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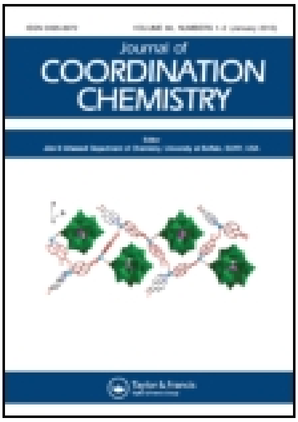

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# Investigations on synthesis, thermolysis, and coordination chemistry of aminophosphine oxides

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# Investigations on synthesis, thermolysis, and coordination chemistry of aminophosphine oxides

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Some aminophosphine oxides (AmPOs), $(R_1)(R_2)(R_3)$P=O [$R_1 = R_2 = R_3 = HNCH_2CH{=}CH_2$; $R_1 = R_2 = Ph$, $R_3 = HNCH_2CH{=}CH_2$; $R_1 = R_2 = R_3 = HNNMe_2$; $R_1 = R_2 = Ph$, $R_3 = HNNMe_2$; $R_1 = R_2 = R_3 = NC_4H_8O$; $R_1 = R_2 = Ph$, $R_3 = NC_4H_8O$], have been synthesized. The coordination chemistry of these AmPOs is studied with La(III), Th(IV), and U(VI) salts. The products are characterized by various analytical and spectroscopic techniques, and the thermal properties of the ligands and their complexes examined. The TGA data for these compounds show different decomposition temperatures, as well as thermal stability of the metal complexes. Comparisons are made among different ligands on their selective complexing ability towards some chosen metal salts. Mulliken population analysis shows that the basicity of P=O of ligand increases with an increase in the number of P-bonded amino groups.

*Keywords*: Aminophosphine oxide; Lanthanum(III); Thorium(IV); Uranium(VI) complexes; Thermogravimetric analysis

## 1. Introduction

Ligands containing either trivalent or pentavalent phosphorus have interest throughout inorganic and organic chemistry, due to their wide range of applications as insecticides and antitumor agents and their involvement in a number of catalytic reactions [1–3]. Among these ligand systems, phosphines or phosphine oxides containing P–N bonds represent a major class of molecules as potential precursors to P–N backbone polymeric materials [4], active ligands [5], and various other applications [6]. This area is likely to continue to grow as the demand for carefully designed ligands has been increasing in nuclear industries for treatment and separation of nuclear waste. In this context, understanding the nature of aminophosphine oxide (AmPO) ligands in coordination spheres of selected f-metals is important, especially as they possess potentially reactive P–N linkage and extra donor alkene moiety or $-NMe_2$. Little work has been focused on extraction and coordination chemistry of AmPO ligands with lanthanides and actinides [3, 7, 8].

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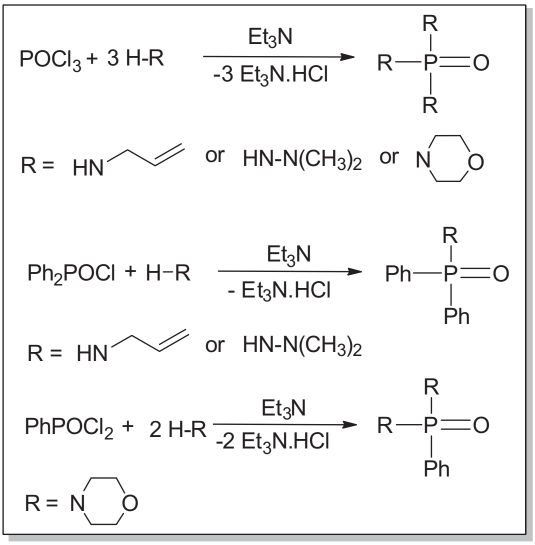
Here, we describe the synthesis, coordination chemistry, and thermolysis of some selected aminophosphine oxides [($R_1$)($R_2$)($R_3$) P=O, where $R_1 = R_2 = R_3 = HNCH_2CH{=}CH_2$; $R_1 = R_2 = Ph$, $R_3 = HNCH_2CH{=}CH_2$; $R_1 = R_2 = R_3 = HNNMe_2$; $R_1 = R_2 = Ph$, $R_3 = HNNMe_2$; $R_1 = R_2 = R_3 = NC_4H_8O$; $R_1 = R_2 = Ph$, $R_3 = NC_4H_8O$]. In order to gain more insight into the nature of metal complexes, further studies have been carried out to observe the effect of substituents on phosphorus. To the best of our knowledge, this contribution represents the first example of thermolysis of various metal–AmPO complexes.

