Andrew T. Breshears, Charles L. Barnes, Durgesh V. Wagle, Gary A. Baker, Michael K. Takase, and Justin R. Walensky*

Structure and spectroscopy of uranyl and thorium complexes with substituted phosphine oxide ligands

Abstract: Phosphine oxide ligands are important in the chemistry of the nuclear fuel cycle. We have synthesized and characterized a series of phosphine oxide ligands with polycyclic aromatic hydrocarbon (PAH) groups to enhance the spectroscopic features of uranyl, UO_2^{2+} , and to make detection more efficient. Complexation of OPPh_2R , $\text{R} = \text{C}_{10}\text{H}_7$ (naphthyl); C_{14}H_9 (phenanthrenyl); C_{14}H_9 (anthracenyl); and C_{16}H_9 (pyrenyl), to $\text{UO}_2(\text{NO}_3)_2$ afforded the eight-coordinate complexes, $\text{UO}_2(\text{NO}_3)_2(\text{OPPh}_2\text{R})_2$. An eleven-coordinate complex, $\text{Th}(\text{NO}_3)_4[\text{OPPh}_2(\text{C}_{14}\text{H}_9)]_3$, $\text{C}_{14}\text{H}_9 = \text{phenanthrenyl}$, was structurally characterized, and was found to be the first thorium compound isolated with three phosphine oxide ligands bound. The phosphine oxide ligands were not fluorescent but the anthracenyl-substituted ligand showed broad, red-shifted emission at approximately 50 nm relative to typical anthracene, making this ligand set a possibility for use in detection. The synthesis and spectroscopy of the uranyl and thorium complexes are presented.

Keywords: Uranyl, Thorium, Phosphine Oxide, X-ray crystallography, Fluorescence.

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1 Introduction

With the increasing population of the world comes a rise in energy consumption which requires diverse solutions. All indications are that nuclear power will remain an im-

portant player for many years. However, the advancement of nuclear energy has the consequence of developing nuclear weapon capability, and to combat these new methods for sensing actinides in complex matrices need to be developed. Uranyl nitrate, $\text{UO}_2(\text{NO}_3)_2$, is a major species throughout the reprocessing step of the nuclear fuel cycle, and therefore we are interested in investigating how to exploit the properties of UO_2^{2+} to enhance its detection. One prominent feature of UO_2^{2+} is its phosphorescence; however, in general, this phosphorescence is quite weak, and our approach is to amplify this property.

Phosphine oxide ligands are ubiquitous in actinide chemistry. For example, tributyl phosphate (TBP), $\text{OP}(\text{O}^n\text{Bu})_3$, is used in the PUREX process in solvent extraction of uranyl into the organic phase. Due to this, many phosphine oxide ligands have been found to coordinate to the actinyl moiety. For example, $\text{AnO}_2(\text{NO}_3)_2(\text{OPPh}_3)_2$, $\text{An} = \text{U}$, Np [1], Pu [2], $\text{AnO}_2\text{Cl}_2(\text{OPPh}_3)_2$, $\text{An} = \text{U}$ [3], Np [1] and $\text{UO}_2(\text{O}_2\text{CCH}_3)_2(\text{OPPh}_3)_2$ [4] have been shown to make actinyl complexes. However, to our knowledge, uranyl complexes with phosphine ligands bearing polycyclic aromatic hydrocarbons (PAHs) have not been reported. Our rationale for using these ligands is to enhance the spectroscopic properties of uranyl and use a phosphine oxide ligand that would be more robust than TBP to radiolysis [5]. Herein, we report the synthesis, characterization, and spectroscopy of uranyl nitrate complexes with phosphine oxide ligands bearing a PAH, $\text{UO}_2(\text{NO}_3)_2(\text{OPPh}_2\text{Ar})_2$, $\text{Ar} = \text{naphthyl}$, anthracenyl , phenanthrenyl , and pyrenyl .

