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# Function of Substituents on Coordination Behaviour, Thermolysis and Ligand Crossover Reactions of Phosphine Oxides

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## Abstract

Some selected aminophosphine oxides (AmPOs) of the type OP(NMe<sub>2</sub>)<sub>3</sub>, OPPh(NMe<sub>2</sub>)<sub>2</sub>, OP(NC<sub>2</sub>H<sub>4</sub>O)<sub>3</sub>, OPPh(NC<sub>2</sub>H<sub>4</sub>O)<sub>2</sub> and their corresponding La(III) and Th(IV) complexes are synthesized and analyzed by FT-IR, <sup>1</sup>H-NMR, <sup>31</sup>P{<sup>1</sup>H}-NMR, elemental analysis and TGA data. The coordination behavior of AmPOs was compared with some of the known ligands that include trioctylphosphine oxide (TOPO), tributylphosphate (TBP) and diethylphosphite (DEP). Thermogravimetric analysis of these complexes showed a distinct decomposition trend either by a single step or multi-step elimination of ligand species, which are strongly dependent on the electronic and steric behaviour of substituents on P=O group and nature of metal. Phosphine oxide based La(III) and Th(IV) complexes undergo three unique intermolecular ligand exchange reactions at room temperature: relative competition among phosphine oxides to form a strong complex by exchanging the weaker ligand and complete ligand transfer from La(III) to Th(IV) metal centers. Ligand crossover is well controlled by priority rules and the trend follows as TOPO > TBP > DEP > AmPO > Ph<sub>3</sub>PO. This tendency closely agrees with the stability constants of metal complexes. On comparison, Th(IV) complexes showed slightly higher stability than La(III) analogues.

**Keywords:** aminophosphine oxide; synthesis; comparative study; ligand crossover reaction; coordination behavior; thermolysis

## Introduction

Pentavalent phosphine oxides (R<sub>3</sub>P=O) are known as reagents or precursors and their association in metal mediated catalytic reactions as dynamic ligands and in bioactivity studies for many years [1-3]. Apart from

this, phosphine oxides with active O-donor functionality were also reported as active ligands in the separation of actinides and lanthanides *e.g.* carbamoylmethylphosphine oxides (CMPOs) are being used in the TRUEX (transuranium extraction) process [4] through the formation of a six-membered chelate ring upon complexation [5]. In general, the extraction efficiency is dependent on the nature of substituents, which can greatly influence the performance of the ligand. When the *N*-substituents are phenyl groups, the resulting less basic carbonyl oxygen improve the extraction selectivity [6]. The basicity of some of the reported ligands with respect to extraction of uranium(VI) and thorium(IV) salts in nitric acid medium was in the following order: TOPO (tri-*n*-octylphosphine oxide) > TEHPO (tris(2-ethylhexyl)phosphine oxide) and HDPM (bis((di-*n*-hexylphosphinyl)methane) > EBDPM (bis[bis(2-ethylbutyl)phosphinyl]methane) [7]. There is a pressing demand to design the ligands with the desired properties for the effective separation of actinides and lanthanides from nuclear waste. In this perspective, it seemed a constructive exercise to compare the nature of AmPO ligands with some selected and known phosphine oxides in order to understand their coordination performance with some selected *f*-metals.

As our recent focus is on the exploration of chemistry of aminophosphine oxides (AmPOs) which are relatively new classes of ligands derived from very well known phosphine oxide family and offer fascinating opportunities [8-11], we have recently reported the synthesis and coordination behavior of AmPOs [12]. The present work describes the synthesis, thermolysis, coordination behavior and ligand crossover reactions of some selected phosphine oxides as given in Chart-1. We now present evidence for complete *intermolecular* ligand crossover among different metal complexes, further extending the flexible nature of these ligands to understand the degree of coordination strength.

(Chart-1 here)

## 2. Experimental Part

### 2.1. Instrumentation

$^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra were recorded on a Bruker DMX-400 spectrometer and all  $^1\text{H}$  chemical shifts were reported relative to the residual proton resonance in deuterated solvents (all at 298 K,  $\text{CDCl}_3$ ). Infrared spectra were recorded on a Shimadzu Affinity 1 FT-IR Spectrometer. Thermogravimetric analyses were carried out on a Perkin Elmer TGA-7 and Mettler Toledo SDTA851e from ambient to about 800 °C under air ( $50 \text{ mL min}^{-1}$ ) and at a heating rate of  $10.0^\circ\text{C min}^{-1}$ . Approximately 5 mg of the samples was used in the TG experiments. Heraeus CHNS rapid micro analyzer was used for elemental analysis.

## 2.2. Materials and methods

All manipulations were carried out under nitrogen atmosphere using Schlenk line techniques, unless otherwise stated. Commercially available solvents were distilled from Na metal/benzophenone ketyl before use. The phosphorus reagents (Merck and Sigma–Aldrich) including  $\text{POCl}_3$ ,  $\text{Ph}_2\text{POCl}$ ,  $\text{PhPOCl}_2$ , TOPO (trioctylphosphine oxide), TBP (tributylphosphate) and DEP (diethoxyphosphate) were used as received and morpholine (Merck) was purified by distillation over KOH [9]. Dimethylamine (40%) solution from Loba (India) was used as such without any further purification. Hydrated metal salts (Loba and Aldrich),  $[\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}]$  and  $[\text{La}(\text{NO}_3)_3 \cdot 7\text{H}_2\text{O}]$  were used as received. UV–vis absorption spectra were recorded with a UNICAM UV4-100 type double-beam spectrophotometer (ATI UNICAM, Cambridge, UK) controlled by a software VISION 3.4. Quartz cuvettes with path length of 1 cm were used.

## 2.3. Experimental

### 2.3.1. Preparation of Aminophosphine Oxides ( $\text{L}_1$ – $\text{L}_4$ )

Tris(morpholino)phosphine oxide ( $\text{L}_1$ ) and bis(morpholino)phenyl phosphine oxide ( $\text{L}_1$ ) were prepared by the literature methods [12,13].

*General procedure for the synthesis of bis(dimethylamino)phenylphosphine oxide ( $\text{L}_3$ ):* To the 40% aqueous solution of dimethylamine (13.33 g, 0.295 mol) was added dichlorophenylphosphine oxide (11.5 g, 0.059 mol) drop wise in ice cold condition for over 2h *via* dropping funnel using 50 mL of dichloromethane as solvent under  $\text{N}_2$  atm under constant stirring. Then the reaction mixture was brought to room temperature and was allowed to stir for 24h. As the products (AmPOs) are highly soluble in water, it is very difficult to extract them from water to organic solvents. In order to overcome this problem and to solubilize these AmPOs into the organic solvents like dichloromethane, the aqueous solution was treated with equal volume of  $\text{CH}_2\text{Cl}_2$  and 10 g of NaCl. The mixture was stirred for 30 min and the two layers were separated. The organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  (5 g) for 30 min. The product ( $\text{L}_3$ ) obtained as a colourless crystalline solid (6.0 g) Yield 60%. m.p. 135-37 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.62-2.63 (s, 12H, - $\text{NCH}_3$ ), 7.45- 7.77 (m, 5H, Ph);  $^{31}\text{P}\{^1\text{H}\}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  29.98. Anal. Calc. for  $\text{C}_{20}\text{H}_{22}\text{Cl}_2\text{N}_4\text{O}_2\text{Si}$ : C, 56.59; H, 8.07; N, 13.20. Found: C, 56.83; H, 8.57; N, 13.28%.

*Synthesis of tris(dimethylamino)phosphine oxide ( $\text{L}_4$ ):* To the solution of dimethylamine in THF (15.09 g, 0.334 mol) was added phosphorous oxychloride (7.66 g, 0.055 mol) drop wise under ice cold temperature for over 2h *via* dropping funnel using dicholoromethane (50 mL) as solvent under  $\text{N}_2$  atm. The work-up of

the reaction mixture was carried out as mentioned above. The product (**L**<sub>4</sub>) was obtained as yellow crystalline solid (3.5 g). Yield 70%. m.p. 122-24°C. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 2.66-2.67 (s, 18H, -NCH<sub>3</sub>); <sup>31</sup>P{<sup>1</sup>H}-NMR (CDCl<sub>3</sub>): δ 20.6. Anal. Calc. for C<sub>6</sub>H<sub>18</sub>N<sub>3</sub>OP: C, 40.21.45; H, 10.12; N, 23.45. Found: C, 40.26; H, 10.16; N, 23.48%. The pure compounds were isolated and characterized by various spectroscopic techniques (Table-1).

