

View Article Online View Journal

RSC Advances

This article can be cited before page numbers have been issued, to do this please use: B. Pavankumar, V. G. E., S. R, S. Akella, V. Kari, A. K. SK, B. R. C.V.S., S. K.N. and P. C. Jha, *RSC Adv.*, 2014, DOI:



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This Accepted Manuscript will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/advances

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

¹B.B. Pavankumar, ¹E. Veerashekhar Goud, ¹R. Selvakumar, ¹S.K. Ashok Kumar, ¹Akella Sivaramakrishna*, and ¹Kari Vijayakrishna

¹Chemistry Division, School of Advances Sciences, VIT University, Vellore 632 014, Tamil Nadu, India ²C.V.S. Brahmananda Rao and ²K.N. Sabharwal

²Chemistry Group, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, Tamil Nadu, India ³Prakash C. Jha

³School of Chemical Sciences, Central University of Gujarat, Sector-30, Gandhinagar, Gujarat, India E-mail: <u>asrkrishna@rediffmail.com</u>

Abstract

Published on 05 December 2014. Downloaded by State University of New York at Binghamton on 06/12/2014 12:26:43.

Some selected aminophosphine oxides (AmPOs) of the type OP(NMe₂)₃, OPPh(NMe₂)₂, OP(NC₂H₄O)₃, OPPh(NC₂H₄O)₂ and their corresponding La(III) and Th(IV) complexes are synthesized and analyzed by FT-IR, ¹H-NMR, ³¹P{¹H}-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 > Ph₃PO. This tendency closely agrees with the stability constants of metal complexes.

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

Introduction

Pentavalent phosphine oxides (R₃P=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

View Article Online DOI: 10.1039/C4RA13645D

Page 2 of 27

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)]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 *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 *inter*molecular 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

¹H, ¹³C, and ³¹P{¹H}-NMR spectra were recorded on a Bruker DMX-400 spectrometer and all ¹H chemical shifts were reported relative to the residual proton resonance in deuterated solvents (all at 298 K, CDCl₃). 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 mL min⁻¹) and at a heating rate of 10.0°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.

Published on 05 December 2014. Downloaded by State University of New York at Binghamton on 06/12/2014 12:26:43.

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 POCl₃, Ph₂POCl, PhPOCl₂, 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), [Th(NO₃)₄.5H₂O)] and [La(NO₃)₃.7H₂O)] 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 (L1-L4)

Tris(morpholino)phosphine oxide (L_1) and bis(morpholino)phenyl phosphine oxide (L_1) were prepared by the literature methods [12,13].

General procedure for the synthesis of bis(dimethylamino)phenylphosphine oxide (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 N₂ 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 CH₂Cl₂ 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 Na₂SO₄ (5 g) for 30 min. The product (L₃) obtained as a colourless crystalline solid (6.0 g) Yield 60%). m.p. 135-37 °C. ¹H NMR (400 MHz, CDCl₃): δ 2.62-2.63 (s, 12H, -NCH₃), 7.45- 7.77 (m, 5H, Ph); ³¹P{¹H}-NMR (CDCl₃): δ 29.98. Anal. Calc. for C₂₀H₂₂Cl₂N₄O₂Si: 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 (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 N₂ atm. The work-up of

Page 4 of 27

ccepted Ma

Ž

()

Ü U

the reaction mixture was carried out as mentioned above. The product (L₄) was obtained as yellow crystalline solid (3.5 g). Yield 70%. m.p. 122-24°C. ¹H-NMR (400 MHz, CDCl₃): δ 2.66-2.67 (s, 18H, -NCH₃); ³¹P{¹H}-NMR (CDCl₃): δ 20.6. Anal. Calc. for C₆H₁₈N₃OP: 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 $[Th(NO_3)_4(L_3)_2]$ complex and the same procedure was followed for the other metal complexes.

A finely powdered solid of Th(NO₃)₄.6H₂O (0.56 g, 0.98 mmol) was added all at once to a stirred solution of L₃ (0.417g, 1.96 mmol) in solvent mixture of CHCl₃ (15mL) and the mixture was stirred for 24h to get the colorless crystalline solid. Yield: 0.82 g, 93%. IR (Nujol mull/cm⁻¹): 970.19 (s) [P=O]. ¹H-NMR (CDCl₃, ppm): δ 7.42–7.79 (m, phenyl), 2.82 (m, CH₂). ³¹P{¹H}-NMR (D₂O): δ -1.16 (s). Then the solid residue was washed with dichloromethane to obtain the pure product, Th(NO₃)₄(L₃)₂.

