

Synthesis and spectral analysis of Mn(II), Co(II), Zn(II) and Cd(II) complexes of a new Schiff base derived from p-vanillin and 4-nitroaniline

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Abstract:

Schiff bases have gained importance in research due to their biological activity and have reported uses in biology, medicine and industry. They are called 'privileged ligands', as they are easily synthesized, cost effective and exhibit unique stereochemistry and reactivity. In the present study, a new Schiff base (HL) is reported, which is the condensation product of p-vanillin, a phenolic aldehyde with anti-microbial properties and 4-nitroaniline, the final intermediate in the industrial synthesis of paracetamol. The ligand and its complexes with Mn(II), Co(II), Zn(II) and Cd(II) metal ions, prepared by magnetic stirring method, have been characterized using UV and IR spectroscopic techniques. The formation of the Schiff base ligand is confirmed by its IR spectrum showing the characteristic vibration of the azomethine group (C=N) at 1658 cm^{-1} . The results indicate that the ligand is bidentate, coordinating with the metal through its azomethine nitrogen and phenolic oxygen in all the cases. All the complexes except the zinc complex, show a wide band in the range of $3200\text{-}3400\text{ cm}^{-1}$, indicating the presence of water molecules.

Index terms: Schiff base, coordination complexes, p-vanillin, 4-nitro-aniline, magnetic stirring method, UV and IR spectroscopy

1 INTRODUCTION:

Coordination Chemistry is a sub-field of chemistry which deals with the chemical interactions between organic and inorganic ligands and metal centres. It involves the study of the physical and chemical properties, syntheses and structures of coordination compounds.

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One of the most important properties of metallic elements is their ability to act as Lewis acids that form complexes with a variety of Lewis bases. A metal complex or coordination compound is 'a compound formed from a Lewis acid and a bronsted base, a Lewis acid being an electron pair acceptor and a bronsted base a proton acceptor. Metal complexes can be neutral, such as $\text{Co}(\text{NH}_3)_3\text{Cl}_3$; positively charged, such as $[\text{Nd}(\text{H}_2\text{O})_9]^{3+}$; or negatively charged, such as $[\text{UF}_8]^{4-}$. Electrically charged metal complexes are sometimes called complex ions[1].

Metal complexes are a feature of the chemistry of more than half the elements. Many industrial catalysts are metal complexes, and such catalysts are steadily

becoming more important as a way to control reactivity. For example, a mixture of a titanium complex and an organometallic compound of aluminum is the catalyst used to produce most of the polyethylene and polypropylene “plastic” items we use every day [1].

The total number of points of attachment to the central metal atom is termed the **coordination number**. It can vary from 2 to at least 9 depending on which the geometry of the molecule can be predicted. Metal complexes with low coordination numbers generally have only one or two possible structures.

The 38 elements in groups 3 through 12 of the periodic table are called transition elements or d-block elements which were found to exhibit numerous intensity and important properties with respect to their magnetic, optical and electronic

behaviour and this is the reason behind the quick development of the field. Now scientists focus on application of transition element only.

Transition metals form coordination complexes. Coordination numbers two and three are common for d^{10} metal ions. [2].

A Schiff base, named after Hugo Schiff, is a compound with a functional-group that contains a carbon-nitrogen double bond with the nitrogen atom connected to an aryl or alkyl group. Schiff bases have the general formula $R^1R^2C=NR^3$, where R is an organic side chain.

It is usually formed by condensation of an aldehyde or ketone with a primary amine [3].



Fig. 1: Synthesis of Salen, a well-known Schiff base

Schiff bases have recently assumed greater importance in view of the fact that several of them have been found to be biologically active and have found uses in biology, medicine as well as in industry [4]. They have been widely used in pigments and dyes, photographic emulsions, heat resistant polymers, high temperature stabilizers, lubricating oils, anticorrosive agents, anti-knocking agents and liquid crystal display composition. They also have been used as antibacterial, antiviral, antifungal, antitumor agents and insecticides [5]. Several Schiff bases which are reported to be therapeutically active possess cytotoxic, anti-inflammatory, antipyretic,

analgesics, diuretic, and antispasmodic activity [5].

Schiff base ligands are considered ‘privileged ligands’, because they are easily prepared. The advantages include

- ✓ Ease-of-synthesis
- ✓ Low cost
- ✓ Stereochemical rigidity
- ✓ Facile substitution at both achiral and prochiral positions
- ✓ High-binding constants

Vanillin (4-hydroxy-3-methoxybenzaldehyde) is a phenolic

aldehyde, which is an organic compound with the molecular formula, $C_8H_8O_3$. Its functional groups include aldehyde, hydroxyl, and ether. It is the primary component of the extract of the vanilla bean. Synthetic vanillin, instead of natural vanilla extract, is now more

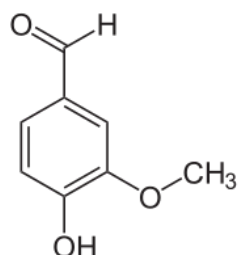


Fig. 2: 4-Hydroxy-3- methoxybenzaldehyde

4-Aminophenol (*p*-aminophenol) is an organic compound with the formula $H_2NC_6H_4OH$. Typically available as a white powder, it is commonly used as a developer in black-and-white film, marketed under the name Rodinal. It is the final intermediate in the industrial synthesis of paracetamol. Treating *p*-aminophenol with acetic anhydride gives paracetamol.

