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Synthesis and Structural Examination of Complexes of Am(IV) and Other Tetravalent Actinides with Lacunary Heteropolyanion α_2-$P_2W_{17}O_{61}^{10-}$

Marina N. Sokolova,[†] **Alexander M. Fedosseev,**[*,†] **Grigory B. Andreev,**[†] **Nina A. Budantseva,**[†] **Alexander B. Yusov,**[†] **and Philippe Moisy**[*,‡]

[†]*A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, 31 Leninskiy pr., Moscow, 119991, Russia, and* [‡]*CEA Marcoule, DRCP/SCPS, BP 17171, 30207 Bagnols sur Cèze Cedex, France*

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This study concerns the formation of complexes with actinides at oxidation state +IV, from Th to Am, through a lacunary heteropolyanion ligand $P_2W_{17}O_{61}^{10-}$. The preparation of original single crystals of complexes with 1:2 stoichiometry provided structural data through single-crystal X-ray diffraction for the entire An(IV) series. An(IV) atoms in these complexes have a coordination number of 8, and their coordination polyhedron is a distorted square antiprism. The data were used to compute a mean (An−O) interatomic distance for each actinide. When the interatomic distance is plotted versus the inverse ionic radius of these tetravalent actinides, it appears that the simple electrostatic model is not suitable for Am(IV) and Pu(IV), although this trend must be confirmed by further investigation with other examples from the An(IV) series.

Introduction

Polyoxometalates have long been considered as prospective reagents in actinide separation processes; the most widely investigated of these is the heteropolyanion $P_2W_{17}O_{61}^{10-}$.[1] Other application involves the use of actinide polyoxometalates in the sequestration, immobilization, and storage of radioactive waste.[2] This possibility has led in recent years to renewed interest in the chemistry of actinide polyoxometalates, especially regarding their synthesis and the structures of new solids including AnO_2^{2+} and AnO_2^{+} compounds.[2−8] The advances in the structural chemistry of actinide polyoxometalates have been recently summarized.[9]

Among others, the monovacant lacunary heteropolyanion $P_2W_{17}O_{61}^{10-}$ remains a rather attractive subject of investigation. It is obtained by removing a $[W(VI){=}O]^{4+}$ group from the plenary Wells−Dawson anion α-$P_2W_{18}O_{62}^{6-}$ and could strongly bind metal ions by four oxygen atoms of "lacuna" forming coordination complexes. The two main isomers of $P_2W_{17}O_{61}^{10-}$, α_1 and α_2, differ by the site from which the $[W(VI){=}O]^{4+}$ group is removed. The complexation and redox properties of actinide complexes with $P_2W_{17}O_{61}^{10-}$ heteropolyanions in solutions and in solids were studied in recent works.[10−19] Tetravalent actinides form extremely strong complexes both by electrostatic interaction of high-charge cations and anions and by 4-fold coordination of cations by oxygen atoms of lacuna. As a result, the redox potentials of An(IV)/An(III), An(V)/An(IV), and An(VI)/An(IV) pairs shift in such a way that tetravalent Np, Pu, Am, Cm, and Bk become much more stable than aqua ions relative to reduction, and U(IV) becomes much more stable relative to oxidation. Such properties allowed authors from

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*To whom correspondence should be addressed. E-mail: philippe.moisy@cea.fr (P.M.), a.fedosseev@gmail.com (A.M.F.).