In a similar way, all the following complexes were prepared by taking the appropriate amounts as given below: $LaCl_3(L_1)_3$ [LaCl_3.7H₂O (0.5 g, 1.346 mmol) and L₁ (1.196 g, 4.039 mmol)], LaCl_3(L_2)_3 [LaCl₃.7H₂O (0.159 g, 0.43 mmol) and L₂ (0.393 g, 1.29 mmol)], LaCl₃(L₃)₃ [LaCl₃.7H₂O (0.5 g, 1.34 mmol) and L₃ (0.853 g, 4.02 mmol)], LaCl₃(L₄)₃ [LaCl₃.7H₂O (0.5 g, 1.34 mmol) and L₄ (0.724 g, 4.02 mmol)], LaCl₃(L₅)₃ [LaCl₃.7H₂O (0.082 g, 0.744 mmol) and L₅ (0.262 g, 2.232 mmol)], LaCl₃(L₆)₃ $[La(NO_3)_3.7H_2O (1.066 g, 2.84 mmol) and L_6 (2.29 g, 8.61mmol)] LaCl_3(L_7)_3 [La(NO_3)_3.7H_2O (1.02g, 1.02g)]$ 2.72 mmol) and L₇ (2.24 g, 8.07 mmol)], LaCl₃(L₈)₃ [La(NO₃)₃.7H₂O (0.6133 g, 1.49 mmol) and L₈ (0.554 g, 4.47 mmol)], Th(NO₃)₄(L₁)₂ [Th(NO₃)₄.5H₂O (1.02 g, 1.78 mmol) and L₁ (1.03 g, 3.51 mmol)], Th(NO₃)₄(L₂)₂ [Th(NO₃)₄.5H₂O (0.26 g, 0.458 mmol) and L₂ (0.279 g, 0.916 mmol)], Th(NO₃)₄(L₄)₂ [Th(NO₃)₄.5H₂O (0.56 g, 0.98 mmol) and L₄ (0.35 g, 1.96 mmol)], Th(NO₃)₄(L₅)₂ [Th(NO₃)₄.5H₂O (0.54 g,0.79 mmol) and L₅ (0.62 g, 1.59 mmol)], Th(NO₃)₄(L₆)₂ [Th(NO₃)₄.5H₂O (1.68 g, 2.96 mmol) and L₆ (1.569 g, 5.92 mmol)], Th(NO₃)₄(L₇)₂ [Th(NO₃)₄.5H₂O (0.51 g, 0.871 mmol) and L₇ (0.588 g, 1.75 mmol)], Th(NO₃)₄(L₈)₂ [Th(NO₃)₄.5H₂O (0.240 g, 0.876 mmol) and L₈ (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 vacuuo 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(NO₃)₄(L₅)₂ (21.24 mg, 0.0798 mmol) and L₆ (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 ³¹P NMR. The formation of mixed ligand complex was confirmed by ³¹P{¹H}-NMR. In the similar way, other reactions were carried out by taking Th(NO₃)₄(L₆)₂ (12 mg, 0.012 mmol) complex, L₅ (9.15 mg, 0.0237 mmol); LaCl₃(L₅)₃ (24 mg, 0.017 mmol), L₆ (40 mg, 0.153 mmol) and LaCl₃(L₅)₃ (12 mg, 0.0115 mmol), L₆ (13.3 mg, 0.0345 mmol) [L₅ = TOPO, L₆ = TBP].

3. Results and Discussion

3.1. Synthesis and characterization of ligands (L_1-L_4) :

The compounds L_3 and L_4 were prepared as given in the Eq.1. The ¹H-NMR spectra of the free ligands L_5 – L_8 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 ³¹P-NMR spectra (Table 2). By comparing the ³¹P NMR results of the free ligand (for example L_3 shows δ 29.98) as well as the corresponding metal complexes of [Th(NO₃)₄(L_3)₂] (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 ³¹P{¹H}-NMR spectra of L_3 and L_4 showed single peaks at 29.6 and 20.0 ppm respectively, indicating the formation of a single compound. The chemical shifts in ¹H⁻NMR pertaining to the aromatic protons in the range of 7.2-8.4 ppm and two signals for NMe₂ protons in the range of 2.59-2.62 ppm were obtained for L_3 . In a similar way, the structural confirmation of L_4 was carried out using IR and NMR spectral data. All the metal complexes derived from various ligands L_1 to L_8 were characterized by IR and NMR spectral analysis (Table-3).

