Organophosphorus-Modified Lanthanide Nitrates as Potential Actinide Oxide Aerosol Surrogates

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ABSTRACT: In search of suitable simulants for aerosol uranium waste products from Plutonium Uranium Redox Extraction (PUREX) process burns, a series of lanthanide nitrate hydrates ([$Ln(\kappa^2-NO_3)_3\cdot nH_2O$]) were dissolved in the presence of tributylphosphate (O= P(O(CH₂)₃CH₃)₃) referred to as TBP) in kerosene or triphenylphosphate (O=P(O(C₆H₅)) referred to as TPhP) in acetone. The crystal structure of the TPhP derivatives of the lanthanide nitrate series and uranium nitrate were solved as [$Ln(\kappa^2-NO_3)_3$ (TPhP)₃] (**Ln** = **La**, **Ce**, **Pr**, **Nd**, **Sm**, **Eu**, **Gd**, **Tb**, **Dy**, **Ho**, **Er**, **Tm**, **Yb**, **Lu**) and [$U(O)_2(\kappa^2-NO_3)_2$ (TPhP)₂] (**U**), respectively. The lanthanide-TBP, **Ln**, and **U** were further characterized using FTIR spectroscopy, ³¹P NMR spectroscopy, thermogravimetric analysis, and X-ray fluorescence spectroscopy. Further, thermal treatment of the lanthanide-TBP, **Ln**, and **U** using a box furnace to mimic pyrolysis conditions was found by PXRD analyses to generate a phosphate phase [LnP_3O_9 or UP_2O_7) for all systems. The resultant nuclear waste fire contaminant particulates will impact both aerosol transport and toxicity assessments.



I. INTRODUCTION

The Plutonium Uranium Redox Extraction (PUREX) process relies on solubilizing actinide oxide waste through the acidification of the waste stream using nitric acid. In order to separate the actinides from other metals, this mixture is then transferred to a kerosene system employing organophosphorus compounds. Historically, this process has been found to generate a red colored, unspecified organic phase consisting of a trialkylphosphate and nitric acid, which is referred to as "Red Oil".¹⁻¹¹ When this material is heated above 120 °C, explosions and fires have occurred, resulting in several incidents in the United States and across the world.¹⁻¹¹ Due to the potential risks within this system, a great deal of research into characterizing the properties of Red Oil and identifying the products formed during this process has been undertaken.^{1–14} Studies concerning the scattering of the particulates from actinide-containing fires rely heavily on particle dispersion data collected in the early 1970s.¹⁵ As part of a revamping of these outdated data, this effort focused on identifying the various components of the solution system and characterizing the particulates formed during a burn event. Particulate behavior of this system has been reported in additional reports.^{16,17}

While there is no ideal actinide simulant among the lanthanide cations, the rare earth ceramic oxide materials are often used due to the similarity in chemistry, phases, oxidation states, and lack of radioactivity. In particular, ceria (CeO_2) is widely selected as a surrogate for uranium dioxide (UO_2) due to its similar mineral phase and oxidation state (4+).¹⁸⁻³⁰ For

both oxide structures, the metals are 8-coordinated, which consists of eight-coordinate Ce4+ cations and tetrahedrally bound O²⁻ anions. This approach is valid for a wide number of research efforts concerning stability to radiation exposure; however, for aerosol transport during a fire, as would occur in a Red Oil explosion, the density of the metal oxide is believed to be a more important parameter. The composition, mobility, and distribution of aerosolized metal oxide particulates in the ambient atmosphere are of critical importance for the modeling aspects of thermal processing of actinide waste materials. As can be discerned from the density of the oxides listed in Table 1, CeO2 may not be the best lanthanide surrogate choice for actinide oxide waste processing.³¹ The heavier, late lanthanide cations (Yb and Lu) appear to be the most similar in terms of oxide density. While UO_x is the main actinide of study, it is of note that plutonium oxide (PuO_r) is also of particular interest for these types of studies, but it is not feasible to study this material under the same conditions. Therefore, it is surprising that the solubility and aerosol transport behavior of these potential simulants in comparison to UO_x have not been previously reported.

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Table 1. List of Potential Lanthanide Oxide Simulants, Phase, Density Data from Ref 35, and General Solubility in the TBP/Kerosene Mixture

oxide	crystal structure (space group)	density (g/cm ³)
CeO ₂	cubic (fluorite)	7.22
Ce ₂ O ₃	hexagonal $(P\overline{3}m1)$	6.2
Pr ₂ O ₃	hexagonal $(P\overline{3}m1)$	6.9
Nd_2O_3	hexagonal $(P\overline{3}m1)$	7.24
Sm ₂ O ₃	cubic	8.35
Eu_2O_3	monclinic, cubic	7.42
Gd_2O_3	monclinic, cubic	7.407
Tb_2O_3	cubic $(Ia\overline{3})$	7.91
Dy ₂ O ₃	cubic $(Ia\overline{3})$	7.80
Ho ₂ O ₃	cubic $(Ia\overline{3})$	8.41
Er ₂ O ₃	cubic $(Ia\overline{3})$	8.64
Tm_2O_3	cubic $(Ia\overline{3})$	8.6
Yb ₂ O ₃	cubic	9.17
Lu_2O_3	cubic	9.42
U_3O_8	layered	8.3
UO ₂	cubic (fluorite)	11.0
PuO ₂	cubic (fluorite)	11.5

Lacking in the literature is the structure that the lanthanide precursor adopts in this process, the degree of solvation, and the material conversion properties. The most commonly used organophosphorus reagent in the PUREX system is tri-nbutylphosphate (TBP; $O=P(OBu^n)_3$); however, there does not appear to be any published structures of lanthanide or actinide ions ligated by TBP. In our hands, we were not able to crystallize any of these cations with TBP either. Other modifiers such as triphenyl (TPhP; $O=P(OPh)_3$), triisobutyl (TIP), triethyl (TEP), or trimethylphosphate (TMP) have also been employed. $^{12-14,32-36}$ A search of crystallographically characterized organophosphate-modified lanthanide cations³⁷ yields only a handful of compounds that have been identified^{34,35,38-45} with only two possessing a nitrate^{34,35} coligand. It is of note that other lanthanide nitrates modified by phosphate derivatives have been structurally characterized,³⁷ but due to their polydenticity in comparison to the monodentate organophosphates, different structure types have been reported.^{35,46-48} A few monomeric and U species with nitrate and organophosphate ligands have been reported as monomeric species $[U(O)_2(\kappa^2-NO_3)_2(O=P(OR)_3)_2]$ (OR = OMe⁴⁹ and OCH₂(C(CH₃)₂)⁵⁰). The dimeric complex $[U(O)_{2}(\kappa^{2}-NO_{3})(O=P(OMe)_{3})(\mu-O_{2}P(OMe)_{2}]_{2}^{14}$ has also been found when an acid phosphate ligands is employed.

In this study, a series of lanthanide nitrates ([Ln(κ^2 -NO₃)₃: nH₂O]) were mixed with organophosphorus ligands (i.e., TBP (eq 1) or TPhP (eq 2)), and the resulting products generated were characterized and evaluated as potential actinide aerosol simulants. The crystal structures of the lanthanide series and uranium nitrate⁵¹ using TPhP (eq 2) were solved as [Ln(κ^2 -NO₃)₃(TPhP)₃] (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu collectively referred to as Ln) and [U(O)₂(κ^2 -NO₃)₂(TPhP)₂] (U). The lanthanide-TBP, Ln, and U were further characterized using FTIR, ³¹P NMR spectroscopy, and thermal gravimetric analysis (TGA). The thermally treated products from the lanthanide-TBP, Ln, and U precursors were surprisingly found to form a phosphate phase by powder X-ray diffraction (PXRD) and X-ray fluorescence (XRF) studies.

