



Studies on Transition Metal Complexes of Th(IV), La(III) and Ce(III) with Bidentate Ligands.

M. A. Sakhare*, S. V. Thakur¹, O.S.Chavan², L.S.Gadekar³

*Department of Chemistry, Balbhim College, Beed (M.S.), India.

¹Department of Chemistry, Milliya college, Beed (M.S.), India

²Department of Chemistry, B.R.Barwale College, Jaha (M.S.), India

³Department of Chemistry, P.V.P.College, Patoda (M.S.), India

E-mail: sakharema.chem@gmail.com

ABSTRACT

The Schiff base bidentate ligand were prepared by condensation of salicylaldehyde and 2-amino phenol in 1:1 molar ratio and its complexes of Th(IV), La(III) and Ce(III) has synthesized and characterized by elemental analysis, FT-IR, ¹H NMR spectra and screened for antibacterial activity. From the micro analytical data, the stoichiometry of the complexes has been found to be 2:1. The Ligand and their metal complexes were screened for antibacterial activity against *Staphylococcus aureus* and *Escherichia coli*.

Keywords: Bidentate ligand complexes, FT-IR, Antibacterial activity etc.

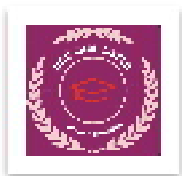
1. INTRODUCTION

Schiff base complexes play a major role in the development of coordination chemistry [1]. Because they have antimicrobial, anticancer, analgesic, anti-inflammatory, antifertility, and herbicidal applications [2,3]. Also they have more importance in the field of catalysis, agriculture, analytical, polymer sciences, food and dyes industry and antiseptic agents [4-7]. Some of them have been used as complexing agent [8-9] and powerful corrosion inhibitors [10]

In view of these facts, the present investigation deals with synthesis and characterization of complexes of Th(IV), La(III) and Ce(III) with Schiff base ligand (L) derived from salicylaldehyde and 2- amino phenol. Structure of the resulting complex was investigated using spectroscopic techniques. The results of this study are reported in this paper.

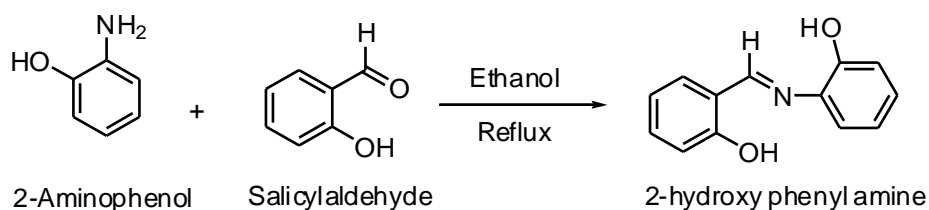
2. MATERIALS AND METHODS

All the chemicals used for experimental work were of AR-grade. Purity of synthetic ligands was checked by TLC. The C,H and N were determined on Elementar Vario EL III analyzer. FTIR spectra were recorded on Spectrum RX-I spectrometer using KBr pellets. ¹H NMR spectra of ligand were measured in CDCl₃ +DMSO using TMS as internal standard.



2.1 Synthesis of Ligand (L)

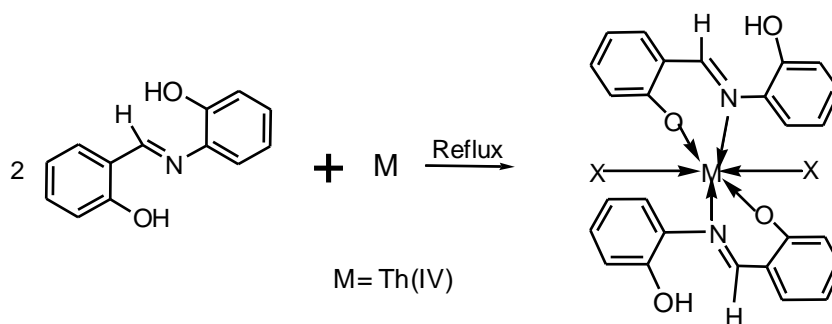
Salicylaldehyde (0.2 mm) and 2-amino phenol (0.1mm) was mixed in 100 ml Round Bottom Flask and reaction mixture was refluxed for 4-5 Hrs. On cooling, a solid yellow precipitate appeared, which was filtered, washed with cold EtOH. The product was dried at room temperature and recrystallized with ethanol. The purity of Schiff Base checked by TLC.[11]