Published on 05 December 2014. Downloaded by State University of New York at Binghamton on 06/12/2014 12:26:43.

3.2. Synthesis and characterization of metal complexes:

The metal complexes were synthesized using phosphine oxides, L_1-L_8 (chart-1) with LaCl₃ and Th(NO₃)₄ are shown in Table-2. The subsequent studies gave satisfactory yields of metal complexes with 1:2 ratio with Th(NO₃)₄ salts and 1:3 ratio for LaCl₃ salts, the reactions were carried out at room temperature for 12 h using CHCl₃ as solvent. The solvent was concentrated in *vaccuo* resulting colourless products, [LaCl₃(L₁)₃], [LaCl₃(L₂)₃], [LaCl₃(L₃)₃], [LaCl₃(L₄)₃], [LaCl₃(L₆)₃], [LaCl₃(L₇)₃], [LaCl₃(L₇)₃], [LaCl₃(L₄)₃], [LaCl₃(L₄)₃], [LaCl₃(L₄)₃], [LaCl₃(L₆)₃], [LaCl₃(L₇)₃], [LaCl₃(L₆)₃], [Th(NO₃)₄(L₁)₂], [Th(NO₃)₄(L₂)₂], [Th(NO₃)₄(L₃)₂], [Th(NO₃)₄(L₄)₂], [Th(NO₃)₄(L₅)₂], [Th(NO₃)₄(L₆)₂], [Th(NO₃)₄(L₇)₂] and [Th(NO₃)₄(L₈)₂] which on further washed with chloroform to remove unreacted phosphine oxide later dried in *vaccuo* 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 L₁-L₈ 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(NO₃)₄(L_3)₂] appear at δ 2.59 and δ 2.63 respectively. Additionally the IR spectra of the metal complexes derived from the ligands L_1 - L_8 for a v(P=O) ranges from 1015 cm⁻¹ to 1138 cm⁻¹ as strong bands, depending on the nature of substituents on the phosphorus atom (free ligands ranging from 1124– 1192 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 cm⁻¹. The IR spectrum of v(P=O) stretch for the free ligand of TOPO showing strong band at 1190 cm⁻¹ where as the v(P=O) stretch of the [Th(NO₃)₄(L_5)₂] observed at 1090 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 cm⁻¹ for P=O and the corresponding metal complex showed in the range of 1052-1024 cm⁻¹.

vances Accepted Manu

View Article Online DOI: 10.1039/C4RA13645D

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 ³¹P-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 δ 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: TOPO > TBP > DEP > TMPO > PPh₃PO for Th(IV) complexes.

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, Ph₃PO 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 Ph₃PO, 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 LaCl₃(TOPO)₃ was mixed with two equivalents of Th(NO₃)₄.5H₂O in chloroform at room temperature, ³¹P-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(NO₃)₄(TOPO)₂ (δ 65.64) was formed. The stability of the complexes follows the trend: **Th(NO₃)₄(TOPO)₂ > LaCl₃(TOPO)₃**. After heating the reaction mixture at 70°C for 2h it showed peaks (³¹P-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(NO₃)₄(TOPO)(TBP).

(iii) Formation of mixed ligand complex

The ³¹P-NMR of LaCl₃(TOPO)₃ 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(NO₃)₄(TOPO)₂ (δ 65.64), Th(NO₃)₄(TOPO)(TBP) (δ 58.93) and LaCl₃(TBP)₃ (δ -0.30) were formed [21]. The reaction mixture was heated at 70°C and the reaction was monitored at regular intervals using ³¹P-NMR as a tool. For instance the ³¹P-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(NO₃)₄(TOPO)₂] reacts with TBP at ambient temperature in CDCl₃ solution, within minutes new signals in the ³¹P NMR spectrum indicate that ligand TOPO has formally replaced TBP. On heating at 120°C, the mixture showed new signals in ³¹P-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 ³¹P NMR spectral analysis a shown Fig.1.