 $[\operatorname{Ln}(\kappa^2 - \operatorname{NO}_3)_3 \cdot 6H_2 O] + (\operatorname{xs})TBP/\operatorname{kerosene} \to \operatorname{``Ln}(\kappa^2 - \operatorname{NO}_3)_3(TBP)_x"$ (1)

$$[\operatorname{Ln}(\kappa^2 - \operatorname{NO}_3)_3 \cdot 6H_2O] + 3TPhP/acetone \rightarrow [\operatorname{Ln}(\kappa^2 - \operatorname{NO}_3)_3(TPhP)_3]$$
(2)

II. EXPERIMENTAL SECTION

The various $[Ln(\kappa^2-NO_3)_3\cdot 6H_2O]$ compounds were obtained from Aldrich Chemical Company and used without further purification. Depleted uranium metal (d-U(0)) was obtained from Los Alamos National Laboratories and handled with appropriate personal protective equipment with all manipulations performed with double-glove, taped lab-coat in a glovebox, or hood. Additional chemicals were used as received from Aldrich Chemical Company, including the following: TBP, TPhP, kerosene, acetone, nitric acid, and potassium bromide (KBr). All samples were handled under ambient conditions in a hood. DI-water was freshly collected from a Millipore Milli-Q Integral water purification system employing a Progard T3 reverse osmosis filter system. All ³¹P NMR spectroscopic data were collected on a Magritek SpinSolve 60 NMR spectrometer using an aliquot from each reaction mixture. Elemental analyses were performed on a PerkinElmer 2400 CHN-S/O elemental analyzer. All samples were externally referenced to an aqueous solution of tetraphenylphosphonium chloride.

30% TBP/Kerosene Stock Solution. In a hood, a 30% v/v stock solution was prepared under ambient conditions consisting of TBP (30 mL) and kerosene (70 mL). This mixture was stirred for 0.5 h, transferred to an amber colored glass bottle, sealed, and stored until needed.

 $[U(O)_2(\kappa^2-NO_3)_2(H_2O)_2]\cdot H_2O]$. In an argon filled glovebox, d-U(0) (1.0 g, 4.2 mmol) was placed in a beaker, and (conc, aq) HNO₃ (~20 mL) was added. After the bubbling subsided, the clear yellow solution was removed from the glovebox and placed in a hood. The reaction mixture was allowed to slowly evaporate the volatile component until crystals formed. The mother liquor was decanted, and the crystalline product was further air-dried and used without further purification. Yields were not determined but assumed to be quantitative, as the metal was completely consumed, and the solution was clear. The structure of the final crystalline material was consistent with that reported by Burns et al.⁵¹

⁴*U*(*O*)₂(k^2 -*NO*₃)₂(*TBP*)₂". [U(O)₂(k^2 -NO₃)₂(H₂O)₂·H₂O] (0.500 g, 1.00 mmol) was added to the 30% organophosphorus/kerosene stock solution (5 mL) and allowed to stir for 24 h. FTIR (KBr, cm⁻¹) 3432(m, br), 2928(w), 2347(w), 1725(m), 1589(m), 1530(m), 1487(m), 1384(m), 1280(w), 1227(m, sh), 1195(m), 946(m), 904(m), 783(m), 753(m), 687(m), 528(s, sh), 505(s). ³¹P NMR δ 0.11.

 $[U(O)_2(\kappa^2-NO_3)_2(TPhP)_2]$. $[U(O)_2(\kappa^2-NO_3)_2(H_2O)_2 \cdot H_2O]$ (0.500 g, 1.00 mmol) was dissolved in acetone, and TPhP (0.978g, 3.00 mmol) was added with stirring. After 12 h, the reaction mixture was set aside with the cap loose to allow for slow evaporation until crystals formed. Yield 80.4% (0.742 g). FTIR (KBr, cm⁻¹) 3064(w), 2557(w), 2299(w), 1946(m), 1901(m), 1780(w), 1735(m), 1591(m), 1485(m), 1456(m), 1384(w), 1280(m), 1228(m), 1090(w), 1072(w), 1016(m), 946(m), 902(m), 809(m), 779(s), 752(s), 721(m, sh), 685(s), 663(m, sh), 616(m), 584(s), 561(m), 528(s), 505(s), 491(s, sh), 442(m). ³¹P NMR δ –18.15.

a. General Molecular Synthesis. a.i. Lanthanides/TBP. In a vial, the appropriate $[Ln(\kappa^2-NO_3)_3 \cdot 6H_2O]$ (0.50 g) was added to a stirring solution (~5 mL) of the TBP stock solution. After 12 h, the reaction was set aside with the cap off to allow any volatile components to evaporate. In our hands, crystals of the TBP derivative could not be isolated, but powders were obtained for each reaction by slow evaporation or oven drying at 120 °C. ³¹P NMR spectra for several of the "Ln(κ^2 -NO₃)₃(TBP)_x" (Ln = Gd, Tb, Dy, Ho, and Tm) could not be obtained. Meaningful yields could not be calculated due to the presence of excess TBP in each reaction. "La(κ^2 -NO₃)₃(TBP)_x". [La(κ^2 -NO₃)₃·6(H₂O)] (0.500 g, 1.15 mmol). FTIR (KBr, cm⁻¹) 2927(w), 2371(w), 2346(w), 1656(m), 1384(w, sh), 1086(s, br.), 722(w), 493(m). ³¹P NMR δ 18.88(d).

" $Ce(\kappa^2 - NO_3)_3(TBP)_{\chi}$ ". [$Ce(\kappa^2 - NO_3)_3(6H_2O)$] (0.500 g, 1.15 mmol). FTIR (KBr, cm⁻¹) 3414(w), 2960(w), 1654(w), 1384(m, sh), 1185(m, br), 1072(s, br), 552(m), 473(m). ³¹P NMR δ 14.17(s).

"Pr(κ^2 -NO₃)₃(TBP) χ". [Pr(κ^2 -NO₃)₃·6(H₂O)] (0.500 g, 1.15 mmol). FTIR (KBr, cm⁻¹) 3414(m, br), 2927(w), 2391(w), 2127(w), 1618(s), 1384(w, sh), 1090(s, br), 487(m). ³¹P NMR δ 38.86(s).

"Nd(κ^2 -NO₃)₃(TBP)_x". [Nd(κ^2 -NO₃)₃·6(H₂O)] (0.500 g, 1.14 mmol). FTIR (KBr, cm⁻¹) 3458(m, br), 2925(w), 2644(w), 2385(w), 2176(w), 1641(m), 1384(w, sh), 1222(s, br), 1093(s, br), 918(m), 704(w), 498(m). ³¹P NMR δ 53.94(s).

" $Sm(\kappa^2-NO_3)_3(TBP)_x$ ". [$Sm(\kappa^2-NO_3)_3\cdot 6(H_2O)$] (0.500 g, 1.13 mmol). FTIR (KBr, cm⁻¹) 3403(m, br), 2971(w), 2371(w), 2144(w), 1637(m), 1383(w), 1233(s, br), 1101(s, br), 952(s), 737(w), 497(m). ³¹P NMR δ –7.73(s).

"Eu(κ^2 -NO₃)₃(TBP)_x". [Eu(κ^2 -NO₃)₃·6(H₂O)] (0.500 g, 1.12 mmol). FTIR (KBr, cm⁻¹) 3383(m, br), 2926(w), 2070(w), 1650(m), 1091(s, br), 897(w), 734(w), 608(w), 468(m). ³¹P NMR δ -12.48(s).

 $"Gd(\kappa^2-NO_3)_3(TBP)_x"$. [Gd(κ^2-NO_3)_3·6(H₂O)] (0.500 g, 1.11 mmol). FTIR (KBr, cm⁻¹) 3425(m, br), 2133(w), 1637(s), 1097(m, br), 670(w), 586(w), 473(w). ³¹P NMR signal not observed.

 ${}^{\prime}Tb(\kappa^2 - NO_3)_3(TBP)_x''$. [Tb($\kappa^2 - NO_3$)_3·6(H₂O)] (0.500 g, 1.10 mmol). FTIR (KBr, cm⁻¹) 3455(m, br), 2932(w), 2383(w), 2137(w), 1643(m), 1384(m, sh), 1254(s), 1108(s, br), 913(m), 803(w), 718(w), 565(w), 488(m). {}^{31}P NMR signal not observed.