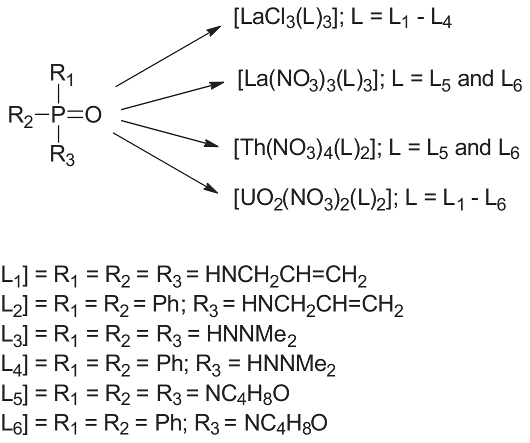
## 2. Results and discussion

### 2.1. *Synthesis and characterization of ligands and metal complexes*

Condensation between amines and phosphorus(V)oxychlorides was used for the preparation of aminophosphine oxides and phenyl aminophosphine oxides as given in scheme 1. The reactions of $La(NO_3)_3$, $LaCl_3$, $UO_2(NO_3)_2$, and $Th(NO_3)_4$ with selected AmPOs are shown in scheme 2. Though the preliminary reactions were performed with 1 : 6 metal to ligand molar ratio, subsequent studies gave satisfactory yields of metal complexes with 1 : 3 M ratio for U and Th salts and 1 : 3.5 for La salts at room temperature for 10 h. Complexes of multicoordinate ligands (**L₁**–**L₆**) with salts of lanthanum and uranium in a solvent mixture of $CH_2Cl_2$ and ethanol (5 : 1) were isolated as crystalline solids. $[LaCl_3(\mathbf{L_1})_3]$, $[LaCl_3(\mathbf{L_2})_3]$, $[LaCl_3(\mathbf{L_3})_3]$, $[LaCl_3(\mathbf{L_4})_3]$, $[La(NO_3)_3(\mathbf{L_5})_3]$, $[La(NO_3)_3(\mathbf{L_6})_3]$, $[UO_2(NO_3)_2(\mathbf{L_1})_2]$, $[UO_2(NO_3)_2(\mathbf{L_2})_2]$, $[UO_2(NO_3)_2(\mathbf{L_3})_2]$, $[UO_2(NO_3)_2(\mathbf{L_4})_2]$, $[UO_2(NO_3)_2(\mathbf{L_5})_2]$, $[UO_2(NO_3)_2(\mathbf{L_6})_2]$, $[UO_2(NO_3)_2(dppeO_2)]$, $[Th(NO_3)_4(\mathbf{L_5})_2]$, and $[Th(NO_3)_4(\mathbf{L_6})_2]$ were further purified by washing with $CHCl_3$ (2 × 10 mL) to remove unreacted free ligands and further characterized by spectroscopic and analytical techniques. Most of these complexes were soluble in polar solvents like $CH_3CN$ and DMSO. All analytical and spectroscopic data of the metal complexes of $\mathbf{L_1}$–$\mathbf{L_4}$ are given in table 1. Table 2 reveals characterization data of metal complexes associated with $\mathbf{L_5}$ and $\mathbf{L_6}$.



Scheme 1. Synthesis of aminophosphine oxide ligands.



$[L_1] = R_1 = R_2 = R_3 = HNCH_2CH{=}CH_2$
$[L_2] = R_1 = R_2 = Ph; R_3 = HNCH_2CH{=}CH_2$
$[L_3] = R_1 = R_2 = R_3 = HNNMe_2$
$[L_4] = R_1 = R_2 = Ph; R_3 = HNNMe_2$
$[L_5] = R_1 = R_2 = R_3 = NC_4H_8O$
$[L_6] = R_1 = R_2 = Ph; R_3 = NC_4H_8O$

Scheme 2. Preparation of metal complexes with AmPOs.

The reaction mixtures always posed the problem of separating the desired compounds from amine hydrochloride salts, which are byproducts of the reaction. The fractional crystallization method was sufficient to obtain the target AmPOs in a pure form from the reaction mixtures. The AmPOs were subsequently recrystallized from chloroform and *n*-hexane to obtain them as colorless crystalline solids.

Formation of neutral AmPO–metal complexes from pure ligands was observed at room temperature in chloroform, dichloromethane, and methanol. $^1$H NMR spectra of all the complexes with $\mathbf{L_1}$ and $\mathbf{L_2}$ did not indicate coordination of 1-alkene to the metal center, i.e. the position of chemical shifts for $–CH{=}CH_2$ protons in ligands (at $\delta$ 5.82 and 5.06, respectively) was not altered in complexes. Also, the $^1$H NMR of $[UO_2(NO_3)_2(\mathbf{L_3})_2]$ (where $\mathbf{L_3} = OP(NHNMe_2)_3$) revealed a significant difference in the chemical shifts of the methyl protons of $NNMe_2$ in the hydrazine, depending on the solvent used. For example, the position of methyl protons of $NNMe_2$ of free hydrazine ($\mathbf{L_3}$) and $[UO_2(NO_3)_2(\mathbf{L_3})_2]$ appears at $\delta$ 2.57 and 2.85, respectively, in $CDCl_3$ whereas in $C_6D_6$ the same compound showed peaks at $\delta$ 2.59 and 2.76.

The $^1$H NMR spectrum of $[UO_2(NO_3)_2(\mathbf{L_6})_2]$ showed signals pertaining to $N–CH_2$ and $O–CH_2$ at $\delta$ 3.05 and 3.65, respectively, which slightly differs from signals of free ligand ($\delta$ 3.10 and 3.71, respectively). A similar trend was observed with $\mathbf{L_5}$ and these results are in agreement with the literature [9].