(Fig.1 here)

In this type of exchange, equimolar amounts of any two of the differently coordinated La(III) and Th(IV) complexes $[LaCl_3(TOPO)_3]$ and $[Th(NO_3)_4(TBP)_2]$ are mixed in chloroform-*d* solution at room temperature, and complete crossover of ligand is observed (Eq.5). This is seen in the ³¹P-NMR spectra of the mixture of $[LaCl_3(TBP)_3]$ and $[Th(NO_3)_4(TOPO)_2]$, 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 Ph₃PO 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 (1) 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 [M] when [L] >> [M]. A plot of x = 1/[M] vs y = Ao/(Ao-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 TOPO > TBP > DEP > AmPO \approx Ph₃PO. This sequence is identical to the observed order for the ³¹P-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 °C min⁻¹, and the weight loss was measured from the ambient temperature up to 700°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°C for thorium complexes where as that of lanthanum complexes exhibited 70 to 120 °C. The initial weight loss occurring in the temperature range of 70°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 portraits the thermal stability of Th(IV) and La(III) complexes in solid state as in the following order: TOPO > TBP > DEP > AmPO > PPh_3PO (Th(IV) complexes) and TOPO > TBP > DEP \approx AmPO > PPh_3PO (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, ¹H NMR, ³¹P-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 P=O group and nature of metal. The

ccepted Manu

Ž

Advances

Page 11 of 27

RSC Advances

View Article Online DOI: 10.1039/C4RA13645D

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

Dr ASRK is highly thankful to DAE-BRNS (INDIA) (No. 2012/37C/6/ BRNS/623) for the financial assistance. BBPK thanks VIT University for the fellowship. Dr. ASRK and his group members thank DST-VIT-FIST for NMR and SIF-VIT University for other instrumentation facilities.

References

- E.P. Horwitz, W.W. Shulz, in The TRUEX Process: A Vital Toll for Disposal of US Defense Nuclear Waste, Elsevier, London 1991 21.
- a) E.P. Horwitz, D.G. Kalina, H. Diamond, D.G. Vandegrift and W.W. Schultz, Solvent Extr. Ion Exch. 3 (1985) 75; b) Kolodiazhnyi, Tetrahedron: Asym. 23 (2012) 1–46; c) R. A. Cherkasov, A. R. Garifzyanov, S. A. Koshkin, and N. V. Davletshina, Russ. J. Gen. Chem. 82 (2012) 1453–1454.
- 3. a) L. Spjuth, J.O. Liljenzin, M.J. Hudson, M.G.B. Drew, P.B. Iveson, C. Madic, Solvent Extr. Ion Exch. 18 (2000) 1; b) G.K. Ingle, Y. Liang, M.G. Mormino, G. Li, F.R. Fronczek, J.C. Antilla, Org. Lett. 13 8 (2011) 2054;
- 4. a) L. Ackermann, Syn. Lett. (2007) 507-526; b) J. Blümel, Coord. Chem. Rev. 252 (2008) 2410-2423;
 c) C.J. Wallis, D. Virieux, H.J. Cristau, Encyclopedia of Reagents for Organic Synthesis. 2001, John Wiley & Sons, Ltd., Chichester, UK; d) L. Ackermann, Editor(s): A. Boerner (Editor), Phosphorus Ligands in Asymmetric Catalysis 2 (2008) 831-847; e) B. Schaeffner, A. Boerner, A. Boerner (Editor), Phosphorus Ligands in Asymmetric Catalysis. 2 (2008) 785-805; f) C. Baillie, L. Xu, J. Xiao, S.M.

Roberts Ed(s), Catalysts for Fine Chemical Synthesis. 3 (2004) 77-81; g) A. Gajda, T. Gajda, Curr. Org. Chem. 11 (2007) 1652-1668; h) P. MLynarz, E. Rudzinska, L. Berlicki, P. Kafarski, Curr. Org. Chem. 11 (2007) 1593-1609.