"Dy(κ^2 -NO₃)₃(TBP)_x". [Dy(κ^2 -NO₃)₃·6(H₂ \tilde{O})] (0.500 g, 1.10 mmol). FTIR (KBr, cm⁻¹) 3399(m, br), 2955(w), 2916(w), 2838(w), 2393(w), 2143(w), 1666(m), 1384(m, sh), 1257(m), 1098(s, br), 1014(s), 718(w), 572(w), 458(m). ³¹P NMR signal not observed.

"Ho(κ^2 -NO₃)₃(TBP)_x". [Ho(κ^2 -NO₃)₃·6(H₂O)] (0.500 g, 1.09 mmol). FTIR (KBr, cm⁻¹) 3438(w, br), 2961(w), 2922(w), 2841(w), 2393(w), 2146(w), 1656(w), 1380(m, sh), 1244(s), 1095(s), 1020(s), 952(m), 744(w), 702(w), 481(m). ³¹P NMR signal not observed.

^{*w*}Er(κ^2 -NO₃)₃(TBP)_x^{*w*}. [Er(κ^2 -NO₃)₃·6(H₂O)] (0.500 g, 1.08 mmol). FTIR (KBr, cm⁻¹) 2875 (w, br), 2034(w, br), 1633(w), 1142(m), 1001(s),913(s), 664(m). ³¹P NMR δ –34.02(s).

"*Tm*(κ^2 -*NO*₃)₃(*TBP*)_{κ}". [Tm(κ^2 -NO₃)₃·6(H₂O)] (0.500 g, 1.08 mmol). FTIR (KBr, cm⁻¹) 2941(w), 2880(w), 2822(w), 2356(m), 1819(m, br), 1473(m), 1311(s), 1098(m), 1011(m), 943(w), 758(m), 679(s). ³¹P NMR signal not observed.

"Yb(κ^2 -NO₃)₃(TBP)_x". [Yb(κ^2 -NO₃)₃·6(H₂O)] (0.500 g, 1.07 mmol). FTIR (KBr, cm⁻¹) 3386(m, br), 1634(m), 1533(s), 1471(s), 1325(s), 1273(s), 1241(s), 1023(s), 803(m), 757(s). ³¹P NMR δ -26.67(s).

"Lu(κ^2 -NO₃)₃(TBP)_x". [Lu(κ^2 -NO₃)₃·6(H₂O)] (0.500 g, 1.06 mmol). FTIR (KBr, cm⁻¹) 3451(w, br), 2961(w), 2870(w), 1662(w), 1468(m), 1273(s), 1173(m), 1114(m), 1023(s), 989(s), 893(w), 841(w), 744(m), 656(w). ³¹P NMR δ –3.39(s).

a.ii. Lanthanides/TPhP. In a vial, the appropriate $[Ln(\kappa^2-NO_3)_3 \cdot 6H_2O]$ was added to a stirring solution (~1.5 mL) of acetone and TPhP (3 equiv). The mixture was sonicated, allowed to stir 15 min, and then slowly dried *in vauco*. Samples resulted in off-yellow/brown oils that ultimately crystallized over time. Meaningful ³¹P NMR spectra for some of the $[Ln(\kappa^2-NO_3)_3)(TPhP)_3]$ (Ln = Gd, Tb, and Tm) species could not be obtained.

[$La(\kappa^2-NO_3)_3$ (*TPhP*)_3] (*La*). [$La(\kappa^2-NO_3)_3$ ·6(H₂O)] (0.500 g, 1.16 mmol) and TPhP (1.13 g, 3.47 mmol). Yield 98.0% (1.49 g). FTIR (KBr, cm⁻¹) 3386(m, br), 2480(w), 2363(w), 1632(m), 1426(s), 1292(s), 1160(s), 1042(m), 943(m), 817(m), 744(m), 672(m). ³¹P NMR δ –14.15(s). Elemental Analysis for C₅₄H₄₅LaN₃O₂₁P₃ (MW = 1303.78) Calc'd: 49.75, C%; 3.48, H%; 3.22, N%. Found: 50.08, C%; 3.97, H%; 2.84, N%.

 $[Ce(\kappa^2-NO_3)_3(TPhP)_3]$ (Ce). $[Ce(\kappa^2-NO_3)_3(G(H_2O))]$ (0.250 g, 0.576 mmol) and TPhP (0.563 g, 1.73 mmol). Yield 98% (0.736 g). FTIR

(KBr, cm⁻¹) 3065(w), 1566(m), 1475(s), 1454(s), 1292(s), 1168(s), 1072(w), 1011(s), 946(s), 904(s), 747(s), 686(s). ³¹P NMR δ –15.61(s). Elemental Analysis for C₅₄H₄₅CeN₃O₂₁P₃ (MW = 1304.99) Calc'd: 49.70, C%; 3.48, H%; 3.22, N%. Found: 49.69, C %; 3.80, H%; 3.20, N%.

[$Pr(\kappa^2-NO_3)_3(TPhP)_3$] (Pr). [$Pr(\kappa^2-NO_3)_3$ ·6(H₂O)] (0.250 g, 0.575 mmol) and TPhP (0.563 g, 1.72 mmol). Yield 98% (0.741 g). FTIR (KBr, cm⁻¹) 3337(w, br), 3065(w), 1677(w), 1583(w), 1487(s), 1290(m) 1250(m), 1213(m), 1152(s), 1011(s), 979(s), 934(m), 901(m), 747(s), 683(s). ³¹P NMR δ –16.73(s). Elemental Analysis for C₅₄H₄₅N₃O₂₁P₃Pr (MW = 1303.78) Calc'd: 49.67, C%; 3.47, H%; 3.22, N%. Found: 50.07, C%; 3.87, H%; 3.24, N%.

[*Nd*(κ^2 -*NO*₃)₃(*TPhP*)₃] (*Nd*). [Nd(κ^2 -*NO*₃)₃·6(H₂O)] (0.250 g, 0.570 mmol) and TPhP (0.558 g, 1.71 mmol). Yield 95.3% (0.712 g). FTIR (KBr, cm⁻¹) 3337(w, br), 3061(w), 1588(w), 1482(s). 1290(m), 1250(m), 1215(m), 1157(s), 1016(m), 976(s), 943(m), 899(m), 749(s), 683(s). ³¹P NMR δ –14.37(s). Elemental Analysis for C₅₄H₄₅N₃NdO₂₁P₃ (MW = 1309.21) Calc'd: 49.54, C%; 3.46, H %; 3.21, N%. Found: 49.97, C%; 3.68, H%; 3.00, N%.

 $[Sm(\kappa^2-NO_3)_3(TPhP)_3]$ (Sm). $[Sm(\kappa^2-NO_3)_3\cdot 6(H_2O)]$ (0.250 g, 0.562 mmol) and TPhP (0.550 g, 1.69 mmol). Yield 95.0% (0.703 g). FTIR (KBr, cm⁻¹) 3070(w), 1585(w), 1475(s), 1290(m), 1241(m), 1215(m), 1154(s), 1009(m), 9799s), 936(m), 894(m), 744(s), 678(s). ³¹P NMR δ –15.54(s). Elemental Analysis for C₅₄H₄₅N₃O₂₁P₃Sm (MW = 1315.24) Calc'd: 49.31, C%; 3.45, H%; 3.19, N%. Found: 49.57, C%; 2.60, H%; 3.06, N%.

 $[Eu(\kappa^2-NO_3)_3(TPhP)_3] (Eu). [Eu(\kappa^2-NO_3)_3 \cdot 6(H_2O)] (0.250 g, 0.560 mmol) and TPhP (0.549 g, 1.68 mmol). Yield 98.6% (0.729 g). FTIR (KBr, cm⁻¹) 3403(m, br), 2974(w), 2911(w), 1672(m), 1637(m), 1491(s), 1451(s), 1445(s), 1405(m), 1337(m), 1283(s), 1194(s), 1037(s), 906(m), 810(s), 742(s), 693(m). ³¹P NMR <math>\delta$ –24.89(s). Elemental Analysis for C₅₄H₄₅EuN₃O₂₁P₃ (MW = 1316.84) Calc'd: 49.25, C%; 3.44, H%; 3.19, N%. Found: 49.60, C%; 3.71, H%; 3.20, N %.

