligand -2C₅H₄N₂- was decomposed in third step at 360-430°C (calculated 38.60%, experimental 38.12% of weight). At temperature above 600°C the complex formed as Cd/CdO [35, 36]. The proposed degradation pathway [37]

of the synthesized Cd(II) complex showing order and steps of possible elimination of atoms and groups as shown in (Fig. 3).

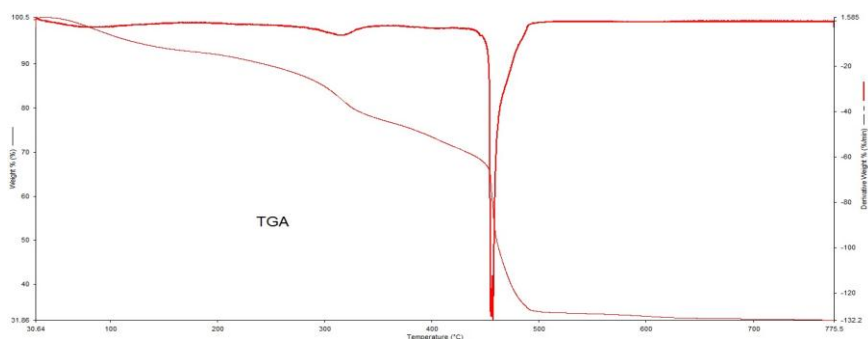


Fig. 1. TGA and DTG curve of $[C_{24}H_{18}FeN_4O_2] \cdot H_2O$

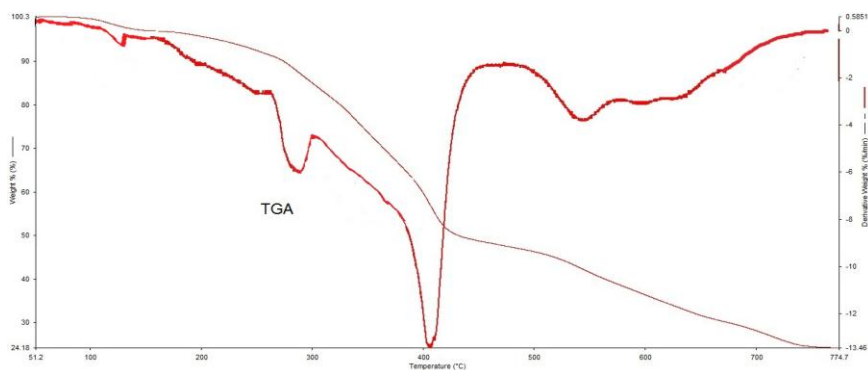
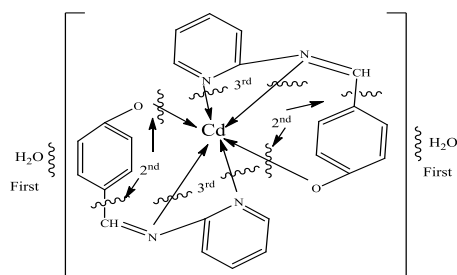


Fig 2. TGA and DTG curve of $[C_{24}H_{18}CdN_4O_2] \cdot 2H_2O$

Table 4. Thermal data of Fe(II) and Cd(II) complexes.

Complexes	Steps	Temperature Range/ °C	DTG Peak/°C	TG mass loss% calc./found	Assignments
$[C_{24}H_{18}FeN_4O_2] \cdot H_2O$	1 st	62 -360		3.83/3.75	H ₂ O
	2 nd	450-490	330	84.01/82.03	2C ₁₂ H ₉ N ₂ O
	3 rd	>500	455	11.96/11.68	Fe/ FeO
$[C_{24}H_{18}CdN_4O_2] \cdot 2H_2O$	1 st	60-140		6.61/6.10	2 H ₂ O
	2 nd	160-290	140	32.34/32.15	2C ₆ H ₅ O ⁻
	3 rd	360-430	285	38.60/38.12	2C ₅ H ₄ N ₂ ⁻
	4 th	>600	410	20.58/20.10	Cd/CdO

Fig 3. Possible degradation pathway of $[C_{24}H_{18}CdN_4O_2] \cdot 2H_2O$

3.5. Antibacterial properties

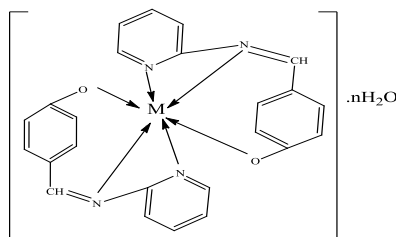
The free Schiff base ligand and their metal complexes were screened for their antibacterial activity against the strains the *Escherichia coli*, *Pseudomonas aeruginosa*, *Acetobacter aceti*. The compounds were tested at a concentration of 40 $\mu\text{g}/0.01\text{ mL}$ in DMSO solution using the paper disc diffusion method [38,39]. The susceptibility zones were measured in diameter (mm) and the result are listed in (Table 5). 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.

Table 5. Antibacterial screening activity of Schiff base metal complexes.

Tested Bacteria	Diameter of zone inhibition(mm) of tested compounds					Ampicillin (20 $\mu\text{g}/0.02$ mL/disc)
	Ligand	Mn-complex	Fe-comp	Co-comp	Cd-comp	
<i>E.coli</i>	11	12	12	13	07	17
<i>Acetobacter aceti</i>	10	10	11	11	12	16
<i>Pseudomonas Aeruginosa</i>	10	09	10	11	11	16

4. Conclusion

In this paper we have explored the synthesis and coordination chemistry of Mn(II), Fe(II), Co(II) and Cd(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 thermogravimetric analysis confirmed the proposed octahedral structure of metal complexes (Fig. 4). TGA analysis Indicated that Fe(II) complex are more stable than that of Cd(II) complex. Biological activity revealed that the ligand and its metal complexes have good antibacterial activity as compared to the standard antibiotic (Ampicillin).



Where, M= Mn(II), Fe(II),Co(II) and Cd(II)

Fig. 4. Proposed structure of M(II) complexes. where, n=1 or 2

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