- a) L. Ackermann, Synthesis (2006) 1557-1571; b) L. Ackermann, R. Born, J.H. Spatz, A. Althammer, C.J. Gschrei, Pure Appl. Chem. 78 (2006) 209-214.
- 6. a) D. Leca, L. Fensterbank, E. Lacote, M. Malacria, Chem. Soc. Rev. 34 (2005) 858-865; b) N. V. Dubrovina, A. Boerner, Angew. Chem., Int. Ed. 43 (2004) 5883-5886.
- V.V. Grushin, Chem. Rev. 104 (2004) 1629-1662; b) G. Keglevich, H. Forintos, H. Szelke, A. Tamas, A. Vasko, K. Gyongyver, K. Janos T. Kortvelyesi, L. Kollar, L. Toke, Phosphorus, Sulfur Silicon Rel. Elem. 177 (2002) 1681-1684.
- 8. (a) N.J. Farrer, R. McDonald, T. Piga, J.S. McIndoe, Polyhedron 29 (2010) 254-261; (b) H.H. Dam, D.N. Reinhoudt, W. Verboom, Chem. Soc. Rev. 36 (2007) 367-378; (c) R. Engel, J.I. Rizzo, Curr. Org. Chem. 10 (2006) 2393-2405.
- 9. M. Kim, F. Sanda, T. Endo, Polym. Bull. 46 (2001) 277-283.
- 10. (a) J.G. Verkade, K.J. Coskram, Organophosphorus Compounds, G.M. Kosolapoff, L. Eds. Maier, Wiley, New York, 2 (1972) 1-53; (b) A.H. Cowley, R.E. Davies, K. Remadna, Inorg. Chem. 20 (1981) 2146-2152; (c) M.R.I. Zubiri, J.D. Woollins, Comments Inorg. Chem., 24 (2003) 189-252; (d) S.A. Katz, V.S. Allured, A.D. Norman, Inorg. Chem., 33 (1994) 1762-1769; (e) G. Ewart, D.S. Payne, A.L. Porte, A.P. Lane, J. Chem. Soc., (1962) 3984-3990; (f) D.S. Payne, A.P. Walker, J. Chem. Soc. (1966) 498-499; (g) P.W. Dyer, M.J. Hanton, R.D.W. Kemmitt, R. Padda, N. Singh, Dalton Trans. (2003) 104-113.
- (a) S. Singh, K.M. Nicholas, Chem. Commun. (1998) 149-150; (b) J.J. Brunet, R. Chauvin, Chiffre, S. Huguet, P. Leglaye, J. Organomet. Chem. 566 (1998) 117-123; (c) N.R. Price, J. Chambers, The Chemistry of Organophosphorus Compounds, F. R. Hartley, (Ed.), Wiley, Chichester, 1 (1990) 649; (d) J. Ansell, M. Wills, Chem. Soc. Rev. 31 (2002) 259-268; (e) M.C.B. Dolinsky, W.O. Lin, M. L. Dias, J. Mol. Catal. A: Chem. 258 (2006) 267-274.
- E.V.S. Goud, B.B. Pavankumar, A. Paul, Y. Shruthi, A. Sivaramakrishna, K. Vijayakrishna, H.S. Hadley, C.V.S.B. Rao, and K.N. Sabharwal, J. Coord. Chem., 66 (2013) 2647-2658.
- a) J.T. Donoghue, E. Fernadez, D.A. Peters, Inorg. Chem. 8 (1968) 1191-1194.; b) Christian Romming, Jon Songstad, Acta Chem. Scand. A 36 (1982) 665-671; c) J.T. Donoghue, Bull. Chem. Soc. Jpn. 43 (1970) 932-934; d) J.T. Donoghue, E. Fernadez, Bull. Chem. Soc. Jpn. 43(1970) 271-273.
- a) Y.A. El-Nadi, Hydrometallurgy, 119-120 (2012) 23-29; b) K.S.R. Murthy, R.J. Krupadam, Y. Anjaneyulu, J. Chromatogr. Sci. 36 (1998) 595-599.

Published on 05 December 2014. Downloaded by State University of New York at Binghamton on 06/12/2014 12:26:43

RSC Advances

- 15. a) K.M.A. Malik, J.W. Jeffery, Acta Cryst. (1973). B29, 2687; b) M.R. Yaftian, M.E. Eshraghi, L. Hassanzadeh, Iran. J. Chem. & Chem. Eng. 22 (2003) 71-76; c) J.M.P.J. Verstegen, J. Inorg. Nucl. Chem. 26 (1964) 25-35; d) N. Kumar, Dennis G. Tuck, Can. J. Chem. 62 (1984) 1701-1704.
- 16. a) E. Jorjani, M. Shahbazi, Arab. J. Chem. (2012), http://dx.doi.org/10.1016/j.arabjc.2012.04.002;
 b) B. Mokili, C. Poitrenaud, Sol. Extr. Ion Exch. 15(3), 455-481 (1997).
- 17. a) M.D. Reinoso Lopez, S. Gonzalez Garcia, Ars Pharmaceutica 27 (1986) 435-45; b) K. Changkrueng, D. Chatsiriwech, J. Rare Earths, 29 (2011) 896-901; c) V. Vallet, I. Grenthe, Sol. Extr. Ion Exch. 31(2013) 358-369.
- a) M.J. Glazier, W. Levason, M.L. Matthews, P.L. Thornton, M. Webster, Inorg. Chim. Acta 357 (2004) 1083–1091; b) D.R. Cousins, F.A. Hart, J. Inorg. Nucl. Chem. 30 (1968) 3009-3015; c) B. C. Smith, Marguerite A. Wassef, J. Chem. Soc. (A), (1968) 1817-1818.
- G. Manca, M. Caporali, A. Ienco, M. Peruzzini, C. Mealli, J. Organomet. Chem. 760 (2014) 177-185; b) H.P. Benschop, M. Halmann, J.C.S. Perkin II, 1972, 1095.
- 20. The ³¹P-NMR chemical shifts for TOPO (free ligand), LaCl₃(TOPO)₃ are δ 48.93 and δ 54.72 respectively.
- 21. 50 mg (0.0355 mmol) of [LaCl₃(TOPO)₃] was mixed with 36 mg (0.0355 mmol) of [Th(NO₃)₄(TBP)₂] and stirred the mixture for 30 min in chloroform under different temperatures.
- 22. M. Kadar, A. Biro, K. Toth, B. Vermes, P. Huszthy, Spectrochim. Acta Part A 62 (2005) 1032–1038;
 b) I. D. Kuntz, Jr., F. P. Gasparro, M. D. Johnston, Jr., R. P. Taylor, J. Am. Chem. Soc. 90 (1968) 4778; c) H.A. Benesi, J.H. Hildebrand, J. Am. Chem. Soc. 1949, 71, 2703.