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the CEA (Commissariat à l'Énergie Atomique, France) to use α_2-$P_2W_{17}O_{61}^{10-}$ as a reagent for the confinement and offline analysis of U(IV) as part of the PUREX process.[11] The SESAME and PARC processes were developed by the CEA and JAERI (Japan Atomic Energy Research Institute) to exploit the chemistry of α_2-$P_2W_{17}O_{61}^{10-}$ for separating Am from trivalent elements through selective oxidation of Am(III) to Am(IV, VI).[20−22] It is worth noting that the redox potential shift and shielding of the central actinide ion from aqua molecules even allows the existence of dioxo-free U^{5+}, that is, as a bare ion.[10,23,24]

Most structural investigations to date, however, have concerned complexes of trivalent f elements involving both α_2- and α_1-$P_2W_{17}O_{61}^{10-}$ isomers,[25−30] and their scope continues to broaden. The structural data for solid compounds of tetravalent f elements were first obtained for a Ce(IV) complex, $K_{16}Ce(P_2W_{17}O_{61})_2 \cdot nH_2O$,[31] in which Ce(IV) occupies the central position in an anti-square prismatic environment and $P_2W_{17}O_{61}^{10-}$ anions form the "wings" of a butterfly-shaped structure. A similar coordination environment occurs for U(IV) and Th(IV) compounds with α_2-$P_2W_{17}O_{61}^{10-}$.[32,33] Some crystal data and metrics for $[U(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{16-}$ as well as for $[Th(\alpha_1\text{-}P_2W_{17}O_{61})_2]^{16-}$ and a few other complexes are given in ref 33. The authors demonstrated that, when both ligands are α_2 isomers, the solid state structure of U(IV) and Ce(III) adopts a syn conformation of the ligands. When one or both ligands are α_1-$P_2W_{17}O_{61}^{10-}$, crystals of ammonium or potassium salts of the U(IV) and Ce(III) complexes contain anti conformers, while Th forms a syn complex. In solution, U(IV) and Ce(III) complexes exist as a mixture of two major diastereomers, syn and anti forms.

Several studies involve NMR spectroscopy (usually ^{31}P) of dissolved $K_{16}An(P_2W_{17}O_{61})_2 \cdot nH_2O$ (An = U, Th).[32,34] This method demonstrated that a plane of symmetry passes through the U atom and that the structure of the complexation site (tungsten vacancy) is identical for $PW_{11}O_{39}^{7-}$ and α_2-$P_2W_{17}O_{61}^{10-}$.[32] Far IR spectra of solid U(IV) complexes with α_2-$P_2W_{17}O_{61}^{10-}$ reveal the similarity of their structure with the U(IV) complexes with $XW_{11}O_{39}^{n-}$ anions.[32]

No published information appears to exist on the structure of solid complexes of tetravalent transuranium elements with $P_2W_{17}O_{61}^{10-}$, although the complexation in solution has been proved for Np(IV), Pu(IV),[35,36] Am(IV),[35] and even for Cm(IV)[35,37,38] and Cf(IV).[38,39] The latter two could be obtained by the oxidation of Cm(III) and Cf(III) complexes with a 1:2 An(III)/$P_2W_{17}O_{61}^{10-}$ composition. Solid compounds of U(IV), Np(IV), and Pu(IV) with a 1:2 metal/$P_2W_{17}O_{61}^{10-}$ ratio were separated as potassium and cesium salts and studied by physicochemical methods.[36] Some structural data on complexes with α_2-$P_2W_{17}O_{61}^{10-}$ in the Th(IV)−U(IV)−Np(IV)−Pu(IV) series were recently obtained using extended X-ray absorption fine structure/X-ray absorption near edge structure (EXAFS−XANES).[40]

The known data are thus generally consistent with the composition and structure of $An(P_2W_{17}O_{61})_2^{16-}$ (An = Th, U, and, possibly, Np and Pu) analogous to the $Ce(P_2W_{17}O_{61})_2^{16-}$ anion. However, single-crystal X-ray diffraction analysis involves difficulties in obtaining suitable quality crystals and with the high radioactivity of transuranium elements. The present work is devoted to the synthesis and structural examination of complexes of α_2-$P_2W_{17}O_{61}^{10-}$ with tetravalent actinides. Among others, the complex with Am(IV), which is usually easily reduced to Am(III) in aqueous solution, has been synthesized and structurally and spectroscopically characterized.