The purity of all the samples has been established by spectral and analytical data, especially by observing one sharp singlet in their $^{31}$P NMR spectra (tables 1 and 2). By comparing $^{31}$P NMR results of the free ligand (for example $\mathbf{L_6}$ shows $\delta$ 23.5), as well as the corresponding metal complexes (ranging from $\delta$ 19.2–20.4), it is evident that the metal complexes showed a signal shift with relation to the free ligand, showing evidence of bonding through the phosphoryl. The solubility of these AmPO–metal complexes in organic solvents increases with increasing number of allylamino substituents on phosphorus.

Attempts have been made to compare the coordination and thermolysis behavior of AmPO–metal complexes with $[UO_2(NO_3)_2(dppeO_2)]$ (dppe = 1,2-bis(diphenylphosphino)ethane), as various diphosphine dioxides are well-known ligands in lanthanide and actinide metal chemistry [10]. The reaction of $[UO_2(NO_3)_2{\cdot}6H_2O]$ with $dppeO_2$ in ethanol yielded $[UO_2(NO_3)_2(dppeO_2)]$. The IR spectrum shows the ligand coordinated through both

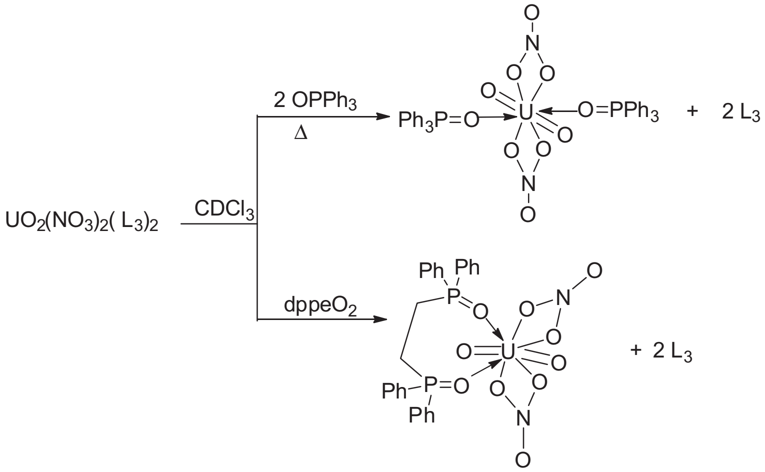
Table 1. Spectroscopic data of La(III) and U(VI) complexes containing $\mathbf{L_1}$–$\mathbf{L_4}$.

| Sl. no. | Complex | Yield (%) | m.p. (°C) | $^1$H NMR (ppm) | $^{31}$P NMR (ppm) | Elemental analysis (calculated) | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | %C | %H | %N |
| 1. | $[LaCl_3(\mathbf{L_1})_3]$ | 85 | 226–230 | 4.1 (*s*, 9H, –NH), 3.22 (*d*, 18H, –NCH$_2$), 4.40–4.55 (*m*, 18H, = CH$_2$), 5.52–5.64 (*m*, 9H, =CH) | 16.8 | 36.72 (36.77) | 5.66 (5.14) | 14.42 (14.29) |
| 2. | $[LaCl_3(\mathbf{L_2})_3]$ | 76 | 158–162 | 7.26–8.18 (*m*, 30H, Ph), 4.1 (*s*, 3H, –NH), 3.22 (*d*, 6H, –NCH$_2$), 4.40–4.55 (*m*, 6H, =CH$_2$), 5.52–5.64 (*m*, 3H, =CH) | 16.9 | 31.64 (31.99) | 5.45 (5.37) | 12.42 (12.44) |
| 3. | $[LaCl_3(\mathbf{L_3})_3]$ | 84 | 236–248 | 4.1 (*s*, 9H, –NH), 3.22 (*s*, 54H, –NCH$_3$) | 20.4 | 22.66 (22.39) | 7.08 (7.02) | 26.43 (25.98) |
| 4. | $[LaCl_3(\mathbf{L_4})_3]$ | 85 | 202–216 | 7.26–8.18 (*m*, 30H, Ph), 4.1 (*s*, 3H, –NH), 3.22 (*s*, 54H, –NCH$_3$) | 19.6 | 20.88 (20.78) | 6.25 (6.10) | 24.56 (24.23) |
| 5. | $[UO_2(NO_3)_2(\mathbf{L_1})_2]$ | 90 | 184–192 | 4.1 (*s*, 6H, –NH), 3.22 (*d*, 12H, –NCH$_2$), 4.40–4.55 (*m*, 12H, =CH$_2$), 5.52–5.64 (*m*, 6H, =CH) | 22.6 | 26.33 (26.41) | 3.66 (3.69) | 13.41 (13.69) |
| 6. | $[UO_2(NO_3)_2(\mathbf{L_2})_2]$ | 86 | 146–158 | 7.26–8.18 (*m*, 20H, Ph), 4.1 (*s*, 2H, –NH), 3.22 (*d*, 4H, –NCH$_2$), 4.40–4.55 (*m*, 4H, =CH$_2$), 5.52–5.64 (*m*, 2H, =CH) | 21.8 | 26.46 (26.22) | 4.68 (4.40) | 13.68 (13.59) |
| 7. | $[UO_2(NO_3)_2(\mathbf{L_3})_2]$ | 77 | 163–172 | 4.1 (*s*, 6H, –NH), 3.22 (*s*, 36H, –NCH$_3$) | 34.6 | 16.41 (16.22) | 5.28 (5.11) | 22.32 (22.15) |
| 8. | $[UO_2(NO_3)_2(\mathbf{L_4})_2]$ | 82 | 152–159 | 7.26–8.18 (*m*, 30H, Ph), 4.1 (*s*, 2H, –NH), 3.22 (*s*, 12H, –NCH$_3$) | 22.4 | 17.18 (17.11) | 5.29 (5.02) | 23.35 (23.27) |
| 9. | $[UO_2(NO_3)_2(dppeO_2)]$ | 57 | >250 | 6.92–7.88 (*m*, 20H, Ph), 2.8–3.1 (*m*, 4H, P–CH$_2$) | 44.3 | 38.28 (37.88) | 3.63 (2.93) | 3.42 (3.40) |