Graphical Abstract





Published on 05 December 2014. Downloaded by State University of New York at Binghamted on 05 December 2014. Downloaded by State University of New York at Binghamted on 05 December 2014.



Chart-1: Ligands employed in this study

S1.	Metal salt taken	Ligand taken	Structural Formula of the	% Yield, (wt of the	m.p.	$(\lambda_{\max}),$	P=O stretch	[Ref]
No.	mmol (amount)	(amount in	formed complex	product)		nm	in FT-IR,	
		mmol)					cm ⁻¹	
	1.346 (0.5 g)	4.039 (1.196 g)	$[LaCl_3(L_1)_3]$	79.2 (1.21 g)	235 (dec)	240	1028	[12]
	0.43 (0.159 g)	1.29 (0.393 g)	$[LaCl_3(L_2)_3]$	78.3 (0.391 g)	205 (dec)	216	1112	[12]
	1.34 (0.5 g)	4.02 (0.853 g)	$[LaCl_3(L_3)_3]$	92.0 (1.09 g)	>250	265	1105	
	1.34 (0.5 g)	4.02 (0.724 g)	$[LaCl_3(L_4)_3]$	89.0 (0.94 g)	>250		1016	
La	0.744 (0.082 g)	2.232 (0.262 g)	$[LaCl_3(L_5)_3]$	81.7 (0.85 g)	L	242	1060	[14,15]
-	2.87 (1.066 g)	8.61 (2.29 g)	$[LaCl_3(L_6)_3]$	82.9 (2.48 g)	L	224, 300	1033	[16,17]
	2.69 (1.0 g)	8.07 (2.24 g)	$[LaCl_3(L_7)_3]$	81.0 (2.36 g)	>250	255	1052	[18]
	1.49 (0.6133 g)	4.47 (0.554 g)	$[LaCl_3(L_8)_3]$	80.0 (0.781 g)	105	263	1047	
	1.75 (1.0 g)	3.5 (1.039 g)	$[Th(NO_3)_4(L_1)_2]$	85.4 (1.598 g)	213-215 (dec)	258	1132,1111	[12]
	0.458 (0.26 g)	0.916 (0.279 g)	$[Th(NO_3)_4(\mathbf{L_2})_2]$	82.5 (0.412 g)	217-218 (dec)	248	1138	[12]
	0.98 (0.56 g)	1.96 (0.417 g)	$[Th(NO_3)_4(\mathbf{L_3})_2]$	93.0 (0.82 g)	>250	230, 260	1055	
	0.98 (0.56 g)	1.96 (0.35 g)	$[Th(NO_3)_4(L_4)_2]$	91.0 (0.75 g)	>250	225, 295	1031	
Th	0.79 (0.45 g)	1.59 (0.62 g)	$[Th(NO_3)_4(L_5)_2]$	80.8 (0.80 g)	L	244	1024	[14,15]
	2.96 (1.68 g)	5.92 (1.569 g)	$[Th(NO_3)_4(L_6)_2]$	80.9 (2.42 g)	L	232	1033	[16,17]
	0.87 (0.5 g)	1.75 (0.488 g)	$[Th(NO_3)_4(L_7)_2]$	83.0 (0.75 g)	265	260	1024	[18]
	0.876 (0.240 g)	1.75 (0.5 g)	$[Th(NO_3)_4(\mathbf{L_8})_2]$	81.0 (0.54 g)	L	274	1035	

