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Synthesis and Structure of $(Ph_4P)_2MCl_6$ (M = Ti, Zr, Hf, Th, U, Np, Pu)

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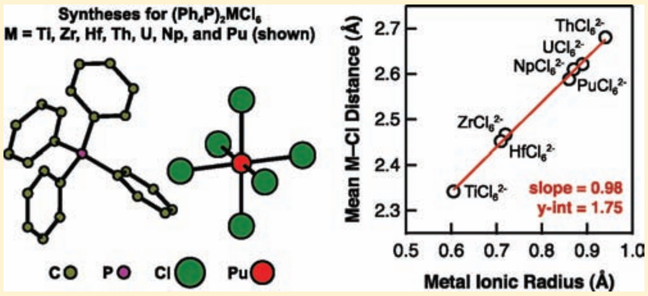
Supporting Information



ABSTRACT: High-purity syntheses are reported for a series of first, second, and third row transition metal and actinide hexahalide compounds with equivalent, noncoordinating countercations: $(Ph_4P)_2TiF_6$ (**1**) and $(Ph_4P)_2MCl_6$ (M = Ti, Zr, Hf, Th, U, Np, Pu; **2**–**8**). While a reaction between MCl_4 (M = Zr, Hf, U) and 2 equiv of Ph_4PCl provided **3**, **4**, and **6**, syntheses for **1**, **2**, **5**, **7**, and **8** required multistep procedures. For example, a cation exchange reaction with Ph_4PCl and $(NH_4)_2TiF_6$ produced **1**, which was used in a subsequent anion exchange reaction with Me_3SiCl to synthesize **2**. For **5**, **7**, and **8**, synthetic routes starting with aqueous actinide precursors were developed that circumvented any need for anhydrous Th, Np, or Pu starting materials. The solid-state geometries, bond distances and angles for isolated $ThCl_6^{2-}$, $NpCl_6^{2-}$, and $PuCl_6^{2-}$ anions with noncoordinating counter cations were determined for the first time in the X-ray crystal structures of **5**, **7**, and **8**. Solution phase and solid-state diffuse reflectance spectra were also used to characterize **7** and **8**. Transition metal MCl_6^{2-} anions showed the anticipated increase in M–Cl bond distances when changing from M = Ti to Zr, and then a decrease from Zr to Hf. The M–Cl bond distances also decreased from M = Th to U, Np, and Pu. Ionic radii can be used to predict average M–Cl bond distances with reasonable accuracy, which supports a principally ionic model of bonding for each of the $(Ph_4P)_2MCl_6$ complexes.

■ INTRODUCTION

Recent advances in actinide synthesis[1−16] are correlated with the availability of convenient preparations for actinide starting materials. For molecular systems, actinide halides have emerged as the most attractive reagents for anhydrous synthesis[17−31] and have also served as analytes for both spectroscopic and theoretical studies.[32−35] The $AnCl_4$ (An = Th, U, Np) compounds are well established starting materials for exploring the anhydrous chemistry of the early actinides. While synthesis and use of UCl_4 is still widespread, the lack of commercial sources for $ThCl_4$ has prompted the search for alternative entries into nonaqueous thorium chemistry.[31] Using $NpCl_4$ has become less attractive because it requires significant laboratory infrastructure to support the high temperature (ca. 200 °C) air and moisture sensitive synthesis with hexachloropropene, and associated production of large quantities of flammable organic neptunium waste. Tetravalent $PuCl_4$ has been observed in the gas phase, but has not been established as a viable starting material and is reported to decompose readily in the solid-state.[36] In this sense, actinide hexachloride dianions (MCl_6^{2-}) are promising alternatives to the tetrachlorides because they are stable for all of the light actinides (M = Th to Pu).[37−39]

Octahedral binary chlorides are also attractive for systematic spectroscopic and theoretical studies. They are known for most metals in the periodic table, and their octahedral ligand environment provides a well-defined platform from which actinide electronic structure and bonding can be compared with that of the main group, transition metal, and lanthanide elements. As part of a recent effort to better understand trends in M–Cl orbital mixing as a function of 3d, 4d, 5d, 5f, and 6d orbital energies and occupancies, transition metal and actinide hexachlorides MCl_6^{2-} (M = Ti, Zr, Hf, Th, U, Np, Pu) were targeted for Cl K-edge X-ray absorption spectroscopy (XAS) and time-dependent density functional theory (DFT) studies.[40] Syntheses have been reported previously for numerous octahedral MCl_6^{2-} salts with alkali metal or noncoordinating tetraalkylammonium, phosphonium, or arsonium countercations (Table 1). However, high-purity syntheses for MCl_6^{2-} complexes with equivalent noncoordinating countercations that met all the spectroscopic requirements of Cl K-edge XAS had not been developed. Of the known salts that had been structurally characterized, the M–Cl bond distances varied widely with different countercations (see Table 1 for crystallographically characterized examples). Reported here is the synthesis and structural characterization of a comprehensive series of d and f block transition metal MCl_6^{2-} dianions with two common Ph_4P^+ countercations. Each compound was

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Table 1. Previously Published MCl_6^{2-} Salts (M = Ti, Zr, Hf, Th, U, Np, Pu) with Alkali Metal or Tetraalkylpnictogenium Cations and Average M−X Bond Distances Where Available[a]

cation	$TiCl_6^{2-}$	$ZrCl_6^{2-}$	$HfCl_6^{2-}$	$ThCl_6^{2-}$	UCl_6^{2-}	$NpCl_6^{2-}$	$PuCl_6^{2-}$
K^+	2.35(3)[75]						2.570(2)[67]
Rb^+	2.33(5)[76]	2.4(1)[76]					2.6799(7)[67]
Cs^+	2.35(5)[76]	2.5(1)[76]		2.81(6)[64]	2.621(4)[77,78]		2.7(2)[68]
R_4N^+	2.3344(7)[79]	2.452(9)[80]	2.452(9)[80]				
Ph_4P^+ [b]	2.336(7)[48]	2.46(1)[44]	2.44(2)[49]		2.60(2)[47]		
Ph_4As^+	2.34(1)[81]				2.611(3)[82]		

[a] Published examples of MX_6^{2-} salts where M is not six coordinate are not included. Errors indicated in parentheses are equal to the standard deviation in the average M−X bond distances. Where only one M−X bond distance is observed, the error is taken from the published estimated standard deviation. [b] These structures were reported with cocrystallized CH_2Cl_2 solvent molecules.