(Table-1 here)

**2.3.2. General Procedure for the preparation of metal complexes:** The following general procedure was used for the preparation of [Th(NO<sub>3</sub>)<sub>4</sub>(L<sub>3</sub>)<sub>2</sub>] complex and the same procedure was followed for the other metal complexes.

A finely powdered solid of Th(NO<sub>3</sub>)<sub>4</sub>.6H<sub>2</sub>O (0.56 g, 0.98 mmol) was added all at once to a stirred solution of L<sub>3</sub> (0.417g, 1.96 mmol) in solvent mixture of CHCl<sub>3</sub> (15mL) and the mixture was stirred for 24h to get the colorless crystalline solid. Yield: 0.82 g, 93%. IR (Nujol mull/cm<sup>-1</sup>): 970.19 (s) [P=O]. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, ppm): δ 7.42–7.79 (m, phenyl), 2.82 (m, CH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H}-NMR (D<sub>2</sub>O): δ -1.16 (s). Then the solid residue was washed with dichloromethane to obtain the pure product, Th(NO<sub>3</sub>)<sub>4</sub>(L<sub>3</sub>)<sub>2</sub>.

In a similar way, all the following complexes were prepared by taking the appropriate amounts as given below: LaCl<sub>3</sub>(L<sub>1</sub>)<sub>3</sub> [LaCl<sub>3</sub>.7H<sub>2</sub>O (0.5 g, 1.346 mmol) and L<sub>1</sub> (1.196 g, 4.039 mmol)], LaCl<sub>3</sub>(L<sub>2</sub>)<sub>3</sub> [LaCl<sub>3</sub>.7H<sub>2</sub>O (0.159 g, 0.43 mmol) and L<sub>2</sub> (0.393 g, 1.29 mmol)], LaCl<sub>3</sub>(L<sub>3</sub>)<sub>3</sub> [LaCl<sub>3</sub>.7H<sub>2</sub>O (0.5 g, 1.34 mmol) and L<sub>3</sub> (0.853 g, 4.02 mmol)], LaCl<sub>3</sub>(L<sub>4</sub>)<sub>3</sub> [LaCl<sub>3</sub>.7H<sub>2</sub>O (0.5 g, 1.34 mmol) and L<sub>4</sub> (0.724 g, 4.02 mmol)], LaCl<sub>3</sub>(L<sub>5</sub>)<sub>3</sub> [LaCl<sub>3</sub>.7H<sub>2</sub>O (0.082 g, 0.744 mmol) and L<sub>5</sub> (0.262 g, 2.232 mmol)], LaCl<sub>3</sub>(L<sub>6</sub>)<sub>3</sub> [La(NO<sub>3</sub>)<sub>3</sub>.7H<sub>2</sub>O (1.066 g, 2.84 mmol) and L<sub>6</sub> (2.29 g, 8.61mmol)], LaCl<sub>3</sub>(L<sub>7</sub>)<sub>3</sub> [La(NO<sub>3</sub>)<sub>3</sub>.7H<sub>2</sub>O ( 1.02g, 2.72 mmol) and L<sub>7</sub> (2.24 g, 8.07 mmol)], LaCl<sub>3</sub>(L<sub>8</sub>)<sub>3</sub> [La(NO<sub>3</sub>)<sub>3</sub>.7H<sub>2</sub>O (0.6133 g, 1.49 mmol) and L<sub>8</sub> (0.554 g, 4.47 mmol)], Th(NO<sub>3</sub>)<sub>4</sub>(L<sub>1</sub>)<sub>2</sub> [Th(NO<sub>3</sub>)<sub>4</sub>.5H<sub>2</sub>O (1.02 g, 1.78 mmol) and L<sub>1</sub> (1.03 g, 3.51 mmol)], Th(NO<sub>3</sub>)<sub>4</sub>(L<sub>2</sub>)<sub>2</sub> [Th(NO<sub>3</sub>)<sub>4</sub>.5H<sub>2</sub>O (0.26 g, 0.458 mmol) and L<sub>2</sub> (0.279 g, 0.916 mmol)], Th(NO<sub>3</sub>)<sub>4</sub>(L<sub>4</sub>)<sub>2</sub> [Th(NO<sub>3</sub>)<sub>4</sub>.5H<sub>2</sub>O (0.56 g, 0.98 mmol) and L<sub>4</sub> (0.35 g, 1.96 mmol)], Th(NO<sub>3</sub>)<sub>4</sub>(L<sub>5</sub>)<sub>2</sub> [Th(NO<sub>3</sub>)<sub>4</sub>.5H<sub>2</sub>O (0.54 g, 0.79 mmol) and L<sub>5</sub> (0.62 g, 1.59 mmol)], Th(NO<sub>3</sub>)<sub>4</sub>(L<sub>6</sub>)<sub>2</sub> [Th(NO<sub>3</sub>)<sub>4</sub>.5H<sub>2</sub>O (1.68 g, 2.96 mmol) and L<sub>6</sub> (1.569 g, 5.92 mmol)], Th(NO<sub>3</sub>)<sub>4</sub>(L<sub>7</sub>)<sub>2</sub> [Th(NO<sub>3</sub>)<sub>4</sub>.5H<sub>2</sub>O (0.51 g, 0.871 mmol) and L<sub>7</sub> (0.588 g, 1.75 mmol)], Th(NO<sub>3</sub>)<sub>4</sub>(L<sub>8</sub>)<sub>2</sub> [Th(NO<sub>3</sub>)<sub>4</sub>.5H<sub>2</sub>O (0.240 g, 0.876 mmol) and L<sub>8</sub> (0.5 g, 1.75 mmol)]. The unreacted ligands were collected from the worked up solvent mixtures of dichloromethane and petroleum ether (3:1) and this indirectly supports the metal-ligand stoichiometries. The metal complexes were dried *in vacuo* over anhydrous calcium chloride. The complete list of isolated metal complexes is given in Table 1.

### 2.3.3. General procedure for ligand crossover reactions:

A series of experiments were carried out to investigate the priority of the ligands in complex formation with Th(IV) and La(III) salts.

Th(NO<sub>3</sub>)<sub>4</sub>(L<sub>5</sub>)<sub>2</sub> (21.24 mg, 0.0798 mmol) and L<sub>6</sub> (50 mg, 0.0398 mmol) were taken in 5 mL of chloroform. This reaction mixture was heated at different temperatures for different time intervals and monitored by <sup>31</sup>P NMR. The formation of mixed ligand complex was confirmed by <sup>31</sup>P{<sup>1</sup>H}-NMR. In the similar way, other reactions were carried out by taking Th(NO<sub>3</sub>)<sub>4</sub>(L<sub>6</sub>)<sub>2</sub> (12 mg, 0.012 mmol) complex, L<sub>5</sub> (9.15 mg, 0.0237 mmol); LaCl<sub>3</sub>(L<sub>5</sub>)<sub>3</sub> (24 mg, 0.017 mmol), L<sub>6</sub> (40 mg, 0.153 mmol) and LaCl<sub>3</sub>(L<sub>5</sub>)<sub>3</sub> (12 mg, 0.0115 mmol), L<sub>6</sub> (13.3 mg, 0.0345 mmol) [L<sub>5</sub> = TOPO, L<sub>6</sub> = TBP].

## 3. Results and Discussion

### 3.1. Synthesis and characterization of ligands (L<sub>1</sub>-L<sub>4</sub>):

The compounds L<sub>3</sub> and L<sub>4</sub> were prepared as given in the Eq.1. The <sup>1</sup>H-NMR spectra of the free ligands L<sub>5</sub>-L<sub>8</sub> and their corresponding metal complexes were shown good agreement with the literature results [12-18]. The pure nature of all the samples prepared has been established by spectral and elemental analysis data, especially by observing characteristic peaks in <sup>31</sup>P-NMR spectra (Table 2). By comparing the <sup>31</sup>P NMR results of the free ligand (for example L<sub>3</sub> shows δ 29.98) as well as the corresponding metal complexes of [Th(NO<sub>3</sub>)<sub>4</sub>(L<sub>3</sub>)<sub>2</sub>] (δ -1.16 ppm), it is evident that the metal complexes showed significant chemical shift with relative to the free ligands, showing evidence of bonding through the phosphoryl group.