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

Page 17 o	f 27		RSC Advances				
Binghar	Tabl	e 2: ${}^{31}P{}^{1}H$ -NMR	chemical shifts of all the liga	ands and their metal con	nplexes		
v York at	Ligands Used ³¹ P{ ¹ H}- NMR for Free ligand		Expected structure of complex	³¹ P{ ¹ H}-NMR spectral data, ppm	Elemental Analysis of the metal complexes obtained (calculated)		
of Nev		(ppm)	-		% C	% H	% N
niversity	ТОРО	48.5	Th(TOPO) ₂ (NO ₃) ₄	70.0	46.12 (46.00)	8.31 (8.20)	4.52 (4.47)
State U1			La(TOPO) ₃ Cl ₃	54.72	61.62 (61.54)	11.07 (10.97)	-
aded by	ТРРО	29.3	Th(TPPO) ₂ (NO ₃) ₄	45.5	41.84 (41.71)	2.96 (2.92)	5.44 (5.40)
Downlo		-	La(TPPO) ₃ Cl ₃	35.0	45.64 (45.62)	5.44 (5.36)	-
oer 2014.	Diethylphosphite	9.48, 5.21	Th(DEPO) ₂ (NO ₃) ₄	4.92, 10.86	12.73 (12.71)	2.95 (2.93)	7.42 (7.41)
Decemt			La(DEPO) ₃ Cl ₃	2.36, -1.64	21.91 (21.85)	5.11	-
ed on 05	Bis(dimethylamino)phenyl	29.6	Th(BDMPO) ₂ (NO ₃) ₄	-1.1	26.84	3.82 (3.79)	12.43 (12.39)
Publish	phosphille onlice	-	La(BDMPO) ₃ Cl ₃	35.1	40.92	5.87	9.61
	Tris(dimethylamino)phosphine	20.0	Th(TDMPO) ₂ (NO ₃) ₄	22.2	17.26	4.86	16.74
	UNICE	-	La(TDMPO) ₃ Cl ₃	-2.5	27.68	(4.33) 6.99 (6.95)	16.14
	Dimorpholinephenylphosphine	24.6	Th(DMPO) ₂ (NO ₃) ₄	29.0	(27.02) 31.48* (31.35)	(0.93) 4.08 (3.95)	10.54 (10.45)
	UXIC	-	La(DMPO) ₃ Cl ₃	28.71	44.52	(5.93) 5.62	7.50 (7.41)
	Trimorpholinephosphine oxide	20.5	Th(TMPO) ₂ (NO ₃) ₄	23.0	(44.48) 24.12 (24.20)	(3.00) 4.23 (4.03)	11.41 (11.76)
			La(TMPO) ₃ Cl ₃	2181	(24.20) 37.28 (27.24)	(4.03) 6.30 (6.25)	10.91 (10.86)
	Tributylphosphate	-0.75	Th(TBP) ₂ (NO ₃) ₄	-1.21	(37.24) 28.54 (28.46)	(6.23) 5.42 (5.27)	5.56
		-	La(TBP) ₃ Cl ₃	-0.30	(28.46) 37.11 (37.06)	(3.37) 7.06 (7.00)	- (3.33)

