

# Synthesis and Characterization of Neodymium (III) and Praseodymium (III) Complexes Containing Bis (Salicylaldehyde) Orthophenylenediamine as Ligand

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**Abstract:-** The solid complexes of Nd(III) and Pr(III) were synthesized from a tetradentate Schiff base, bis(salicylaldehyde) orthophenylenediamine. The schiff base ligand was prepared from condensation of o-phenylenediamine (1, 2-diamine benzene) with salicylaldehyde. The prepared Schiff base reacts with Neodymium (III) to give a complex with stoichiometric ratio of (1:2) (metal: ligand) and the Praseodymium reacts to give a complex with stoichiometric ratio (1:1) (metal : ligand). The complexes have been characterized by elemental analysis, molar conductance, electronic absorption, infrared, HNMR and  $C^{13}$  NMR spectral studies. Possible structures were suggested for Nd(BSOPD)<sub>2</sub> and PrBSOPD which were based on the results.

**Keywords:** Schiff Base, Metal Complexes, Stoichiometry

## I. INTRODUCTION

Schiff bases derived from the aromatic amines and aldehydes have a wide variety and are important class of ligands in coordination chemistry; and find extensive applications in different fields, e.g., inorganic, biological and analytical chemistry<sup>1</sup>. Schiff bases play important roles in coordination chemistry as they easily form stable complexes with most transition metal ions<sup>2</sup>. Imines are formed when either ammonia or primary amine reacts with a ketone or an aldehyde under proper conditions. Schiff base complexes find important position in coordination chemistry and schiff base complex with transition metals are used in organic synthesis, analytical reagents, and catalysts and in medicine<sup>3, 4</sup>. A large number of Schiff base complexes have been studied because of their important properties which include catalytic activity<sup>5,6</sup> and complex formation towards metal ions<sup>7,8</sup> corrosion inhibition and transfer of amino groups<sup>9</sup>. According to literature review on the Schiff bases<sup>10-11</sup> much of the work done are based on transition metal complexes. However in this research work, synthesis and characterization of Neodymium (III) and Praseodymium (III) complexes containing Bis (salicylaldehyde) orthophenylenediamine as ligand were investigated.

## II. MATERIALS AND METHODS

All the reagents and solvents used were analytical grade and were used as supplied unless otherwise stated. The melting points of the ligand and complexes were determined using Electrothermal point apparatus. The IR spectra were recorded using a KBr disc technique MB 3000 spectrophotometer

(SHIMADZU) in the range of 400-4000  $cm^{-1}$ . The electronic spectra in the range 200-800 nm were obtained in DMF on a Shimadzu spectrophotometer. The Conductivity of the ligands and the complexes were determined in DMF using WTW model; LF 90 conductivity meter in the units of  $\mu S cm^{-1}$ . The solubility of the ligand and the complexes in the various solvents were determined at room temperature.

*Synthesis of Schiff base-Bis (salicylaldehyde) orthophenylenediamine-BSOPD*

The Schiff based formed from 1, 2 diamine benzene and salicylaldehyde was prepared according to the method by Dharmarajan and Gruber<sup>12-13</sup> with some modifications.

5.405g (0.05M) of 1, 2 diamine was dissolved in 50.0  $cm^3$  of absolute ethanol. 2.0  $cm^3$  of 0.1M NaOH was added slowly followed by 10.45 $cm^3$  (12.22g) of 0.1M salicylaldehyde. The final reaction mixture, yellow in colour was refluxed for 2hours at 55-60°C. The precipitate formed was allowed to cool to room temperature. The clear supernatant was discarded, the precipitate washed with cold ethanol in batch, using 50 $cm^3$  of the ethanol. The washed precipitate was recrystallized in ethanol, dried in the oven at a temperature of 50°C. The product, having orange yellow colour was then dried in dessicator over calcium chloride.

*Synthesis of Complexes [Nd (BSOPD)<sub>2</sub>(NO<sub>3</sub>) and [Pr<sub>4</sub>(BSOPD)<sub>4</sub>.12(NO<sub>3</sub>)<sub>2</sub>4(H<sub>2</sub>O)*

The complexes of Nd(III) and Pr(III) were prepared by mixing requisite amount of the ligand with the metal salt to form a 1:2 (M:L) metal ligand ratio for Nd(III) and 1:1 for Pr(III). The procedure involved adding an ethanolic solution (10 $cm^3$ ) of the metal salt dropwisely to hot ethanolic solution of the ligand BSOPD (30 $cm^3$ ). The resulting solution was refluxed for 4-6 h with an observable colour change<sup>15</sup>. The solution was reduced to 15 $cm^3$ . The resulting solution was allowed to stand in an ice bath over night; the resulting solid complex was filtered, washed thoroughly with successive portions of ethanol followed by diethyl ether. The complex was dried in dessicator over calcium chloride.

*Determination of Stoichiometry of Metal to ligand Ratio:*

This was done using Job's method.

### III. RESULTS AND DISCUSSION

The physical characteristics, micro analytical and molar conductivity data of the ligand and its Nd(III) and Pr(III) complexes are given in Table 1. The synthesized complexes are stable at room temperature in the solid state. The metal

complexes are soluble in DMF and DMSO and insoluble in common organic solvents. The observed values of molar conductivity of the complexes show that they are electrolytes. The complexes were characterized using the following physical studies.