Table 2. Analytical and spectral data of La(III), Th(IV), and U(VI) complexes containing $\mathbf{L_5}$ and $\mathbf{L_6}$.

| Sl. no. | Complex | Yield (%) | m.p. (°C) | $^1$H NMR (ppm) | $^{31}$P NMR (ppm) | Elemental analysis (calculated) | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | %C | %H | %N |
| 1. | $[La(NO_3)_3(\mathbf{L_5})_3]$ | 80.2 | 228–230 | 2.4 (*m*, 36H, –N–$CH_2$), 3.1 (*m*, 36H, –O–$CH_2$) | 16.2 | 34.24 (34.84) | 5.94 (5.80) | 14.02 (13.55) |
| 2. | $[UO_2(NO_3)_2(\mathbf{L_5})_2]$ | 76.6 | 236 (dec) | 2.4 (*m*, 24H, –N–$CH_2$), 3.1 (*m*, 24H, –O–$CH_2$) | 16.5 | 25.62 (26.08) | 4.32 (4.35) | 10.21 (10.14) |
| 3. | $[Th(NO_3)_4(\mathbf{L_5})_2]$ | 68.8 | 214 (dec) | 2.4 (*m*, 24H, –N–$CH_2$), 3.1 (*m*, 24H, –O–$CH_2$) | 17.5 | 24.12 (24.20) | 4.23 (4.03) | 11.41 (11.76) |
| 4. | $(UO_2(NO_3)_2(\mathbf{L_6})_2]$ | 81.0 | 200 (dec) | 7.26–8.18 (*m*, 20H, Ph), 2.4 (*m*, 8H, –N–$CH_2$), 3.1 (*m*, 8H, –O–$CH_2$) | 20.4 | 34.11 (34.08) | 4.31 (4.26) | 8.52 (8.52) |
| 5. | $[Th(NO_3)_4(\mathbf{L_6})_2]$ | 82.2 | 218 (dec) | 6.86–7.82 (*m*, 20H, Ph), 2.4 (*m*, 8H, –N–$CH_2$), 3.1 (*m*, 8H, –O–$CH_2$) | 19.5 | 32.62* (32.61) | 4.08 (4.05) | 11.02 (10.23) |
| 6. | $[La(NO_3)_3(\mathbf{L_6})_3]$ | 82.4 | 208 (dec) | 7.02–7.96 (*m*, 30H, Ph), 2.4 (*m*, 12H, –N–$CH_2$), 3.1 (*m*, 12H, –O–$CH_2$) | 19.2 | 41.77 (41.56) | 5.32 (5.23) | 10.42 (10.39) |

*With 0.25 M of toluene.



Scheme 3. Ligand exchange reactions.

phosphine oxide oxygens to uranium by replacing all the waters. $^{31}$P NMR of this complex showed a singlet at $\delta$ 44.3 and no signal at $\delta$ 35.8 for free dppe$O_2$, indicating bonding from both the phosphoryl oxygens with the metal.

IR spectra of the metal complexes derived from $\mathbf{L_1}$–$\mathbf{L_6}$ for $\nu$(P=O) range from 1063 to 1070 cm$^{-1}$ as strong bands, depending on the nature of substituents on phosphorus (free ligand ranging from 1120 to 1174 cm$^{-1}$ as strong bands), indicating coordination through phosphoryl oxygen. All the bands of nitrates at 1524 (*s*), 1308 (*s*) and 1276 (*m*) cm$^{-1}$ indicate coordinated bidentate nitrates in **3**, **4**, **7** and **10–12** [8c]. Broad and weak bands for La–Cl are assigned at 220–240 cm$^{-1}$. A band at 930 cm$^{-1}$ is assigned to O=U=O as reported earlier [10f].

In order to expand the relatively unexplored ligand addition chemistry of these AmPO–metal complexes, investigations into their reactivities with various types of ligands were carried out. The reactivity of $[UO_2(NO_3)_2(\mathbf{L_3})_2]$, where $\mathbf{L_3} = OP(NHNMe_2)_3$, was studied with $OPPh_3$ and 1,10-phenanthroline, and there was no reaction observed at room temperature even after several days.