2 Experimental

All reactions were conducted in air unless otherwise specified. $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_6$ was used as is from legacy stock, $\text{Th}(\text{NO}_3)_4(\text{H}_2\text{O})_4$ (Strem) was used as received. All other chemicals were purchased (Aldrich) at 95% or higher purity and used as received. All ^1H , ^{13}C , and ^{31}P NMR data were obtained on a 250 MHz ARX, 300 MHz DRX or 500 MHz DRX Bruker spectrometer. ^1H NMR shifts given

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were referenced internally to the residual protio impurities at δ 5.32 ppm (CDHCl_2). ^{13}C NMR shifts were referenced internally to the residual peaks at δ 53.52 ppm (CD_2Cl_2). ^{31}P NMR spectra were externally referenced to 0.00 ppm with 85% H_3PO_4 in D_2O . Infrared spectra were recorded from KBr pellets on a Perkin-Elmer Spectrum One FT-IR spectrometer. Absorbance spectra were obtained using a Varian Cary 50 Bio UV-Vis spectrophotometer and luminescence spectra were acquired on a Varian Cary Eclipse fluorimeter. Elemental analyses were performed by Atlantic Microlab, Inc. (Norcross, GA).

2.1 Synthesis of phosphines and phosphine oxides, 1–4

Phosphines $\text{P}(\text{C}_6\text{H}_5)_2(\text{C}_{10}\text{H}_7)$ (C_{10}H_7 = naphthyl) [6], $\text{P}(\text{C}_6\text{H}_5)_2(\text{C}_{14}\text{H}_9)$, (C_{14}H_9 = phenanthrenyl), $\text{P}(\text{C}_6\text{H}_5)_2(\text{C}_{14}\text{H}_9)$, (C_{14}H_9 = anthracenyl), $\text{P}(\text{C}_6\text{H}_5)_2(\text{C}_{16}\text{H}_9)$, (C_{16}H_9 = pyrenyl) [7], and phosphine oxides, $\text{OP}(\text{C}_6\text{H}_5)_2(\text{C}_{10}\text{H}_7)$, (C_{10}H_7 = naphthyl), **1**, $\text{OP}(\text{C}_6\text{H}_5)_2(\text{C}_{14}\text{H}_9)$, (C_{14}H_9 = phenanthrenyl), **2**, $\text{OP}(\text{C}_6\text{H}_5)_2(\text{C}_{14}\text{H}_9)$, (C_{14}H_9 = anthracenyl), **3**, and $\text{OP}(\text{C}_6\text{H}_5)_2(\text{C}_{16}\text{H}_9)$, (C_{16}H_9 = pyrenyl), **4** were synthesized according to literature procedures [8].

2.2 $\text{UO}_2(\text{NO}_3)_2[\text{OP}(\text{C}_6\text{H}_5)_2(\text{C}_{10}\text{H}_7)]_2$, **5**

In a 20 mL scintillation vial, $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_6$ (100 mg, 0.199 mmol) was suspended in 10 mL of THF. **1** (171 mg, 0.521 mmol) was added to the mixture and then stirred for 2 h. The solvent was reduced under vacuum to one-fifth of the original volume and the compound was then placed in a freezer at 0°C overnight to yield a pale orange solid (245 mg, 90%). ^1H NMR (CD_2Cl_2 , 500 MHz, 21°C): δ 6.9–7.8 (m, 20H), 7.1–8.5 ppm (m, 14H) ppm. ^{13}C NMR (CD_2Cl_2 , 125 MHz, 21°C): δ 124.3 (naph), 126.5 (naph), 127.2 (Ph), 127.5 (naph), 128.7 (Ph), 128.9 (naph), 129.6 (Ph), 131.0 (naph), 132.0 (naph), 132.7 (naph), 133.3 (naph), 133.5 (Ph), 133.8 (naph), 134.0 (naph) ppm. ^{31}P NMR (CD_2Cl_2 , 101 MHz, 21°C): δ 52.08 ppm. IR (KBr, cm^{-1}): 1548 (s, N=O), 1495 (s, C=C), 1474 (s), 1296 (s, NO_3), 1124 (s, P=O), 1079 (s, P–O), 1024 (w), 935 (s, U=O), 832 (w), 806 (m), 776 (m, =C–H), 753 (w), 727 (w), 558 (m), 543 (s), 505 (w). Anal. Calcd for $\text{C}_{44}\text{H}_{34}\text{N}_2\text{O}_{10}\text{P}_2\text{U}$: C, 50.30%; H, 3.25%; N, 2.67%. Found: C, 50.18%; H, 3.52%; N, 2.65%.

