
Research Article

Theme- New horizons in chemical sciences.

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Synthesis, Spectral and Antibacterial Studies of Some Transition Metal Complexes Derived from Schiff Base Ligand.

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ABSTRACT

N-N bis (salicylidene) ethylene-1, 2-diamine (salen) Ligand derived from the 2:1 molar condensation of Salicylaldehyde and ethylenediamine by simple stirring method and characterized by elemental analysis, FT-IR, ¹H NMR analysis. The transition metal complexes of salen have been characterized by UV-visible FT-IR, TGA-DTA. Ligand and their transition metal complexes were screened for antibacterial activity against *Escherichia coli*, *pseudomonas aeruginosa* and *Bacillus spp.*

KEYWORDS

Salicylaldehyde, Schiff bases, N-N bis (salicylidene) ethylene-1, 2-diamine (salen), Metal Complexes, Spectral Studies, Biological studies.

1. INTRODUCTION

Schiff base complexes have remained an important and popular area of research due to their simple synthesis, versatility and diverse range of applications [1]. Metal complexes of Schiff base ligands possess a variety of applications in the biological, analytical, clinical and industrial areas. In recent times, transition metal complexes of Schiff base ligands have gained considerable attention, not only due to their spectroscopic properties and applications but also due to their remarkable antifungal, antibacterial and antitumor activities [2-7]. Due to presence of the imine group, the electron cloud of the aromatic ring and electro negative nitrogen, oxygen and Sulphur atoms are in the Schiff's base molecules, these compound effectively prevent corrosion of mild steel, copper, Aluminum, zinc in acidic medium [8]. Transition metal complexes with salen ligands are used in catalytic reactions. Such salen complexes are used to catalyze the peroxidation reaction of olefins. For example, Mn^{2+} salen complex has been used for chiral peroxidation [9-11]. In view of these facts, reaction of the transition metal salts and Schiff bas ligands has been carried out and structure of the resulting complex was investigated using spectroscopic techniques and Thermal analysis. The results of this study are reported in this paper.

2. MATERIALS AND METHODS

All chemicals used included Metal salts like $(CH_3COO)_2Mn \cdot 4H_2O$, $(CH_3COO)_2 Co \cdot 6H_2O$, $(CH_3COO)_2$, $(CH_3COO)_2Cu \cdot 2H_2O$ and $(CH_3COO)_2Zn \cdot 2H_2O$ were high AR grade. Salicylaldehyde and ethylenediamine was supplied by Sigma Aldrich. IR spectra were recorded on Perkin-Elmer FT-IR Spectrophotometer in range $4000-400\text{ cm}^{-1}$. IR spectra of metal complexes were recorded in KBr at $4000-400\text{ cm}^{-1}$ at Deogiri College, Aurangabad. Electronic spectral studies were carried out using a Shimadzu UV-2101 spectrophotometer in the range 200-900 nm at Crystal Growth Laboratory Department of Physics, Milliya College, Beed. 1H NMR spectra were obtained on a Perkin-Elmer 300 MHz spectrophotometer using TMS as internal standard in $CDCl_3$ as the solvent.

2.1. Preparation of *N-N bis (salicylidene)ethylene-1,2-diamine (salen)* by green Approach

Salicylaldehyde was mixed with Ethylene-diamine drop wise 2:1 molar ratio in 100 ml beaker. The reaction mixture stirred with glass rod for about 2 min without solvent. The shiny yellow precipitate was obtained and washed with two to three times with absolute alcohol and finally dried under vacuum. The reaction monitored by Thin Layer Chromatography. (Yield 60 %)

Scheme 1. Synthesis of the Schiff Base ligands.

2.2. Preparation of transition metal complexes

Ethanol solution of corresponding metal salt was mixed to a hot ethanolic solution of the Schiff base ligands with stoichiometric proportion (1:1 mole). The reaction mixture was refluxed with stirring for about 3–4 hrs. On cooling a coloured complex precipitated out, which was filtered washed with cold ethanol and dried in vacuum (yield 54–64%) [12].