Table 2. Summary of Crystallographic Data Collection and Refinement for 1−4

	$(Ph_4P)_2TiF_6{\cdot}CH_3CN$	$(Ph_4P)_2TiCl_6{\cdot}4CH_3CN$	$(Ph_4P)_2ZrCl_6{\cdot}4CH_3CN$	$(Ph_4P)_2HfCl_6{\cdot}4CH_3CN$
	1	2	3	4
empirical formula	$C_{50}H_{43}F_6NP_2Ti$	$C_{56}H_{52}Cl_6N_4P_2Ti$	$C_{56}H_{52}Cl_6N_4P_2Zr$	$C_{56}H_{52}Cl_6N_4P_2Hf$
formula weight (g/mol)	881.69	1103.56	1146.88	1234.15
T (K)	140(2)	140(2)	140(2)	140(2)
radiation	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
crystal system	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	9.9307(16)	9.4866(16)	9.5282(12)	9.5378(13)
b (Å)	10.5367(13)	19.326(3)	19.366(2)	19.356(3)
c (Å)	11.0318(16)	14.839(3)	14.9522(18)	14.942(2)
alpha (deg)	74.432(6)	90	90	90
beta (deg)	72.6920(10)	98.234(2)	98.159(2)	98.112(2)
gamma (deg)	79.405(3)	90	90	90
volume (Å^3)	1054.8(3)	2692.6(8)	2731.2(6)	2730.9(6)
Z	1	2	2	2
density (calcd) (g/cm^3)	1.388	1.361	1.395	1.501
crystal color	colorless	yellow	colorless	colorless
absorption coefficient (mm^{-1})	0.342	0.557	0.594	2.303
crystal size (mm)	0.20 × 0.18 × 0.16	0.18 × 0.10 × 0.06	0.36 × 0.10 × 0.06	0.30 × 0.04 × 0.04
θ range for data collection (deg)	1.99 to 25.31	2.11 to 26.73	2.10 to 27.48	2.10 to 25.30
$F(0\ 0\ 0)$	456	1140	1176	1240
no. reflns collected	10335	28139	28487	25846
no. of data/restrnts/params	3830/48/325	5694/0/315	6174/0/315	4963/0/315
goodness-of-fit on F^2	1.038	1.036	1.002	1.003
R_1, wR_2 ($I > 2\sigma(I)$)	0.0412, 0.0991	0.0360, 0.0744	0.0479, 0.0931	0.0332, 0.0735
R_1, wR_2 (all data)	0.0514, 0.1058	0.0549, 0.0823	0.0919, 0.1085	0.0509, 0.0804

obtained in high-purity as crystalline solids. In addition, the first X-ray crystal structures containing discrete $ThCl_6^{2-}$, $NpCl_6^{2-}$, and $PuCl_6^{2-}$ anions supported by noncoordinating cations are presented. The metrical parameters obtained from single crystal X-ray diffraction are evaluated as a function of the increasing ionic radii of the metals, and the resulting implications for ionic and covalent models of M−Cl bonding are discussed.

■ EXPERIMENTAL SECTION

General Considerations. *Caution! The ^{232}Th and ^{238}U isotopes are low specific-activity α-particle emitting radionuclides, and their use presents hazards to human health. ^{237}Np and ^{239}Pu isotopes are high specific activity α-particle emitting radionuclides, and their use presents extreme hazards to human health. This research was conducted in a radiological facility with appropriate analyses of these hazards and implementation of controls for the safe handling and manipulation of these toxic and radioactive materials.*

Where noted, all manipulations were performed with rigorous exclusion of air and moisture using Schlenk and glovebox techniques under an atmosphere of argon or helium. All glassware was dried at 150 °C for at least 12 h. Toluene (anhydrous, Fisher) and tetrahydrofuran (THF, anhydrous, Fisher) were vacuum distilled from potassium metal and benzophenone, and degassed by three freeze−pump−thaw cycles. Acetonitrile (anhydrous, Fisher) was dried over CaH_2, degassed by three freeze−pump−thaw cycles, and vacuum distilled before use. Ph_4PCl (Aldrich) was exposed to vacuum (10^{-3} Torr) for 24 h and stored under He in a glovebox prior to use. Me_3SiCl (Aldrich) was transferred to a Teflon sealable Schlenk flask for storage and used as received. $(NH_4)_2TiF_6$ (American Elements), $ZrCl_4$ (anhydrous, Strem), and $HfCl_4$ (anhydrous, Strem) were used as received. UCl_4 was prepared as previously described from UO_3 and hexachloropropene.[17] Aqueous manipulations were performed with >18 Ω water from a Millipore purification system. Electronic absorption spectra were collected at room temperature using a Varian Cary 6000i UV−vis−NIR spectrophotometer with a 0.2 nm spectral bandwidth. Solid diffuse reflectance spectra were collected using a Varian Cary 500 with an Internal Diffuse Reflectance Accessory. Elemental analyses were carried out by Midwest MicroLab, LLC (Indianapolis, IN), and infrared spectra were recorded on a Nicolet Magna-IR System 750 spectrometer as KBr pellets.

Table 3. Summary of Crystallographic Data Collection and Refinement for 5−8

	$(Ph_4P)_2ThCl_6{\cdot}4CH_3CN$ 5	$(Ph_4P)_2UCl_6{\cdot}4CH_3CN$ 6	$(Ph_4P)_2NpCl_6$ 7	$(Ph_4P)_2PuCl_6{\cdot}4CH_3CN$ 8
empirical formula	$C_{56}H_{52}Cl_6N_4P_2Th$	$C_{56}H_{52}Cl_6N_4P_2U$	$C_{48}H_{40}Cl_6P_2Np$	$C_{56}H_{52}Cl_6N_4P_2Pu$
formula weight (g/mol)	1287.7	1293.69	1128.49	1294.72
T (K)	140(1)	120(1)	141(2)	140(1)
radiation	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
crystal system	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a (Å)	9.6163(8)	9.5987(11)	10.178(6)	9.6574(5)
b (Å)	19.4637(16)	19.413(2)	10.316(6)	19.7997(10)
c (Å)	15.1524(12)	15.0841(17)	12.108(7)	15.2266(8)
alpha (deg)	90	90	93.067(7)	90
beta (deg)	98.0870(10)	98.085(1)	99.243(7)	98.8540(10)
gamma (deg)	90	90	116.144(6)	90
volume (Å^3)	2807.9(4)	2782.5(5)	1115.3(11)	2876.8(3)
Z	2	2	1	2
density (calcd) (g/cm^3)	1.523	1.544	1.634	1.498
crystal color	Colorless	Blue-Green	Colorless	Yellow
absorption coefficient (mm^{-1})	3.037	3.302	2.758	1.519
crystal size (mm)	0.14 × 0.16 × 0.18	0.22 × 0.10 × 0.08	0.26 × 0.26 × 0.32	0.10 × 0.12 × 0.14
θ range for data collection (deg)	2.09 to 25.34	2.10 to 28.37	2.10 to 25.05	2.06 to 28.41
$F(0\ 0\ 0)$	1276	1280	538	1284
no. reflns collected	26950	31206	10535	32300
no. of data/restrnts/params	5136/0/315	6561/0/315	3924/0/259	6820/0/315
goodness-of-fit on F^2	1.24	0.933	1.096	0.974
R_1, wR_2 ($I > 2\sigma(I)$)	0.0287, 0.0417	0.0202, 0.0526	0.0288, 0.0911	0.0263, 0.0542
R_1, wR_2 (all data)	0.0466, 0.0443	0.0275, 0.0564	0.0299, 0.0920	0.0475, 0.0614