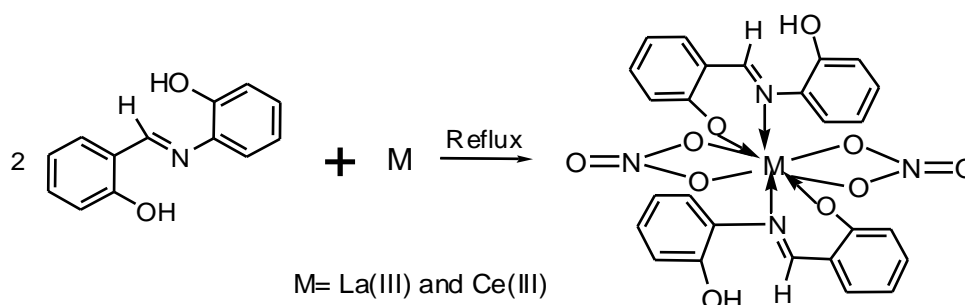
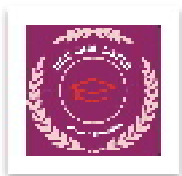
Scheme 1 Synthesis of Ligand.

2.2. Preparation of metal complexes:-

The Schiff's base metal complexes were synthesized by mixing the Schiff's base (0.2 mm) in hot ethanolic solution, with hot ethanolic solution of (0.1 mm) metal salt. The reaction mixture was refluxed for 3-4 hours. On cooling, a solid colored precipitate appeared, which was filtered, washed with cold EtOH.[11]



Scheme 2 Synthesis of Th(IV) complexes.



Scheme 3 Synthesis of La(III) and Ce(III) complexes

3. RESULTS AND DISCUSSION

Physical characteristics, micro analytical data of ligand and metal complexes are given in Table 1. The analytical data of complexes reveal 2:1 molar ratio. The general formula for Th(IV) complexes is $[M L_2 X_2]$. Where X = Cl and the general formula for La(III) and Ce(III) complexes is $[M L_2 X_2] \cdot X \cdot H_2O$ Where X = NO_3 . The presence of water molecules was confirmed FT-IR spectroscopy.

3.1 1H NMR spectral data of Ligand,

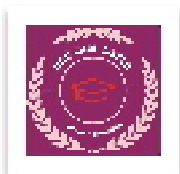
1H NMR ($CDCl_3$ -DMSO) of Ligand L : 6.70–8.10 (m, 8H, Ar-H), 8.5 (s, 1H, H-C=N), 11.5 (s, 2H, Ar-OH).

3.2 Physical parameters of the ligands and Metal complexes.

The prepared ligand is crystalline yellow, it is soluble in common organic solvents but insoluble in water. The Th(IV), La(III) and Ce(III) complexes of schiff base prepared are coloured and their decomposition temperature was more than 300 $^{\circ}C$. These high decomposition temperatures, revealed the stability of the complex compounds.

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

| Ligand/complexes | F.W. | M.P. ($^{\circ}C$) | Colour | %Yield | % Found (Calcd.) | | | |
|----------------------|------|-------------------------|--------|--------|------------------|----------------|----------------|-------|
| | | | | | C | H | N | M |
| $[C_{13}H_{11}NO_2]$ | 184 | 138 | Orange | 50.27 | 84.40 (84.78) | 6.05 (5.97) | 7.65 (7.60) | ----- |



| | | | | | | | | |
|---|-----|------|--------|-------|------------------|----------------|----------------|------------------|
| [Th(IV) L ₂ (Cl) ₂] | 727 | >300 | Yellow | 46.10 | 48.79 (48.91) | 2.86 (2.75) | 3.89 (3.85) | 31.78 (31.91) |
| [La(III) L ₂ (NO ₃) ₂] NO ₃ 2H ₂ O | 785 | >300 | Yellow | 61.23 | 39.67 (39.74) | 3.00 (3.05) | 9.05 (8.91) | 17.85 (17.70) |
| [Ce(III) L ₂ (NO ₃) ₂] NO ₃ 2H ₂ O | 786 | >300 | Brown | 49.58 | 39.60 (39.69) | 3.00 (3.05) | 8.96 (8.90) | 17.92 (17.81) |

3.3 FT-IR spectra

The IR spectrum of the ligand (L) shows a ν (C=N) and ν (C-O) peak at 1631 and 1275 cm⁻¹ respectively. The IR spectra of Th(IV), La(III) and Ce(III) complexes, the medium to strong bands appeared in the region 1604-1608 cm⁻¹ are assigned to ν (C=N) stretching vibration modes. A downward shift of the band by 20 to 30 cm⁻¹ in complexes indicates that the ν (C=N) group of the Ligand is coordinated to the metal ion via its azomethine nitrogen [12]. The ν (C-O) stretching vibration shows downward shift in complexes indicates that the ν (C-O) group of the Ligand is coordinated to the metal ion. The ν (OH) vibration of the phenolic proton appears as a broad band in the region 3200-3600 cm⁻¹ probably due to the overlapping of the symmetric and antisymmetric ν (OH) stretching vibrations of lattice water [13]. The bands in the 464–486 cm⁻¹ and 597-601 cm⁻¹ regions may be assigned to ν (M-N) and ν (M-O) stretching vibrations [14]