3. RESULTS AND DISCUSSION

All the complexes are having different colours, non-hygroscopic solids. They are soluble in DMSO, slightly soluble in DMF and insoluble in ethanol and methanol. Physical characterization and analytical data of ligand and its metal complexes are shown in (Table 1).

3.1. ¹H NMR spectra of Ligand

¹H NMR (CDCl₃): δ=4.13 (s, 4H, –CH₂-CH₂-), 6.76–7.45 (m, 8H, Ar–H), 8.11 (s, 2H, N=C–H), 13.2(s, 2H, Ar-OH) [13]. NMR spectrum of Ligand is shown in fig. 1

3.2. Infrared spectra

The Schiff base ligands show a strong IR band in the 1613-1630 cm⁻¹ region characteristic of azomethine absorption (CH=N). This band shifted to lower frequencies (15-20 cm⁻¹) and appeared at 1595- 1600 cm⁻¹ in the metal complexes, indicating coordination of the nitrogen atom of Schiff base to the metal. If the Schiff bases coordinated via the nitrogen atom, a reduction in the >(C=N) frequency due to a lowering of electron density is to be expected [13]. The band in the 510-550 cm⁻¹ and 410-440 cm⁻¹ can be assigned to the stretching modes of the metal to ligands bonds, ν (M-O) and ν (M-N) respectively [14]. Thus, the IR spectra give clear

evidence that bonding of the ligand to the metal ion can occur through nitrogen and oxygen atoms and that the ligands act in a tetradentate donor. Results are as shown in (Table 2).

3.3. Electronic absorption spectra

Electronic spectra of the Schiff base and metal complexes were taken in DMSO (10^{-3} molar) in the range 50000-11111 cm^{-1} . The UV-Visible spectra of the free ligand in ethanol appeared a high, intense absorption bands at 32894 (304) and 26109 (383) $\text{cm}^{-1}(\text{nm})$. These bands may be attributed to $\pi-\pi^*$ and $n-\pi^*$ transitions respectively. The UV-Visible spectra of the complexes displayed absorptions at 301-334 nm assigned for ligand field. Results are as shown in (Table 3).

3.4. Thermal analysis

The simultaneous TGA analysis of metal complexes was studied from ambient temperature to 700 °C in nitrogen. The Ni(II), Cu(II) and Fe(II) complexes of ligand were chosen for thermal study. Thermogravimetric analysis shows that the transition metal complexes of ligand exhibit high thermal stability. The lattice water is removed in the temperature range of 55–110 °C [15] and the coordinate water molecules are removed in the 120–360 °C range [12]. Thermogravimetric data of the Ni(II), Cu(II) and Fe(II) complexes are as shown in (Table 4). TGA-DTA Spectrum of Cu(II) complex is shown in fig.2.

3.5. Antibacterial activities

The antibacterial activity of ligand and its metal complexes were evaluated against bacteria such as *Escherichia coli*, *pseudomonas aeruginosa* and *Bacillus spp.* by paper disc plate method [16]. Sterile (10 mm) diameter Whatmann No. 42 paper discs were soaked in 100 ppm concentrations of the ligand/complexes in DMSO dried and then placed on the lawn culture of nutrient agar plates [17]. The plates were then incubated for 24 h at 34 °C and the inhibition zone around each disc was measured. The results obtained were compared with known antibiotics, Chloramphenicol. Three replicates were taken and average values are given in (Table 5). All complexes show moderate antibacterial activity as compared to known antibiotics, Chloramphenicol. From Tables 5, it is clear that the inhibition by metal chelates is higher than that of ligand and the results are in good agreement with previous findings with respect to comparative activity of free ligand and its complexes [18].