Crystallographic Details. Crystals of the Np and Pu-containing compounds **7** and **8** were prepared with three appropriate layers of containment prior to single crystal X-ray diffraction studies by following modifications of the published procedures.[15,41,42] Single crystals were coated with epoxy and then mounted inside 0.5 mm capillaries. The capillaries were sealed with additional epoxy, and their external surfaces were coated with a thin film of acrylic dissolved in ethyl acetate (Hard as Nails nail polish). Otherwise, single crystals of **1**−**6** were mounted on nylon loops with Paratone-N oil (Hampton Research) and immediately cooled to 140 K in a cold nitrogen gas stream on a Bruker CCD platform diffractometer. Standard peak search and indexing procedures, followed by least-squares refinement yielded the cell dimensions given in Tables 2 and 3. The measured intensities were reduced to structure factor amplitude, and their estimated standard deviations by correction for background and Lorentz and polarization effects. No corrections for crystal decay were necessary. Systematically absent reflections were deleted and symmetry equivalent reflections were averaged to yield the set of unique data. All unique data were used in the least-squares refinements. The analytical approximations to the scattering factors were used, and all structure factors were corrected for both real and imaginary components of anomalous dispersion. Correct atomic position(s) were deduced from an E-map (SHELX); least-squares refinement and difference Fourier calculations were used to locate atoms not found in the initial solution.

Where noted, all manipulations were performed with rigorous exclusion of air and moisture using Schlenk and glovebox techniques under an atmosphere of argon or helium. All glassware was dried at 150 °C for at least 12 h. Toluene (anhydrous, Fisher) and tetrahydrofuran (THF, anhydrous, Fisher) were vacuum distilled from potassium metal and benzophenone, and degassed by three freeze−pump−thaw cycles. Acetonitrile (anhydrous, Fisher) was dried over CaH_2, degassed by three freeze−pump−thaw cycles, and vacuum distilled before use. Ph_4PCl (Aldrich) was exposed to vacuum (10^{-3} Torr) for 24 h and stored under He in a glovebox prior to use. Me_3SiCl (Aldrich) was transferred to a Teflon sealable Schlenk flask for storage and used as received. $(NH_4)_2TiF_6$ (American Elements), $ZrCl_4$ (anhydrous, Strem), and $HfCl_4$ (anhydrous, Strem) were used as received. UCl_4 was prepared as previously described from UO_3 and hexachloropropene.[17] Aqueous manipulations were performed with >18 Ω water from a Millipore purification system. Electronic absorption spectra were collected at room temperature using a Varian Cary 6000i UV−vis−NIR spectrophotometer with a 0.2 nm spectral bandwidth. Solid diffuse reflectance spectra were collected using a Varian Cary 500 with an Internal Diffuse Reflectance Accessory. Elemental analyses were carried out by Midwest MicroLab, LLC (Indianapolis, IN), and infrared spectra were recorded on a Nicolet Magna-IR System 750 spectrometer as KBr pellets.

Bis(tetraphenylphosphonium) Titanium Hexafluoride, $(Ph_4P)_2TiF_6$ (1). Compound **1** was synthesized using a modification of a previously published procedure.[43] $(NH_4)_2TiF_6$ (0.21 g, 1.05 mmol) and Ph_4PCl (0.78 g, 2.09 mmol) were each dissolved in boiling water (10 mL), and the solutions were stirred together. The resulting solution was allowed to cool and stored at room temperature for 24 h, which resulted in formation of white crystals. Following filtration, the crude product was isolated from the reaction mixture as small white crystals. These solids were dried under vacuum (10^{-3} Torr) at elevated temperature (60 °C) for 24 h, brought into a helium-filled glovebox, and dissolved in hot (60 °C) CH_3CN (15 mL). The solution was allowed to cool slowly to room temperature and then placed in a freezer (−20 °C) overnight. Compound **1** was isolated as single crystals suitable for X-ray diffraction studies in 22% yield (0.20 g, 0.22 mmol). Higher crystalline yields are achieved by isolating a second crop of crystals, which can be obtained by concentrating the mother liquor and repeating the crystallization procedure. IR (cm^{-1}): 695 (s), 724 (s), 762 (s), 770 (m), 997 (m), 1027 (w), 1108 (s), 1166 (w), 1190 (w), 1317 (w), 1385 (w), 1437 (m), 1444 (m), 1483 (w), 1584 (w), 3022 (w), 3073 (w). Anal. Calcd for $C_{48}H_{40}P_2TiF_6$: C, 68.58; H, 4.80; F, 13.56. Found: C, 68.48; H, 4.84; 13.66.

Bis(tetraphenylphosphonium) Titanium Hexachloride, $(Ph_4P)_2TiCl_6$ (2). In a helium-filled glovebox, an excess of Me_3SiCl (10 mL) was added to a flask containing a solution of **1** (0.51 g, 0.60 mmol) in CH_3CN (10 mL). This caused immediate precipitation of a yellow solid. The volatiles were removed in vacuo (10^{-3} Torr), and the resulting solids were redissolved in CH_3CN. Slow diffusion of Et_2O

into this solution produced compound **2** as single crystals suitable for X-ray diffraction in 35% yield following filtration (0.58 g, 0.18 mmol). Higher crystalline yields are achieved by isolating a second crop of crystals, which can be obtained by concentrating the mother liquor and repeating the crystallization procedure. IR (cm^{-1}): 669 (w), 691 (s), 723 (s), 757 (w), 997 (m), 1028 (w), 1108 (s), 1166 (w), 1187 (w), 1318 (w), 1384 (w), 1438 (s), 1483 (w), 1585 (w), 2218 (w), 2249 (w), 2925 (w), 3058 (w). Anal. Calcd for $C_{48}H_{40}P_2TiCl_6$: C, 61.37; H, 4.29. Found: C, 61.10; H, 4.65.