Schiff base complexes of manganese, though well known, continue to generate interest due to their potential applications in fields as diverse as homogeneous catalysis and magnetic materials. Complexes of general formula $Mn(SB)X$, where SB is a tetra-dentate Schiff base and X is usually an anionic ligand, often crystallize as phenoxo-bridged dimers which may exhibit a range of magnetic interactions depending upon the bridge geometry. Some of these complexes have been investigated in detail for their SMM (single molecule magnet) properties [8]. Cobalt is another metal of biological importance.

often used as a flavoring agent in foods, beverages, and pharmaceuticals. Schiff bases containing *o*-vanillin possesses antifungal, antibacterial properties [6]. It presents improved antifungal properties when forming Schiff bases [7].

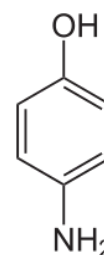


Fig. 3: Structure of 4-aminophenol

The importance of zinc for stabilization of protein loops in enzymes, zinc fingers etc., has generated new interest in the field of zinc coordination chemistry [9].

2 EXPERIMENTAL SECTION

2.1 MATERIALS

All chemicals were obtained from commercial sources and used as received. Vanillin (assay 99%) was purchased from LOBA chemie and 4-nitroaniline (assay 95%) was purchased from Sisco Research Laboratories. Manganese chloride tetrahydrate (assay 95%), cobalt chloride hexahydrate (assay 99.9%), Anhydrous zinc chloride (assay 95%) and cadmium chloride (assay 99.9%) are the metal chlorides used in the syntheses. Ethanol (assay 99.9%) was used as the reaction medium.

2.2 SYNTHESIS OF THE SCHIFF BASE LIGAND (HL)

The ligand was synthesized by standard chemical method [10] involving the condensation of vanillin and p-nitroaniline. The aldehyde and the amine were taken in 1:1 molar ratio. To an ethanolic solution (15ml) of 4-nitroaniline (0.2071g, 1 mmol), a 15 ml ethanolic solution of vanillin (0.2282g, 1 mmol) was slowly added in

drops with constant magnetic stirring at room temperature. One drop of con. HCl was added as a catalyst. The solution was stirred for 2 hours. A yellow coloured solid of starts separating from the solution. The progress of the reaction was monitored using TLC. The collected precipitate was washed by using petroleum ether and then dried in air. The yield was stored in a desiccator.

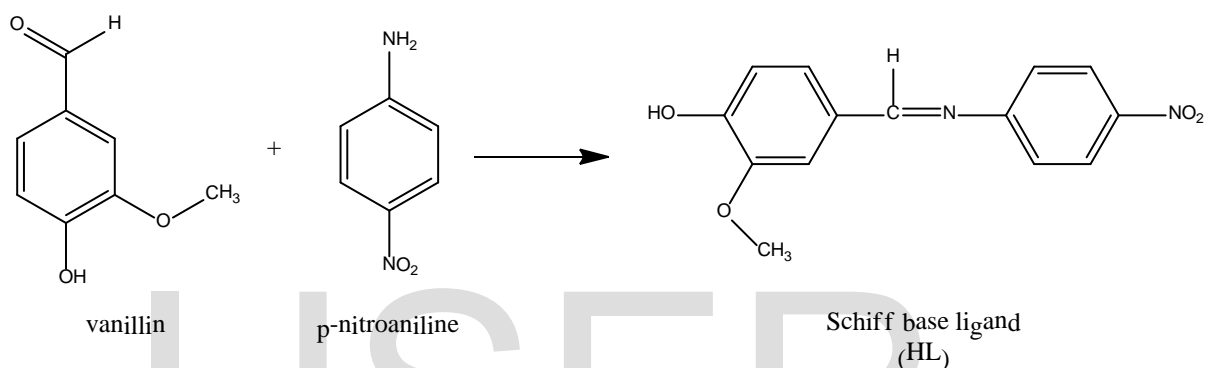


Fig. 4: Synthesis of HL

2.3 SYNTHESIS OF MANGANESE(II) COMPLEX

To the ethanolic solution (10 ml) of the ligand (0.2722 g, 0.1 mol), an solution of manganese(II) chloride (0.1619 g, 0.1 mol) in ethanol (10 ml) was added slowly in drops with constant magnetic stirring at room temperature. The solution was stirred till the colour changes from yellow to dark red colour. The mixture was kept undisturbed in a dry place over a night. Then the reaction mixture was kept in sun light and dried completely. The progress of the reaction was monitored using TLC. Fine brown coloured powder was obtained. The product was stored in desiccator for further studies.