(Table 2 here)

(Eq.1 here)

The <sup>31</sup>P{<sup>1</sup>H}-NMR spectra of L<sub>3</sub> and L<sub>4</sub> showed single peaks at 29.6 and 20.0 ppm respectively, indicating the formation of a single compound. The chemical shifts in <sup>1</sup>H-NMR pertaining to the aromatic protons in the range of 7.2-8.4 ppm and two signals for NMe<sub>2</sub> protons in the range of 2.59-2.62 ppm were obtained for L<sub>3</sub>. In a similar way, the structural confirmation of L<sub>4</sub> was carried out using IR and NMR spectral data. All the metal complexes derived from various ligands L<sub>1</sub> to L<sub>8</sub> were characterized by IR and NMR spectral analysis (Table-3).

(Table-3 here)

### 3.2. Synthesis and characterization of metal complexes:

The metal complexes were synthesized using phosphine oxides,  $L_1$ - $L_8$  (chart-1) with  $LaCl_3$  and  $Th(NO_3)_4$  are shown in Table-2. The subsequent studies gave satisfactory yields of metal complexes with 1:2 ratio with  $Th(NO_3)_4$  salts and 1:3 ratio for  $LaCl_3$  salts, the reactions were carried out at room temperature for 12 h using  $CHCl_3$  as solvent. The solvent was concentrated in *vacuo* resulting colourless products,  $[LaCl_3(L_1)_3]$ ,  $[LaCl_3(L_2)_3]$ ,  $[LaCl_3(L_3)_3]$ ,  $[LaCl_3(L_4)_3]$ ,  $[LaCl_3(L_5)_3]$ ,  $[LaCl_3(L_6)_3]$ ,  $[LaCl_3(L_7)_3]$ ,  $[LaCl_3(L_8)_3]$ ,  $[Th(NO_3)_4(L_1)_2]$ ,  $[Th(NO_3)_4(L_2)_2]$ ,  $[Th(NO_3)_4(L_3)_2]$ ,  $[Th(NO_3)_4(L_4)_2]$ ,  $[Th(NO_3)_4(L_5)_2]$ ,  $[Th(NO_3)_4(L_6)_2]$ ,  $[Th(NO_3)_4(L_7)_2]$  and  $[Th(NO_3)_4(L_8)_2]$  which on further washed with chloroform to remove unreacted phosphine oxide later dried in *vacuo* and further characterized by spectroscopic and analytical techniques. Most of these complexes were soluble in high polar solvents like water and DMSO. All the analytical and spectroscopic data of the metal complexes of  $L_1$ - $L_8$  are given in Table-1. Reaction of thorium nitrate with tertiary phosphine oxides in solvents like dichloromethane or methanol has afforded the corresponding complexes having coordination number 10. All lanthanum(III) complexes indicated the coordination number as 6 (Chart-2).

(Chart-2 here)

$^1H$ -NMR spectra of all the complexes derived from  $L_1$ -  $L_8$  ligands showed significant downfield shifts for their respective metal complexes. For example, the position of methyl protons of  $-NMe_2$  groups ( $L_3$ ) and the complex  $[Th(NO_3)_4(L_3)_2]$  appear at  $\delta$  2.59 and  $\delta$  2.63 respectively. Additionally the IR spectra of the metal complexes derived from the ligands  $L_1$ - $L_8$  for a  $\nu(P=O)$  ranges from  $1015\text{ cm}^{-1}$  to  $1138\text{ cm}^{-1}$  as strong bands, depending on the nature of substituents on the phosphorus atom (free ligands ranging from  $1124$ – $1192\text{ cm}^{-1}$  as strong bands), indicating coordination through the phosphoryl oxygen. The broad and weak bands for La-Cl modes are assigned in the range of  $221$ - $243\text{ cm}^{-1}$ . The IR spectrum of  $\nu(P=O)$  stretch for the free ligand of TOPO showing strong band at  $1190\text{ cm}^{-1}$  where as the  $\nu(P=O)$  stretch of the  $[Th(NO_3)_4(L_5)_2]$  observed at  $1090\text{ cm}^{-1}$  this shows the coordination of phosphine oxide with metal centre. The free ligand (DEP) shows a band in the range of  $1052$ - $1024\text{ cm}^{-1}$  for P=O and the corresponding metal complex showed in the range of  $1052$ - $1024\text{ cm}^{-1}$ .

The trends related to phosphoryl stretching frequencies show that the infrared band shift of La(III) and Th(IV) complexes follow the increasing trend :  $L_4 > L_1 > L_3 > L_8 > L_7 > L_5 > L_3 > L_2$  and  $L_5 = L_7 > L_4 > L_6 > L_8 > L_3 > L_1 > L_2$  respectively with regard to the free ligand bands (Table-2). These results further indicate that the coordination strength of ligands strongly depending on the nature of substituents attached to the P=O group.

The absorption pattern of the complexes (205 to 300 nm range) depends on the nature of substituents on phosphoryl group and the nature of metal ions. The electronic absorption of these ligands could be due to  $n \rightarrow \pi^*$  transitions as per the literature reports [19]. The metal complexes coordinated with ligands containing both electron withdrawing groups and electron donating groups respectively exhibited bathochromic shifts compared to the free ligands of phosphine oxides and metal salt precursors in solution. It may be speculated that this unusual trend could be due to the character of the metal complexes associated with the nature of substituents on phosphoryl group.

### 3.3. Ligand exchange reactions

Phosphine oxide based La(III) and Th(IV) complexes undergo three unique intermolecular ligand exchange reactions: relative competition among phosphine oxides to form a strong complex by exchanging the weaker ligand and complete ligand transfer from La(III) to Th(IV) metal centers. Ligand crossover is well controlled by priority rules. The evidence for complete intermolecular ligand crossover among different metal complexes, further extending the flexible nature of these ligands to understand the degree of coordination strength is obtained.

Three unique intermolecular exchange reactions are described below:

#### (i) Ligand crossover reactions among Th(IV) or La(III) complexes

The ligand crossover reactions were monitored in chloroform solutions by  $^{31}\text{P}$ -NMR spectral data. The data showed that TOPO can easily replace the other ligands in both the complexes of Th(IV) and La(III). This was confirmed by obtaining two new signals at  $\delta$  63.4 for the complex of TOPO and the released free ligand(s) at their respective positions as given in the Table-2. Among the other ligands, aminophosphine oxide ligands have not shown any significant effect in chloroform solution on the coordination. The schematic representation of ligand crossover reactions is given in Eq.2. The priority of the ligand crossover in chloroform solution is observed as follows:  $\text{TOPO} > \text{TBP} > \text{DEP} > \text{TMPO} > \text{PPh}_3\text{PO}$  for Th(IV) complexes.

(Eq.2 here)



Perhaps the most striking feature of this exchange is its apparent irreversibility: within NMR detection limits, the replacement of any ligand such as TBP, DEP, TMPO, Ph<sub>3</sub>PO and by TOPO is *quantitative* and *irreversible*. This is demonstrated here by the example shown in Eq.2, in which addition of a large excess of Ph<sub>3</sub>PO, TMPO and DMP did not result in reversal of the reaction and detection of even a trace of free TOPO.

*(ii) Complete ligand transfer from La(III) to Th(IV) metal centers.*

When LaCl<sub>3</sub>(TOPO)<sub>3</sub> was mixed with two equivalents of Th(NO<sub>3</sub>)<sub>4</sub>·5H<sub>2</sub>O in chloroform at room temperature, <sup>31</sup>P-NMR spectrum of this reaction mixture was flanked with new peaks at δ 65.82 and 71.13 (Eq.3) [20]. It clearly indicates that Th(NO<sub>3</sub>)<sub>4</sub>(TOPO)<sub>2</sub> (δ 65.64) was formed. The stability of the complexes follows the trend: **Th(NO<sub>3</sub>)<sub>4</sub>(TOPO)<sub>2</sub> > LaCl<sub>3</sub>(TOPO)<sub>3</sub>**. After heating the reaction mixture at 70 °C for 2h it showed peaks (<sup>31</sup>P-NMR spectrum) at δ 75.98, 71.79, 66.35, and 58.31. After prolonged heating for 12 h and 24 h, the formation of new signals was observed due to the formation of mixed ligand complex, Th(NO<sub>3</sub>)<sub>4</sub>(TOPO)(TBP).