Bis(tetraphenylphosphonium) Zirconium Hexachloride, $(Ph_4P)_2ZrCl_6$ (3). In a helium-filled glovebox, a modified version of the literature procedure was followed.[44] A solution of Ph_4PCl (0.32 g, 0.85 mmol) in acetonitrile (6 mL) was added to a stirred solution of $ZrCl_4$ (0.10 g, 0.43 mmol) in CH_3CN (6 mL), resulting in the immediate formation of a white crystalline solid. After isolating the solid by centrifugation it was dissolved in hot CH_3CN. This solution was allowed to cool slowly to room temperature and then placed in a freezer at −6 °C. The resulting white crystals were isolated by filtration and desolvated by exposure to vacuum for several hours. This provided compound **3** in 49% yield (0.21 g, 0.21 mmol). The desolvated product was used for analytical measurements. Single crystals suitable for X-ray diffraction were obtained by slow-cooling of a hot saturated solution of **3** in CH_3CN. Higher crystalline yields are achieved by isolating a second crop of crystals, which can be obtained by concentrating the mother liquor and repeating the crystallization procedure. IR (cm^{-1}): 689 (s), 722 (s), 756 (m), 996 (m), 1027 (w), 1107 (s), 1164 (w), 1188 (w), 1315 (w), 1437 (s), 1483 (w), 1585 (w), 3057 (w). Anal. Calcd for $C_{48}H_{40}P_2ZrCl_6$: C, 58.66; H, 4.10. Found: C, 58.04; H, 4.04.

Bis(tetraphenylphosphonium) Hafnium Hexachloride, $(Ph_4P)_2HfCl_6$ (4). The procedure for **3** was modified, using instead $HfCl_4$ (0.10 g, 0.31 mmol) and Ph_4PCl (0.24 g, 0.63 mmol). Compound **4** was isolated as white crystals, desolvated by exposure to vacuum for several hours, and obtained in 49% yield (0.16 g, 0.15 mmol). Single crystals suitable for X-ray diffraction were formed by slow-cooling of a hot saturated solution of **4** in CH_3CN. The crystals which had been desolvated by exposure to vacuum for several hours were used for other analytical measurements. Higher crystalline yields can be achieved by isolating a second crop of crystals, which can be obtained by concentrating the mother liquor and repeating the crystallization procedure. IR (cm^{-1}): 669 (w), 691 (s), 723 (s), 761 (m), 996 (m), 1027 (w), 1108 (s), 1165 (w), 1187 (w), 1316 (w), 1338 (w), 1368 (w), 1438 (s), 1483 (w), 1585 (w), 3059 (w). Anal. Calcd for $C_{48}H_{40}P_2HfCl_6$: C, 53.88; H, 3.77. Found: C, 54.01; H, 3.86.

Bis(tetraphenylphosphonium) Thorium Hexachloride, $(Ph_4P)_2ThCl_6$ (5). An adaptation of the published synthesis of $(NH_4)_4Th(SO_4)_4$ was followed.[45] In a fume hood, ThO_2 (0.26 g, 0.98 mmol) and $(NH_4)_2SO_4$ (0.79 g, 6.0 mmol) were ground together in a mortar and pestle, placed in a Pt foil boat, and slowly heated in a quartz tube to 365 °C for 3 h. The product, $(NH_4)_4Th(SO_4)_4$, was then dissolved in H_2O (100 mL). While monitoring with a pH meter, concentrated aqueous NH_4OH was added dropwise until the pH was slightly below 9. A white precipitate, which was formulated as a poly hydrated thorium hydroxide, was isolated on a medium glass frit, washed liberally with aqueous NH_4OH (0.1 M), and redissolved in aqueous HCl (1 M, 10 mL). The solution was transferred to an Erlenmeyer flask and the solvent removed using a Meker burner. After drying in an oven (100 °C),[46] the resulting powder was dissolved in CH_3CN and a solution of Ph_4PCl (0.71 g, 1.9 mmol) in CH_3CN (5 mL) was added, resulting in a rapid formation of a white precipitate. The product was isolated on a medium glass frit, washed with cold CH_3CN, and dried in vacuo (10^{-3} Torr) at 60 °C for 24 h. This desolvated form of compound **5** was isolated with 70% overall yield as a white powder (0.77 g, 0.69 mmol). Crystals of compound **5** suitable for X-ray diffraction studies were grown by slow diffusion of Et_2O vapor into saturated solutions of **5** in CH_3CN. Higher crystalline yields can be achieved by isolating a second crop of crystals, which can be obtained by concentrating the mother liquor and repeating the crystallization procedure. IR (cm^{-1}): 689 (s), 723 (s), 754 (m), 760 (m), 997 (m), 1027 (w), 1108 (s), 1165 (w), 1189 (w), 1316 (w), 1338 (w), 1384 (w), 1440 (s), 1484 (m), 1586 (m), 3059 (m). Anal. Calcd for $C_{48}H_{40}P_2ThCl_6$: C, 51.3; H, 3.59. Found: C, 51.5; H, 3.69.

Bis(tetraphenylphosphonium) Uranium Hexachloride, $(Ph_4P)_2UCl_6$ (6). A modification of the literature procedure was followed.[47] A vial containing UCl_4 (0.22 g, 0.58 mmol) and THF (10 mL) was heated (70 °C) while stirring in a helium-filled glovebox until all of the UCl_4 dissolved. In a separate vial, CH_3CN (10 mL) was added dropwise to a white suspension of Ph_4PCl (0.48 g, 1.3 mmol) in THF (10 mL) and heated at 70 °C until all the Ph_4PCl dissolved. The Ph_4PCl solution was then added rapidly to the solution of UCl_4 causing immediate precipitation of a pale blue-green solid. After stirring for 1 h, the mixture was centrifuged and the supernatant was decanted and discarded. The remaining solids were washed with hot THF (3 × 5 mL) and dissolved in boiling CH_3CN (15 mL). After filtration, the solution was cooled to −25 °C and after 24 h formed pale blue-green crystals, which were isolated by decanting the supernatant, washing with cold THF (10 mL), and drying in vacuo (10^{-3} Torr). The desolvated product was obtained as a crystalline solid (0.42 g, 0.37 mmol) in 64% yield. Single crystals suitable for X-ray crystallographic analysis were obtained by slow cooling of a hot concentrated solution of **6** in CH_3CN. Higher crystalline yields can be achieved by isolating a second crop of crystals, which can be obtained by concentrating the mother liquor and repeating the crystallization procedure. IR (cm^{-1}): 689 (s), 723 (s), 754 (m), 760 (m), 996 (m), 1027 (w), 1108 (s), 1165 (w), 1188 (w), 1315 (w), 1338 (w), 1385 (w), 1438 (s), 1483 (m), 1585 (m), 3058 (m). Anal. Calcd for $C_{48}H_{40}P_2UCl_6$: C, 51.04; H, 3.57. Found: C, 51.15; H, 3.66.