 $[Gd(\kappa^2-NO_3)_3(TPhP)_3]$ (Gd). $[Gd(\kappa^2-NO_3)_3\cdot 6(H_2O)]$ (0.250 g, 0.554 mmol) and TPhP (0.542 g, 1.66 mmol). Yield 97.2% (0.712 g). FTIR (KBr, cm⁻¹) 3412(w, br), 3063(w), 2969(w), 1679(m), 1634(w), 1578(m), 1470(s), 1281(s), 1253(s), 1215(s)m 1154(s), 1030(s), 979(s), 904(m), 815(m), 754(s), 683(s). ³¹P NMR signal not observed. Elemental Analysis for $C_{54}H_{45}GdN_3O_{21}P_3$ (MW = 1322.13) Calc'd: 49.06, C%; 3.43, H%; 3.18, N%. Found: 48.81, C%; 3.47, H%; 3.17, N%.

 $[Tb(\kappa^2-NO_3)_3(TPhP)_3]$ (*Tb*). $[Tb(\kappa^2-NO_3)_3\cdot 6(H_2O)]$ (0.250 g, 0.552 mmol) and TPhP (0.540 g, 1.65 mmol). Yield 87.2% (0.637 g). FTIR (KBr, cm⁻¹) 3396(w, br), 2969(w), 1677(m), 1644(w), 1588(w), 1468(s), 1283(s), 1248(s), 1161(s), 1039(s), 981(m), 906(m), 803(m), 751(s), 683(s). ³¹P NMR signal not observed. Elemental Analysis for $C_{54}H_{45}N_3O_{21}P_3$ Tb (MW = 1323.80) Calc'd: 48.99, C%; 3.43, H%; 3.17, N%. Found: 48.87, C%; 3.44, H%; 3.23, N%.

[Dy(κ^2 -NO₃)₃(TPhP)₃] (Dy). [Dy(κ^2 -NO₃)₃·6(H₂O)] (0.250 g, 0.548 mmol) and TPhP (0.536 g, 1.64 mmol). Yield 98.1% (0.713 g). FTIR (KBr, cm⁻¹) 3419(w, br), 3061(w), 2976(w), 1677(w), 1644(w), 1588(w), 1473(s), 1288(s), 1255(s), 1215(m), 1166(s), 1028(s), 974(s), 904(m), 808(m), 747(s), 688(s). ³¹P NMR δ -37.25(s). Elemental Analysis for C₅₄H₄₅DyN₃O₂₁P₃ (MW = 1327.38) Calc'd: 48.86, C%; 3.42, H%; 3.17, N%. Found: 48.87, C%; 3.63, H%; 3.20, N%.

[*H*0(κ^2 -*NO*₃)₃(*TPhP*)₃] (*H*0). [H0(κ^2 -*NO*₃)₃·6(H₂O)] (0.250 g, 0.544 mmol) and TPhP (0.533 g, 1.63 mmol). Yield 70.2% (0.508 g). FTIR (KBr, cm⁻¹) 3424(w, br), 3058(w), 2974(w), 2360(w), 1681(w), 1637(w), 1583(w), 1473(s), 1292(s), 1255(s), 1220(m), 1154(s), 1035(s), 967(s), 932(s), 901(m), 812(m), 751(s), 686(s). ³¹P NMR δ -32.55(s). Elemental Analysis for C₅₄H₄₅HoN₃O₂₁P₃ (MW = 1329.81) Calc'd: 48.77, C%; 3.41, H%; 3.16, N%. Found: 49.08, C%; 3.99, H%; 2.97, N%.

 $\begin{array}{l} [Er(\kappa^2-NO_3)_3(TPhP)_3] \ (Er). \ [Er(\kappa^2-NO_3)_3\cdot 6(H_2O)] \ (0.250 \ g, \ 0.549 \ mmol) \ and \ TPhP \ (0.530 \ g, \ 1.63 \ mmol). \ Yield \ 99.2\% \ (0.716 \ g). \ FTIR \ (KBr, \ cm^{-1}) \ 3574(w, \ br), \ 3080(w), \ 2529(w), \ 1869(w), \ 1580(w), \ 1506(m), \ 1480(s), \ 1311(m), \ 1239(s), \ 1210(s), \ 1149(s), \ 1014(s), \ 975(s), \ 939(s), \ 894(m), \ 784(s), \ 747(s), \ 683(s). \ ^{31}P \ NMR \ \delta \end{array}$

nitrate	P=Ostretch FTIR (cm ⁻¹)	³¹ P NMR ^{<i>a</i>} (δ , acetone)	TGA/DSC temp (°C)	PXRD phase (1000 °C)	XRF ^b
TBP	1275 (s)	-0.98(s)			
La	1086 (s, br)	18.88 (d)	240	LaP ₃ O ₉ (PDF00-033-07176)	La, P
Ce	1072 (s, br)	14.17 (s)	265	CeP ₃ O ₉ (<i>PDF00-033-0336</i>)	Ce, P
Pr	1090 (s, br)	38.86 (s)	230	PrP ₃ O ₉ (<i>PDF00-033-1077</i>)	Pr, P
Nd	1093 (s, br)	53.94 (s)	235	NdP ₃ O ₉ (<i>PDF00-027-0322</i>)	Nd, P
Sm	1101 (s, br)	7.73 (s)	240	Sm(PO ₄)· <i>x</i> H ₂ O (<i>PDF01-084-0918</i>)	Sm, P
Eu	1091 (s, br)	-12.48 (s)	240	Eu(PO ₃) ₃ (<i>PDF00-034-1453</i>)	Eu, P
Gd	1097 (m, br)	NSO ^a	250	Gd(PO ₃) ₃ (<i>PDF00-052-1761</i>)	Gd, P
Tb	1108 (s, br)	NSO	210	TbP ₃ O ₉ (<i>PDF00-031-1379</i>)	Tb, P
Dy	1098 (s, br)	NSO	245	Dy(PO ₃) ₃ (<i>PDF00-052-1760</i>)	Dy, P
Ho	1095 (s)	NSO	240	Ho(PO ₃) ₃ (<i>PDF00-052-1763</i>)	Ho, P
Er	1001 (s)	-34.02 (s)	205	Er(PO ₃) ₃ (<i>PDF00-055-0209</i>)	Er, P
Tm	1011 (m)	NSO	190	Tm(PO ₃) ₃ (<i>PDF00-052-1759</i>)	Tm, P
Yb	1023 (s)	26.67(s)	260	YbP ₃ O ₉ (<i>PDF00-045-0653</i>)	Yb, P
Lu	1023 (s)	3.39(s)	260	Lu(PO ₃) ₃ (<i>PDF00-035-0399</i>)	Lu, P
U	1227 (m)	0.11 (s)	175	U(P ₂ O ₇) (PDF04-019-3508)	U, P
TPhP	1189 (s)	-17.65			TPhP
La	1160 (s)	-14.15 (s)	155(24%), 235(36%)	La(PO ₄) (<i>PDF 04-002-9468</i>)	La, P
Ce	1011 (s)	-15.61 (s)	195(10%), 250(56%)	Ce(PO ₄) (<i>PDF00-032-0199</i>)	Ce, P
Pr	1152 (s)	-16.73 (s)	220	$Pr(PO_4)$ (<i>PDF00-032-0885</i>)	Pr, P
Nd	1157 (s)	-14.37 (s)	230	Nd(PO ₄) (<i>PDF00-025-1066</i>)	Nd, P
Sm	1154 (s)	-15.54 (s)	235	Sm(PO ₄) (<i>PDF00-032-0938</i>)	Sm, P
Eu	1194 (s)	-24.89 (s)	175(15%), 245(40%)	EuP ₃ O ₉ (<i>PDF04-001-9480</i>)	Eu, P
Gd	1154 (s)	NSO	240	Gd(PO ₄) (<i>PDF04-008-8499</i>)	Gd, P
ть	1161 (s)	NSO	215	TbP ₃ O ₉ (<i>PDF04-006-0692</i>)	Tb, P
				Tb(PO ₄) (04-002-0128)	
Dy	1166 (s)	-37.25 (s)	245	Dy(PO ₄) (<i>PDF00-026-0593</i>)	Dy, P
Но	1154 (s)	-32.55 (s)	220	Ho(PO ₄)·3H ₂ O (<i>PDF00-020-0476</i>)	Но, Р
				Ho(PO ₃) ₃ (<i>PDF00-052-1763</i>)	
Er	1149 (s)	-38.01 (s)	210	Er(PO ₄) (<i>PDF04-008-3615</i>)	Er, P
Tm	1154 (s)	NSO	180(5%), 250(34%)	TmP ₃ O ₉ (<i>PDF04-001-9474</i>)	Tm, P
Yb	1011 (s)	-18.63 (s)	180(5%), 255(30%)	Yb(PO ₄)·3H ₂ O (<i>PDF00-020-1398</i>)	Yb, P
Lu	1011 (s)	-14.10 (s)	220	Lu(PO ₄) (<i>PDF00-043-0003</i>)	Lu, P
U	1228 (m)	-18.15 (s)	180	U(P ₂ O ₇) (PDF04-019-3508)	U, P
aNSO = not	o single observed. ^b Argon and	d Ca were observed as well	from the background gas	and holder, respectively.	