2.3 $\text{UO}_2(\text{NO}_3)_2[\text{OP}(\text{C}_6\text{H}_5)_2(\text{C}_{14}\text{H}_9)]_2$, **6**

In a 20 mL scintillation vial, $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_6$ (100 mg, 0.199 mmol) was suspended in 10 mL of THF. **2** (176 mg, 0.465 mmol) was added to the mixture and then stirred for 2 h. The solvent was reduced *in vacuo* to one-fifth of the original volume and then placed in a freezer at 0°C overnight to yield a pale green-yellow solid (274 mg, 99%). ^1H NMR (CD_2Cl_2 , 500 MHz, 21°C): δ 7.11–7.29 (m, 4H, Ph), 7.43–7.56 (m, 8H, Ph), 7.53–7.68 (m, 8H, Ph), 7.74–7.84 (m, 4H, phenan), 7.81–7.94 (m, 2H, phenan), 8.35–8.41 (m, 4H, phenan), 8.63–8.74 (m, 4H, phenan), 8.76–8.81 (m, 4H, phenan) ppm. ^{13}C NMR (CD_2Cl_2 , 125 MHz, 21°C): δ 123.0 (phenan), 123.53 (phenan), 127.4 (Ph), 127.5 (phenan), 128.1 (Ph), 129.0 (phenan), 129.1 (phenan), 129.6 (phenan), 130.1 (Ph), 130.2 (phenan), 130.3 (phenan), 131.2 (phenan), 131.4 (phenan), 132.3 (phenan), 132.4 (Ph), 132.8 (phenan), 133.7 (phenan), 137.1 (phenan) ppm. ^{31}P NMR (CD_2Cl_2 , 101 MHz, 21°C): δ 49.13 ppm. IR (KBr, cm^{-1}): 3061 (m), 2974 (m), 2869 (m), 1612 (w), 1588 (m), 1521 (s, N=O), 1438 (s, C=C), 1384 (m), 1285 (s, NO_3), 1197 (w), 1134 (s, P=O), 1089 (s, P–O), 1035 (m), 998 (w), 963 (m), 930 (s, U=O), 904 (w), 859 (w), 811 (w), 748 (s, =C–H), 721 (s), 696 (s), 610 (m), 572 (s), 531 (s), 517 (m). Anal. Calcd for $\text{C}_{52}\text{H}_{38}\text{N}_2\text{O}_{10}\text{P}_2\text{U}$: C, 54.27%; H, 3.33%; N, 2.43%. Found: C, 53.18%; H, 3.67%; N, 2.40%.

2.4 $\text{UO}_2(\text{NO}_3)_2[\text{OP}(\text{C}_6\text{H}_5)_2(\text{C}_{14}\text{H}_9)]_2$, **7**

In a 20 mL scintillation vial, $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_6$ (100 mg, 0.199 mmol) was suspended in 10 mL of THF. **3** (171 mg, 0.452 mmol) was added to the mixture and then stirred for 2 h. The solvent was reduced *in vacuo* to one-fifth of the original volume and the complex was placed in a freezer at 0°C overnight to yield a pale yellow solid (262 mg, 96%). ^1H NMR (CD_2Cl_2 , 500 MHz, 21°C): δ 6.99 (d, 8H, Ph, $^1J_{\text{H-H}} = 7$ Hz), 7.14 ppm (t, 4H, Ph, $^1J_{\text{H-H}} = 7$ Hz), 7.4–7.6 ppm (m, 8H, anth), 7.82–7.90 ppm (m, 8H, Ph), 8.0–8.2 (m, 8H, anth) 8.47 (s, 2H, anth) ppm. ^{13}C NMR (CD_2Cl_2 , 125 MHz, 21°C): δ 125.4 (Ph), 126.8 (anth), 129.2 (Ph), 129.7 (anth), 131.7 (anth), 131.8 (Ph), 132.0 (anth), 134.5 (anth), 135.0 (Ph), 135.5 (anth), 135.9 (anth), 136.7 (anth) ppm. ^{31}P NMR (CD_2Cl_2 , 101 MHz, 21°C): δ 48.19 ppm. IR (KBr, cm^{-1}): 3064 (w), 1619 (w), 1517 (s, N=O), 1438 (s, C=C), 1384 (w), 1284 (s, NO_3), 1125 (s, P=O), 1083 (s, P–O), 1034 (w), 935 (s, U=O), 844 (w), 824 (w), 756 (w), 737 (m, =C–H), 697 (m), 563 (w), 530 (m). Anal. Calcd for $\text{C}_{52}\text{H}_{38}\text{N}_2\text{O}_{10}\text{P}_2\text{U}$: C, 54.27%; H, 3.33%; N, 2.43%. Found: C, 53.46%; H, 3.28%; N, 2.38%.