*(iii) Formation of mixed ligand complex*

The <sup>31</sup>P-NMR of LaCl<sub>3</sub>(TOPO)<sub>3</sub> showed single peak at δ 54.72 and after mixing with thorium complex it showed a signal at δ -3.10, 58.93, 66.40 and 67.64. It indicates that Th(NO<sub>3</sub>)<sub>4</sub>(TOPO)<sub>2</sub> (δ 65.64), Th(NO<sub>3</sub>)<sub>4</sub>(TOPO)(TBP) (δ 58.93) and LaCl<sub>3</sub>(TBP)<sub>3</sub> (δ -0.30) were formed [21]. The reaction mixture was heated at 70 °C and the reaction was monitored at regular intervals using <sup>31</sup>P-NMR as a tool. For instance the <sup>31</sup>P-NMR taken after 2h and 12 h gave signals at δ 68.19, 66.47, 59.04, -3.19 and δ 68.02, 66.40, 59.08, -3.29 respectively with little shift in their values. When [Th(NO<sub>3</sub>)<sub>4</sub>(TOPO)<sub>2</sub>] reacts with TBP at ambient temperature in CDCl<sub>3</sub> solution, within minutes new signals in the <sup>31</sup>P NMR spectrum indicate that ligand TOPO has formally replaced TBP. On heating at 120 °C, the mixture showed new signals in <sup>31</sup>P-NMR spectrum affording a mixed ligand complex as shown in Eq.4. The product was identified by its spectral analogy with the independently characterized sample, and progress of the reaction was monitored by <sup>31</sup>P NMR spectral analysis as shown Fig.1.

**(Eq.3 here)**

**(Eq.4 here)**

(Fig.1 here)

In this type of exchange, equimolar amounts of any two of the differently coordinated La(III) and Th(IV) complexes  $[\text{LaCl}_3(\text{TOPO})_3]$  and  $[\text{Th}(\text{NO}_3)_4(\text{TBP})_2]$  are mixed in chloroform-*d* solution at room temperature, and complete crossover of ligand is observed (Eq.5). This is seen in the  $^{31}\text{P}$ -NMR spectra of the mixture of  $[\text{LaCl}_3(\text{TBP})_3]$  and  $[\text{Th}(\text{NO}_3)_4(\text{TOPO})_2]$ , in which signals for all four species are well resolved.

(Eq.5 here)

Studies on exchange of ligands in water were not possible for TOPO, TBP and  $\text{Ph}_3\text{PO}$  ligands as they are water insoluble. However, AmPOs were shown better affinity towards Th(IV) and La(III) than DEP.

### 3.4. Calculation of Stability Constants

The spectroscopic parameters (extinction coefficient in ultraviolet measurements and chemical shifts in the NMR studies) are the fundamental properties of the pure molecular complex and they do not depend upon the choice of a concentration scale. When complex (M---L) formation by the addition of ligand to the metal salt in solution is followed spectroscopically, the absorbance of the complex (*A*) at the path length (*l*) is measured at different concentrations of the components.

The Benesi-Hildebrand analysis of *K* involves the measurement of the M---L absorbance as a function of varied  $[\text{M}]$  when  $[\text{L}] \gg [\text{M}]$ . A plot of  $x = 1/[\text{M}]$  vs  $y = A_0/(A_0 - A)$  gives a y-intercept =  $1/\epsilon$  and slope =  $(1/K_f\epsilon)$  as defined by the Benesi-Hildebrand equation [22]. Then the stability constant (*K*) was calculated by dividing intercept with slope.

As shown in Table-4, TOPO complexes of Th(IV) and La(III) showed highest stability followed by TBP complexes. The decreasing trends of stability constants follow the sequence  $\text{TOPO} > \text{TBP} > \text{DEP} > \text{AmPO} \approx \text{Ph}_3\text{PO}$ . This sequence is identical to the observed order for the  $^{31}\text{P}$ -NMR trends during the ligand exchange reactions as well as thermal stability trends. It is significant to note that the substituent groups on central phosphorus atom influence the ligand exchange behavior and thermal stability of the metal complexes. For example, Fig.2 and Fig.3 depict the absorption patterns for Th(IV) and La(III) solutions in the presence of DEP in DMSO respectively. Further the stability constants were calculated from the slope as shown in Fig.4.

(Fig.2 here), (Fig.3 here), (Fig.4 here)

(Fig. 5 here) (Table-4 here)

### 3.5. Thermogravimetric analysis

In the present study, the heating rate was suitably controlled at  $10\text{ }^{\circ}\text{C min}^{-1}$ , and the weight loss was measured from the ambient temperature up to  $700^{\circ}\text{C}$ . The residues were found to be rare earth oxides, as reported earlier. The weight loss for each chelate was calculated within the temperature range at which the hydrated water molecules were expelled. The experimentally found and calculated weight losses are listed in Table-5.

(Table-5 here)

(Fig. 6 here) & (Fig.7 here)

On comparison, all the thorium complexes clearly showed better thermal stability than the corresponding lanthanum complexes. The minimum temperature ranges at which the decomposition initiated were found to be from  $100$  to  $380^{\circ}\text{C}$  for thorium complexes where as that of lanthanum complexes exhibited  $70$  to  $120^{\circ}\text{C}$ . The initial weight loss occurring in the temperature range of  $70^{\circ}\text{C}$  may be interpreted as loss of crystal water molecules for the respective Th(IV) and La(III) complexes. The TG curves showed the step-wise decomposition of the ligands till a constant weight, in which the metal oxide residue is formed as final product. The basicity of the ligands portrays the thermal stability of Th(IV) and La(III) complexes in solid state as in the following order:  $\text{TOPO} > \text{TBP} > \text{DEP} > \text{AmPO} > \text{PPh}_3\text{PO}$  (Th(IV) complexes) and  $\text{TOPO} > \text{TBP} > \text{DEP} \approx \text{AmPO} > \text{PPh}_3\text{PO}$  (La(III) complexes). The thermogravimetric analysis of some TMPO complexes of Th(IV) and La(III) complexes were reported earlier and the trends are in good agreement with the corresponding metal complexes of DMPO.

### 4. Conclusion:

As phosphine oxides are key ligand systems due to the hard nature of the oxygen atom and are proficient extracting agents in radioactive waste treatment plants, the current focus is on synthesis and coordination behavior of some selected aminophosphine oxides. All the products were characterized by FT-IR,  $^1\text{H}$  NMR,  $^{31}\text{P}$ -NMR, TGA and UV/Vis Spectroscopic techniques. The coordination behavior of AmPOs was compared with some of the known ligands that include trioctylphosphine oxide (TOPO), tributylphosphate (TBP) and diethoxyphosphate (DEP). Thermogravimetric analysis of these complexes showed a distinct decomposition trends either single step or multi-step elimination of ligand species, which are strongly dependent on the electronic and steric behaviour of substituents on  $\text{P}=\text{O}$  group and nature of metal. The

tendency in thermal stability of these complexes is almost similar to the trends in ligand crossover reactions. The changes in chemical shifts can be attributed to variations in the extent and degree of coordination of donor atoms towards metal(s). The present work describes the influence of various substituents attached to the tetracoordinate phosphorous atom on the basicity of phosphoryl group and this work is significant in designing the new ligands of the required properties. The priority of ligands explains the influence of ligands for example the ability of TOPO ligand to exchange all other ligands in organic solutions. Thermogravimetric analysis of the complexes showed the elimination of ligands in a step wise manner in most of the complexes but the amino phosphine oxide indicates the removal of ammine group from the ligands by breaking the PN bonds this further supports the flexibility of P-N bonds and they are weaker than O-M bond dative bond. Changes in the substituents of 'P=O' groups can influence the thermal and coordination behaviour of the corresponding La(III) and Th(IV) complexes. In summary, the results reported in the present work will increase our knowledge of phosphorus chemistry and these findings may be useful for tailoring new complexes for catalytic and medical applications.