8 8 8

-38.01(s). Elemental Analysis for $C_{54}H_{45}ErN_3O_{21}P_3~(MW=1332.13)$ Calc'd: 48.69, C%; 3.41, H%; 3.15, N%. Found: 48.97, C %; 3.78, H%; 3.43, N%.

 $[Tm(\kappa^2-NO_3)_3(TPhP)_3]$ (Tm). $[Tm(\kappa^2-NO_3)_3\cdot 6(H_2O)]$ (0.250 g, 0.540 mmol) and TPhP (0.528 g, 1.62 mmol). Yield 99.8% (0.719 g). FTIR (KBr, cm⁻¹) 3354(w, br), 2981(w), 1684(w), 1641(w), 1470(s), 13679w), 1278(s), 1255(s), 1154(s), 1025(s), 972(m), 904(m), 798(m), 749(s), 681(m). ³¹P NMR signal not observed. Elemental Analysis for $C_{54}H_{45}N_3O_{21}P_3Tm$ (MW = 1333.81) Calc'd: 48.63, C%; 3.40, H%; 3.15, N%. Found: 49.18, C%; 4.05, H%; 2.84, N %.

[Yb(κ^2 -NO₃)₃(TPhP)₃] (Yb). [Yb(κ^2 -NO₃)₃·6(H₂O)] (0.250 g, 0.535 mmol) and TPhP (0.524 g, 1.61 mmol). Yield 98.3% (0.706 g). FTIR (KBr, cm⁻¹) 3391(w, br), 3072(w), 3012(w), 1951(w), 1583(m), 1480(s), 1318(m), 1295(s), 1269(m), 1245(s), 1152(s), 1014(s), 976(s), 899(s), 808(m), 777(s), 747(s), 681(s). ³¹P NMR δ –18.63(s). Elemental Analysis for C₅₄H₄₅N₃O₂₁P₃Yb (MW = 1338.94) Calc'd: 48.44, C%; 3.46, H%; 3.14, N%. Found: 48.87, C%; 3.44, H%; 3.23, N%.

[*Lu*(κ^2 -*NO*₃)₃(*TPhP*)₃] (*Lu*). [*Lu*(κ^2 -*NO*₃)₃·6(H₂O)] (0.250 g, 0.533 mmol) and TPhP (0.525 g, 1.60 mmol). Yield 93.3% (0.670 g). FTIR (KBr, cm⁻¹) 3335(w, br), 1677(w), 1578(w), 1484(s), 1229(m), 1248(m), 1213(m), 1145(s), 1030(s), 1011(s), 979(s), 939(m), 904(m), 808(w), 749(s), 679(s). ³¹P NMR δ –14.10(s). Elemental Analysis for C₅₄H₄₅LuN₃O₂₁P₃ (MW = 1340.85) Calc'd: 48.37, C%; 3.46, H%; 3.13, N%. Found: 47.93, C%; 4.05, H%; 2.92, N%.

X-ray Crystal Structure Information. For each sample, the individual single crystals were mounted onto a loop from a pool of Fluorolube or Parabar 10312 and immediately placed in a 100 K N₂ vapor stream. X-ray intensities were measured using a Bruker APEX-II CCD diffractometer with MoK α radiation ($\lambda = 0.71070$ Å) for all compounds. Indexing, frame integration, and structure solutions were performed using the BrukerSHELXTL^{52–54} software package within Apex3⁵⁴ and/or OLEX2⁵⁵ suite of software. All final CIF files were checked using the CheckCIF program (http://www.iucr.org/). Additional information concerning the data collection and final structural solutions can be found in the Supporting Information or by accessing CIF files through the Cambridge Crystallographic Data Base.³⁷ The unit cell parameters for all compounds are available in Table S1 (see the Supporting Information). Due to the isostructural nature of 1–14, crystal structures were solved using the Condinates of the Sm adduct (5) as a basis for refinement.

For each analysis, the samples generated from the above mixtures were dried (*in vacuo*), the resulting powder was ground and further dried, and a free-flowing powder remained. These powders were used without further manipulation.

Fourier Transformed Infrared Spectroscopy (FTIR). The dried powders were pressed into KBr pellets on the benchtop. Spectra were collected on a Bruker Vector 22 MIR spectrometer under an atmosphere of flowing nitrogen.

Thermogravimetric Analysis/Differential Scanning Calorimetry (TGA/DSC). All powder samples were carefully loaded under ambient conditions into a prefired (1000 °C) ceramic boat using a



Figure 1. Structure plot for $[Yb(\kappa^2-NO_3)_3(TPhP)_3]$ (Yb). Thermal ellipsoids are drawn at 30% for the heavy atoms. Hydrogen atoms are omitted for clarity. The dotted lines represent the bonds for the two (50%) occupancy disordered O53 O atoms.

Mettler Toledo TGA/DSC 1 Star^e System. All analyses were conducted under a flowing argon atmosphere from room temperature to 1000 $^\circ C$ at a ramp rate of 10 $^\circ C/min.$

Thermal Processing. For all thermal processing, the sample solutions were carefully loaded into a prefired (1000 $^{\circ}$ C) ceramic boat and heated in a ThermoScientific Thermolyne (FB1315m) Box furnace under ambient atmosphere in a ventilated hood. Each sample was heated to preselected temperatures (450, 650, and 1000 $^{\circ}$ C), and after each temperature, the room temperature powder was analyzed by PXRD.

Powder X-ray Diffraction (PXRD). Powder X-ray diffraction (PXRD) was performed by a PANalytical X'Pert Pro diffractometer employing Cu K_{α} radiation (1.5406 Å) and a RTMS X'Celerator detector. Data were collected over a 2θ range of $10-100^{\circ}$ at a scan rate of 0.15° /s, and a zero-background holder was employed. The XRD patterns were analyzed using JADE 9 software (Materials Data, Inc., Livermore CA) and indexed using The Powder Diffraction File PDF-4+ 2013.

X-ray Fluorescence (XRF) Spectroscopy. Elemental concentrations were determined using a ThermoFisher ARL (West Palm Beach, FL, US) Quant'X EDXRF spectrometer utilizing UniQuant software that was used for all analyses. The system uses a Fundamental Parameters approach based on the Sherman equation for direct measurement of elemental concentrations based on integrated fluorescent peak intensities. In air, using a medium count rate, a 1 repetition, multiscan excitation [C Thin (5 kV, 60 s); Al (12 kV, 100 s), Pd Thick (28 kV, 100 s); Cu Thick (50 kV, 100 s)] was used to evaluate each sample.