The reaction of $[UO_2(NO_3)_2(\mathbf{L_3})_2]$ with $OPPh_3$ yielded a mixture of products in refluxing $CDCl_3$. The formation of a known complex showing $\delta$ 37.2 for $[UO_2(NO_3)_2(OPPh_3)_2]$ [11] by exchanging $\mathbf{L_3}$ was observed by $^{31}$P NMR spectrum. On the contrary, the $^{31}$P NMR spectrum of $[UO_2(NO_3)_2(\mathbf{L_3})_2]$ did not show any dissociation on refluxing with a large excess of 1,10-phenanthroline. $^{31}$P NMR spectral analysis shows that dppe$O_2$ can smoothly exchange with $\mathbf{L_3}$ in $[UO_2(NO_3)_2(\mathbf{L_3})_2]$. This could be due to the chelating nature of diphosphine dioxide as shown in scheme 3.

## 2.2. *Theoretical calculations*

The electron distributions in aminophosphine oxides $(R_2N)_nR_{(3-n)}P{=}O$ were analyzed through an electrostatic charge analysis. Although atomic charges are not an observable in quantum mechanics, they are appropriate to get an idea on the electron distribution. In this study, the Mulliken population analysis was employed. In table 3, Mulliken atomic charges are reported for the six ligands.

Table 3. Selected Mulliken atomic charges for $(R_2N)_nR_{(3-n)}P{=}O$.[a]

| Ligand | P=O | P=O | P–N | P–C |
|---|---|---|---|---|
| $(H_2N)_3P{=}O$ | −0.654 | +1.262 | −0.637; −0.637; −0.641 | |
| $(Me_2N)_3P{=}O$ | −0.680 | +1.444 | −0.649; −0.649; −0.648 | |
| $(Me_2N)_2MeP{=}O$ | −0.661 | +1.297 | −0.626; −0.639 | −0.566 |
| $(Me_2N)Me_2P{=}O$ | −0.645 | +1.146 | −0.605 | −0.547; −0.548 |
| $(Et_2N)_3P{=}O$ | −0.686 | +1.457 | −0.641; −0.650; −0.652 | |
| $({}^nPr_2N)_3P{=}O$ | −0.681 | +1.456 | −0.639; −0.640; −0.659 | |

[a] Electron units (charge of electron is equal to −1).

From our results, it is clear that the alkyl chain length of the amino moiety has a negligible effect on the atomic charge at oxygen. However, as the number of amino groups attached to phosphorus increase, the atomic charge at the oxygen increases significantly from −0.645 in $(Me_2N)Me_2P{=}O$ to −0.680 in $(Me_2N)_3P{=}O$. The Mulliken population analysis is useful for qualitative purposes and provides an effective indicator of the basicity of the O-donor of the incoming ligand. We can interpret these data to show that as the number of P-bonded amino groups increase, the σ-basicity of the P=O group of the ligand increases.

### 2.3. *Thermogravimetric analysis*

Different examples of AmPOs and their metal complexes were subjected to thermogravimetric analysis and decomposition of these compounds begins at different temperatures. The differences in thermal stability are a reflection of the influence that substituents on phosphorus have on the thermal behavior. However, a feature common to most of them is that they decompose essentially in a single step. The decomposition temperatures of these compounds are given in table 4.

TGA curves of metal–AmPO complexes were obtained from 25 to 700 °C. Weight loss below 100 °C for two of the complexes, i.e. $[UO_2(NO_3)_2(\mathbf{L_3})_2]$ and $[LaCl_3(\mathbf{L_3})_3]$, where $\mathbf{L_3} = OP(NHNMe_2)_3$, was ascribed to the evaporation of solvent from the crystal lattice, as reported earlier [12]. Weight loss at lower temperatures also indicates the thermal instability of the complexes. Weight loss temperatures for the other complexes were in the range of 150–350 °C, indicating more thermal stability (i.e. no involvement of water or any solvent in thermal stability of these compounds). The TGA of some of the ligands were carried out in order to compare the thermal stability with their corresponding metal complexes (table 4). Stability of ligands in the presence of metal salts was relatively high in most cases. Thermal stability of various metal complexes derived from the ligands is $dppeO_2 > \mathbf{L_6} > \mathbf{L_5} > \mathbf{L_1} > \mathbf{L_3}$. The shapes of the TG curves obtained for $[UO_2(NO_3)_2L_2]$ (L = AmPO) are nearly the same except for $[UO_2(NO_3)_2(dppeO_2)]$. Mass loss percentages (TGA and calculated) and temperature ranges of some selected ligands and complexes obtained in the studies are summarized in table 4. The TGA curves of ligands as well as complexes are given in figure 1 and Supplementary material. $[(UO_2(NO_3)_2(\mathbf{L_5})_2)]$ undergoes decomposition at 260–303 °C, producing a stable residue. Mass losses and IR spectra suggest $(UO_2)_2P_2O_7$ as the final product. Residues from other metal complexes were their corresponding metal phosphates and pyrophosphates, which is in agreement with earlier work [13].