2.4 SYNTHESIS OF COBALT (II) COMPLEX

To the ethanolic solution (10 ml) of the ligand (0.2722 g, 0.1 mol), a solution of cobalt(II) chloride (0.2379 g, 0.1mmol) in ethanol (10ml) was added slowly in drops with constant magnetic stirring at room temperature. Then the mixture was then refluxed 5h on a water bath at 70 °C. A green colour solution was obtained. The complex formation was confirmed by Thin Layer Chromatography technique. The mixture is allowed to evaporate. Fine black coloured powder was obtained.

2.5 SYNTHESIS OF ZINC(II) COMPLEX

To the ethanolic solution (10 ml) of the ligand (0.2722 g, 0.1 mol), a solution of zinc(II) chloride (0.1363 g, 0.1 mol) in ethanol (10 ml) was added slowly in drops

with constant magnetic stirring at room temperature. The solution was stirred till the colour changes from yellow to dark red colour. The mixture was kept undisturbed in a dry place over a night. Then the reaction mixture was kept in sun light and dried completely. The progress of the reaction was monitored using TLC. Fine orange coloured powder was obtained. The product was stored in desiccator for further studies.

2.6 SYNTHESIS OF CADMIUM (II) COMPLEX

To the ethanolic solution (10 ml) of the ligand (0.2722 g, 0.1 mol), a solution of cadmium(II) chloride (0.2379 g, 0.1mmol) in ethanol (10ml) was added slowly in drops with constant magnetic stirring at room temperature. Then the mixture was stirred till a yellow coloured precipitate starts separating from the solution. The complex formation was confirmed by Thin Layer Chromatography technique. The mixture is allowed to evaporate. Fine brick red coloured powder was obtained.

3 RESULTS AND DISCUSSION

3.1 IR SPECTROSCOPY

Figures 5-9 show the IR spectra of the ligand and the four complexes, respectively. In the Schiff base ligand, the strong peak observed at 1658 cm^{-1} can be assigned to the $\nu(\text{C}=\text{N})$ azomethine stretching vibration as reported in the earlier literature [6].

On complexation, this peak has shifted to lower frequencies 1629 cm^{-1} and 1590 cm^{-1} in the spectra of Mn(II) and Co(II) complexes indicating the coordination of the azomethine nitrogen to the central metal ions. The (O-H)

stretching frequency in the complexes is in the range of 3200 to 3400 cm^{-1} indicating the coordination of water molecules in both the complexes. In the complexes, weak bands in the $470\text{--}580\text{ cm}^{-1}$ range, can be attributed to (M-N) vibration and those in the 400 to 470 cm^{-1} range can be assigned to (M-O) vibration. Thus the metal ion in both the complexes form two coordinate bonds, one with the azomethine nitrogen and another with the phenolic oxygen and hence the ligand acts as a bidentate ligand.

In the case of the other two complexes also, the band obtained for azomethine stretching vibration was shifted to a lower frequency in the $1590\text{--}1630\text{ cm}^{-1}$ range indicating the coordination of the azomethine nitrogen atom to the central metal ion, Zn(II) and Cd(II). The $\nu(\text{O-H})$ phenolic band in the complexes was shifted to lower frequency 3076 cm^{-1} in the case of the Cd(II) complex and the band is absent in the case of the Zn(II) complex indicating the involvement of the phenolic oxygen in bond formation and is in accordance with the literature [9] that the ligand loses its proton when it involves in coordination with a metal. In the complexes, weak bands in the $570\text{--}600\text{ cm}^{-1}$ range, can be attributed to $\nu(\text{M-N})$ vibration and those in the 400 to 470 cm^{-1} range can be assigned to $\nu(\text{M-O})$ vibration. Thus the ligand is a bidentate ligand. In the case of cd(II) the wide band in the $3200\text{--}3650\text{ cm}^{-1}$ range represents the coordination of water molecule to the central metal atom. Absence of peaks in the $300\text{--}350\text{ cm}^{-1}$ range indicates the absence of M-Cl bond in the complexes.