Experimental Section

Caution! *^{237}Np, ^{239}Pu, and ^{243}Am are higly radioactive isotopes and have to be handled in dedicated facilities with appropriate equipment for radioactive materials.*

The "Wells−Dawson" ion, $P_2W_{18}O_{62}^{6-}$ as the ammonium salt, and the α_2 lacunary isomer, K_{10}-α_2-$P_2W_{17}O_{61}^{10-}$, were prepared using known methods[41,42] and identified by IR spectroscopy.

Synthesis of $K_{10}H_6[Th(\alpha_2\text{-}P_2W_{17}O_{61})_2] \cdot 26H_2O$ (1). A total of 0.051 g (0.099 mmol) of solid thorium oxalate, $Th(C_2O_4)_2 \cdot 6H_2O$, was mixed with 1 g (about 0.21 mmol) of $K_{10}P_2W_{17}O_{61}$, and 25 mL of H_2O was added. On heating to 80 °C with agitation, the mixture was completely dissolved. The solution was stored in an open vessel at 5 °C in a refrigerator, and after 4 days, colorless crystals suitable for single-crystal X-ray analysis were obtained.

Synthesis of $K_{12}H_4U(\alpha_2\text{-}P_2W_{17}O_{61})_2 \cdot 32H_2O$ (2). A total of 0.068 g (0.130 mmol) of solid uranium(IV) oxalate, $U(C_2O_4)_2 \cdot 6H_2O$, was mixed with 1.42 g (about 0.29 mmol) of $K_{10}P_2W_{17}O_{61}$, and 25 mL of H_2O was added. On heating to 80 °C with agitation, the mixture was completely dissolved, and the solution became dark reddish-violet. The solution was stored in an open vessel at room temperature, and after 5 days, deep purple crystals suitable for single-crystal X-ray analysis were obtained.

Synthesis of $K_{16}Np(\alpha_2\text{-}P_2W_{17}O_{61})_2 \cdot 42H_2O$ (3). A total of 0.02 g (0.0383 mmol) of solid neptunium(IV) oxalate was mixed with 0.377 g (about 0.077 mmol) of $K_{10}P_2W_{17}O_{61}$, and 30 mL of H_2O was added. On heating to 80 °C with agitation, the mixture was slowly dissolved, and the solution became orange. The solution was stored in an open vessel at room temperature,

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Table 1. Crystallographic Data and Refinement Parameters for Compounds **1**−**5**

compound	**1** (Th)	**2** (U)	**3** (Np)	**4** (Pu)	**5** (Am)
outer sphere cations	$K_{20}+H_{12}$	$K_{12}+H_4$	K_{16}	$K_{12}+H_4$	$K_{10}+H_6$
number of water molecules	52	32	42	19	30
cryst syst	triclinic	monoclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	21.9886(8)	23.0333(6)	14.5053(4)	12.6062(18)	15.7207(9)
b, Å	25.8002(9)	12.9572(3)	22.3173(7)	22.350(3)	20.1531(12)
c, Å	27.5180(10)	46.2652(12)	24.5068(8)	23.080(3)	22.7596(13)
α, deg	64.699(2)	90.00	95.250(2)	91.387(4)	85.866(4)
β, deg	78.962(2)	95.0770(10)	102.152(2)	100.267(4)	85.253(4)
γ, deg	80.648(2)	90.00	100.539(2)	90.003(5)	88.358(4)
vol., $Å^3$	13795.3(9)	13753.5(6)	7554.6(4)	6396.6(16)	7165.4(7)
Z	2	4	2	2	2
R	0.0814	0.0669	0.0700	0.0944	0.0685

and after 14 days, orange-brown crystals suitable for single-crystal X-ray analysis were obtained.