2.5 $\text{UO}_2(\text{NO}_3)_2[\text{OP}(\text{C}_6\text{H}_5)_2(\text{C}_{16}\text{H}_9)]_2, \mathbf{8}$

In a 20 mL scintillation vial, $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_6$ (100 mg, 0.199 mmol) was suspended in 10 mL of THF. **4** (176 mg, 0.438 mmol) was added to the mixture and then stirred for 2 h. The solvent was reduced *in vacuo* to one-fifth of the original volume and the complex placed in a freezer at 0 °C overnight to yield a pale green-yellow solid (274 mg, 99%). ^1H NMR (CD_2Cl_2 , 500 MHz, 21 °C): δ 8.92 (d, 4H, py, $^1J_{\text{H-H}} = 9.5$ Hz), 8.25 (m, 8H), 8.08 (m, 8H), 7.79-7.46 (m, 18H) ppm. ^{13}C NMR (CD_2Cl_2 , 125 MHz, 21 °C): δ 123.7 (py), 125.0 (py), 125.2 (Ph), 125.7 (py), 126.2 (Ph), 126.4 (py), 126.5 (py), 126.6 (py), 127.2 (py), 128.7 (Ph), 129.9 (py), 130.4 (py), 130.7 (Ph), 131.3 (py), 132.0 (py), 132.1 (py), 132.2 (py), 133.0 (py), 133.8 (py), 134.3 (py) ppm. ^{31}P NMR (CD_2Cl_2 , 101 MHz, 21 °C): δ 51.21 ppm. IR (KBr, cm^{-1}): 3049 (w), 2963 (w), 2852 (w), 1626 (w), 1591 (w), 1519 (s, N=O sym str.), 1437 (m), 1384 (s), 1280 (s, asym. str. NO_3), 1208 (w), 1138 (s, P=O str.), 1097 (s, P–O), 1029 (m), 999 (w), 971 (w), 933 (s, U=O), 928 (m), 856 (m), 824 (w), 753 (w), 726 (w), 692 (m), 551 (m), 528 (m), 504 (w). Anal. Calcd for $\text{C}_{52}\text{H}_{38}\text{N}_2\text{O}_{10}\text{P}_2\text{U}$: C, 54.27%; H, 3.33%; N, 2.43%. Found: C, 53.18%; H, 3.67%; N, 2.40%.

2.6 $\text{Th}(\text{NO}_3)_4[\text{OP}(\text{C}_6\text{H}_5)_2(\text{C}_{14}\text{H}_9)]_3, \mathbf{9}$