Table 4. Thermogravimetric analysis data of some AmPOs and their metal complexes.

| Compound | Temperature range (°C) | % Weight loss obtained | Calculated weight loss (%) for loss of fragment |
|---|---|---|---|
| $\mathbf{L_1}$ | 25–410; 410–700 | 21.3;<br>77.3 | 21.8 ($NHCH_2CH{=}CH_2$);<br>78.2 ($Ph_2PO$) |
| $\mathbf{L_3}$ | 100–320; 320–700 | 26.4;<br>73.3 | 24.2 ($NHNMe_2$);<br>76.1 ($Ph_2PO$) |
| $[UO_2(NO_3)_2(\mathbf{L_1})_2]$ | 60–340; 340–700 | 27.3;<br>26.8 | 28.3 ($NHCH_2CH{=}CH_2$);<br>28.3 ($NHCH_2CH{=}CH_2$) |
| $[UO_2(NO_3)_2(\mathbf{L_3})_2]$ | 50–160; 160–220 | 32.5;<br>22.5 | 56.7 ($NHNMe_2$);<br>23.3 ($NO_2$) |
| $[LaCl_3(\mathbf{L_3})_3]$ | 25–290 | 36.4 | 34.2 ($NHNMe_2$) |
| $\mathbf{Dppe(O)_2}$ | 170–700 | 98.5 | Decomposes completely |
| $[UO_2(NO_3)_2(D\mathbf{ppeO_2})]$ | 50–360; 380–700 | 28.3;<br>22.6 | 35.3 ($dppeO_2$);<br>23.3 ($NO_2$) |
| $\mathbf{L_5}$ | 150–238 | 84.1 | 81.1 ($OC_4H_8N–$ & $C_6H_5–$) |
| $\mathbf{L_6}$ | 150–266 | 82.2 | 80.7 ($OC_4H_8N–$ & $C_6H_5–$) |
| $[UO_2(NO_3)_2(\mathbf{L_5})_2]$ | 266–303 | 62.5 | 61.2 ($OC_4H_8N–$ & $NO_2$) |
| $[Th(NO_3)_4(\mathbf{L_5})_2]$ | 245–294 | 69.1 | 65.6 ($OC_4H_8N–$ & $NO_2$) |
| $[Th(NO_3)_2(\mathbf{L_6})_2]$ | 235–340 | 68.4 | 62.4 ($OC_4H_8N–$ & $NO_2$) |

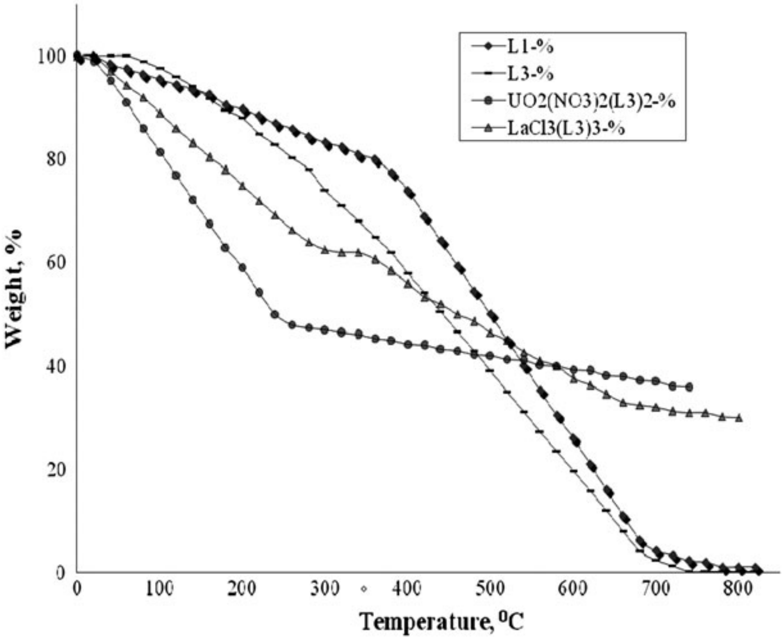


Figure 1. TGA curves of $\mathbf{L_1}$ and $\mathbf{L_3}$ ligands and their complexes $[UO_2(NO_3)_2(\mathbf{L_3})_2]$ and $[LaCl_3(\mathbf{L_3})_2]$.

## 3. Experimental

### 3.1. *Instrumentation*

$^1$H, $^{13}$C, and $^{31}$P NMR spectra were recorded on a Bruker DMX-400 spectrometer and all $^1$H chemical shifts are reported relative to the residual proton resonance in deuterated solvents (all at 298 K, $CDCl_3$). Microanalyses (C, H, N) were conducted with a Thermo

Flash 1112 Series CHNS-O Elemental Analyzer instrument and Heraeus CHN rapid microanalyzer. Infrared spectra were recorded on a Perkin-Elmer Spectrum One FT-IR Spectrometer, Perkin Elmer 1430, Shimadzu UV-240 (and/or Shimadzu NIR 3100), and JEOL JNM JGX-400 instruments, respectively. 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.