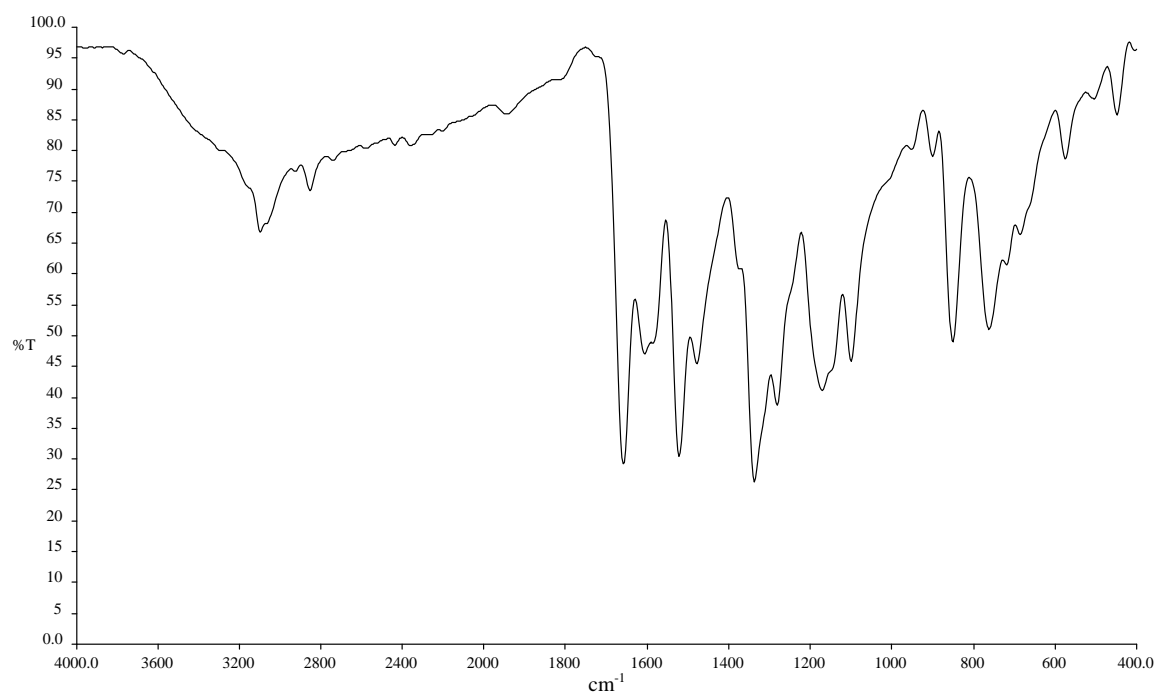


Fig. 5: IR spectrum of the ligand (HL)