4. CONCLUSION

Based on analytical, infrared, electronic spectral data and TGA-DTA all these complexes exhibit coordination number Six. Biological studies of these complexes reveal that these complexes show better activity compared to their respective ligands and moderate activity compared to known antibiotics, Chloramphenicol. The FTIR spectral data suggest that the ligand behaves as a tetradentate ligand with N_2O_2 donor atoms towards central metal ion. Thermal study reveals thermal stability of complexes.

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Table 1. Physical characterization and analytical data of ligand and its metal complexes.

Compound/ complex	M.W.	M.P. °C	Colour	Yield %	Elemental Analysis % found (Cal.)			
					C	H	N	M
Ligands	268.31	121	Shiny Yellow	90.11	71.15 (71.64)	5.98 (5.97)	10.26 (10.44)	-----
[Fe(salen)2H ₂ O	358.16	>250	Reddish Brown	62.32	53.68 (53.65)	5.00 (5.06)	7.40 (7.82)	16.07 (16.38)
[Cu (salen)]	329.85	>250	Green	61.01	57.21 (58.26)	4.51 (4.27)	8.32 (8.49)	18.63 (19.26)
[Ni (salen)]	325	200	Brown	63.10	57.16 (59.13)	4.27 (4.34)	8.45 (8.62)	19.30 (18.05)
[Zn(salen)]	331.71	>250	Pale Yellow	54.74	56.47 (57.93)	4.22 (4.25)	7.14 (8.44)	17.21 (17.69)

Table 2. FT-IR spectra of the ligand (L) and its Metal complexes (cm⁻¹).

Compound	$\nu(\text{C-H})$	$\nu(\text{HC=N})$ azomethine	$\nu(\text{C=C})$ aromatic	M-N	M-O
Ligands	3027	1630	1481	-----	----
[Fe(salen)2H ₂ O	3011	1610	1467	498	515
[Cu (salen)]	3008	1608	1470	501	520
[Ni (salen)]	3013	1617	1462	491	517
[Zn(salen)2H ₂ O	2997	1619	1468	490	520

Table 3. Electronic absorption Spectral data of metal complexes.

Compound	$\pi-\pi^*(\text{nm})$	$n-\pi^*(\text{nm})$
[Fe(salen)2H ₂ O	223	292
[Cu (salen)]	230	289
[Ni (salen)]	230	280
[Zn(salen)2H ₂ O	245	296

Table 4. Thermogravimetric data of the Fe(II), Cu(II) and Ni(II) of salen Ligand.

Complexes	Temp. range(°C)	Weight loss (%)		Explanations
		Observed	Calculated	
[Fe(salen)2H ₂ O]	50-110	00	00	Absence of lattice water molecules.
	110-280	9.07	10.11	Two coordinated water molecules are lost.
	280-520	74.55	75.10	Ligand is lost and final residue FeO
[Cu (salen)]	50-310	00	00	Absence of lattice and coordinated water molecules
	310-600	83.07	82.39	Ligand is lost and final residue CuO
[Ni (salen)]	50-340	00	00	Absence of lattice and coordinated water molecules
	340-550	76.55	80.90	Ligand is lost and final residue NiO

Table 5. Antibacterial activity of ligand L and their metal complexes.

Ligand/complexes	Diameter of inhibition zone (mm)		
	Bacillus spp.	E. coli	P. aeruginosa
L	9	12	10
[Fe(salen)2H ₂ O]	14	14	13
[Cu (salen)]	13	16	15
[Ni (salen)]	12	14	16
[Zn(salen)2H ₂ O]	10	16	15
Chloramphenicol (Reference)	23	20	22
DMSO	6	7	6