In a 20 mL scintillation vial, $\text{Th}(\text{NO}_3)_4(\text{H}_2\text{O})_4$ (100 mg, 0.181 mmol) was suspended in 10 mL of THF. **2** (301 mg, 0.795 mmol) was added to the stirring solution and overnight turned a deep red color. The solvent was removed *in vacuo* to one-fifth of the original volume, and the complex was placed in the freezer at 0 °C to yield a light yellow powder and polycrystalline beads. The beads were recrystallized out of a concentrated solution of benzene to produce yellow crystalline product of **9** (150 mg, 50% yield). ^1H NMR (CD_2Cl_2 , 300 MHz, 21 °C): δ 8.84 (d, 6H, $^1J_{\text{H-H}} = 8$ Hz), 8.32 (bs, 3H), 7.99-7.89 (m, 7H), 7.85-7.73 (m, 20H), 7.62-7.45 (m, 12H), 7.41-7.24 (m, 9H) ppm. ^{13}C NMR (CD_2Cl_2 , 75 MHz, 21 °C): δ 123.8 (phenan), 124.3 (Ph), 126.3 (phenan), 128.3 (phenan), 128.5 (Ph), 129.1 (phenan), 129.2 (phenan), 130.0 (Ph), 130.2 (phenan), 130.5 (phenan), 131.1 (phenan), 131.5 (phenan), 131.8 (phenan), 133.4 (phenan), 133.6 (phenan), 134.3 (phenan), 139.0 (Ph), 140.0 (phenan) ppm. ^{31}P NMR (CD_2Cl_2 , 101 MHz, 21 °C): δ 44.9 ppm. IR (KBr, cm^{-1}): 3057(w), 1506 (s, N=O), 1438 (s, O–N str.), 1384 (s, P–C), 1299 (s, asym. str. NO_3), 1127 (s, P=O str.), 1082 (s, P–O str.), 1028(m), 961(w), 810(w), 748(w), 724(s), 693(m), 620(m), 572(m), 533(s, Th–O), 499(m). Anal. Calcd for $\text{C}_{52}\text{H}_{38}\text{N}_2\text{O}_{10}\text{P}_2\text{U}$: C, 58.00%;

H, 3.56%; N, 3.47%. Found: C, 57.31%; H, 3.80%; N, 3.55%.

2.7 Crystallographic data collection and structure determination

The selected single crystal was mounted on nylon cryoloop using viscous hydrocarbon oil. X-ray data collection was performed at 173(2) or 100(2) K. The X-ray data were collected on a Bruker CCD diffractometer with monochromated Mo K_α radiation ($\lambda = 0.71073$ Å). The data collection and processing utilized the Bruker Apex2 suite of programs [9]. The structures were solved using direct methods and refined by full-matrix least-squares methods on F^2 using Bruker SHELX-97 program [10]. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were added on idealized positions and not allowed to vary. Thermal ellipsoid plots were prepared by using X-seed [11] with 50% of probability displacements for non-hydrogen atoms. Crystal data and detail for data collection for complexes **5–9** are provided in Table 1, and significant bond distances and angles are gathered in Tables 4 and 5.

3 Results and discussion

3.1 Synthesis and spectroscopy

The phosphine oxide ligands, **1–4**, were prepared as previously reported [8]. Reaction of two equivalents of the phosphine oxide ligands with $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_6$ in THF yielded new products as discerned by ^{31}P NMR spectroscopy, Table 2. The phenanthrenyl-substituted phosphine oxide ligand, $\text{OPPh}_2(\text{C}_{14}\text{H}_9)$, **2**, also coordinates to the thorium metal center when reacted with $\text{Th}(\text{NO}_3)_4(\text{H}_2\text{O})_4$, Table 2. The ligand, **2**, was chosen due to its propensity to form isolable products which can be readily characterized by X-ray diffraction analysis. The uranyl complexes were found to be soluble in THF and CH_2Cl_2 , but only sparingly soluble in arene solvents, while **9** shows more solubility in toluene. The ^1H , ^{13}C , and ^{31}P NMR spectra for each uranyl complex showed only one set of aryl and phosphorus resonances, indicating a symmetric coordination environment. Coordination of the phosphine oxide to uranyl leads to a downfield shift in the ^{31}P NMR spectrum. This can be attributed to less electron density on the phosphorus atom due to the actinide metal center siphoning electron density from the oxide. There does not seem to be a trend with respect to

Table 1: X-ray crystallography parameters for complexes 5–9.