Bis(tetraphenylphosphonium) Neptunium Hexachloride, $(Ph_4P)_2NpCl_6$ (7). In an argon-filled negative pressure purge box, an aliquot (0.10 mL, 0.14 mmol) of a green stock solution of dilute aqueous HCl containing NpO_2^+ (1.4 M) was transferred to a flask containing a Zn/Hg amalgam. Following a brief agitation by shaking, which resulted in a color change from green to blue, the solution was decanted from the reducing agent and exposed to an atmosphere of air. After approximately 2 h, the complete oxidation from blue Np^{3+} to yellow Np^{4+} was confirmed by UV−vis−NIR spectroscopy. The water was removed via distillation, a solution of Ph_4PCl (0.11 g, 0.28 mmol) in hot CH_3CN (5 mL) was added, and the mixture was heated until all the solids had dissolved. Vapor diffusion of Et_2O into this concentrated solution produced colorless single crystals of **7** suitable for X-ray diffraction studies, and were isolated in 41% yield (0.063 g, 0.056 mmol) following filtration from the supernatant. Radiological concerns prohibited evaluation of the elemental composition of **7**.

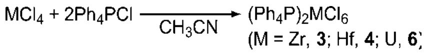
Alternative Synthesis of Bis(tetraphenylphosphonium) Neptunium Hexachloride, $(Ph_4P)_2NpCl_6$ (7). In a fume hood, an aliquot of a stock solution containing mixed NpO_2^+ and NpO_2^{2+} oxidation states in HCl (309 μL, 0.44 M, 0.14 mmol), was diluted with additional HCl (1 mL, 6.0 M). The Np oxidation state was adjusted to Np^{4+} by adding $NH_2OH{\cdot}HCl$ and heating the solution. Oxidation state purity was verified by UV−vis−NIR spectroscpy. This green solution was evaporated to dryness by flowing argon gas for 12 h over the opening of a vial containing the solution. The orange solid residue was suspended in CH_3CN (1 mL), a solution of Ph_4PCl (0.095 g, 0.25 mmol) in CH_3CN (2 mL) was added, and the mixture was stirred for 10 min producing a cloudy white suspension. Et_2O (8 mL) was added, and the mixture was stirred at room temperature for 20 min. After settling, the supernatant was pipetted away from the white solid, which was transferred to a negative-pressure helium atmosphere drybox and dried in vacuo to yield a crude powdered product (0.10 g, 0.092 mmol) in 66% yield. The product could be purified further by dissolving in CH_3CN (9 mL) at 50 °C, filtering, and crystallizing by diffusion of Et_2O vapor into the concentrated CH_3CN solution at −35 °C for 3 d. Following filtration and drying in vacuo, colorless crystals suitable for X-ray diffraction were obtained in 61% yield (0.096 g, 0.085 mmol).

Bis(tetraphenylphosphonium) Plutonium Hexachloride, $(Ph_4P)_2PuCl_6$ (8). In a fume hood, an aliquot of a Pu^{4+} stock solution (0.15 mL, 0.71 M, 0.10 mmol) in HCl was diluted with HCl (0.5 mL, 6 M) and stirred briefly until homogeneous. This red solution was evaporated to dryness by flowing argon gas for 12 h over the opening of a vial containing the solution. A solution of Ph_4PCl (0.079 g, 0.21 mmol) dissolved in CH_3CN (3 mL) was added to this solid residue, which quickly produced a yellow precipitate. The reaction was allowed to go to completion while stirring at room temperature for 5 min, then 40 °C for 10 min, and finally allowed to cool back to room temperature. The resulting mixture contained both a yellow solution and a yellow precipitate. To force precipitation of the partially soluble yellow product, Et_2O (12 mL) was added while stirring over 10 min. The supernatant was then pipetted away from the solids, which were subsequently transferred to a negative-pressure He atmosphere drybox and dried in vacuo to yield a crude powdered product (0.10 g, 0.092 mmol) in 88% yield. For further purification, this yellow solid was dissolved in CH_3CN (6 mL), heated to 50 °C, and filtered. Storing the filtrate at −35 °C for 5 h followed by filtration gave **8** as X-ray quality single crystals in 82% yield (0.097 g, 0.086 mmol). Radiological concerns prohibited evaluation of the elemental composition of **8**.

■ RESULTS AND DISCUSSION

Synthesis. The general reaction involving combination of the anhydrous MCl_4 and Ph_4PCl in organic solvent consistently provided large quantities (crystalline yields ranging 49 to 69%) of pure zirconium, hafnium, and uranium hexachlorides (**3**, **4**, and **6**) following crystallization from CH_3CN (Scheme 1).

Scheme 1

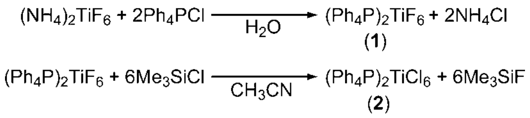


$$MCl_4 + 2Ph_4PCl \xrightarrow[CH_3CN]{} (Ph_4P)_2MCl_6 \quad (M = Zr, \mathbf{3}; Hf, \mathbf{4}; U, \mathbf{6})$$

Some syntheses have been reported for MCl_6^{2-} salts (M = Ti, Zr, Hf, U) with noncoordinating Ph_4P^+ countercations,[44,47−49] However, the $(Ph_4P)_2MCl_6$ salts typically cocrystallized with chlorinated CH_2Cl_2 solvent molecules, which are not compatible with our interest in conducting Cl K-edge XAS studies focused on the MCl_6^{2-} anions.[50] The elemental analysis and single crystal X-ray structures (see below) confirm that the syntheses reported herein provided $(Ph_4P)_2MCl_6$ salts with rigorous exclusion of a secondary chlorine species.

Upon initial inspection the synthetic approach used for **3**, **4**, and **6** seemed appropriate for all the $(Ph_4P)_2MCl_6$ complexes. However, this was not feasible for the Ph_4P^+ salts of $TiCl_6^{2-}$ (**2**), $ThCl_6^{2-}$ (**5**), $NpCl_6^{2-}$ (**7**), or $PuCl_6^{2-}$ (**8**), and alternative syntheses of these anhydrous materials were designed. For example, because $TiCl_4$ reacts with many solvents that solubilize Ph_4PCl (such as CH_3CN), **2** was prepared in two steps from commercially available $(NH_4)_2TiF_6$ (Scheme 2).