Synthesis of $K_{12}H_4Pu(\alpha_2\text{-}P_2W_{17}O_{61})_2\cdot 19H_2O$ (4). About 0.016 mM plutonium(IV) oxalate was precipitated, and excess $H_2C_2O_4$ was washed away. Wet $Pu(C_2O_4)_2\cdot 6H_2O$ was mixed with $K_{10}P_2W_{17}O_{61}$ (0.146 g, about 0.032 mmol, $K_{10}P_2W_{17}O_{61}$/Pu molar ratio = 2:1, suggesting that Pu(IV) oxalate was obtained with 100% yield). A total of 5 mL of H_2O was added, and the mixture was completely dissolved upon heating to 90−95 °C with agitation. The solution became pale rose. The solution was stored in an open vessel at room temperature, and after 5 days, pale rose crystals suitable for single-crystal X-ray analysis were obtained.

Synthesis of $K_{10}H_6Am(\alpha_2\text{-}P_2W_{17}O_{61})_2\cdot 30H_2O$ (5). The solid Am(III) oxalate obtained from Am(III) nitrate solution was evaporated with $HClO_4$ by heating. The residue was dissolved in 0.01 mol/L HNO_3, and the Am(III) concentration was tested by radiometry and spectrophotometry ($\lambda = 503$ nm, $\varepsilon = 440$ $M^{-1}cm^{-1}$). A total of 1 mL of 10^{-2} mol/L $Am(NO_3)_3$ in 0.01 mol/L HNO_3 was evaporated to dryness at about 100−120 °C. The residue was dissolved in a minimum quantity of water under moderate heat. A saturated solution of $K_{10}P_2W_{17}O_{61}$ was added up to a 2:1 $K_{10}P_2W_{17}O_{61}$/Am molar ratio, and finally the solid $K_2S_2O_8$ was added up to an Am/$K_2S_2O_8$ molar ratio of about 1:2. The mixture was heated to about 90−95 °C. In half a minute, the solution became dark red-brownish, and after cooling to 6−10 °C in 1 h, dark red-brown crystals were obtained. Conserving the solution with the crystals at the above-mentioned temperature led to recrystallization, and sufficiently large crystals (up to 0.3 mm) were obtained. No visible changes in the crystals separated from the supernatant were observed after 3−4 days of storage. When the reaction mixture was allowed to dry, some yellow-orange crystals of Am(III) compounds were present among the red-brown crystals of Am(IV) complex.

X-Ray Crystallography. All X-ray data for compounds **1**−**5** were obtained on a Bruker KAPPA APEX II area-detector diffractometer (Mo Kα radiation, graphite monochromator) at 100 K. Absorption correction was made using the SADABS procedure.[43] The structures were solved using a direct method (SHELXS97[44]) and refined on F^2 with the full-matrix least-squares procedure (SHELXL97[44]) using all reflections. In all of these compounds, H atoms were not localized. All phosphorus atoms in compound **2** were refined anisotropically and in compounds **1**, **3**, **4**, and **5** isotropically. A total of 77 oxygen atoms of the polyoxotungstate cage and 11 oxygen atoms of crystallization water in **1** were refined isotropically. Main crystallographic data are presented in Table 1.

Results and Discussion

One of the most important results of this work is obtaining a solid Am(IV) compound. Due to the high oxidation potential of the Am(IV)/Am(III) couple, Am(IV) could be readily reduced to Am(III) by products of water radiolysis due to ^{243}Am (with a half-life of about 7300 years). Therefore, (i) the oxidation state of Am in the complex was tested by spectrophotometry (Figure S1, Supporting Information) and (ii) the ligand stability in the Am complex was tested by infrared spectroscopy (Figure S2, Supporting Information).

Whereas the electronic absorption spectrum of the aqueous solution Am(IV) complex contains only an almost structureless broad band in the 400−700 nm range, the 516−517 nm peak is characteristic of the Am(III) complex.[35] Figure S1 in the Supporting Information shows the electronic absorption spectra of the obtained Am complex with α_2-$P_2W_{17}O_{61}^{10-}$. Spectrum 1 of the solid compound contains no visible peak at 517 nm, indicating the absence of Am(III). As well, no Am(IV) f−f transitions are observed. It is normal for the narrow spectral region depicted in Figure S1 (Supporting Information). Indeed, spectra of Am(IV) complexes with α_2-$P_2W_{17}O_{61}^{10-}$ in aqueous solutions demonstrate only weak narrow bands of presumably f−f transitions in the region 660−1000 nm with a molar absorptivity of 50−60 M^{-1} cm^{-1}.[35] In the spectrum of the solid, these narrow bands are almost invisible due to lesser spectrum quality. No narrow peaks appear at wavelengths less than 650 nm since the molar absorptivity of the charge transfer band becomes here much higher than the molar absorptivity of possible f−f transitions.