III. RESULTS AND DISCUSSION

The PUREX system has established the utility of organophosphorus compounds in terms of extraction of actinide waste. Due to the use of nitric acid to solubilize the various metals found in the process, nitrate ligated species are expected to be found in the aqueous solution.^{1–13,56} Some of the organophosphate uranium nitrate products that have been crystallographically identified include the monomeric $[UO_2(\kappa^2-NO_3)_2(L)_2]$ (where L = TMP, TEP, TIP) or dimeric $[UO_2(\kappa^2-NO_3)(\mu-L)(L)]_2$ (where L = TMP, TEP) compounds.^{12,13,32,33,57} As mentioned, lanthanide cations are often used as simulants to mitigate the complications Table 3. List of Select, Average Metrical Data for (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) and $[U(O)_2(\kappa^2-NO_3)_2(TPhP)_2]$ (U)^b

	distan	ces (Å)	angles (deg)			
Ln-TPhP	Ln- O=P	Ln– O ₂ NO	Ln– O–N	0- N-0	Ln– O=P	ref
La	2.50	2.59	96.5	116.8	154.3	а
Ce	2.46	2.53	96.4	116.9	153.8	а
Pr	2.44	2.53	96.5	116.2	153.6	а
Pr-dmpp	2.45	2.60	102.1	117.3	153.7	35
Nd	2.43	2.51	96.6	115.7	153.6	а
Sm	2.39	2.49	95.9	116.6	152.6	а
Eu	2.38	2.48	96.2	116.0	152.5	а
Gd	2.36	2.47	95.9	116.2	152.1	а
ть	2.34	2.45	95.7	116.4	151.7	а
Ho	2.32	2.43	94.4	118.23	150.9	а
Dy	2.34	2.44	95.5	116.5	151.2	а
Dy-dipp	2.24	2.47	95.3	116.7	141.6	34
Ho	2.32	2.43	94.4	118.23	150.9	а
Ho-dipp	2.22	2.47	95.1	116.4	142.9	34
Er	2.31	2.42	95.8	115.5	150.7	а
Er-dipp	2.22	2.44	95.5	115.9	140.0	34
Tm	2.29	2.42	95.3	116.4	149.9	а
Yb	2.29	2.41	95.6	115.6	149.9	а
Lu	2.28	2.40	95.6	115.4	149.5	а
U	2.42	2.50	97.4	114.4	139.0	а
U - OBu^i	2.37	2.51	97.6	114.3	164.3	33

^{*a*}This work. ^{*b*}The model compounds have been added near the particular cation for completeness. TPhP = triphenylphosphate; dmpp = (dimethylphosphonato)phenylmethanol; dipp = 2,6-diisopropylphenylphosphate.

encountered using radioactive materials; however, the structures adopted by organophosphorus modified $[Ln(\kappa^2 - NO_3)_3 \cdot 6H_2O]$ salts and the subsequent materials they are converted to are less explored. In fact, only two nitrate organophoste derivatives have been reported: $[Pr(\kappa^2 - NO_3)_3(\kappa^2 - L)]$ where L = (dimethylphosphonato)-

Table 4. H-Bonding Interactions between P–OPh and NO_3 Moieties for Gd

H-bond interaction (atoms)	С-О (Å)	Н–О (Å)	C-H-O (deg)	symmetry
C(523)-H(523)-O(22)	3.47	2.55	163.8	$x - \frac{1}{2}, \frac{11}{2} - \frac{1}{2}, \frac{1}{2}$
C(533)-H(533)-O(22)	3.592	2.69	158.3	$x - \frac{1}{2}, \frac{1}{2} - \frac{1}{2}$
C(623)-H(623)-O(21)	3.515	2.61	158.2	2-x,y-1/2, 11/2-z
C(535)-H(535)-O(33)	3.314	2.44	157.8	x-1,y,z
C(424) - H(424) - O(33)	3.418	2.52	157.3	x-1,y,z
C(543)-H(543)-O(33)	3.374	2.63	135.9	$x - \frac{1}{2}, \frac{1}{2} - y,$ 1 - z
C(533)-H(533)-O(32)	3.408	2.67	135.5	$x - \frac{1}{2}, \frac{1}{2} - \frac{1}{2}$
C(442)-H(442)-O(23)	3.354	2.72	124.9	x-1,y,z
C(626)-H(626)-O(13)	3.084	2.94	89.6	x-1,y,z

phenylmethanol³⁵ and a series of polymeric lanthanide dimethylphosphate compounds.³⁶ It is of note that a wide range of complex organophosphate ligands are available for the lanthanide cations, including the following: tris(bis(2,6dimethylphenyl)hydrogen phosphate)-tris(bis(2,6dimethylphenyl)phosphato)-neodymium(iii) benzene solvate,⁴² tetrakis(m-bis(2,6-dimethylphenyl)phosphato)-(bis-(2,6-dimethylphenyl)hydrogen phosphate)-bis(bis(2,6dimethylphenyl)phosphato)-dineodymium(III) benzene solvate,⁴² catena(tris(μ -dimethylphosphato-O,O'')-(trimethylphosphate-O)-lanthanum),³⁸ catena-(dodecakis(µ-diethylphosphato)-bis(triethylphosphate)tetracerium(III)),⁴⁵ bis(triisobutylphosphonato-O)-tris(4-benzoyl-3-methyl-1-phenyl-5pyrazolonato-O,O')-europium, ^{40,58} hexakis (μ_2 - η^5 -cyclopentadienylcarboxylato)-bis($\mu - \eta^5$ -cyclopentadienylcarboxylato)tetrakis(trimethyl phosphate)-tetracosacarbonyl-dierbium-nonamanganese toluene solvate,⁴⁴ and tris(diethyl(1-methylvinyl)phosphate)-tris(picrato)-europium(III).⁴³

As can be determined from this family of compounds, the molecules formed from the standard TBP or TPhP ligands with the lanthanide cations have not been previously crystallographically characterized. In order to fill this void, the synthesis of the $[Ln(\kappa^2-NO_3)_3\cdot nH_2O]$ series in the presence of TBP and TPhP was undertaken, and the organophosphorus lanthanide products formed were evaluated by FTIR spectroscopy, ³¹P NMR spectroscopy, TGA, and single crystal X-ray studies when possible. The compounds were also thermally processed to mimic pyrolysis, and the final materials were characterized by PXRD and XRF.

Sample Preparation. Full dissolution of the $[Ln(\kappa^2-NO_3)_3\cdot 6H_2O]$ in the 30% TBP/kerosene stock solution was facile for the majority of starting materials, but low heating was required for $[Ln(\kappa^2-NO_3)_3\cdot 6H_2O]$ (TBP: Ln = Yb, Lu). There was no visual evidence of any changes upon dissolution for these samples with the solution adopting the color of the powders used. Due to solubility of the TPhP, the appropriate $[Ln(\kappa^2-NO_3)_3\cdot 6H_2O]$ was dissolved in acetone, and then a stoichiometric amount (3 equiv) of TPhP was added. No samples required heating to dissolve. The mixtures were stirred for 12 h with a pale-yellow color forming over time for the noncolored samples. Slow evaporation of the volatile component of the TBP/kerosene led to oils, while the TPhP/acetone mixtures led to a mixture of crystalline materials in an organic matrix. Other attempts to generate crystals (i.e.,

cooling, antisolvents) from this mixture or stoichiometric reactions also failed to produce acceptable crystalline materials.

The oils formed with the TBP derivatives may be a reflection of the alkyl chain present, polymer formation, or potential hydrolysis products that alkyl phosphates reportedly undergo. ^{59,60} In order to distinguish between the crystallographically characterized species, the TBP compounds have been identified using quotes, inferring only potential empirical formulations. For the TPhP samples, other minor byproducts were observed that are currently being fully investigated. In order to produce "pure" materials, the reaction mixture was generated, sonicated, and then slowly dried in vacuo to eliminate any "aged" products. For the samples that crystallized, the structures obtained were identical to those previously observed, and the additional analytical data of either the 12 h sample or the sonicated TPhP reactions were self-consistent. Analytical data (FTIR, ³¹P NMR, TGA/DSC, PXRD, XRF, and elemental analyses) were independently collected on the product material to characterize the products.