Scheme 2



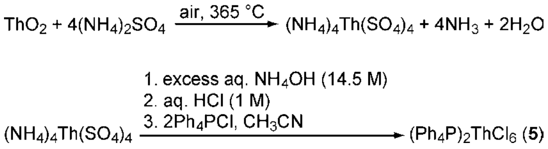
$$(NH_4)_2TiF_6 + 2Ph_4PCl \xrightarrow[H_2O]{} \underset{(\mathbf{1})}{(Ph_4P)_2TiF_6} + 2NH_4Cl$$

$$(Ph_4P)_2TiF_6 + 6Me_3SiCl \xrightarrow[CH_3CN]{} \underset{(\mathbf{2})}{(Ph_4P)_2TiCl_6} + 6Me_3SiF$$

First, compound **1** was prepared in low crystalline yield (22%) using a modification of the published procedure for $(Ph_4P)_2ZrF_6$,[43] which involved a cation exchange reaction between $(NH_4)_2TiF_6$ and Ph_4PCl. The product **1** was precipitated from H_2O, dried at elevated temperature under vacuum, and crystallized from CH_3CN. A subsequent anion exchange reaction between **1** and Me_3SiCl conducted with rigorous exclusion of air and moisture provided **2** in 35% yield following crystallization from Et_2O/CH_3CN.

The synthesis of the Th analogue (**5**) was achieved beginning with ThO_2 because of the limited commercial availability of more favorable Th starting materials such as $ThCl_4$.[31] In contrast to redox active actinide oxides (MO_2, M = U, Np, and Pu), ThO_2 is not easily dissolved. As a result, ThO_2 was first converted to water-soluble $(NH_4)_4Th(SO_4)_4$ by reaction with $(NH_4)_2SO_4$ at 365 °C, using a procedure similar to that described by Mudher and co-workers (Scheme 3).[45] The ammonium thorium sulfate was dissolved in H_2O, precipitated with NH_4OH, and redissolved in dilute HCl. After removing the water at elevated temperature using a Meker burner, the resulting solid was treated with Ph_4PCl in CH_3CN. Anhydrous **5** was obtained by gently heating the reaction product under vacuum, and isolated as single crystals in 49% yield from a Et_2O/CH_3CN solution.

Scheme 3

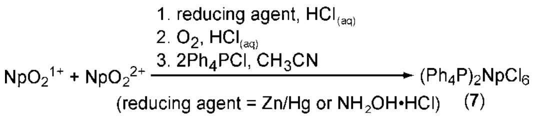


$$ThO_2 + 4(NH_4)_2SO_4 \xrightarrow{\text{air, 365 °C}} (NH_4)_4Th(SO_4)_4 + 4NH_3 + 2H_2O$$

$$(NH_4)_4Th(SO_4)_4 \xrightarrow{\substack{\text{1. excess aq. } NH_4OH \text{ (14.5 M)} \\ \text{2. aq. HCl (1 M)} \\ \text{3. } 2Ph_4PCl, CH_3CN}} (Ph_4P)_2ThCl_6 \ (\mathbf{5})$$

Aqueous synthetic routes were also investigated to obtain sufficient quantities of $(Ph_4P)_2NpCl_6$ (**7**) and $(Ph_4P)_2PuCl_6$ (**8**), and are related to those used to generate Cs_2NpCl_6 and Cs_2PuCl_6.[51,52] Pure stock solutions of Np^{4+} were prepared by reducing a mixed stock solution containing NpO_2^{2+} and NpO_2^{+} with either Zn/Hg amalgam or $NH_2OH·HCl$ (Scheme 4).

Scheme 4

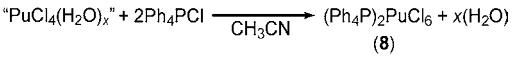


$$NpO_2^{1+} + NpO_2^{2+} \xrightarrow[\text{(reducing agent = Zn/Hg or } NH_2OH\bullet HCl)]{\substack{\text{1. reducing agent, } HCl_{(aq)} \\ \text{2. } O_2, HCl_{(aq)} \\ \text{3. } 2Ph_4PCl, CH_3CN}} \underset{(\mathbf{7})}{(Ph_4P)_2NpCl_6}$$

UV−visible spectroscopy indicated that if a solution containing NpO_2^{2+}/NpO_2^{+} was reduced with Zn/Hg amalgam, a solution containing almost exclusively Np^{3+} was generated which subsequently oxidized to Np^{4+} upon exposure to air (for ca. 2 h).[53−55] Alternatively, if the milder $NH_2OH·HCl$ reducing agent was used, Np^{3+} was not observed and a clean tetravalent Np solution was obtained directly. After obtaining a pure Np^{4+} solution, removal of the solvent followed by reactions with Ph_4PCl in CH_3CN provided colorless **7** in moderate crystalline yields, which ranged from 41% when using Zn/Hg, to 61% if $NH_2OH·HCl$ was used. A similar approach was developed for the Pu salt (**8**); however, no valence adjustment step was required because solutions containing exclusively Pu^{4+} were readily available from anion exchange purification procedures, which are routinely employed in aqueous Pu chemistry.[56] After removing the water, the Pu^{4+} solid was partially dissolved in CH_3CN and treated with Ph_4PCl. From this saturated solution, yellow X-ray quality single crystals of **8** were obtained in 82% yield (Scheme 5).

Optical Spectroscopy of 7 and 8. Diffuse solid-state reflectance spectra and the UV/visible/NIR absorbance spectra of solutions of **7** and **8** in CH_3CN show the anticipated f → f and f → d transitions associated with the Np^{4+} (f^3) and Pu^{4+}

Scheme 5



$$\text{“}PuCl_4(H_2O)_x\text{”} + 2Ph_4PCl \xrightarrow[CH_3CN]{} \underset{(\mathbf{8})}{(Ph_4P)_2PuCl_6} + x(H_2O)$$

(f^4) ions (Figures 1 and 2). For both compounds, the number and intensity of bands observed in the visible region are consistent with the usually pale colors observed for single crystals of **7** (colorless) and **8** (yellow). The solid and solution-state optical spectra are very similar, and in agreement with previous reports on $NpCl_6^{2-}$ and $PuCl_6^{2-}$ with different cations.[57−61] They exhibit a series of well-resolved absorptions in the near-IR region, which is a characteristic of Np^{4+} and Pu^{4+} coordination compounds and suggests that the speciation for the neptunium and plutonium ions in solution is equivalent to that in the solid state.