### Acknowledgments

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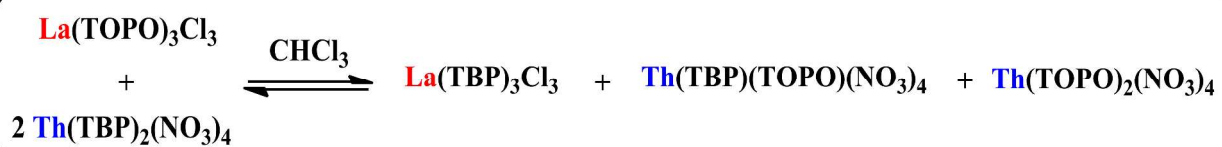
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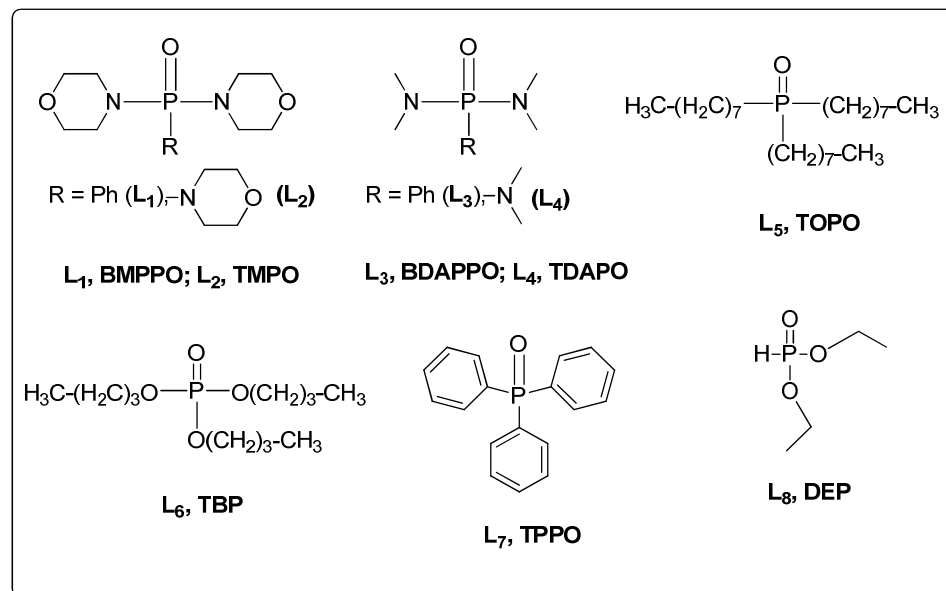
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20. The  $^{31}\text{P}$ -NMR chemical shifts for TOPO (free ligand),  $\text{LaCl}_3(\text{TOPO})_3$  are  $\delta$  48.93 and  $\delta$  54.72 respectively.
21. 50 mg (0.0355 mmol) of  $[\text{LaCl}_3(\text{TOPO})_3]$  was mixed with 36 mg (0.0355 mmol) of  $[\text{Th}(\text{NO}_3)_4(\text{TBP})_2]$  and stirred the mixture for 30 min in chloroform under different temperatures.
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## Graphical Abstract



**L = Ph<sub>3</sub>PO, TBP,  
TMPO, DEP**





**Chart-1:** Ligands employed in this study



**Table 1:** Characterization of synthesized La(III) and Th(IV) metal complexes of phosphine oxides

Sl. No.	Metal salt taken mmol (amount)	Ligand taken (amount in mmol)	Structural Formula of the formed complex	% Yield, (wt of the product)	m.p.	( $\lambda_{\max}$ ), nm	P=O stretch in FT-IR, $\text{cm}^{-1}$	[Ref]
<b>La</b>	1.346 (0.5 g)	4.039 (1.196 g)	$[\text{LaCl}_3(\text{L}_1)_3]$	79.2 (1.21 g)	235 (dec)	240	1028	[12]
	0.43 (0.159 g)	1.29 (0.393 g)	$[\text{LaCl}_3(\text{L}_2)_3]$	78.3 (0.391 g)	205 (dec)	216	1112	[12]
	1.34 (0.5 g)	4.02 (0.853 g)	$[\text{LaCl}_3(\text{L}_3)_3]$	92.0 (1.09 g)	>250	265	1105	
	1.34 (0.5 g)	4.02 (0.724 g)	$[\text{LaCl}_3(\text{L}_4)_3]$	89.0 (0.94 g)	>250	----	1016	
	0.744 (0.082 g)	2.232 (0.262 g)	$[\text{LaCl}_3(\text{L}_5)_3]$	81.7 (0.85 g)	L	242	1060	[14,15]
	2.87 (1.066 g)	8.61 (2.29 g)	$[\text{LaCl}_3(\text{L}_6)_3]$	82.9 (2.48 g)	L	224, 300	1033	[16,17]
	2.69 (1.0 g)	8.07 (2.24 g)	$[\text{LaCl}_3(\text{L}_7)_3]$	81.0 (2.36 g)	>250	255	1052	[18]
	1.49 (0.6133 g)	4.47 (0.554 g)	$[\text{LaCl}_3(\text{L}_8)_3]$	80.0 (0.781 g)	105	263	1047	
<b>Th</b>	1.75 (1.0 g)	3.5 (1.039 g)	$[\text{Th}(\text{NO}_3)_4(\text{L}_1)_2]$	85.4 (1.598 g)	213-215 (dec)	258	1132, 1111	[12]
	0.458 (0.26 g)	0.916 (0.279 g)	$[\text{Th}(\text{NO}_3)_4(\text{L}_2)_2]$	82.5 (0.412 g)	217-218 (dec)	248	1138	[12]
	0.98 (0.56 g)	1.96 (0.417 g)	$[\text{Th}(\text{NO}_3)_4(\text{L}_3)_2]$	93.0 (0.82 g)	>250	230, 260	1055	
	0.98 (0.56 g)	1.96 (0.35 g)	$[\text{Th}(\text{NO}_3)_4(\text{L}_4)_2]$	91.0 (0.75 g)	>250	225, 295	1031	
	0.79 (0.45 g)	1.59 (0.62 g)	$[\text{Th}(\text{NO}_3)_4(\text{L}_5)_2]$	80.8 (0.80 g)	L	244	1024	[14,15]
	2.96 (1.68 g)	5.92 (1.569 g)	$[\text{Th}(\text{NO}_3)_4(\text{L}_6)_2]$	80.9 (2.42 g)	L	232	1033	[16,17]
	0.87 (0.5 g)	1.75 (0.488 g)	$[\text{Th}(\text{NO}_3)_4(\text{L}_7)_2]$	83.0 (0.75 g)	265	260	1024	[18]
	0.876 (0.240 g)	1.75 (0.5 g)	$[\text{Th}(\text{NO}_3)_4(\text{L}_8)_2]$	81.0 (0.54 g)	L	274	1035	

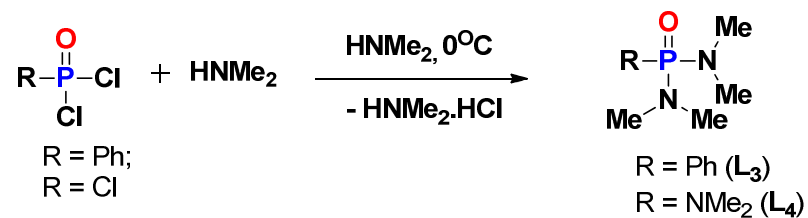
**Table 2:**  $^{31}\text{P}\{^1\text{H}\}$ -NMR chemical shifts of all the ligands and their metal complexes