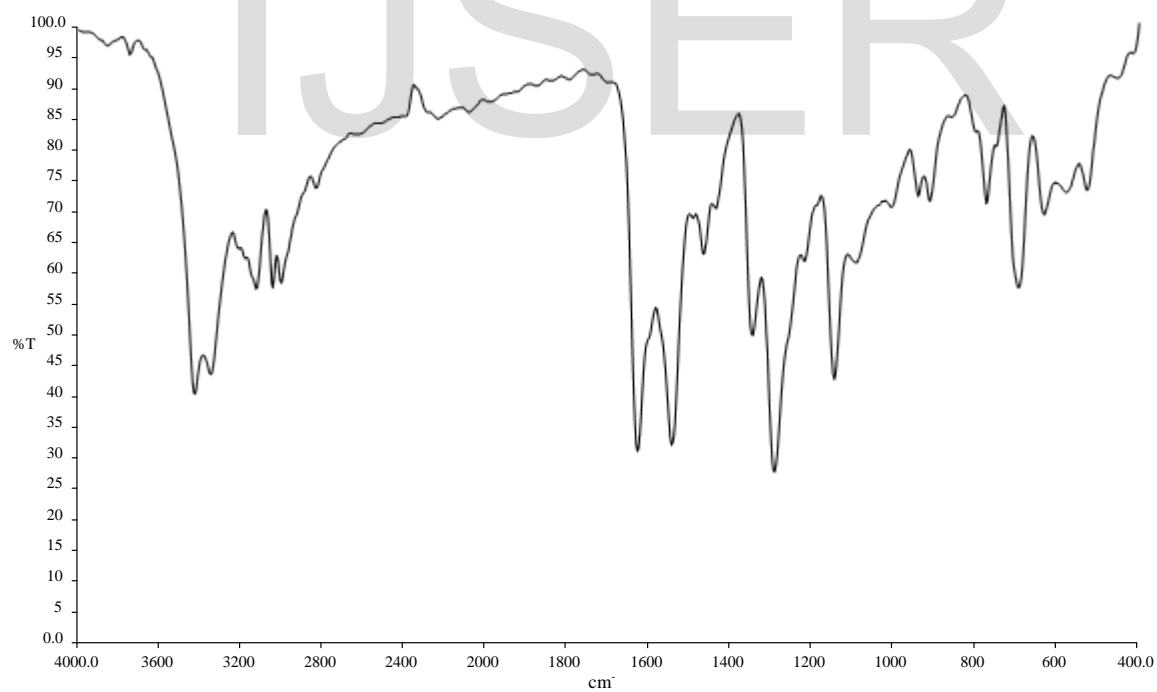


Fig. 6: IR spectrum of the Manganese(II) complex

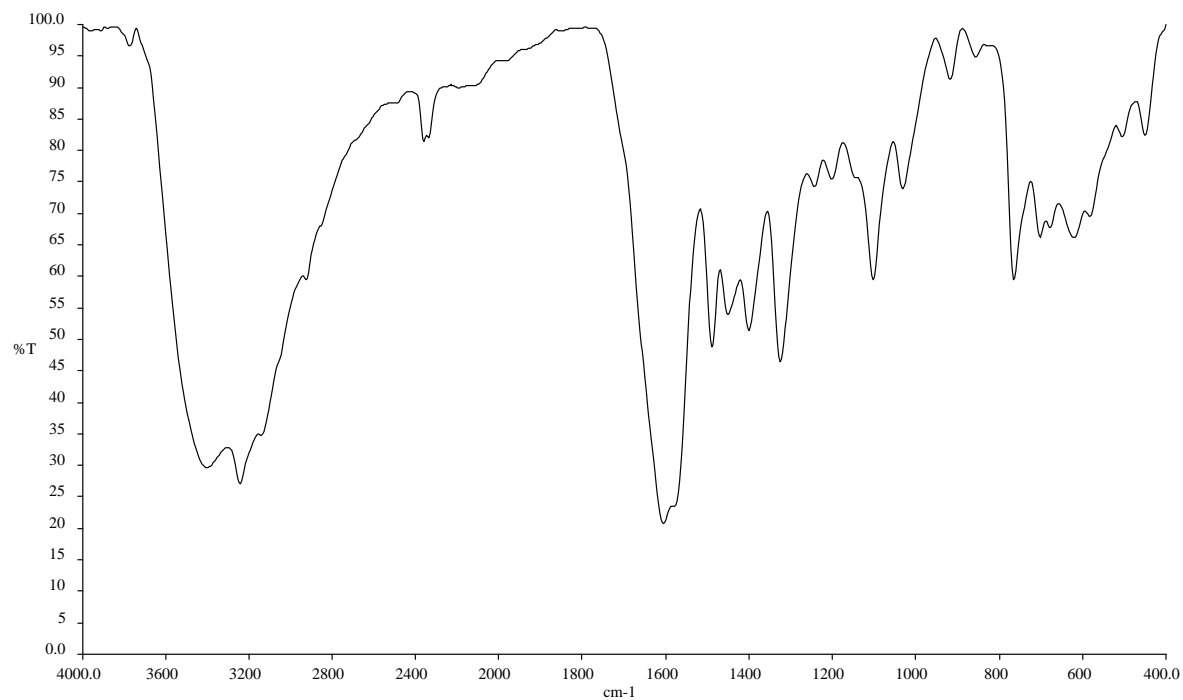


Fig. 7: IR spectrum of the Cobalt(II) complex

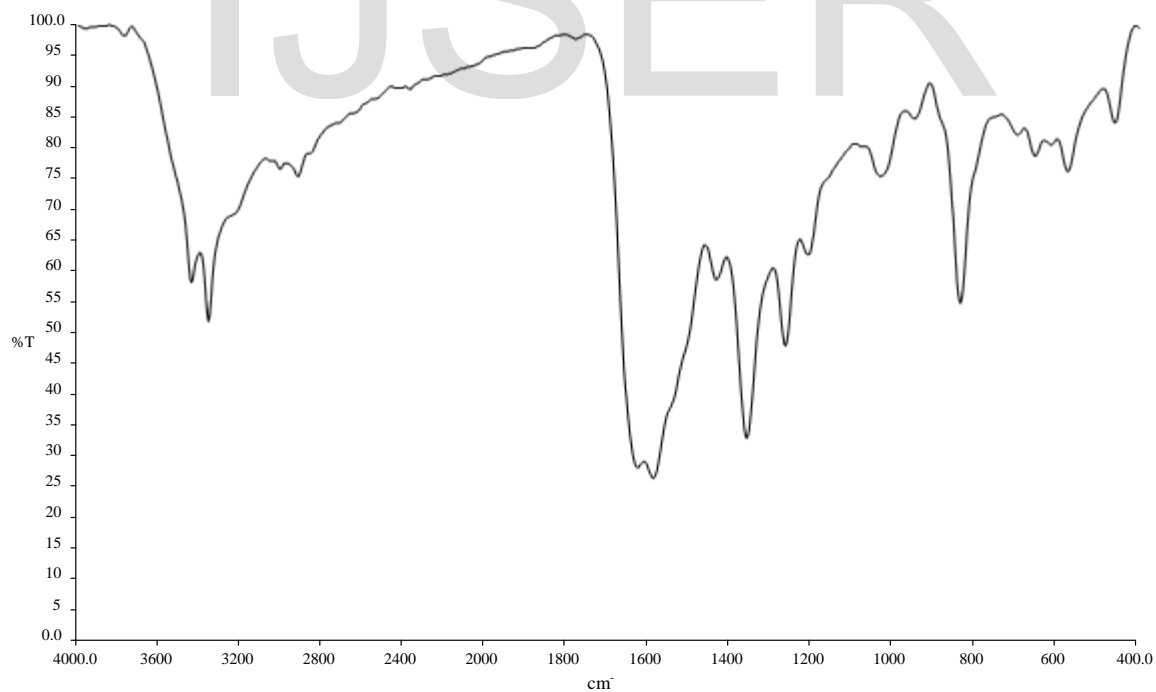


Fig. 8: IR spectrum of Zinc(II) complex

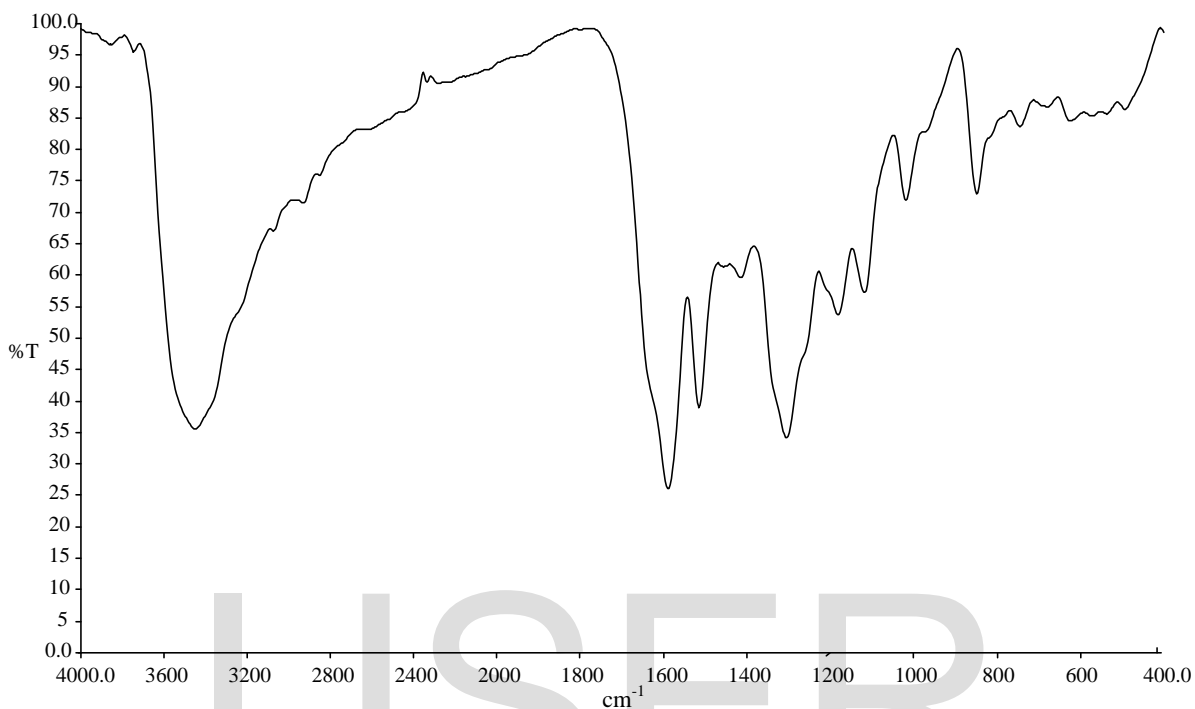


Fig. 9: IR spectrum of Cadmium(II) complex

Table 1: IR Spectral Data of the ligand and the complexes

Ligand/Complex	$\nu(\text{C}=\text{N})$	$\nu(\text{O}-\text{H})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$
HL	1658.78	3100.60	-	-
Manganese(II) Complex	1629.57	3432.58	420.67	579.63
Cobalt(II) Complex	1590.16	3455.01	494.80	574.27
Zinc(II) Complex	1629.81	-	460.73	576.15
Cadmium(II) Complex	1516.22	3076.05	425.23	528.51

3.2 UV SPECTROSCOPY

The absorption spectra of the ligand, HL and the four complexes are given in the figures

10-14 respectively. The spectra of the ligand shows three bands with λ_{max} at 311 nm, 364 nm and 416 nm which are assigned for $\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively.

In the spectrum of the manganese complex, the wavelengths (λ_{\max} values) representing the $\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions are present. However, in the case of Mn(II) complex there is a shift in the positions of all the three bands to a much lower wavelength. Also in addition, there is an additional band in the range 400-480 nm with λ_{\max} value at 432.62 nm. This shows the interaction between the ligand and the metal ion.

Similarly, the spectrum of the Co(II) complex shows three bands similar to that of the ligand, however with a mild shift in the respective λ_{\max} values.

In the spectrum of the zinc complex, the wavelengths (λ_{\max} values) representing the $\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions are present. However, there is a shift in the positions of all the three bands to a lower wavelength when compared to the λ_{\max} values in the spectrum of the ligand, from which formation of the complex can be confirmed.