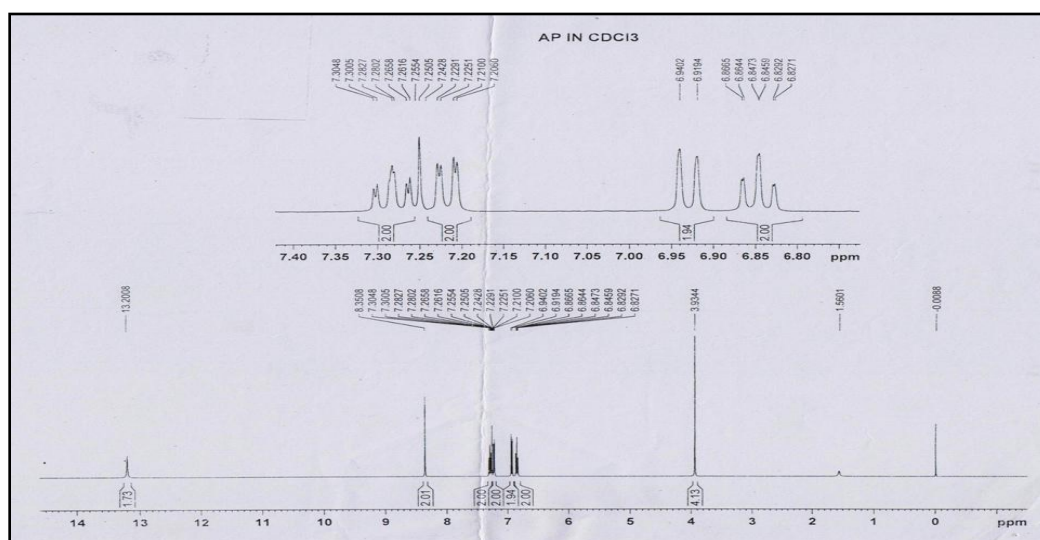


Fig. 1. ¹H Nuclear magnetic resonance spectrum of ligand.

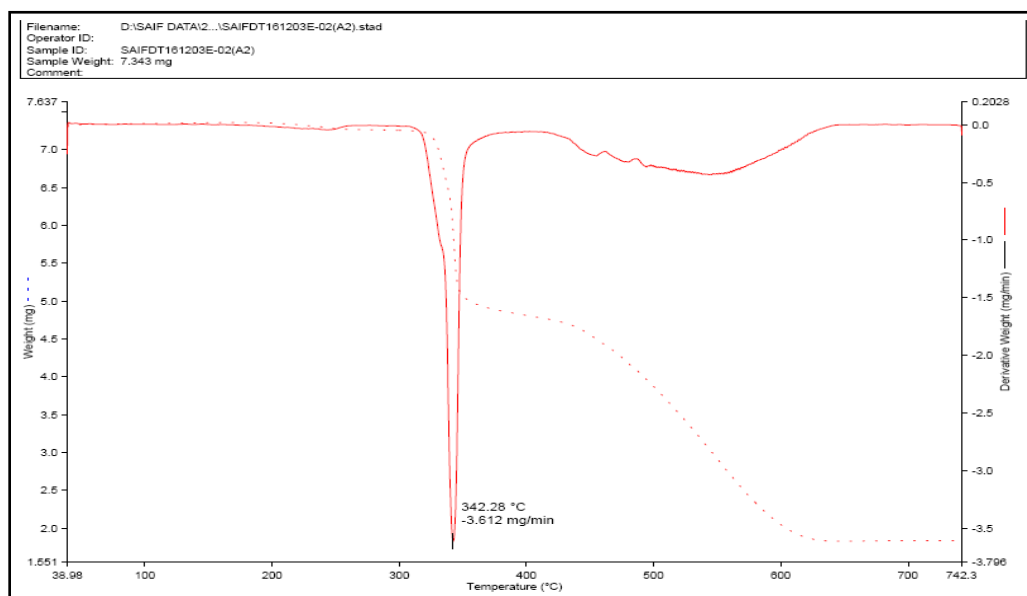


Fig. 2. TGA-DTA Spectrum of Cu(II) complex.