	5	6	7	8	9
CCDC Deposit Number	1005324	1005321	1005323	1005325	1005322
Empirical Formula	C ₄₄ H ₃₄ N ₂ O ₁₀ P ₂ U	C ₅₂ H ₃₈ N ₂ O ₁₀ P ₂ U	C ₅₂ H ₃₈ N ₂ O ₁₀ P ₂ U	C ₅₆ H ₃₈ N ₂ O ₁₀ P ₂ U	C ₉₉ H ₇₈ N ₄ O ₁₅ P ₃ Th ₁
Formula weight (g/mol)	1050.70	1150.80	1150.80	1202.87	1888.6
Crystal Habit, color	Needle, Colorless	Prism, Colorless	Block, Colorless	Prism, Colorless	Prism, Colorless
Temperature (K)	100(2)	173(2)	173(2)	173(2)	100(2)
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1	<i>P</i> -1
Crystal system	<i>Triclinic P</i>	<i>Triclinic P</i>	<i>Monoclinic P</i>	<i>Triclinic P</i>	<i>Triclinic P</i>
Volume (Å ³)	2023.31(6)	1635.5(3)	2288.57(4)	1307.35(3)	4207.65(5)
<i>a</i> (Å)	9.4887(15)	9.0855(10)	14.383(8)	9.014(2)	12.7596(9)
<i>b</i> (Å)	10.8116(17)	9.7152(10)	9.735(5)	12.511(3)	14.0268(10)
<i>c</i> (Å)	20.710(3)	16.3826(18)	17.526(9)	13.168(3)	25.5719(19)
α (°)	102.658(3)	73.856(1)	90.00	109.143(3)	89.984(1)
β (°)	91.102(3)	82.960(1)	111.156(6)	105.180(3)	84.026(10)
γ (°)	101.955(3)	80.505(1)	90.00	98.700(3)	67.700(1)
<i>Z</i>	2	1	2	1	2
Calculated density (Mg/m ³)	1.725	1.575	1.670	1.614	1.491
Absorption coefficient (mm ⁻¹)	4.153	3.10	3.68	3.23	1.90
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0305 w <i>R</i> 2 = 0.0619	<i>R</i> 1 = 0.020 w <i>R</i> 2 = 0.052	<i>R</i> 1 = 0.030 w <i>R</i> 2 = 0.067	<i>R</i> 1 = 0.033 w <i>R</i> 2 = 0.066	<i>R</i> 1 = 0.030 w <i>R</i> 2 = 0.066

Table 2: ³¹P NMR chemical shifts for complexes 1–9.

Compound	³¹ P NMR Chemical Shift (ppm)
1	31.5
2	31.8
3	34.6
4	32.0
5	52.1
6	48.2
7	49.1
8	51.2
9	44.9

³¹P NMR chemical shift vs. ligand electron withdrawing strength. The ³¹P NMR spectrum of **9** showed a broad resonance at 44.9 ppm, which is unusual for a diamagnetic species. This was attributed to fluxional behavior of the phosphine oxide ligand in solution with two or three ligands coordinated to thorium.

In accordance with the ³¹P NMR chemical shifts indicative of less electron density on the phosphorus atoms and weakening of the P–O bond, the infrared spectra of uranyl complexes, **5–8**, have a corresponding red shift of the P–O stretching frequency, Table 3. For example, in free OPPh₂(C₁₆H₉), **4**, a stretch at 1171 cm⁻¹ is observed and is located at 1138 cm⁻¹ in UO₂(NO₃)₂[OPPh₂(C₁₆H₉)]₂, **8**.

Table 3: Infrared stretching frequencies (cm⁻¹) of phosphine oxide ligands, **1–4**, uranyl, **5–8**, and thorium complex, **9**.

Bond stretching frequency (cm ⁻¹)	1	2	3	4	5	6	7	8	9
$\nu(\text{U=O})_{\text{asym}}$	–	–	–	–	935	935	930	930	–
$\nu(\text{P=O})$	1182	1187	1179	1171	1124	1124	1134	1138	1127

3.2 X-ray crystallography analysis

Single crystal X-ray diffraction analysis of complexes **5–9** was performed to examine their structural features. The structure of **5**, Figure 1, exhibits a seven-coordinate complex with *C*₁ symmetry, with one of the nitrate ligands coordinating κ^1 –(O) instead of κ^2 –(O,O). The uncoordinated oxygen atom (O9) on the nitrate has a hydrogen bond, 2.378 Å, with the closest hydrogen on an adjacent naphthyl ring (H39), Figure 1A. Due to the κ^1 –(O) bonding of the nitrate ligand, there is a contraction of that U–O bond from 2.4813(3) to 2.3720(3) Å. The remaining uncoordinated oxygen (O10) also hydrogen bonds with a hydrogen atom (H8) on the adjacent naphthyl ring at 2.671 Å, Figure 1A. However, this effect is only observed in the solid state as the ¹H NMR spectrum of **5** indicates that the complex is symmetric.