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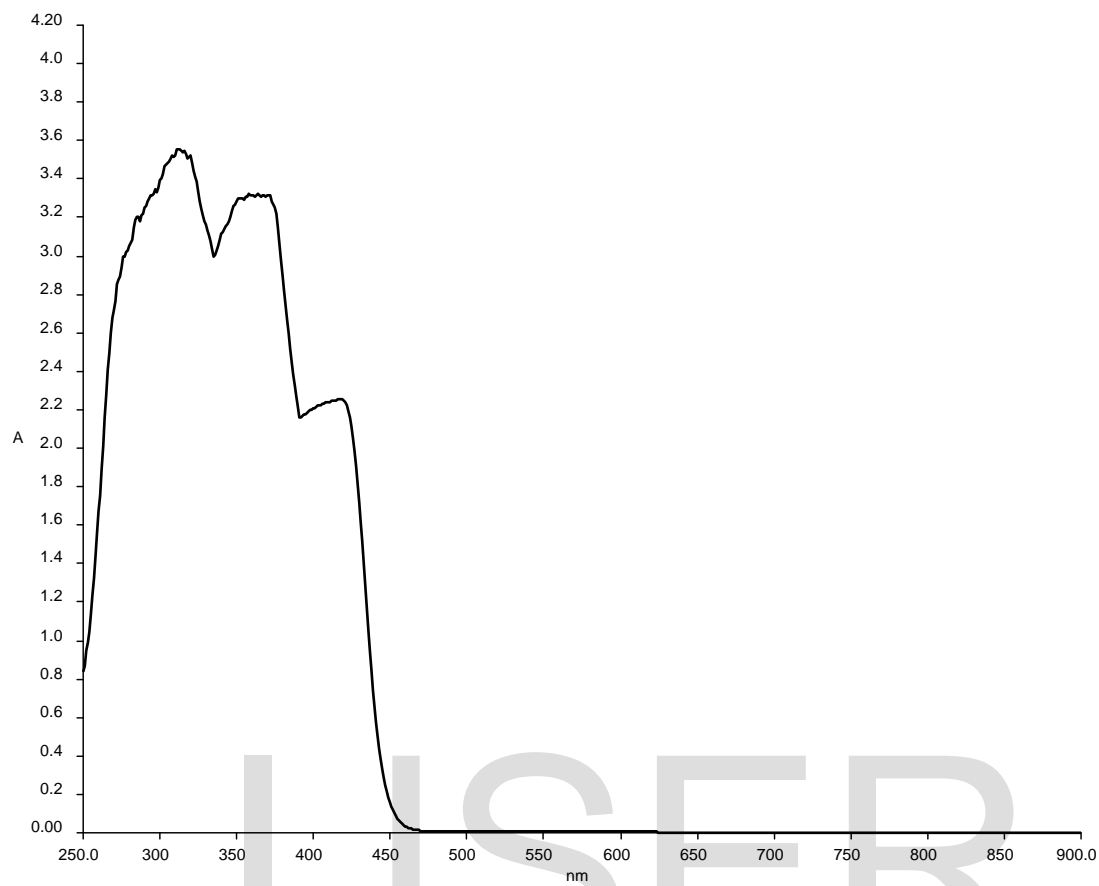


Fig. 10: Absorption spectrum of the ligand (HL)