Sample Characterization. The FTIR spectrum of the organophosphorus precursors TBP and TPhP readily displayed the P=O stretches at 1275 and 1189 cm⁻¹, respectively. A fresh solution of the various $[Ln(\kappa^2-NO_3)_3 \cdot 6H_2O]/organo$ phosphorus reactions was dried to a powder, whereupon each sample clearly displayed both NO_3 and P=O bends and stretches. While the NO3 bends and stretches were consistent with the parent precursors, the P=O of the organophosphate stretches were shifted. Table 2 lists the P=O stretches observed for the lanthanide TBP and Ln powders. These shifts are similar to other lanthanide organophosphate species $([Ln_5(\mu_3-OH)(dipp)_6(\kappa^2-NO_3)_x(CH_3OH)_y(H_2O)_z]^{2+} dipp =$ 2,6-diisopropylphenylphosphate])³⁴ which had strong absorptions for P=O noted at 1100 cm⁻¹. Based on these data, it is clear that the organophosphates have bound to the various metals without displacing the nitrates.

Further characterization of these powders redissolved in the parent solution was undertaken using NMR spectroscopy. The paramagnetic nature of the various Ln cations prevents obtaining sharp peaks in the spectral data. Further, all attempts for the TBP compounds were obfuscated by the excess TBP or kerosene solvent necessary for dissolution. For the TPhP samples, the ¹H NMR spectra revealed road peaks for the phenyl ring and did not significantly add to an understanding of the purity of the final compounds. Therefore, efforts focused on using ³¹P NMR, with the resultant data being tabulated in Table 2. For the "free" organophosphates, a single ^{31}P resonance was observed: TBP ($\delta = -0.98$ ppm, kerosene) and TPhP ($\delta = -17.65$ ppm, acetone). When a ³¹P signal could be obtained on the lanthanide-TBP or TPhP (Ln) samples, only a single resonance was noted. Addition of the free ligand to these mixtures only resulted in a shift of the signal and not an ingrowth of a new resonance. This is attributed to the rapid exchange the Ln cations are known to undergo, especially for monodentate ligands. In some instances when the Ln samples did not display a ³¹P signal, but this was overcome by running samples at higher concentrations. Therefore, all samples were ultimately analyzed at as high concentration as possible. A ³¹P signal was not observed for the following cations: TBP derivatives: Gd, Tb, Tm, Dy, and Ho versus TPhP derivatives: Gd, Tb, Tm. This may be a reflection of low solubility or the signal being outside of the ³¹P spectral window of the instrument used. Further, while lanthanides have unpaired electrons and f-orbitals, electron spin can be

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Figure 2. PXRD pattern of processed (a) YbP₃O₉ (PDF 00-045-0653) from "Yb(κ^2 -NO₃)₃(TBP)_x" and (b) YbPO₄·3H₂O (PDF 00-020-1398) from [Yb(κ^2 -NO₃)₃(TPhP)₃] (Yb).

delocalized into σ and π orbitals of the ligand. For the *n*-Bu and Ph moieties of the TBP and TPhP ligands, respectively, different σ and π orbitals will be available and may also explain the variation noted above for active ³¹P signals. While the collective observed lanthanide-TBP ³¹P resonances were shifted downfield of the TBP free ligand, the observed TPhP-lanthanide shifts appear to be more aligned with what nuclei they are bound to. The early (La-Sm) and late (Yb-Lu)



Figure 3. Structure plot of $[U(O)_2(NO_3)_2(TPhP)_2]$ (U). Thermal ellipsoids are drawn at 30% for the heavy atoms. Hydrogen atoms are omitted for clarity.

were shifted downfield, and the middle cations either were not observed or shifted significantly upfield.

The structure literature indicates two organophosphorus ligands should be present on the uranium^{12,13,32,33,} and possibly four for Ln³⁵ (two bidentate phosphates) nitrate species. All attempts to crystallize the final products to aid in identifying the TBP binding were not successful in our hands; however, the Ln species all successfully crystallized. The isomorphous family of compounds were identified as monomeric compounds, where the lanthanide cation adopts a 9-coordinated, tricapped trigonal prismatic (ttp) geometry. Figure 1 shows the general structure type, using Yb as the representative compound (note: there was some disorder in the oxygen of one of the ligands indicated by dashed lines to the 50% occupancy). For each of these structures, the three κ^2 -NO₃ ligands were located in the capping position, and the TPhP ligands were coplanar in the equatorial (trigonal) positions. For the structure solutions, all of the heavier Ln cations were found to have slightly disordered OPh groups, which did not occur for the lighter metals. This is produced from an offset of the phenyl ring, in one of two positions, as noted in the Ln-O-C angle. The metrical data of the first lanthanide nitro-triphenyl phosphate derivatives reported were self-consistent (see Table 3). For comparison, literature data for related compounds^{35,36} are included in the table.

All of the **Ln** structures isolated in this work are isomorphous and isostructural, crystallizing in the $P2_12_12_1$ space group, which has only translational symmetry. Approximately 90% of the crystals isolated in this space group are chiral, and enantiomeric pairs should therefore be available. For each structure, the coordinates of **Sm** were used as a starting point for refinement; thus, only one of the two possible packing patterns occurs, and the material spontaneously resolves upon crystallization as the same enantiomer. Remarkably the structures all refined to Flack parameters of 0 (±0.05), indicating that the 14 structures all adopt the same enantiomeric structure. If the odds of 14 examples of a binary choice are the same, this sets a lower limit for $\Delta G < 5.2$ kcal/ mol (i.e., $K = 2^{14}$ or 16384); as there are nine C–H…O hydrogen bonds, the enantiomers must differ by at least an av of 0.58 kcal/mol (5.2 kcal/mol/9 bonds). Differences in Hbonding energies of this magnitude are reasonable and could account for the failure to observe the missing enantiomer. It would be useful to compare these intermolecular interactions with the enantiomeric partner, but again, surprisingly, none were isolated.

Further evaluation of the model Gd system, reveals nine C-H…O hydrogen bonding interactions between molecules (see Table 4). The bonds represent donations from a C-H group of an OC₆H₅ ring to an oxygen on a NO₃ ligand: five to terminal and four to Gd-bonded NO₃ oxygens, with no clear difference between the two types. A structure literature search for a C–H group from a P–OPh ring that H-bonds to a NO_3 ion yielded 26 structures.³⁷ Of these, the H-bonding was found to primarily occur through the meta phenyl ring H, and some para interactions but no ortho protons were involved in Hbonding. The majority of structures (17) has one such interaction, six have two, two have three, and one has four OPh-H-NO₃ bonds.³⁷ In contrast, the Ln structures reported here have eight (the last entry in Table 4 should not be considered a H-bond) and are the principle force guiding the packing of the final molecules. The metrical parameters found for the C-H…O hydrogen bonds of these Ln species are consistent with those observed in the literature.³

Elemental analyses of the resulting products were undertaken for the TPhP samples. Again, the TBP products were not evaluated by this means as they could not be meaningfully analyzed due to the excess TBP present. The data proved to be consistent with three TPhP species bound to a hydrate free " $Ln(NO_3)_3$ ". Further, if this analysis was a result of the simple mixture of the two components in the correct stoichiometry, significantly less %C would be available. For example, the **Lu** sample for mixed (C, 44.79; H, 3.97; N, 2.90%) versus reacted (C, 48.37; H, 3.46; N, 2.90%) illustrate the difference. Therefore, the bulk materials were consistent with the observed crystal structures.

