

# Synthesis, Structure, and Properties of Cs<sub>4</sub>Th<sub>4</sub>P<sub>4</sub>Se<sub>26</sub>: A Quaternary Thorium Selenophosphate Containing the (P<sub>2</sub>Se<sub>9</sub>)<sup>6-</sup> Anion

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Orange crystals of Cs<sub>4</sub>Th<sub>4</sub>P<sub>4</sub>Se<sub>26</sub> were grown from the reaction of <sup>232</sup>Th and P in a Cs<sub>2</sub>Se<sub>3</sub>/Se molten salt flux at 750 °C. Cs<sub>4</sub>Th<sub>4</sub>P<sub>4</sub>Se<sub>26</sub> crystallizes in the orthorhombic space group *Pbca* with the unit cell parameters: *a* = 12.0130(6), *b* = 14.5747(7), *c* = 27.134(1) Å; *Z* = 8. The compound exhibits a three-dimensional structure, consisting of dimeric [Th<sub>2</sub>Se<sub>13</sub>] polyhedral units. The two crystallographically independent, nine-coordinate, bicapped trigonal prismatic thorium atoms share a triangular face to form the dimer, and each dimer edge-shares two selenium atoms with two other dimers to form kinked chains along the [010] direction. While this structure shares features of the previously reported Rb<sub>4</sub>U<sub>4</sub>P<sub>4</sub>Se<sub>26</sub>, including phosphorus in the 5+ oxidation state, careful inspection of the structure reveals that the selenophosphate anion that knits the structure together in three directions in both compounds is a unique (P<sub>2</sub>Se<sub>9</sub>)<sup>6-</sup> anion. The formula may be described best as [Cs<sub>2</sub>Th<sub>2</sub>(P<sub>2</sub>Se<sub>9</sub>)(Se<sub>2</sub>)<sub>2</sub>]<sub>2</sub>. The (P<sub>2</sub>Se<sub>9</sub>)<sup>6-</sup> anion features a nearly linear Se–Se–Se backbone with an angle of 171° and Se–Se distances that are approximately 0.2–0.3 Å longer than the typical single Se–Se bond. Magnetic studies confirm that this phase contains Th(IV). Raman data for this compound is reported, and structural comparisons will be drawn to its uranium analogue, Rb<sub>4</sub>U<sub>4</sub>P<sub>4</sub>Se<sub>26</sub>.

## Introduction

Recent developments in alkali metal actinide chalcogenide chemistry have given rise to several new and interesting layered and low-dimensional structures.<sup>1–7</sup> Some of these compounds, such as the layered CsTh<sub>2</sub>Te<sub>6</sub>, feature networks of chalcogenide anions that have short interatomic distances that are longer than the typical single bond but shorter than the van der Waals contact.<sup>1</sup> Due to the presence of the short chalcogenide interatomic distances, the formal oxidation state of the actinide metal or chalcogenide is somewhat arbitrary and cannot be absolutely assigned. A recent discussion of the chalcogen's ability to catenate and the ambiguity of magnetic susceptibility measurements and An–Q bond distances in the uranium and thorium chalcogenide systems highlights the problem of assigning formal oxidation states in many of these systems.<sup>6</sup> In our ongoing investigations of quaternary alkali actinide chalcogenides synthesized via the molten salt flux method,<sup>8</sup> we

have isolated a new quaternary phase with the composition Cs<sub>4</sub>Th<sub>4</sub>P<sub>4</sub>Se<sub>26</sub>. This new compound has the same stoichiometric composition as, and is isostructural to, the previously reported Rb<sub>4</sub>U<sub>4</sub>P<sub>4</sub>Se<sub>26</sub>,<sup>5</sup> however, the formal oxidation state of the metal center in both the uranium phase and now our thorium phase is the subject of debate. We will rationalize the formulation of a new [P<sub>2</sub>Se<sub>9</sub>]<sup>6-</sup> anion that can be described for both compounds based on valence electron concentrations, a formulation that supports an oxidation state of An(IV) for each.

## Experimental Section

**General Synthesis.** Red phosphorus powder (99.9%) was obtained from Cerac. Selenium shot (99.999%) was purchased from Johnson Matthey. <sup>232</sup>Th ribbon was obtained from Los Alamos National Laboratory, and the surface oxide was removed with a file before use. Cs<sub>2</sub>Se<sub>3</sub> was prepared from a stoichiometric ratio of the elements in liquid ammonia as described elsewhere.<sup>9</sup> *N,N*-dimethylformamide (DMF) was obtained from Aldrich and used without further purification. Ampules for the reactions were all fused-silica tubes with 4 mm inner diameter and 6 mm outer diameter. All reagents were stored and manipulated in a helium filled glovebox. **WARNING:** <sup>232</sup>Th is a radioactive element with a half-life of 1.41 × 10<sup>10</sup> years. Although its own activity is low, the inevitable daughter products of decay can render samples highly radioactive over time (gamma).

**Preparation of Cs<sub>4</sub>Th<sub>4</sub>P<sub>4</sub>Se<sub>26</sub>.** Cs<sub>2</sub>Se<sub>3</sub> (0.0171 g, 0.0340 mmol), P (0.0085 g, 0.274 mmol), Se (0.0406 g, 0.512 mmol), and <sup>232</sup>Th (0.0077 g, 0.0332 mmol) were loaded into a quartz ampule in the approximate ratio 1:8:15:1, respectively. The ampule was flame sealed under vacuum (<10 mTorr) and placed in a programmable furnace. The reaction was heated to 750 °C at 50 °C/h. After 100 h, the sample was cooled to 200 °C at a rate of 4 °C/h. The ampule was opened to reveal an

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(1) Cody, J. A.; Ibers, J. A. *Inorg. Chem.* **1996**, *35*, 3836–3838.