Complexes **6–8** are all eight-coordinate UO₂(NO₃)₂(OPPh₂Ar)₂ complexes. The U–O (phosphine oxide) bond lengths of 2.3627(16), 2.370(3), and

Table 4: Structural parameters for complexes 5–8.

Bond distance (Å)/ angle (°)	5	6	7	8
U1–O (oxo)	1.767(2)	1.7661(17)	1.757(3)	1.765(3)
U1–O (nitrate)	2.373(2)	2.5179(18)	2.527(3)	2.520(3)
U1–O (nitrate)	2.482(2)	2.5406(18)	2.546(3)	2.532(2)
U1–O (OPPh ₂ Ar)	2.313(2)	2.3627(16)	2.370(3)	2.343(2)
P1–O4	1.511(2)	1.5066(17)	1.511(3)	1.502(2)
O–U1–O (uranyl)	175.11(3)	180.00(4)	180.0	180.0

Fig. 1: (Top) Thermal ellipsoid plot of **5** shown at the 50% probability level. Hydrogen atoms and solvent molecules have been removed for clarity. (Bottom) Thermal ellipsoid plot of **5** with phenyl rings and $\kappa^2(\text{O},\text{O})$ nitrate removed. Dotted lines between H39 and O9 (2.378 Å) as well as H8 and O10 (2.671 Å) have been added to highlight hydrogen bonding.

2.343(2) Å for **6**, Figure 2, **7**, Figure 3, and **8**, Figure 4, respectively, are nearly identical to 2.35–2.36 Å in $\text{UO}_2(\text{NO}_3)_2(\text{OPPh}_3)_2$. Given that the bond distances and angles compare well to previously reported uranyl complexes of the form $\text{UO}_2(\text{NO}_3)_2(\text{OPR}_3)_2$ [1, 12–25], this suggests that PAH-substituted phosphine oxides do not significantly affect sigma donation to the uranium metal center. Another feature in all four complexes is that the PAH is positioned to prevent steric interference, thus even the pyrenyl derivative displays an identical structure

Fig. 2: Thermal ellipsoid plot of **6** shown at the 50% probability level. Hydrogen atoms and solvent molecules have been removed for clarity.

to the phenanthrenyl and anthracenyl. One feature that warrants mention is a small $\sim 3^\circ$ twist from planarity in the anthracenyl ring in **7**, Figure 3. The naphthyl, phenanthrenyl, and pyrenyl are all planar and this twist in the anthracenyl ring may have a consequence on the fluorescence spectrum.

Building on the success with uranyl, we also examined the coordination of **2** with $\text{Th}(\text{NO}_3)_4$. The solid-state structure of **9** revealed an eleven-coordinate complex with $\text{Th}(\text{NO}_3)_4$ and three $\text{OPPh}_2(\text{C}_{14}\text{H}_9)$ ligands coordinated, Figure 5. While NMR spectroscopy has detected thorium complexes with three coordinated phosphine oxide ligands [26, 27], this appears to be the first isolated structure. As previously mentioned, the ^{31}P NMR spectrum of **9** showed a broad resonance and this is most likely due to the fluxional behavior of one of the phosphine oxide ligands associating and dissociating from the thorium center. The increased coordination number also has the effect of forcing a pair of the nitrates to be nonlinear and angle towards the coordination site of the single phosphine oxide with an N–Th–N angle of 149.40° . However, the thorium-oxygen bond lengths of the nitrate ligands in **9** of 2.39 to 2.41 Å compare well to those of 2.31–2.35 Å in $\text{Th}(\text{NO}_3)_4(\text{OPMe}_3)_2$ and 2.33–2.35 Å $\text{Th}(\text{NO}_3)_4(\text{OPPh}_3)_2$.

3.3 Optical spectroscopy

The electronic absorbance spectra for the aromatic phosphine oxide ligands **1–4** in THF are provided in Figure 6 and accord well with the absorbance profiles expected for

Fig. 3: (Left) Thermal ellipsoid plot of **7** shown at the 50% probability level. Hydrogen atoms and solvent molecules have been removed for clarity. (Right) Twist in anthracenyl ligand from planarity is shown.

Fig. 4: Thermal ellipsoid plot of **8** shown at the 50% probability level. Hydrogen atoms and solvent molecules have been removed for clarity.