TGA/DSC. The thermal behavior of the organophosphate modified $[Ln(\kappa^2-NO_3)_3, 6H_2O]$ species was investigated through TGA/DSC experiments. While the overall weight losses could not be calculated accurately for either the TBP or TPhP species due to the inclusion of byproducts or unreacted precursor, the main decomposition temperatures were of interest to understand the various ligand losses and conversion during heating. The TBP derivatives surprisingly had a single weight loss step at ~250 °C except for the Er, Tm, and Tb bearing samples which occurred at lower temperatures (~200 °C). This indicates that the nitrate and TBP ligands are lost at the same temperature, which may have important implications for fire experiments, where the nitrates may act as a fire retardant. In comparison, the majority of TPhP species was also thermally decomposed in a single step around 250 °C, but several species (La, Ce, Eu, Tm, and Yb) had two steps with the first weight loss around ~180 °C. This multistep decomposition may represent the nitrate-TPhP species or other compounds known to be present in the complex mixture. This decomposition and the lack of higher temperature weight loss was found to be consistent with the thermal decomposition of the $[Ln_{5}(\mu_{3}-OH)(dipp)_{6}(\kappa^{2}-NO_{3})_{x}(CH_{3}OH)_{y}(H_{2}O)_{z}]^{2+}$ system.³⁴

The residual powder by XRF analyses indicated the appropriate lanthanide cations were present along with P. The presence of the P was surprising, as literature refers only

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Figure 4. PXRD patterns of $U(P_2O_7)$ (PDF 04-019-3508) from (a) " $U(O)_2(NO_3)_2(TBP)_2$ " and $[U(O)_2(NO_3)_2(TPhP)_2]$ (U).

to oxides being formed.¹⁶ Therefore, additional studies were undertaken where a TPhP stock solution of the $[Sm(\kappa^2-NO_3)_3 \cdot 6H_2O]$ sample was placed in a box furnace and heated to 450 °C in air. The material proved to be amorphous by PXRD. The sample was heated (650, 750, and 850 °C) but remained amorphous until it was heated to 1000 °C, whereupon it was identified by PXRD as samarium phosphate (PDF 01-084-0918). Due to the unexpected phase formed, additional $[Ln(\kappa^2-NO_3)_3\cdot 6H_2O]$ mixed in TBP and TPhP stock solutions was produced and processed at 1000 °C in air. PXRD patterns and XRF spectra were collected, and Figure 2a and 2b show the representative PXRD patterns for the thermal byproduct

for the Yb-TBP and Yb-TPhP (Yb) powders, respectively. Independent of the cation or the organophosphorus modifier used, each sample was found to possess both Ln and P by XRF and to form a phosphate phase (see Table 2). From these data, it was found that the majority of the TBP samples formed the single-phase anhydrous lanthanide metaphosphate phase. The one exception was the Sm derivative that was identified as the phosphate hydrate material. In contrast, the TPhP species mainly generated the anhydrous phosphate powders with both Eu and Tm forming the metaphase. Two samples (Tb and Ho) had both the easily interconverted metaphosphate and phosphate phases present, which was surprising based on the fact that the literature on potential PUREX aerosol efforts has focused on metal oxide behavior. In particular, cerium oxide (CeO_2) is often sprinkled over paper "trash" to mimic contaminated waste.⁶¹ Traditional efforts have merely focused characterizing the percent of transferred metal;^{61,62} however, this may be an erroneous approach due to the actual formation of phosphates from the PUREX route.

Uranium. In order to verify the lanthanide simulants possessed the same chemistry as uranium, a U-nitrate, organophosphorus sample was prepared. Crystalline material (U) was isolated by slow evaporation of the reaction mixture and is shown in Figure 3 (see Table 3 for metrical data). The monomeric U metal center has a central core that consists of two κ^2 -NO₃ and two *trans*-TPhP ligands forming an 8-coordinated geometry best described as a slightly distorted hexagonal bipyramid (D_{6h}), with an ~10° torsional twist in the plane. The remainder of the coordination is filled by the two oxo moieties. The U–O=P and U–O₂NO distances are slightly longer after correction for cation size.⁶³ Interestingly, the U–O=P angle is about 10° smaller than those noted for the Ln compounds.

For comparison, only three uranyl nitrate phosphate derivatives $(O=P(OR)_3 R = Me_1^{13} Et_1^{32,12} and Bu^{33})$ are available. These derivatives are similar to U, adopting a hexagonal bipyramid (hbp) geometry. The best model is the OBuⁱ³³ derivative (see Table 3). Not surprisingly, the metrical data are in agreement except the U–O=P angle. For the other uranium species, this angle ranges from 153.4-166.52°, whereas U has a much smaller angle of 139.0°. This angle reflects the Ph rings bending away from each other, causing the molecule to flatten. In evaluating the Ln species versus the U product, it is obvious that different coordination spheres (coordination and ligands) and oxidation states exist for these compounds: Ln^{3+} (ttp with three TPhP) versus U^{6+} (hbp with two TPhP and two oxides). While this would be problematic in a chemistry sense in terms of surrogates, for materials applications, the similarity of the various ligands present and the monomeric nature bodes well for similar thermal conversion products and their ultimate utility of the Ln as surrogates.

The dried crystalline U was analyzed under identical conditions noted for the Ln species (see Table 2) to determine the utility of these compounds as surrogates. As can be observed within the FTIR data, there is a shift in the O=P stretch upon complexation of the TBP and TPhP ligands versus the free ligands stretch. This overall shift is much smaller for the TPhP ligand than the TBP ligand. Further, the shift for the ligands is much smaller when binding to U in comparison to the lanthanide ions. Thermal analyses revealed a much lower decomposition temperature and a much smaller 31 P chemical shift for U vs the Ln complexes. After processing,

the XRF revealed the presence of both U and P and the PXRD pattern (see Figure 4a and 4b for the TBP and TPhP, respectively, powder patterns) showed the formation of the pyrophosphate (U(P₂O₇): PDF 04-019-3508) phase for both of the U-organophosphorus derivatives. While the phase observed for the final material from the U or the Ln systems was not identical, both were phosphates and not the often used oxide^{61,62} phase for aerosol studies. Stable phosphate phases noted for uranium favor the countercation groups, such as the Autunite group of minerals (M³ⁿ⁽ⁿ⁾⁺[(UO₂)(PO₄)]₂·xH₂O) (M = Ca, Na)⁶⁴ or the Cs[UO₂)_x(HPO₃)_y(H₂O)_z]⁶⁵ family of materials. It is of note that metaphosphate (U(Po₃)₄) has been shown to decompose into the pyrophosphate (U(P₂O₇),⁶⁶ which may explain the variation in the phases noted, as the LnPO₄ materials⁶⁷ are reportedly stable to >900 °C.

IV. SUMMARY AND CONCLUSION

The investigation of the pyrolysis behavior of lanthanide simulants for actinide aerosol PUREX species was undertaken. The synthesis of extraction solutions (kerosene and organophosphorus extractants) with $[Ln(\kappa^2 - NO_3)_3 \cdot 6H_2O)]$ led to the isolation of $[Ln(\kappa^2-NO_3)_3(TPhP)_3]$ for the TPhP solutions, which were crystallographically characterized as 9-coordinated monomers. $[U(O)_2(\kappa^2 - NO_3)_2(TPhP)_2]$ (U) was isolated from a similar reaction mixture, as a 8-coordinated species. Thermal processing of the Ln precursors and U led to the phosphate material, not the oxide, that is often assumed to form upon pyrolysis, which may impact aerosol transport, toxicity, and other safety assessment determinations. In general, the Ln family of organophosphorus nitrates and the U derivative have enough similarities to suggest they would act as reasonable surrogates for aerosol investigations. Studies on the pyrolysis behavior of the resultant materials have been reported elsewhere and indicated substantial differences exist between the lanthanide and uranium organophosphorus species during aerosolization.¹⁶ Efforts to understand the subtle differences that influenced this behavior of these to precursors are underway.

ASSOCIATED CONTENT

1 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c02428.

Crystallographic data for La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and U, respectively (PDF)

Accession Codes

CCDC 2017493–2017507 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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