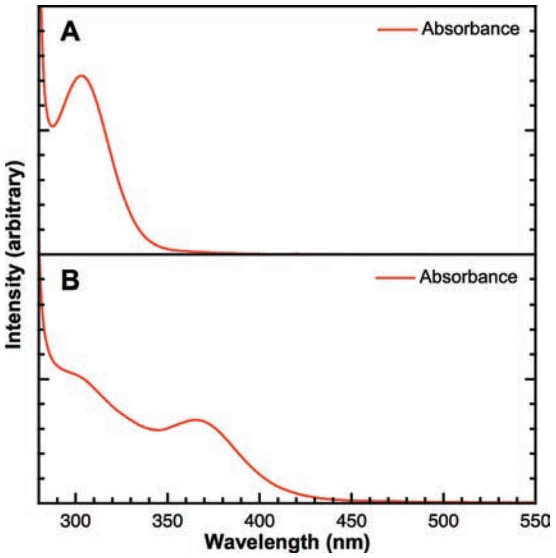


Figure 1. UV spectra of $(Ph_4P)_2NpCl_6$ (panel A) and $(Ph_4P)_2PuCl_6$ (panel B) in CH_3CN.

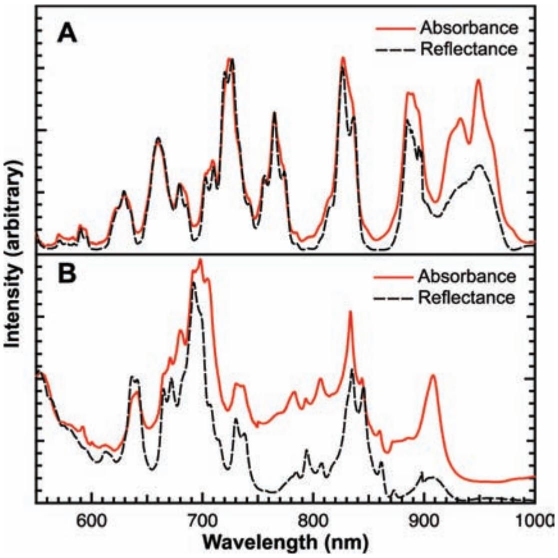


Figure 2. Visible-NIR spectra of $(Ph_4P)_2NpCl_6$ (panel A) and $(Ph_4P)_2PuCl_6$ (panel B), obtained by reflectance of solid samples (black traces) and absorbance of dilute solutions in CH_3CN (red traces).

X-ray Crystal Structure Descriptions. The complexes **2**−**6** and **8** are isomorphous and crystallize in the $P2_1/c$ space group with two molecules of CH_3CN (Tables 2 and 3). For reasons not well understood, compound **7** crystallizes in the $P\bar{1}$ space group without any CH_3CN. Unit cells for crystalline **1**−**8** contain discrete metal halide molecules that are well-separated from the Ph_4P^+ countercations and for **1**−**6** and **8** there are no obvious interactions between MCl_6^{2-} anions and the CH_3CN solvent molecules. A thermal ellipsoid plot for the $PuCl_6^{2-}$ molecule in **8** is shown in Figure 3, and thermal ellipsoid plots for **1**−**7** are provided in the Supporting Information, Figures S1−S7. In each MCl_6^{2-} molecule the metal geometry is best described as octahedral; however, all six M−Cl bond distances are not crystallographically equivalent, and the Cl−M−Cl angles are not rigorously 90 degrees. Each of the three crystallographically inequivalent M−Cl bond distances and angles are given in Table 4, along with the mean M−Cl bond distances and standard deviations from the means (σ).

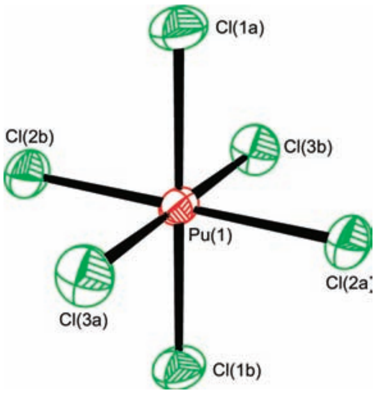


Figure 3. Thermal ellipsoid (50%) plot of **8**. Noncoordinating Ph_4P^+ countercations and acetonitrile molecules have been omitted.

For **1**, the F−Ti−F angles only slightly deviate from 90 degrees (90.49(6), 89.96(6), and 89.92(6) degrees) and the three unique Ti−F bond distances (1.8671(13), 1.8644(14), and 1.8567(14) Å) average 1.863 Å with σ = 0.005 Å. This compares well with the 1.86 Å (σ = 0.01 Å) average distance reported in the crystal structure of TiF_6^{2-} with noncoordinating aminoguanidinium cations.[62,63] In **2**, the average Ti−Cl bond distance is appreciably longer at 2.34 Å (σ = 0.01 Å). Changing the metal from Ti to Zr and Hf increases the M−Cl bond distance, and average values of 2.47 Å (σ = 0.01 Å) and 2.45 Å (σ = 0.01 Å) were observed for **3** and **4**, respectively.

Structures of the thorium and uranium analogues (**5** and **6**) are similar to the transition metal compounds, with an average Th−Cl distance of 2.68 Å (σ = 0.01 Å) and an average U−Cl distance of 2.62 Å (σ = 0.01 Å). The average Th−Cl distance is shorter than what was observed in the X-ray crystal structure of Cs_2ThCl_6 (Th−Cl = 2.81(6) Å; each Cs atom is also coordinated to 12 Cl atoms at an average distance of 3.74 Å).[64] However, because of the large error bars associated with the Cs_2ThCl_6 metric parameters, the Th−Cl bond distances in both crystal structures are equivalent within three σ. The average U−Cl bond distance compares well with that observed in $(Ph_4P)_2UCl_6{\cdot}2CH_2Cl_2$ (average U−Cl = 2.60 Å, σ = 0.02 Å).[47] To the best of our knowledge, the structure of **5** is the only structural report for a $ThCl_6^{2-}$ salt with noncoordinating countercations. Overall, the similarities between observed bond distances and geometries in these MX_6^{2-} molecules (M = Ti, Zr, Hf, Th, U; X = F, Cl) confirm that alternative noncoordinating countercations and cocrystallized solvent molecules have an insignificant effect on the solid-state structure.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Complexes 1−8