Ligands Used	$^{31}\text{P}\{^1\text{H}\}$ - NMR for Free ligand (ppm)	Expected structure of complex	$^{31}\text{P}\{^1\text{H}\}$ -NMR spectral data, ppm	Elemental Analysis of the metal complexes obtained (calculated)		
				% C	% H	% N
TOPO	48.5	$\text{Th}(\text{TOPO})_2(\text{NO}_3)_4$	70.0	46.12 (46.00)	8.31 (8.20)	4.52 (4.47)
		$\text{La}(\text{TOPO})_3\text{Cl}_3$	54.72	61.62 (61.54)	11.07 (10.97)	-
TPPO	29.3	$\text{Th}(\text{TPPO})_2(\text{NO}_3)_4$	45.5	41.84 (41.71)	2.96 (2.92)	5.44 (5.40)
		$\text{La}(\text{TPPO})_3\text{Cl}_3$	35.0	45.64 (45.62)	5.44 (5.36)	-
Diethylphosphite	9.48, 5.21	$\text{Th}(\text{DEPO})_2(\text{NO}_3)_4$	4.92, 10.86	12.73 (12.71)	2.95 (2.93)	7.42 (7.41)
		$\text{La}(\text{DEPO})_3\text{Cl}_3$	2.36, -1.64	21.91 (21.85)	5.11 (5.04)	-
Bis(dimethylamino)phenyl phosphine oxide	29.6	$\text{Th}(\text{BDMPO})_2(\text{NO}_3)_4$	-1.1	26.84 (26.56)	3.82 (3.79)	12.43 (12.39)
		$\text{La}(\text{BDMPO})_3\text{Cl}_3$	35.1	40.92 (40.86)	5.87 (5.83)	9.61 (9.53)
Tris(dimethylamino)phosphine oxide	20.0	$\text{Th}(\text{TDMPO})_2(\text{NO}_3)_4$	22.2	17.26 (17.19)	4.86 (4.33)	16.74 (16.71)
		$\text{La}(\text{TDMPO})_3\text{Cl}_3$	-2.5	27.68 (27.62)	6.99 (6.95)	16.14 (16.10)
Dimorpholinephenylphosphine oxide	24.6	$\text{Th}(\text{DMPO})_2(\text{NO}_3)_4$	29.0	31.48* (31.35)	4.08 (3.95)	10.54 (10.45)
		$\text{La}(\text{DMPO})_3\text{Cl}_3$	28.71	44.52 (44.48)	5.62 (5.60)	7.50 (7.41)
Trimorpholinephosphine oxide	20.5	$\text{Th}(\text{TMPO})_2(\text{NO}_3)_4$	23.0	24.12 (24.20)	4.23 (4.03)	11.41 (11.76)
		$\text{La}(\text{TMPO})_3\text{Cl}_3$	2181	37.28 (37.24)	6.30 (6.25)	10.91 (10.86)
Tributylphosphate	-0.75	$\text{Th}(\text{TBP})_2(\text{NO}_3)_4$	-1.21	28.54 (28.46)	5.42 (5.37)	5.56 (5.53)
		$\text{La}(\text{TBP})_3\text{Cl}_3$	-0.30	37.11 (37.06)	7.06 (7.00)	-

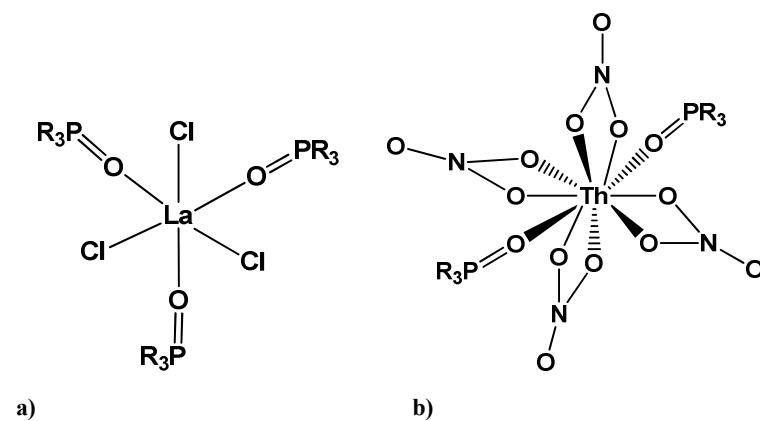
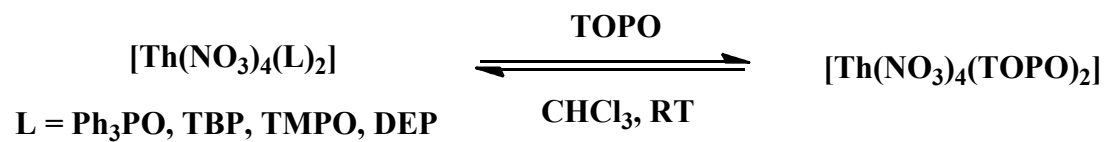
\*with one mole of  $\text{CH}_2\text{Cl}_2$

**Table 3:**  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR data of all the ligands and their metal complexes

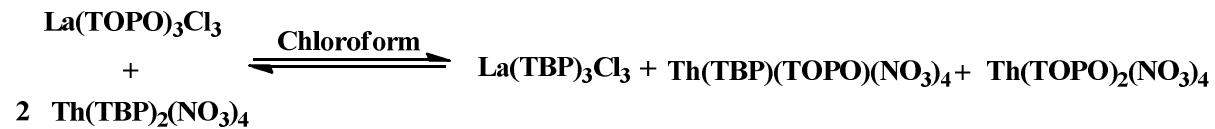
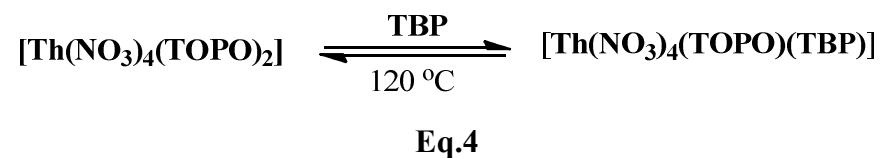
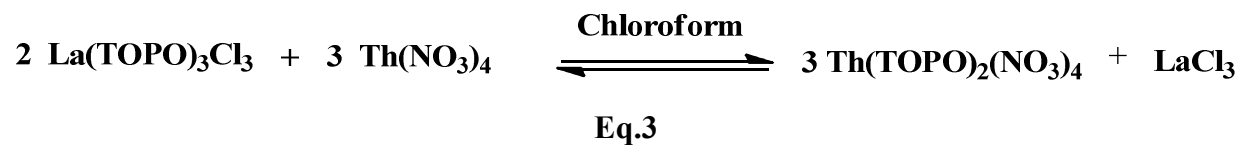
S. No.	Ligand	$^1\text{H}$ -NMR spectral data, ppm			$^{13}\text{C}$ -NMR spectral data, ppm
		Free ligand (L)	$[\text{Th}(\text{NO}_3)_4\text{L}_2]$	$[\text{LaCl}_3\text{L}_3]$	Free ligand (L) $^{13}\text{C}$ NMR (400 MHz, $\text{CDCl}_3$ )
1	TOPO	1.87-1.03 [m, 14H; $\text{CH}_2$ ]	1.92-1.05 [m, 14H; $\text{CH}_2$ ]	1.89-1.03 [m, 14H; $\text{CH}_2$ ]	31.78, 31.12, 29.04, 28.30, 27.66, 22.60, 21.69, 14.04 ( $\text{CH}_2$ and $\text{CH}_3$ )
2	TPPO	7.58-7.39 [m, 5H; Ar-H]	7.60-7.41 [m, 5H; Ar-H]	7.55-7.37 [m, 5H; Ar-H]	133.05, 132.11, 131.92, 128.56, 128.44 (Ph)
3	Diethyl Phosphite	1.31 [t, 6H; $\text{CH}_3$ ], 1.76 [q, 4H; $\text{CH}_2$ ]	1.32 [t, 6H; $\text{CH}_3$ ], 1.77 [q, 4H; $\text{CH}_2$ ]	1.30 [t, 6H; $\text{CH}_3$ ], 1.75 [q, 4H; $\text{CH}_2$ ]	61.62 ( $\text{OCH}_2$ ), 16.15 ( $\text{CH}_3$ )
4	Bis(dimethylamino) phenylphosphine oxide	7.74-7.42 [m, 5H; Ar-H], 2.62 [s, 12H; $\text{CH}_3$ ]	7.83-7.39 [m, 5H; Ar-H], 2.59 [s, 12H; $\text{CH}_3$ ]	7.62-7.74 [m, 5H; Ar-H], 2.51 [s, 12H; $\text{CH}_3$ ]	132.13, 131.03, 129.51, 128.41, 128.28 (Ph), 36.33 ( $\text{N-CH}_3$ )
5	Tris(dimethylamino) phosphine oxide	2.67 [s, 18H; $\text{CH}_3$ ]	2.59 [s, 18H; $\text{CH}_3$ ]	2.61 [s, 18H; $\text{CH}_3$ ]	35.24 ( $\text{N-CH}_3$ )
6	Bis(morpholino) phenylphosphine oxide	7.68-7.47 [m, 5H; Ar-H], 3.58 [t, 8H; $\text{CH}_2$ ], 3.02 [t, 8H; $\text{CH}_2$ ]	7.70-7.51 [m, 5H; Ar-H], 3.59 [t, 8H; $\text{CH}_2$ ], 3.04 [t, 8H; $\text{CH}_2$ ]	7.66-7.45 [m, 5H; Ar-H], 3.55 [t, 8H; $\text{CH}_2$ ], 3.00 [t, 8H; $\text{CH}_2$ ]	132.12, 131.87, 128.81, 128.68 (Ph), 67.08 ( $\text{O-CH}_2$ ), 44.45 ( $\text{N-CH}_2$ )
7	Tris(morpholino) phosphine oxide	3.62 [t, 12H; $\text{CH}_2$ ], 3.06 [t, 12H; $\text{CH}_2$ ]	3.66 [t, 12H; $\text{CH}_2$ ], 3.11 [t, 12H; $\text{CH}_2$ ]	3.63 [t, 4H; $\text{CH}_2$ ], 3.08 [t, 4H; $\text{CH}_2$ ]	67.29 ( $\text{O-CH}_2$ ), 45.17 ( $\text{N-CH}_2$ )
8	TBP	3.90 [t, 6H; $\text{CH}_2$ ], 1.52 [m, 6H; $\text{CH}_2$ ], 1.29 [m, 6H; $\text{CH}_2$ ], 0.813 [t, 6H; $\text{CH}_2$ ]	3.94 [t, 6H; $\text{CH}_2$ ], 1.56 [q, 6H; $\text{CH}_2$ ], 1.30 [m, 6H; $\text{CH}_2$ ], 0.82 [t, 6H; $\text{CH}_2$ ]	3.91 [t, 6H; $\text{CH}_2$ ], 1.53 [q, 6H; $\text{CH}_2$ ], 0.81 [t, 6H; $\text{CH}_2$ ]	67.23 ( $\text{OCH}_2$ ), 32.41 ( $\text{CH}_2$ ), 18.73 ( $\text{CH}_2$ ), 13.43 ( $\text{CH}_3$ )