### 3.2. *Materials and methods*

All manipulations were carried out under nitrogen 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 $POCl_3$, $Ph_2POCl$, and $PhPOCl_2$ were used as received and other reagents (Merck) like morpholine, *n*-allylamine, and N,N-dimethylhydrazine were purified by distillation over KOH [14]. Hydrated metal salts (Loba and Aldrich), $[(ME_x \cdot yH_2O)]$ where M=La, U, Th; E=$NO_3$ ($x=2$ and $y=6$ for U; $x=4$ and $y=5$ for Th; $x=3$ and $y=7$ for La), and E=Cl (x = 3 and y = 7 for La) were used as received. The compounds $PO(NHCH_2CH{=}CH_2)_3$ (**L$_1$**) [15], $Ph_2PO(NHCH_2CH{=}CH_2)$ (**L$_2$**) [16], $PO(NHNMe_2)_3$ (**L$_3$**) [17], and $Ph_2PO(NHNMe_2)$ [18] (**L$_4$**) were prepared according to previous literature procedures. Bis(diphenylphosphino)ethane dioxide [$Ph_2P(O)CH_2CH_2P(O)Ph_2$, dppeO$_2$] was prepared as described earlier [19]. The proton decoupled $^{31}$P NMR chemical shifts of **L$_1$** ($\delta$ 24.9), **L$_2$** ($\delta$ 24.4), **L$_3$** ($\delta$ 26.5), **L$_4$** ($\delta$ 22.5), and **L$_5$** ($\delta$ 25.2) were comparable with the literature.

**3.2.1. Preparation of dimorpholino–phenylphosphine oxide (L$_6$).** To a stirred solution of morpholine (2.95 g, 33.8 mM) and triethylamine (3.6 g, 35 mM) in toluene–hexane (1 : 1, 25 mL) at ice cold temperature, $PhPOCl_2$ (5.08 g, 26.05 mM) of the same solvent mixture (20 mL) was added dropwise through a dropping funnel and allowed to stir for 15 h. The reaction mixture was filtered to separate $Et_3N \cdot HCl$ salt and the volume of filtrate was reduced to ≈ 10 mL under reduced pressure and kept in a refrigerator for 24 h. The obtained colorless crystalline product was separated and dried under vacuum for 4 h to remove all volatiles. The yield was 6.56 g (85%). m.p.: 98–100 °C. $^1$H NMR ($CDCl_3$): $\delta$ 3.10 (*s*, 8H, N–$CH_2$), 3.72 (*s*, 8H, O–$CH_2$), 7.78–7.32 (*m*, 5H, Ph); $^{13}$C NMR: $\delta$ 44.1 (N–$CH_2$), 66.9 (O–$CH_2$), 128.4–131.2 (Ph); $^{31}$P NMR: $\delta$ 23.5; Anal. Calcd for $C_{14}H_{21}N_2O_3P$: C, 56.75; H, 7.09; N, 9.46. Found: C, 56.63; H, 7.31; N, 9.52. In a similar manner, trimorpholino–phosphine oxide (**L$_5$**) [20] was also prepared. The spectroscopic data obtained for **L$_5$** were identical to those previously reported.

**3.2.2. Synthesis of the metal complexes: general procedure for the preparation of metal complexes.** The following general procedure was used for the preparation of $[UO_2(NO_3)_2(\mathbf{L_6})_2]$ and the same procedure was followed for the other metal complexes.

A finely powdered solid of $UO_2(NO_3)_2 \cdot 6H_2O$ (0.28 g, 0.65 mM) was added all at once to a stirred solution of **L$_6$** (1.156 g, 3.9 mM) in $CH_2Cl_2$ and ethanol (5 : 1) and the mixture was stirred for 24 h to get yellow precipitate. The precipitate was washed (3 × 5 mL) with dichloromethane to obtain pure $UO_2(NO_3)_2(\mathbf{L_6})_2$. In a similar way, $LaCl_3(\mathbf{L_1})_3$ [$LaCl_3 \cdot 7H_2O$ (0.121 g, 0.326 mM) and **L$_1$** (0.245 g, 1.1 mM)], $LaCl_3(\mathbf{L_2})_3$ [$LaCl_3 \cdot 7H_2O$ (0.142 g, 0.38 mM) and $\mathbf{L_2}$ (0.342 g, 1.33 mM)], $LaCl_3(\mathbf{L_3})_3$ [$LaCl_3{\cdot}7H_2O$ (0.132 g, 0.355 mM) and $\mathbf{L_3}$ (0.278 g, 1.24 mM)], $LaCl_3(\mathbf{L_4})_3$ [$LaCl_3{\cdot}7H_2O$ (0.115 g, 0.31 mM) and $\mathbf{L_4}$ (0.282 g, 1.08 mM)], $La(NO_3)_3(\mathbf{L_5})_3$ [$La(NO_3)_3{\cdot}7H_2O$ (0.225 g, 0.499 mM) and $\mathbf{L_5}$ (0.533 g, 1.75 mM)], $La(NO_3)_3(\mathbf{L_6})_3$ [$La(NO_3)_3{\cdot}7H_2O$ (0.176 g, 0.39 mM) and $\mathbf{L_6}$ (0.392 g, 1.36 mM)], $Th(NO_3)_4(\mathbf{L_5})_2$ [$Th(NO_3)_4{\cdot}5H_2O$ (0.154 g, 0.27 mM) and $\mathbf{L_5}$ (0.247 g, 0.81 mM)], $Th(NO_3)_4(\mathbf{L_6})_2$ [$Th(NO_3)_4{\cdot}5H_2O$ (0.177 g, 0.31 mM) and $\mathbf{L_6}$ (0.268 g, 0.93 mM)], $UO_2(NO_3)_2(\mathbf{L_1})_2$ [$UO_2(NO_3)_2{\cdot}6H_2O$ (0.202 g, 0.402 mM) and $\mathbf{L_1}$ (0.26 g, 1.2 mM)], $UO_2(NO_3)_2(\mathbf{L_2})_2$ [$UO_2(NO_3)_2{\cdot}6H_2O$ (0.188 g, 0.374 mM) and $\mathbf{L_2}$ (0.289 g, 1.12 mM)], $UO_2(NO_3)_2(\mathbf{L_3})_2$ [$UO_2(NO_3)_2{\cdot}6H_2O$ (0.196 g, 0.39 mM) and $\mathbf{L_3}$ (0.263 g, 1.17 mM)], $UO_2(NO_3)_2(\mathbf{L_4})_2$ [$UO_2(NO_3)_2{\cdot}6H_2O$ (0.146 g, 0.291 mM) and $\mathbf{L_4}$ (0.227 g, 0.873 mM)], and $UO_2(NO_3)_2(\mathbf{L_5})_2$ [$UO_2(NO_3)_2{\cdot}6H_2O$ (0.226 g, 0.45 mM) and $\mathbf{L_5}$ (0.412 g, 1.35 mM)] were prepared. The uranium complexes were synthesized by the reaction of $CH_2Cl_2$ solutions of uranyl nitrate and the ligands. The products obtained were recrystallized from $CH_2Cl_2/Et_2O$ mixture after removing the solvent. The unreacted ligands were collected from the worked-up solvent mixtures 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 tables 1 and 2.