Spectrum 2 of the aqueous solution obtained by dissolving the solid compound confirms the valent state IV of Am in the solid. The spectrum has a wide band with absorption increased in the short-wavelength region. The weak 517 nm peak appears to be due to the reduction of a small amount of Am(IV) during dissolution. Water can partially reduce Am(IV) during dissolution of the solid. However, a more likely explanation is that the radiolytically damaged crystal reacts with water, giving strong reductants that react with Am(IV). However after adding a strong reducing agent, hydrazine, all of the Am(IV) passes into the trivalent state, the wide band practically disappears, and the 517 nm peak becomes the main feature of spectrum 3. It is necessary to note that hydrazine does not reduce W(VI) to W(V) in the $P_2W_{17}O_{61}^{10-}$ anion (deep blue coloration does not appear) in an acidic media, which was used in that experiment.

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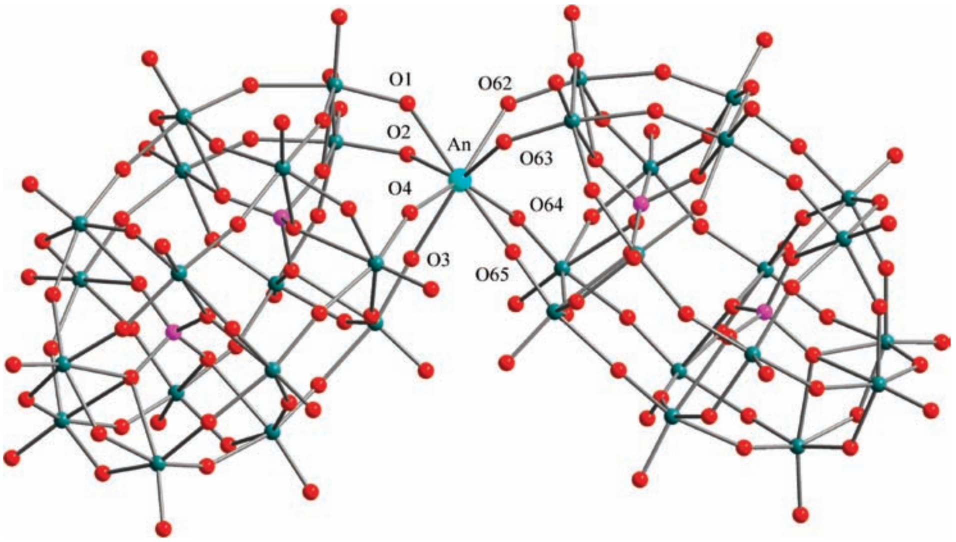

Figure 1. Structure of $[An(P_2W_{17}O_{61})_2]^{16-}$ complex anions in compounds **1**−**6**.

Table 2. Interatomic An−O Distances (Å) in Structures **1**−**5**

bond	Th	Th[a]	U	Np	Pu	Am
An(1)−O(1)	2.405(15)	2.417(16)	2.355(11)	2.349(11)	2.351(14)	2.321(18)
An(1)−O(2)	2.424(14)	2.405(16)	2.377(12)	2.371(11)	2.282(14)	2.381(19)
An(1)−O(3)	2.373(14)	2.390(15)	2.368(12)	2.342(10)	2.231(14)	2.352(18)
An(1)−O(4)	2.437(16)	2.376(15)	2.319(11)	2.278(12)	2.333(13)	2.301(19)
An(1)−O(62)	2.396(17)	2.387(15)	2.352(11)	2.346(11)	2.419(13)	2.270(20)
An(1)−O(63)	2.388(17)	2.416(15)	2.366(12)	2.335(12)	2.312(15)	2.339(18)
An(1)−O(64)	2.387(15)	2.416(16)	2.310(12)	2.313(11)	2.321(13)	2.321(20)
An(1)−O(65)	2.404(15)	2.398(15)	2.380(11)	2.351(11)	2.342(13)	2.321(19)