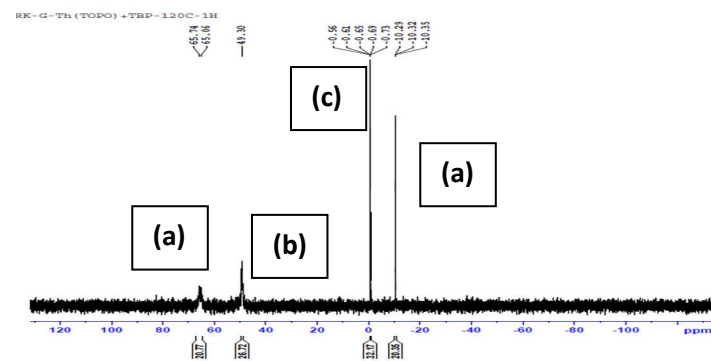
Eq.1

Chart-2: Predicted general structures of  $[\text{LaCl}_3(\text{R}_3\text{PO})_3]$  and  $[\text{Th}(\text{NO}_3)_4(\text{R}_3\text{PO})_2]$ .

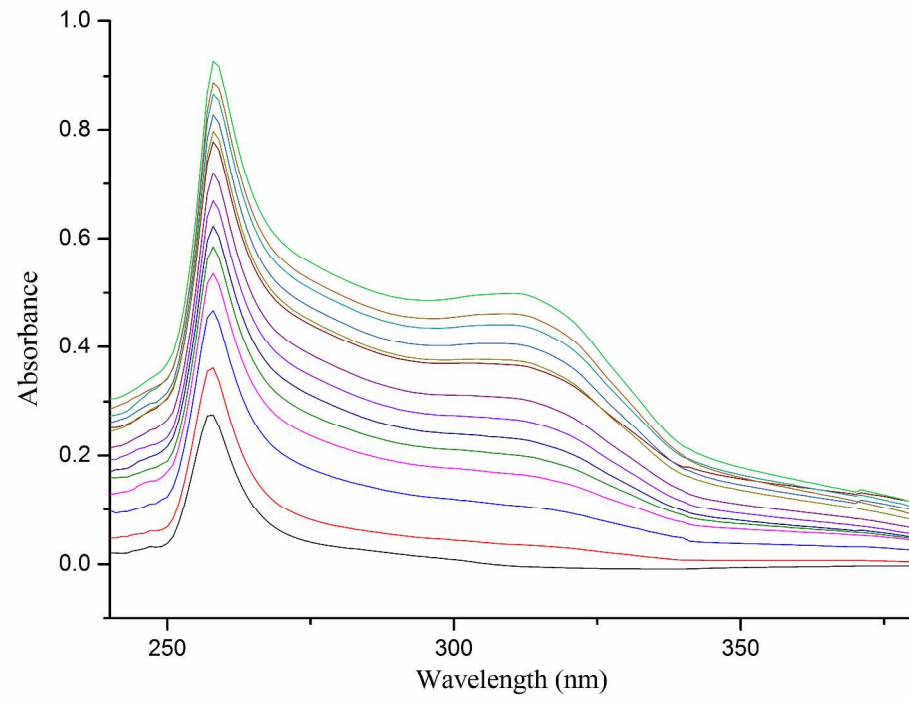
Eq.2: Ligand crossover reactions among Th(IV) complexes



Eq.5: Ligand crossover reactions between Th(IV) and La(III) metal centers



**Fig.1:**  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of mixed ligand complex,  $[\text{Th}(\text{NO}_3)_4(\text{TOPO})(\text{TBP})]$ ;  
(a) -  $[\text{Th}(\text{NO}_3)_4(\text{TOPO})(\text{TBP})]$ , (b) – free TOPO, (c) free TBP

**Fig.2**

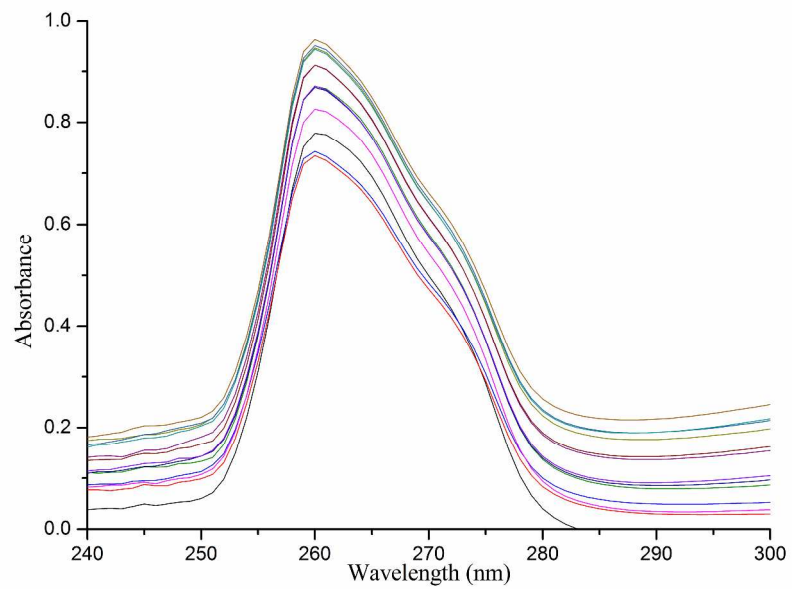


Fig.3

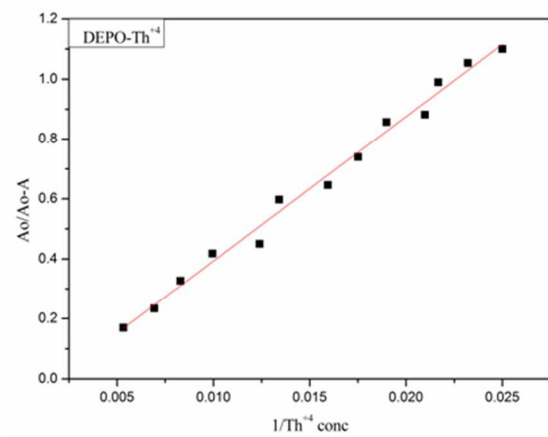


Fig.4



**Table-4: Stability constants of various metal complexes**

S.No.	Ligand	Stability Constants of Th(IV) Complexes*	Stability Constants of La(III) Complexes*
1.	L <sub>1</sub>	6.42	6.23
2.	L <sub>2</sub>	6.78	6.48
3.	L <sub>3</sub>	6.58	6.33
4.	L <sub>4</sub>	7.25	6.67
5.	L <sub>5</sub>	11.7	9.46
6.	L <sub>6</sub>	9.82	8.82
7.	L <sub>7</sub>	7.43	7.13
8.	L <sub>8</sub>	7.04	6.8

\*calculated in DMSO solutions due to the solubility problems associated with some ligands in aqueous solutions.