**3.2.3. Preparation of [$UO_2(NO_3)_2(dppeO_2)$].** $DppeO_2$ (0.270 g, 0.627 mM) was added into a hot ethanol solution (15 mL) of $UO_2(NO_3)_2{\cdot}6H_2O$ (0.302 g, 0.614 mM). The mixture was refluxed for 4 h. The resulting solid was then filtered, washed with ethanol (2 × 10 mL), and dried in vacuo. The product was recrystallized from a methanol–$CH_2Cl_2$ mixture as a yellow crystalline solid. Yield: 0.282 g, 57%. IR (Nujol mull/$cm^{-1}$): 1524 (*s*), 1308 (*s*), 1276 (*w*) ($NO_3$); 1141(*s*) [P=O]; 930 (O=U=O). $^1H$ NMR ($CDCl_3$, ppm): $\delta$ 7.42–7.79 (*m*, phenyl), 2.82 (*m*, $CH_2$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, ppm): $\delta$ 23.4, *s*.

### 3.3. *Computational details*

All calculations were carried out using the DMol3 density functional theory (DFT) code as implemented in the Accelrys Material Studio® 5.0 software package [21]. The non-local generalized gradient approximation (GGA) using the PW91 exchange-correlation functional was used for geometry optimization in all cases [22]. A double numeric, polarized split valence (DNP) basis set was used in this study with a DFT semi-core pseudopotential to account for the core electrons of P. The size of the DNP basis set is comparable to Gaussian 6-31 G**, but the DNP is more accurate than the Gaussian basis set of the same size [23]. Geometry optimizations were performed without symmetry constraints. The convergence criteria for these optimizations consisted of the following threshold values: $1 \times 10^{-5}$ Ha for energy; 0.002 Ha $Å^{-1}$ for gradient and 0.005 Å for displacement convergence, while a self-consistent field density convergence threshold of $1 \times 10^{-6}$ Ha was specified. All optimized geometries were subjected to a full frequency analysis at the same level of theory (GGA/PW91/DNP) to verify the nature of the stationary points. Optimized geometries were characterized by the absence of imaginary frequencies.

## 4. Conclusion

As phosphine oxides are important ligand systems and are versatile extractants in the nuclear waste treatment plants, the present paper describes the synthesis and coordination chemistry of multidentate aminophosphine oxides (AmPOs). The presence of multi-donor sites did not show any influence on the phosphoryl coordination towards lanthanum, thorium, and uranium salts. Theoretical calculations clearly reveal an increase in nucleophilicity of the phosphoryl group with an increase in 'N' character. The changes in chemical shifts can be attributed to variations in the extent and intensity of coordination of donors to metal. TGA studies revealed that all the metal complexes decompose by either single-step or multi-step elimination of ligand species, whereas the free ligands showed single-step decomposition only. Preliminary investigations proved the extractability of hydrated metal salts from aqueous solutions in the presence of AmPOs in chloroform. Various factors including aqueous phase ionic strength, AmPOs concentration in the organic phase, temperature, type of mineral acid, and strength of mineral acid can affect the efficiency of extraction.

The complexation of linear and cyclic carboxylates and polyaminocarboxylates [24] provided more insight into the role of steric differences between the ligands and different donor groups, which can affect complexation strength. In light of this, it is very important to fine-tune the ligand properties toward better solubility and extractability into an organic phase. The functionalization of ligands can be done either by inserting additional groups in the ligand backbone, or by inserting appropriate bulky groups in substituents on phosphorus introducing new properties into a ligand; it can make it more selective toward a metal ion and increase the thermodynamic stability and the kinetic inertness. We are currently working on the coordination behavior of AmPOs having different electronic and steric properties.

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