[a] Column represents data for second crystallographically independent $[Th(P_2W_{17}O_{61})_2]^{16-}$ anion in structure **1**. Values corresponds to interatomic distances between Th(2) and O(123), O(124), O(125), O(126), O(184), O(185), O(186), and O(187) atoms.

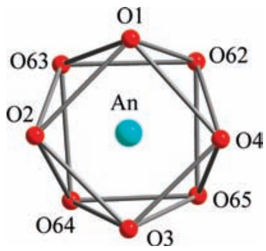

Figure 2. Coordination polyhedron of An atoms in compounds **1**−**6**.

Therefore, hydrazine addition leads to Am(IV) reduction only and does not influence the complex stoichiometry.

The IR spectra (Figure S2, Supporting Information) of the obtained solid complexes resemble the published spectra for $K_{10}P_2W_{17}O_{61}\cdot nH_2O$, $K_{16}U(P_2W_{17}O_{61})_2\cdot nH_2O$, and $K_{16}Th(P_2W_{17}O_{61})_2\cdot nH_2O$.[32,33] The spectra of $K_{10}P_2W_{17}O_{61}\cdot nH_2O$ and the actinide compounds differ only by the band positions. Intense bands are attributable to the vibrations of O−W−O bonds (720−800 cm^{-1}), W═O bonds (880−950 cm^{-1}), and P−O bonds (1080−1090 cm^{-1}).

X-ray structure determination reveals that, in all of the synthesized compounds, An^{4+} ions are strongly chelated by two α_2-$P_2W_{17}O_{61}{}^{10-}$ anions in a butterfly-like structure (Figure 1). An(IV) atoms have a coordination number of 8; their coordination polyhedron (CP) is a distorted square antiprism. The central 5f ion is coordinated by two complex anions in a syn conformation through four oxygen atoms on each in the same manner. Selected interatomic distances for the compounds are listed in Table 2.

Structure **1** contains two crystallographically independent $[Th(P_2W_{17}O_{61})_2]^{16-}$ complex anions. In both anions, Th atoms have a coordination number of 8; the CP of the Th atom is a distorted square antiprism (Figure 2). The Th−O distances range from 2.373(14) to 2.437(16) Å (Table 2), the average values being 2.401(15) Å both for Th(1) and Th(2).

The deviations of O atoms from least-squares planes of two square bases of the Th(1) CP are ±0.005 and ±0.020 Å; the dihedral angle between these planes is 5.5°. At the same time, as shown in Figure 2, the CP is slightly twisted around its 4-fold inversion axis. The angles between the diagonals of the two different bases (i.e., lines O(1)−O(3) and O(62)−O(64); O(2)−O(4) and O(63)−O(65)) are equal to 48.4° and 41.0°, the ideal value being 45°. The angles between two diagonals of the same base (O(1)−O(3) and O(2)−O(4); O(62)−O(64) and O(63)−O(65)) are 89.3° and 88.8°.

The structure of the second crystallographically independent complex anion in **1** is almost the same. Fitting the positions of metal atoms in the two anions gives a root-mean-square deviation of 0.176 Å. The deviations of O atoms from least-squares planes of two square bases of the Th(2) CP are ±0.017 and ±0.009 Å; the dihedral angle between these planes is 3.5°. The angles between the diagonals of the two different bases are 37.2° and 38.5°; the angles between two diagonals of the same base are 88.5° and 89.8°.