	1, TiF_6^{2-}	**2**, $TiCl_6^{2-}$	**3**, $ZrCl_6^{2-}$	**4**, $HfCl_6^{2-}$	**5**, $ThCl_6^{2-}$	**6**, UCl_6^{2-}	**7**, $NpCl_6^{2-}$	**8**, $PuCl_6^{2-}$
M(1)−X(1)	1.8671(13)	2.3543(6)	2.4771(8)	2.4605(10)	2.6901(8)	2.6326(6)	2.6281(16)	2.5944(8)
M(1)−X(2)	1.8644(14)	2.3252(6)	2.4530(8)	2.4414(10)	2.6699(9)	2.6087(5)	2.5826(14)	2.5757(7)
M(1)−X(3)	1.8567(14)	2.3458(6)	2.4699(8)	2.4526(10)	2.6824(8)	2.6224(6)	2.6198(16)	2.5936(8)
av. M(1)−X[a]	1.863(5)	2.34(1)	2.47(1)	2.45(1)	2.68(1)	2.62(1)	2.61(2)	2.59(1)
X(1)−M(1)−X(2)	89.96(6)	90.27(2)	90.50(3)	90.36(3)	91.31(3)	91.048(18)	89.59(6)	90.97(3)
X(1)−M(1)−X(3)	90.49(6)	90.280(19)	90.47(3)	90.38(3)	90.90(3)	89.600(16)	89.93(4)	90.84(3)
X(2)−M(1)−X(3)	89.92(6)	89.89(2)	89.79(3)	89.84(3)	89.57(3)	90.768(16)	88.31(4)	89.61(3)
av. X−M(1)−X[a]	90.1(3)	90.1(2)	90.3(4)	90.2(3)	90.6(9)	90.5(8)	89.3(9)	90.5(8)

[a] The error in the average bond lengths and angles is equal to the standard deviation in the three experimental values.

Although powder X-ray diffraction has been used to characterize Cs_2NpCl_6,[18] to the best of our knowledge, the structure of **7** represents the first single crystal diffraction data containing a $NpCl_6^{2-}$ anion. Three unique Np−Cl bond distances were observed (Table 4), which provide an average Np−Cl bond distance of 2.61 Å (σ = 0.02 Å). For $PuCl_6^{2-}$, powder X-ray diffraction has also been used to characterize $(Me_4N)_2PuCl_6$,[65] and $(Et_4N)_2PuCl_6$,[65,66] but the only single crystal X-ray diffraction studies of the $PuCl_6^{2-}$ anion have been performed on salts with alkali metal countercations. In these studies, Pu−Cl bond distances were found to vary significantly if the countercation was K^+ (2.570(2) Å),[67] Rb^+ (2.6799(8) Å),[67] or Cs^+ (2.7(2) Å).[68] Each of the alkali metals in these crystal structures was coordinated by 12 Cl atoms with K−Cl, Rb−Cl, and Cs−Cl distances that averaged 3.680, 3.643, and 3.71 Å, respectively. The structure of **8** is the first with a $PuCl_6^{2-}$ anion and noncoordinating cations. The mean Pu−Cl distance in **8** is 2.59 Å (σ = 0.01 Å), which more closely resembles the Pu−Cl distance in K_2PuCl_6, than those in the $PuCl_6^{2-}$ salts with Rb^+ or Cs^+ countercations.[67]

In summary, crystallographically equivalent M−Cl bond distances increase when moving from the first row (Ti) to the second (Zr) or third row (Hf), and decrease across the actinide series (Th to Pu).[69] However, average U−Cl, Np−Cl, and Pu−Cl bond distances are equivalent within the standard deviation of the mean. All the transition metal and actinide M−Cl bond distances are essentially invariant when compared to the six coordinate ionic radii. Figure 4 depicts this graphically by showing the linear relationship between mean M−Cl bond distances and metal ionic radii. A linear fit to these data has a near unit slope of 0.98 ± 0.02 and a y-intercept of 1.75 ± 0.02, which is close to the chlorine ionic radius of 1.81 Å.[70] On the basis of previously reported structural criteria for establishing bonding modes,[71] these data indicate that the M−Cl interactions in each of the $(Ph_4P)_2MCl_6$ salts are best described as predominantly ionic in character.

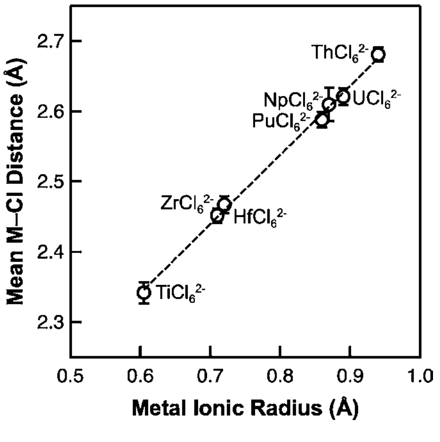


Figure 4. Plot of the mean M−Cl bond distances (Å) in $(Ph_4P)_2MCl_6$ (M = Ti, Zr, Hf, Th, U, Np, Pu) relative to the ionic radius of M.[70] A linear fit to the data (dashed line) gives the equation $y = (1.75 \pm 0.02$ Å$) + (0.98 \pm 0.02)x$. Error bars are taken from the standard deviation in the mean distance of crystallographically inequivalent M−Cl bonds.

CONCLUDING REMARKS

Described here are high-purity syntheses conducted with rigorous exclusion of chlorinated solvents for octahedral TiF_6^{2-} (**1**) and MCl_6^{2-} (M = Ti, Zr, Hf, Th, U, Np, Pu; **2**−**8**) molecules as salts with Ph_4P^+ countercations. By avoiding the introduction of additional Cl atoms into the lattice and using noncoordinating cations to prevent M−Cl−M bridging, the synthetic procedures provide metal hexahalide salts that are compatible with Cl K-edge XAS experiments and guarantee that the M−Cl interactions are probed discretely. Compounds **5**, **7**, and **8** have the potential to serve as well-defined starting materials for nonaqueous Th, Np, and Pu coordination chemistry, and have already been employed as convenient precursors for anhydrous low-valent Pu coordination chemistry.[72,73] Achieving efficient high purity syntheses that do not require extensive manipulations is especially important for the $NpCl_6^{2-}$ and $PuCl_6^{2-}$ salts, because radiological concerns limit the amount of material that can be handled safely.

The M−Cl bond distances follow well-established periodic trends for transition metals and actinides.[69] These trends in bond distance also parallel the ionic radius of the metal, which suggests that the M−Cl bonding in each $(Ph_4P)_2MCl_6$ salt can be described appropriately using a primarily ionic bonding model. On the other hand, a variety of theoretical, spectroscopic and thermodynamic studies indicate that—particularly for actinides—more direct techniques and precise terminology are needed to identify subtle differences in covalent bonding.[32−35,74] Along these lines, we are currently using F and Cl K-edge X-ray absorption spectroscopy as direct probes of electronic structure and metal−ligand orbital mixing for the transition metal and actinide compounds described here.[40]

ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic information files (CIF) and thermal ellipsoid plots for **1**−**8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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