The La(III) and Ce(III) complexes exhibit absorption bands at ~1465 & 1320 cm⁻¹ due to the ν (N=O) (ν_1) and ν_a (NO₂) (ν_5) vibrations, respectively of the coordinated nitrate ion. The ν_s (NO₂) vibration (ν_2) appearing at ~1030 cm⁻¹ is characteristic of a bidentate chelating nitrate. Nitrate ion has a strong preference for bidentate chelation with the lanthanide (III) ions [15, 16]. The presence of strong and sharp band at 1384 cm⁻¹ is characteristic of ionic nitrate [17] (Table 2).

Table 2. FTIR spectral data of the ligand (L) and its Metal complexes (cm⁻¹).

| Ligand/Complexes | (OH) | (C=N) | (C-O) | (M-N) | (M-O) | Ionic nitrate | Coordinated nitrate |
|---|------|-------|-------|-------|-------|---------------|---------------------|
| [C ₁₃ H ₁₁ NO ₂] | 3407 | 1631 | 1275 | ---- | ---- | ---- | |
| [Th(IV) L ₂ (Cl) ₂] | 3368 | 1607 | 1256 | 486 | 597 | ---- | |
| [La(III) L ₂ (NO ₃) ₂] NO ₃ 2H ₂ O | 3408 | 1608 | 1256 | 486 | 601 | 1388 | 1471,1296,1038 |
| [Ce(III) L ₂ (NO ₃) ₂] NO ₃ 2H ₂ O | 3408 | 1604 | 1254 | 464 | 601 | 1382 | 1468,1296,1032 |



3.4 Antibacterial Studies :-

The antibacterial activity of ligand and its metal complexes were evaluated in vitro against bacteria such as gram +ve bacteria (*Bacillus spp.*) and gram -ve bacteria (*E. coli*) by paper disc plate method [16]. Sterile (10 mm) diameter Whatmann No. 42 paper discs were soaked in different concentrations of the ligand/complexes (1000 ppm) in DMF dried and then placed on the lawn culture of nutrient agar plates. The plates were then incubated for 24 h at 37 °C and the inhibition zone around each disc was measured. The results obtained were compared with known antibiotics, Ciprofloxin. Three replicates were taken and average values are given in (Table 3).

From Tables 3, it is clear that results are in good agreement with previous findings with respect to comparative activity of free ligand and its complexes [17-18]. Such enhanced activity of metal chelates is due to the lipophilic nature of the metal ions in complexes [19]. The increase in activity with concentration is due to the effect of metal ions on the normal process. The action of compounds may involve the formation of hydrogen bond with the active center of cell constituents, resulting in interference with the normal cell process [20].

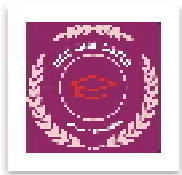
From Tables 3, reveal that the complexes shows moderate activity against *E. coli* and better activity against *Bacillus spp.* compared to their respective ligands

Table 3. Antibacterial activity of ligand and its metal complexes

| Ligand/complexes | Inhibition zone diameter (mm) at 1000 ppm | |
|---|--|----------------|
| | <i>Bacillus spp.</i> | <i>E. coli</i> |
| Ciprofloxin | 16 | 20 |
| [C ₁₃ H ₁₁ NO ₂] | 10 | 09 |
| [Th(IV) L ₂ (Cl) ₂] | 14 | 13 |
| [La(III) L ₂ (NO ₃) ₂] NO ₃ 2H ₂ O | 11 | 12 |
| [Ce(III) L ₂ (NO ₃) ₂] NO ₃ 2H ₂ O | 12 | 13 |

4. CONCLUSION

The synthesized Schiff's base was characterized on the basis of Melting point, TLC, FT-IR. The downward shift of the band in complexes indicates that the ν (C=N) and ν (O-H) group of the Ligand are coordinated to the metal ion via its azomethine nitrogen and phenolic OH. Biological studies of these complexes reveal that these complexes shows moderate activity against *E. coli* and

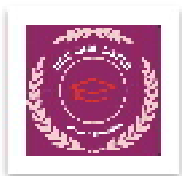


better activity against *Bacillus* spp. compared to their respective ligands. All metal complexes are coloured and thermally stable solid.

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