Compounds **2**, **3**, **4**, and **5** contain only one crystallographically independent complex anion, $An(P_2W_{17}O_{61})_2{}^{16-}$ (An = U, Np, Pu, Am), in a general position. The structure

Table 3. Average An−O Distances (Å) for $\mathrm{An(P_2W_{17}O_{61})_2^{16-}}$ Complexes (An = Th, U, Np, Pu, Am)

< Th−O >	< U−O >	< Np−O >	< Pu−O >	< Am−O >
2.401	2.353	2.336	2.324	2.326
2.38(1) (solid)[a]	2.33(1) (solid)[a]			
	2.35(1) (solution)[a]	2.34(2) (solution)[a]	2.33(2) (solution)[a]	

[a] Data from ref 40.

of $\mathrm{U(P_2W_{17}O_{61})_2^{16-}}$ is very close to that found in **1**. The U−O distances range from 2.310(12) to 2.380(11) Å (Table 2), the average value being 2.353(11) Å (Table 3). Compound **2** crystallizes in the $P2_1/c$ space group, which is different from complexes **1**, **3**, **4**, and **5**, having $P\bar{1}$ symmetry.

The deviations of O atoms from least-squares planes of both square bases of the uranium atom CP are ±0.010 and ±0.004 Å; the dihedral angle between the bases is 4.1°. The angles between diagonals of the two different bases are 40.2° and 41.1°, whereas the angles between two diagonals of the same bases are 89.0° and 88.1°.

The Np−O, Pu−O, and Am−O distances range from 2.278(12) to 2.371(11) Å, from 2.231(14) to 2.419(13) Å, and from 2.270(20) to 2.381(19) Å, respectively, the average values for Np−O, Pu−O, and Am−O bonds being 2.336(11), 2.324(14), and 2.326(19) Å, respectively. The deviations of O atoms from least-squares planes of both square bases of the Np CP are ±0.010 and ±0.001 Å; the dihedral angle between the bases is 4.2°. For Pu and Am compounds, the corresponding values are ±0.009, ±0.014 Å, and 2.4° and ±0.016, ±0.017 Å, and 3.7°. The angles between diagonals of the two different bases are 46.9° and 49.3° for the Np compound, 50.1° and 49.3° for the Pu compound, and 39.0° and 38.1° for the Am compound. The angles between two diagonals of the bases are 89.5° and 88.3° (Np), 89.7° and 89.5° (Pu), and 89.9° and 90.6° (Am).

The greatest distortion in all of the CPs in the studied complexes is thus the twisting of one base of the square antiprism from its ideal position by about 7.8° for the Th(2) complex, or 1.6° for the Np complex. The inner angles of bases range from 85.7° (O63−O62−O65 angle in the Pu complex) to 93.9° (O63−O64−O65 angle in the Th complex); the closest to the ideal value (90.0°) is the O1−O2−O3 angle in the Np complex. Such distortion appears to be inherent in the nature of the complexes.

One of the consequences of the noncentrosymmetric structure of Wells−Dawson-type heteropolyacids is the nonlinearity of all complex anions. In **1**, angles < W1′ > ··· Th1 ··· < W3′ > and < W5′ > ··· Th1 ··· < W6′ > are 124.0° and 121.6° for Th(1) (Figure S3, Supporting Information) and Th(2), respectively. The corresponding values are 123.8° for **2**, 119.5° for **3**, 122.5° for **4**, and 121.2° for **5**. Here, points < W1′ >, < W3′ >, < W5′ >, and < W6′ > designate the centers of mass of triangles whose vertices are the tungsten atoms farthest from the An atom; more specifically, < W1′ >, < W3′ >, < W5′ >, and < W6′ > are the centers of mass of triangles W15−W16−W17, W32−W33−W34, W49−W50−W51, and W66−W67−W68, respectively.