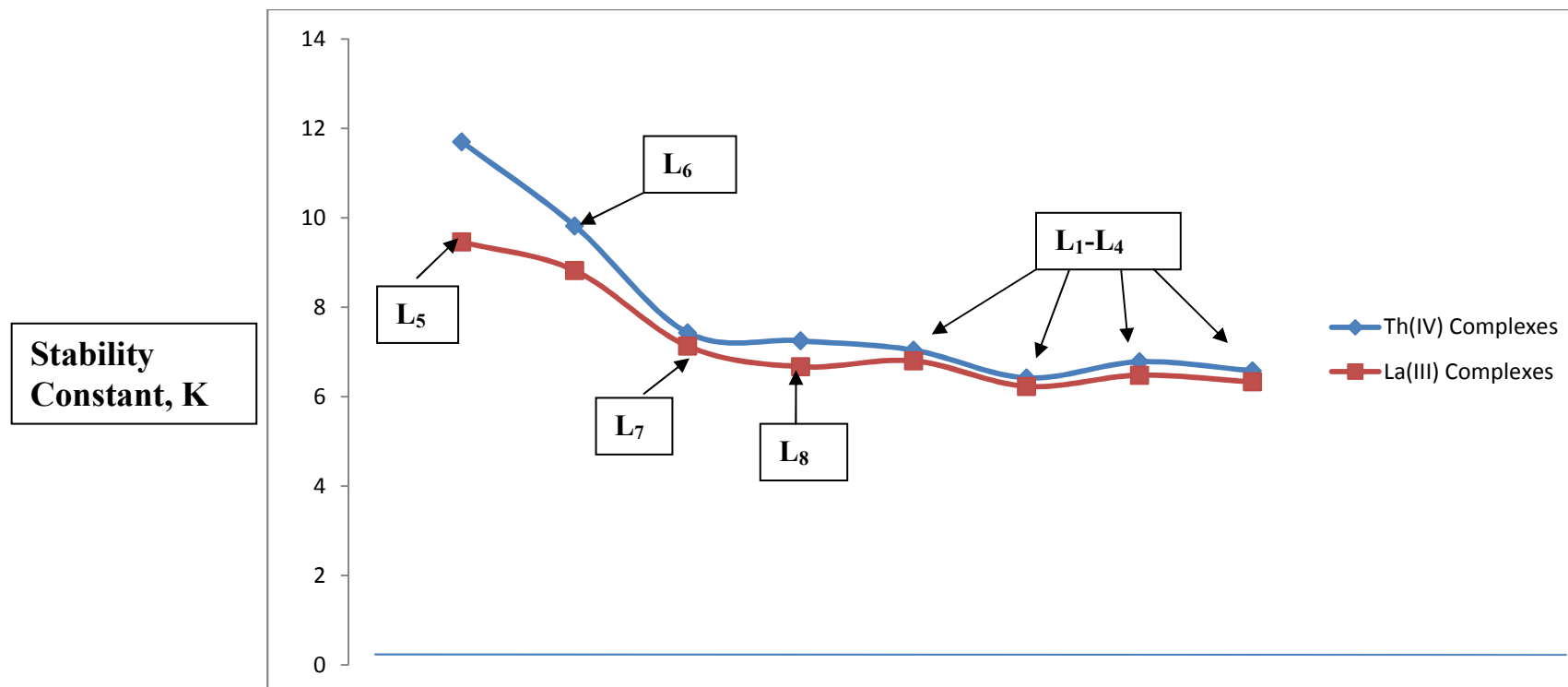


Fig. 5

Various phosphine oxide ligands with different substituents

**Table-5:** Thermogravimetric analysis data of Th(IV) and La(III) Complexes

Complex	Temperature Range, °C	% Weight loss Obtained	Calculated weight loss (%) for loss of fragment
[Th(NO <sub>3</sub> ) <sub>4</sub> .(TBP) <sub>2</sub> ]	220 -330	52%	52.59 for both TBP ligands
[Th(NO <sub>3</sub> ) <sub>4</sub> .(DEPO) <sub>2</sub> ]	140-180; 240-330	18%; 30%	18.26% (monoligand); 36.52% (for two ligands)
[Th(NO <sub>3</sub> ) <sub>4</sub> .(DMPO) <sub>2</sub> ]	100-320	55%	55.28 (for both the ligands)
[Th(NO <sub>3</sub> ) <sub>4</sub> .(TOPO) <sub>2</sub> ]	290-380	61%	61.69% (both DMPO ligands)
[LaCl <sub>3</sub> .(TOPO) <sub>3</sub> ]	120-320	54%	54.50% (for to free ligands)
[LaCl <sub>3</sub> .(TBP) <sub>3</sub> ]	100-180; 300-490	51%	50.91% (free TOPO ligands)
[LaCl <sub>3</sub> .(DMPO) <sub>3</sub> ]	70-190; 410-525	27% and gradual decomposition	26.12% (free DMPO ligands)
[LaCl <sub>3</sub> .(DEPO) <sub>3</sub> ]	70-145; 410-585	20% and gradual decomposition	20.93% (free DEPO ligands)

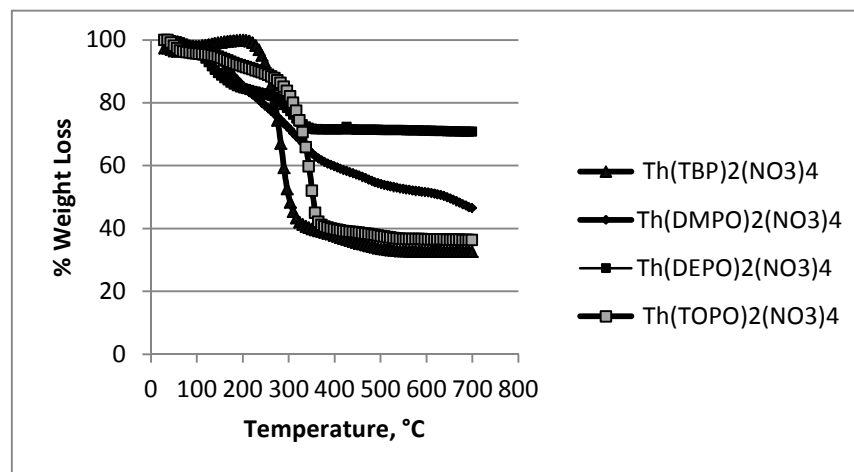


Fig.6: TGA of thorium(IV) complexes

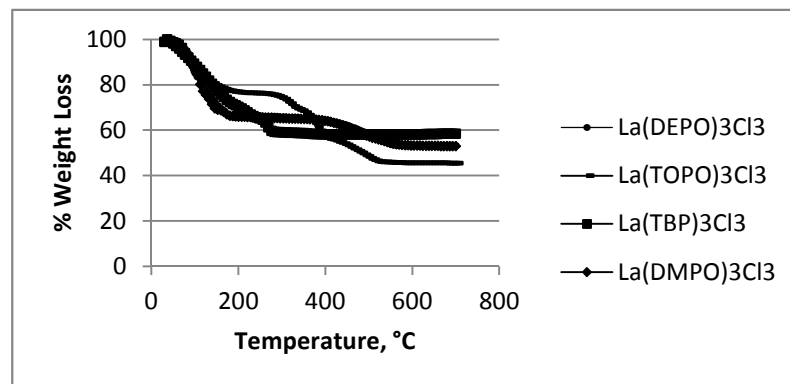


Fig.7: TGA of lanthanum(III) complexes