**Table 1:** Physical and Analytical data of Pr(III) and Nd(III) Complexes

Compound	F.W	Yield %	M:L ratio	MP decom Temp oC	Colour	Conductivity (uScm <sup>-1</sup> )	C% calc. (found)	H% calc. (found)	N% calc. (found)
BSOPD	316.36	77.34		158-160	orange yellow	44.25	75.93 (75.97)	5.10 (5.06)	8.85 (8.91)
Nd(BSOPD) <sub>2</sub> (NO <sub>3</sub> )	836.92	60.00	1:2	150-153	green	168	57.41 (57.91)	3.61 (4.35)	8.37 (8.84)
Pr <sub>4</sub> (BSOPD) <sub>3</sub> .12NO <sub>3</sub> .24H <sub>2</sub> O	2688.80	58.5	4:3	160-162	green	203	26.80 (27.30)	3.60 (3.15)	9.38 (9.99)

MP- Melting Point

#### Infrared Spectral studies

The infrared spectra of the prepared complexes are compared with those of the free ligand in order to determine the site of coordination that may be involved in chelation (Table 2). There are some guiding peaks that are expected to be involved in chelation. The presence of sharp bands at 3456.18 cm<sup>-1</sup> of the stretching vibrations of phenolic OH groups in the IR spectrum of the ligand indicates that the OH groups of the Schiff base is involved in intermolecular hydrogen bonds<sup>16</sup>. From the prepared complexes, the broad bands around 3342.38 for Nd(III) and 3490.90 for Pr(III) cm<sup>-1</sup> in the IR spectra are due to ν(OH) of water molecules. The presence of bands with different intensities in the IR spectrum of the Schiff base at 1191.92cm<sup>-1</sup> is due to C-OH stretching

vibration<sup>17</sup>. In the coordination of the Nd(III) through the phenolic hydroxyl group there is partial deprotonation of the phenolic OH of Nd(BSOPD)<sub>2</sub>.NO<sub>3</sub> and for the Pr<sub>4</sub>(BSOPD)<sub>3</sub>.12NO<sub>3</sub>.24H<sub>2</sub>O the coordination to the Pr(III) is without deprotonation<sup>17</sup>. The IR spectrum of the Schiff base BSOPD show strong C=N stretching band at 1616.23cm<sup>-1</sup>. In the complexes, the C=N stretch band has shifted to 1612.37cm<sup>-1</sup> in Nd(III) and 1637.44cm<sup>-1</sup> in Pr(III) metal ion, this may be attributed to coordination of the imine nitrogen with the metal ion<sup>18</sup>. The ligand coordination to the metal centres are substantiated by Ln-N bands appearing at 802.33 and 817.76cm<sup>-1</sup> for Nd(III) and Pr(III) respectively. Also formation of Ln-O bond is confirmed by the bands at 756.04 and 754.11cm<sup>-1</sup> for Nd-O and Pr-O, respectively. The Ln-Ln bond appears at 351.02cm<sup>-1</sup>

**Table 2:** IR Data of ligand and its Complexes

Peaks for ligand (cm <sup>-1</sup> )BSOPD	Peaks for Nd(III) (cm <sup>-1</sup> )	Peaks for Pr(III) (cm <sup>-1</sup> )	Assignment
3456.18s			ν(O-H) phenol
	3342.38br	3413.75br	ν(O-H) (hydrogen bonded as a result of lattice water)
3060.81m	3062.73w	3064.61w	ν(C-H) aromatic
2923.87m	2929.66w	2927.73w	Aromatic overtones
2854.44m	2852.51w	2856.37w	Aromatic combination bend
1616.23s	1612.37m	1637.44m	ν(C=N)
1483.15m	1458.08m	1458.08m	ν(C=C) of aromatic
1282.57s	1386.72m	1386.72m	ν(C-H) in plane aromatic
1191.92s			ν(C-OH) of phenol
	1153.35w	1134.06w	ν(C-O) of phenol
	1261.35w	1243.99w	ν(C-O) of phenol
910.35s	910.33w	916.12m	ν(C-H) out of plane C-H bending
831.26m	842.83m	838.97m	Coordinated water rocking frequency
	802.33w	817.76m	Ln-N
	756.04m	754.11m	Ln-O
		351.02s	Ln-Ln

S- strong; M- medium; br- broad; W-weak

*Electronic spectra*

The electronic spectra of the ligand and complexes are shown in Fig1. The electronic spectrum of the ligand BSOPD, shows the  $n-\pi^*$  transition at 333 nm and the  $\pi-\pi^*$  transition at 272 nm. The complexes show band in the region of  $n-\pi^*$  at 376 nm and  $\pi-\pi^*$  at 318 nm regions for Nd-BSOPD. The Pr-BSOPD shows  $n-\pi^*$  at 386 nm. The lanthanide (III) complex has no significant absorption in the visible region, this is due to the fact that the 4f orbitals are effectively shielded hence the electrons are not available for bonding<sup>19</sup>.

## IV. CONCLUSION

The Schiff base (BSOPD) was successfully prepared and used to synthesize new metal complexes of Nd(III) and Pr(III) and the complexes have been characterized by physical methods and spectroscopic techniques. Further studies are ongoing to determine the actual structures of the complexes and their potential applications.

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