Fig. 11: Absorption spectrum of Manganese(II) complex

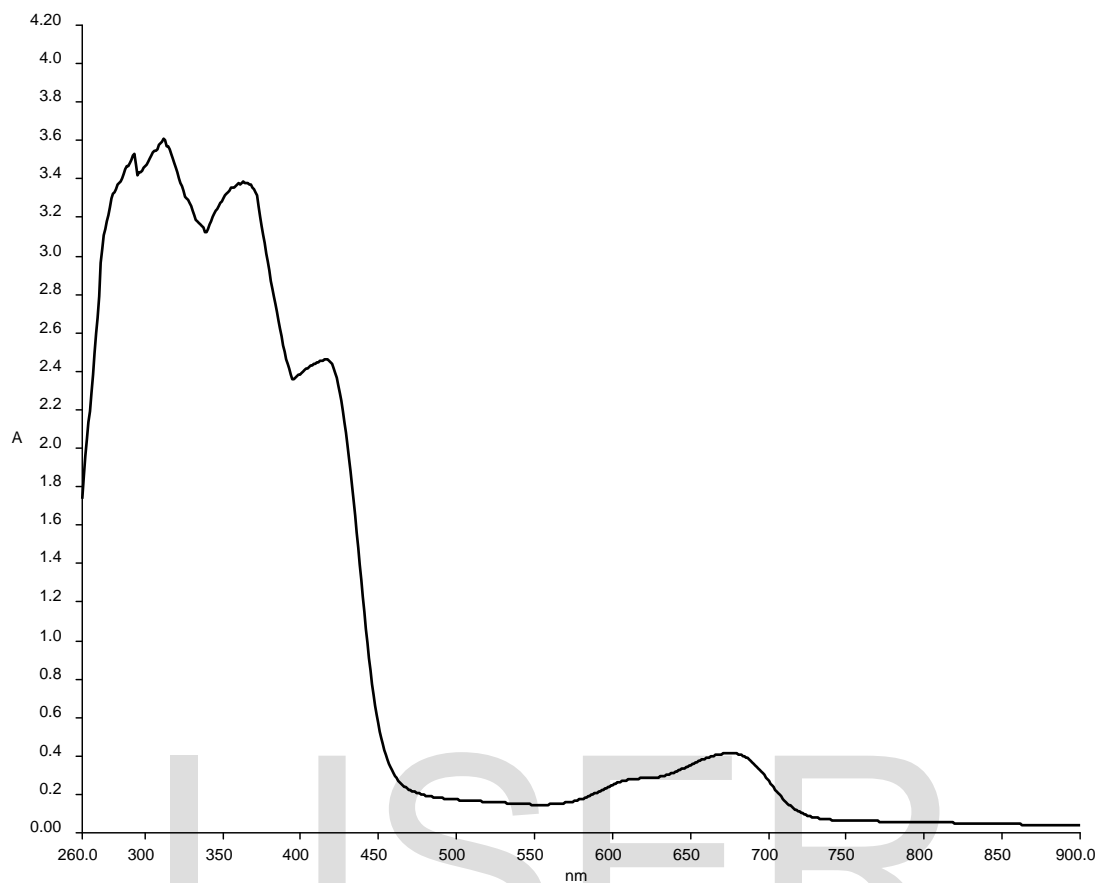


Fig.12. Absorption spectrum of Cobalt(II) complex



Fig. 13 Absorption spectrum of Zinc(II) complex

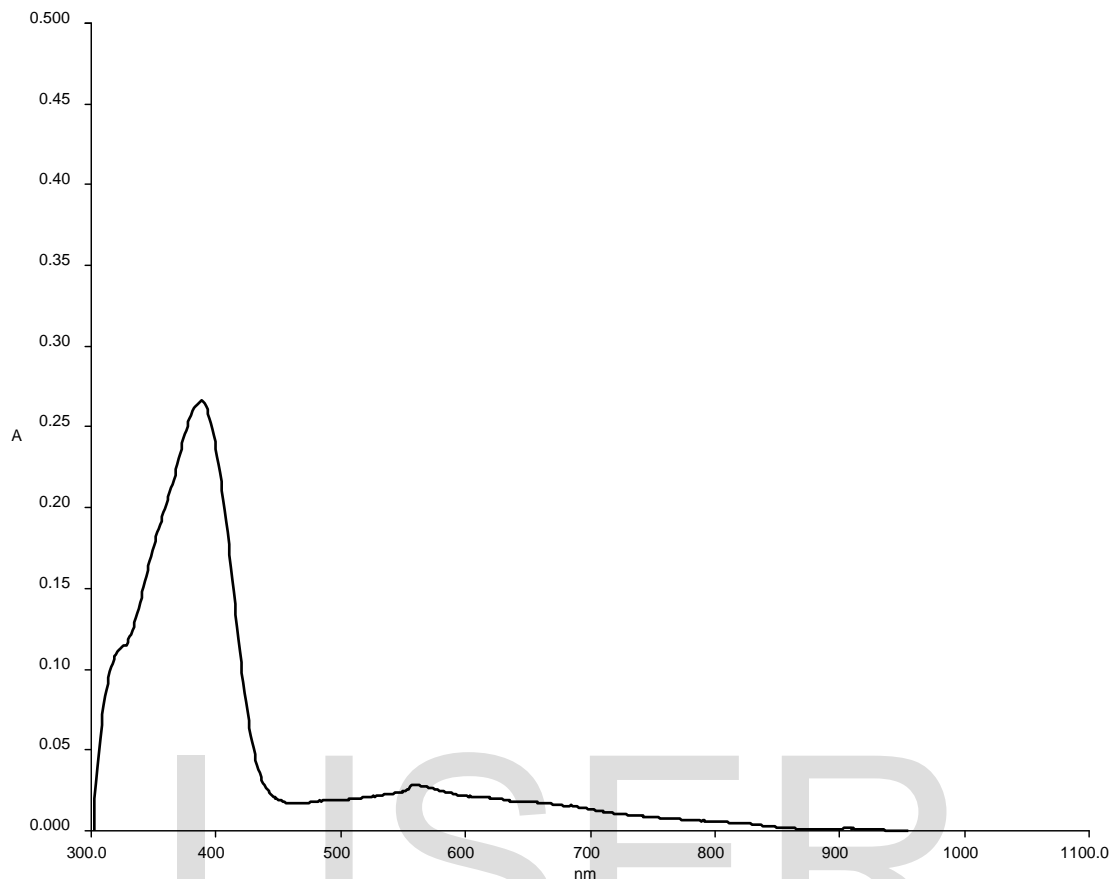


Fig. 14 Absorption spectrum of Cadmium (II) complex

Table 2: UV-Visible Spectral Data of the ligand and the complexes:

Ligand/Complex	$\sigma \rightarrow \sigma^*$ Transition λ_{\max} (nm)	$\pi \rightarrow \pi^*$ Transition λ_{\max} (nm)	$n \rightarrow \pi^*$ Transition λ_{\max} (nm)	$d \rightarrow d$ Transition λ_{\max} (nm)
HL	311.17	364.04	417.81	-
Manganese(II) Complex	279.89	311.19	367.71	432.62
Cobalt(II) Complex	293.29	363.03	416.35	-
Zinc(II) Complex	279.07	310.69	378.10	-
Cadmium(II) Complex	-	335.45	388.62	558.18

4. CONCLUSION

A Schiff Base ligand (HL) has been synthesized from vanillin and 4-aminophenol by condensation reaction. The formation of the ligand is confirmed by the IR spectrum which shows the vibration of the azomethine group (C=N) at 1658 cm^{-1} . Four metal complexes of Mn(II) Co(II), Zn(II) and Cd(II) have been synthesized and studied using the basic spectral techniques like UV-Visible spectroscopy and IR spectroscopy. From the results, it has been found that the ligand acts as a bidentate ligand, coordinating with the metal through the azomethine nitrogen and the phenolic oxygen.

Further studies should be carried out to analyze the complexes' antimicrobial activity and other biological applications.

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