*with one mole of CH₂Cl₂

RSC Advances Accepted Manuscript

C	Lizend ¹ U.NMD spectral data name ¹³ C.NMD spectral da				
S.	Ligand	H	C-NMR spectral data,		
NO.					ррт
		Free ligand (L)	$[Th(NO_3)_4L_2]$	[LaCl ₃ L ₃]	Free ligand (L)
					¹³ C NMR (400 MHz, CDCl3)
1	ТОРО	1.87-1.03 [m, 14H;	1.92-1.05 [m, 14H;	1.89-1.03 [m, 14H;	31.78, 31.12, 29.04, 28.30,
		CH_2]	CH_2]	CH_2]	27.66, 22.60, 21.69, 14.04
		_		_	$(CH_2 \text{ and } CH_3)$
2	TPPO	7.58-7.39 [m, 5H;	7.60-7.41 [m, 5H; Ar-	7.55-7.37 [m, 5H;	133.05, 132.11, 131.92,
		Ar-H]	H]	Ar-H]	128.56, 128.44 (Ph)
3	Diethyl Phosphite	1.31 [t, 6H; CH ₃],	1.32 [t, 6H; CH ₃],	1.30 [t, 6H; CH ₃],	61.62 (OCH ₂), 16.15 (CH ₃)
		1.76 [q, 4H; CH ₂]	1.77 [q, 4H; CH ₂]	1.75 [q, 4H; CH ₂]	
4	Bis(dimethylamino)	7.74-7.42 [m, 5H;	7.83-7.39 [m, 5H; Ar-	7.62-7.74 [m, 5H;	132.13, 131.03, 129.51,
	phenylphosphine	Ar-H], 2.62 [s,	H], 2.59 [s, 12H;	Ar-H], 2.51 [s,	128.41, 128.28 (Ph), 36.33
	oxide	12H; CH ₃]	CH ₃]	12H; CH ₃]	$(N-CH_3)$
5	Tris(dimethylamino)	2.67 [s, 18H; CH ₃]	2.59 [s, 18H; CH ₃]	2.61 [s, 18H; CH ₃]	35.24 (N-CH ₃)
	phosphine oxide				
6	Bis(morpholino)	7.68-7.47 [m, 5H;	7.70-7.51 [m, 5H; Ar-	7.66-7.45 [m, 5H;	132.12, 131.87, 128.81,
	phenylphosphine	Ar-H], 3.58 [t, 8H;	H], 3.59 [t, 8H; CH ₂],	Ar-H], 3.55 [t, 8H;	128.68 (Ph), 67.08 (O-CH ₂),
	oxide	CH ₂], 3.02 [t, 8H;	3.04 [t, 8H; CH ₂]	CH ₂], 3.00 [t, 8H;	44.45 (N-CH ₂)
		CH ₂]		CH ₂]	
7	Tris(morpholino)	3.62 [t, 12H; CH ₂],	3.66 [t, 12H; CH ₂],	3.63 [t, 4H; CH ₂],	67.29 (O-CH ₂), 45.17 (N-
	phosphine oxide	3.06 [t, 12H; CH ₂]	3.11 [t, 12H; CH ₂]	3.08 [t, 4H; CH ₂]	CH ₂)
8	TBP	3.90 [t, 6H; CH ₂],	3.94 [t, 6H; CH ₂],	3.91 [t, 6H; CH ₂],	67.23 (OCH ₂), 32.41 (CH ₂),
		1.52 [m, 6H; CH ₂],	1.56 [q, 6H; CH ₂],	1.53 [q, 6H; CH ₂],	18.73 (CH ₂), 13.43 (CH ₃)
		1.29 [m, 6H; CH ₂],	1.30[m, 6H; CH ₂],	0.81 [t, 6H; CH ₂]	
		0.813 [t, 6H; CH ₂]	0.82 [t, 6H; CH ₂]		

Table 3: ¹H- and ¹³C-NMR data of all the ligands and their metal complexes







Chart-2: Predicted general structures of [LaCl₃(R₃PO)₃] and [Th(NO₃)₄(R₃PO)₂].



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



$$[Th(NO_3)_4(TOPO)_2] \xrightarrow{TBP} [Th(NO_3)_4(TOPO)(TBP)]$$

Eq.4



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

Published on 05 December 2014. Downloaded by State University of New York at Binghamted on back of the state of the stateo



Fig.1: ³¹P{¹H}-NMR spectrum of mixed ligand complex, [Th(NO₃)₄(TOPO)(TBP)]; (a) - [Th(NO₃)₄(TOPO)(TBP)], (b) – free TOPO, (c) free TBP



Fig.2

Published on 05 December 2014. Downloaded by State University of New York at Binghamted on **52** but the state of the stat









Page	24	of	27
------	----	----	----

S.No.	Ligand	Stability Constants of Th(IV) Complexes*	Stability Constants of La(III) Complexes*
1.	L1	6.42	6.23
2.	L ₂	6.78	6.48
3.	L ₃	6.58	6.33
4.	L ₄	7.25	6.67
5.	L ₅	11.7	9.46
6.	L ₆	9.82	8.82
7.	L ₇	7.43	7.13
8.	L ₈	7.04	6.8

Table-4: Stability constants of various metal complexes

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



RSC Advances



Various phosphine oxide ligands with different substituents

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

Published on 05 December 2014. Downloaded by State University of New York at Binghamted on 05 December 2014. Downloaded by State University of New York at Binghamted on 05 December 2014.



Fig.6: TGA of thorium(IV) complexes



Fig.7: TGA of lanthanum(III) complexes