Table 2 shows the decreasing average An−O interatomic distance in the series Th−U−Np−Pu. The average Am−O and Pu−O distances are almost equal (Table 3). These distances agree rather well with previous data obtained by EXAFS and XANES for solutions and solids of the same complexes of Th(IV), U(IV), Np(IV), and Pu(IV).[40]

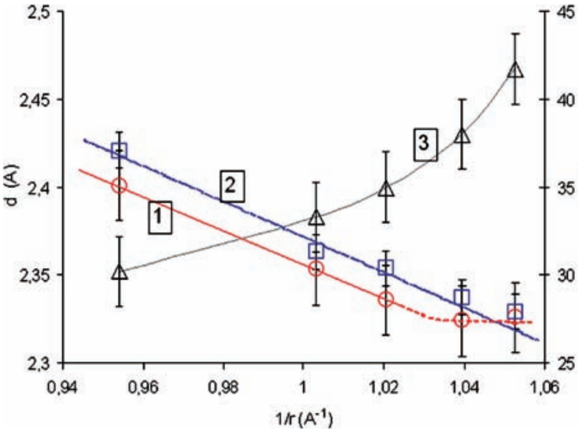

Figure 3. Plot of the interatomic distances (d) for An−O in complexes with $\mathrm{P_2W_{17}O_{61}^{10-}}$ (1) and in actinide dioxides (2) and stability constants of An(IV) complexes with $\mathrm{P_2W_{17}O_{61}^{10-}}$ [47] (3) with appropriate ionic radii ($1/r$) for coordination number 8.[45]

The mean bond length between the metal center and the oxygen atoms of the lacuna is plotted versus the inverse ionic radius ($1/r$) of the actinide ions for a coordination number of 8[45] in Figure 3. The figure also shows the variation of the metal−oxygen bond length for actinide dioxides ($\mathrm{AnO_2}$)[40,46] versus $1/r$ and the logarithm of the constant of formation of the 1:2 stoichiometric complex ($\mathrm{An(P_2W_{17}O_{61})_2^{16-}}$).[47]

The results reveal a linear correlation between the bond length between the metal center and the oxygen of the $\mathrm{P_2W_{17}O_{61}^{10-}}$ lacuna for An(IV) = Th, U, and Np. Considering the experimental measurement uncertainty (±0.02 Å), the distance appears to be constant for Pu(IV) and Am(IV) and almost the same as that observed for Np(IV). However, the linear correlation between the interatomic distance for $\mathrm{AnO_2}$ versus $1/r$ was verified for all of the actinides from Th(IV) to Am(IV), in agreement with published data.[40] Figure 3 also shows that, for the An(IV) series from Th to Am, the constant of formation of ($\mathrm{An(P_2W_{17}O_{61})_2^{16-}}$) complexes increases with $1/r$, as generally acknowledged[40,47−50] given the experimental uncertainties with these constants (±2).

In view of the experimental difficulties encountered with Am(IV), resulting in significant experimental uncertainties, it is difficult at this time to account for the absence of any reduction in the An(IV)−O interatomic distance for $\mathrm{P_2W_{17}O_{61}^{10-}}$ versus $1/r$ in the case of Pu(IV) and Am(IV), whereas the constants of formation of $\mathrm{An(P_2W_{17}O_{61})_2^{16-}}$ complexes increase from Th(IV) to Am(IV). Further investigation with other ligands will be necessary to confirm and discuss this phenomenon.

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Conclusion

This study provided structural data for the complete actinide series from Th to Am at oxidation state +IV. Single-crystal X-ray diffraction measurements allowed us to determine the environment of actinide ions in complexes with 1:2 stoichiometry with $P_2W_{17}O_{61}^{10-}$ lacunary heteropolyanions. These results are necessary for a precise description of the force and nature of the interaction between actinides and ligands. The initial results, especially for plutonium and americium, suggest that a simple electrostatic model is not sufficient for modeling heavy actinides such as Am and Cm.

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Supporting Information Available: Tables of atom parameters, interatomic distances and angles in CIF format, and electron and IR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.