Fig. 5: Thermal ellipsoid plot of **9** shown at the 50% probability level. Hydrogen atoms and solvent molecules have been removed for clarity.

the parent PAH compounds. The corresponding fluorescence excitation and emission spectra are shown in Figure 7. Consistent with an earlier report, the phosphines were observed to be non-fluorescent [8]. The order of the emission intensities for their oxides, however, is $4 > 3 \gg 2 \gg 1$ with ligands **1–3** showing relative intensities of roughly 2.4%, 11%, and 51%, respectively, when compared to the intensity from the 1-pyrenyl ligand **4**. Interestingly, the emission observed from the 9-anthryl phosphine oxide ligand **3** is structureless and red-shifted by *ca.* 50 nm relative to typical anthracene monomer emission, which shows vibronic character. In fact, this was also

seen in earlier work from Akasaka *et al.* [8], but was not specifically mentioned. Broad, red-shifted emission from PAHs is frequently associated with excited-state dimer (excimer) formation; however, this seems an unlikely explanation for the photophysical behavior given the fact that we are operating at highly dilute conditions where intermolecular association during the excited-state lifetime is

Table 5: Selected bond distances (Å) and angles (°) for **9**.

Bond distance (Å)/angle (°)	9
Th–O1 (nitrate)	2.6293(18)
Th–O2 (nitrate)	2.5600(18)
Th–O4 (nitrate)	2.6109(18)
Th–O5 (nitrate)	2.5973(18)
Th–O7 (nitrate)	2.6268(18)
Th–O8 (nitrate)	2.5866(19)
Th–O10 (nitrate)	2.6098(18)
Th–O11 (nitrate)	2.5925(18)
Th–O13 (OPPh ₂ Ar)	2.4108(17)
Th–O14 (OPPh ₂ Ar)	2.3914(17)
Th–O15 (OPPh ₂ Ar)	2.3954(17)
P2–O13	1.5053(18)
P1–O14	1.5161(18)
P3–O15	1.5116(18)
O–Th–O (phosphines)	140.28(6)
	142.31(6)
	77.41(6)
N–Th–N (nonlinear nitrates)	149.40(6)

Fig. 6: Normalized UV-vis absorption spectra of phosphine oxide ligands **1–4** in THF.

unlikely. We tentatively attribute this spectral shift to the bending of the anthracene ring witnessed for this ligand in its uranyl complex (*vide supra*). However, at this point, it is not clear if the same non-planar geometry is assumed for the ring in the free phosphine oxide ligand. This represents a fundamental difference from the results for ligands **1**, **2** and **4** in which the emission appears typical of the monomer-type emission expected on the basis of the parent PAH.

The fluorescence spectra for the uranyl complexes, **5–8**, were also attempted in THF solution at mM concentrations, but it was found that the phosphine oxide ligands dissociated at dilute concentration. This was verified by ³¹P NMR spectroscopy of the 1 mM stock solution which showed the presence of free ligand only. Thus, the fluorescence profile was identical to that of the free ligand and the spectroscopy of the uranyl complexes could not be satisfactorily obtained.

Fig. 7: Normalized excitation (broken profiles) and emission spectra (solid lines) of aromatic phosphine oxide ligands **1–4** in THF at a concentration of 2×10^{-5} M. The emission and excitation wavelengths used to record these spectra were 320/290, 368/260, 440/260, and 377/337 nm for compounds **1**, **2**, **3**, and **4**, respectively.

4 Conclusion

We have synthesized and characterized through ¹H, ¹³C, and ³¹P NMR, as well as IR, UV-Vis, and fluorescence spectroscopy, a series of phosphine oxide ligands bearing a polycyclic aromatic hydrocarbon. Two ligands coordinate to UO₂(NO₃)₂ to form eight-coordinate complexes which were also characterized by X-ray crystallography. In addition, for the first time three phosphine oxide ligands were structurally observed to bind to Th(NO₃)₄ to produce an eleven-coordinate species. The fluorescence spectrum of the anthracenyl-substituted phosphine oxide ligand showed no vibronic coupling and was red-shift approximately 50 nm from free anthracene, providing possible opportunities for use in detection. In the future, we plan to study the stability of these complexes under radiolysis conditions.

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