(2) Pell, M. A.; Ibers, J. A. *Chem. Ber.* **1996**, *130*, 1–8.

(3) Chondroudis, K.; Kanatzidis, M. G. *C. R. Acad. Sci. Paris* **1996**, *t. 322, Serie II b*, 887–894.

(4) Sutorik, A. C.; Kanatzidis, M. G. *Chem. Mater.* **1997**, *9*, 387–398.

(5) Chondroudis, K.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1997**, *119*, 2574–2575.

(6) Narducci, A. A.; Ibers, J. A. *Chem. Mater.* **1998**, *10*, 2811–2823.

(7) Narducci, A. A.; Ibers, J. A. *Inorg. Chem.* **1998**, *37*, 3798–3801.

(8) Briggs Piccoli, P. M.; Abney, K. D.; Schoonover, J. R.; Dorhout, P. K. *Inorg. Chem.* **2000**, *39*, 2970–2976.

(9) Liao, J.-H.; Kanatzidis, M. G. *Inorg. Chem.* **1992**, *31*, 431.

**Table 1.** Crystallographic Parameters for Cs<sub>4</sub>Th<sub>4</sub>P<sub>4</sub>Se<sub>26</sub>.

empirical formula	Cs <sub>2</sub> Th <sub>2</sub> P <sub>2</sub> Se <sub>13</sub>
formula weight	1818.32
space group	<i>Pbca</i> , #61
<i>a</i> (Å)	12.0130(6)
<i>b</i> (Å)	14.5747(7)
<i>c</i> (Å)	27.134(1)
volume	4750.8(4) Å <sup>3</sup>
<i>Z</i>	8
temp (K)	173(2)
wavelength, Mo Kα	0.71073 Å
ρ(calc)	5.084 g/cm <sup>3</sup>
absorption coefficient, μ	35.566 mm <sup>-1</sup>
R1, % <sup>a</sup>	4.00
wR2, % <sup>a</sup>	8.35

<sup>a</sup> R1 =  $\sum(F_o - |F_c|)/\sum|F_o|$ . <sup>b</sup> wR2 =  $[\sum(w(F_o^2 - F_c^2)^2)/\sum(wF_o^2)]^{1/2}$ .

amorphous red flux and clear yellow-orange crystals. A single crystal was manually extracted from the mixture for analysis by X-ray diffraction. The mixture was subsequently washed with DMF to reveal orange crystals suitable for Raman and magnetic analysis. The products appear to be air- and moisture-stable over a period of several months.

**Physical Characterization.** Single-crystal X-ray diffraction was performed on a Siemens P4 four-circle diffractometer using graphite-monochromated Mo Kα radiation and equipped with a SMART CCD system detector. Single-crystal Raman spectra were recorded using a Raman microscope system at Los Alamos National Laboratory.<sup>10</sup> Raman data were corrected for background in postprocessing operations. Laser power was approximately 5 mW at the sample. The crystals from the X-ray structure determination were used in the Raman studies. Magnetic measurements over the temperature range 4–300 K were recorded on a Quantum Design QD5 SQUID magnetometer.

**Structure Determination.** Crystals were selected from the reaction mixtures, mounted in grease, and placed directly into the cold stream of the diffractometer on a glass fiber with the long axis of the crystal oriented roughly parallel to the length of the fiber. Cell constants were initially calculated from reflections taken from approximately 30 frames of reflections. Final cell constants were calculated from all reflections observed in the actual data collection. Table 1 summarizes the crystal structure parameters for Cs<sub>4</sub>Th<sub>4</sub>P<sub>4</sub>Se<sub>26</sub>. The data were processed and corrected for absorption using SADABS. The structure was solved by direct methods using SHELXS-86<sup>11</sup> and refined in full-matrix least-squares using the program SHELXL-93.<sup>12</sup> The final cycle of refinement included all anisotropic displacement parameters. A large electron density peak was found a short distance from one thorium atom that could be reduced upon the application of a DIFABS absorption correction, but no aspects of the structure were affected by this correction. Since this correction made little or no difference in the structure solution except to reduce the peaks and valleys in the residual electron density, hence, lowering the R1 value somewhat, it was not included in the final structure analysis. Additional experimental details are given in the Supporting Information. Table 2 gives final positional parameters and equivalent isotropic displacement parameters, and Table 3 lists selected bond distances and angles.

## Results and Discussion

The structure of Cs<sub>4</sub>Th<sub>4</sub>P<sub>4</sub>Se<sub>26</sub> is shown in Figure 1 and is, in the strictest sense, isostructural to its previously reported uranium analogue, Rb<sub>4</sub>U<sub>4</sub>P<sub>4</sub>Se<sub>29</sub>.<sup>5</sup> Its main features consist of two crystallographically independent thorium atoms, each coordinated to nine selenium atoms. These polyhedra face-share three selenium atoms to form a dimer. There are two (Se<sub>2</sub>)<sup>2-</sup>

**Table 2.** Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å<sup>2</sup> × 10<sup>3</sup>) for Cs<sub>4</sub>Th<sub>4</sub>P<sub>4</sub>Se<sub>26</sub>.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) <sup>a</sup>
Th(1)	0.7844(1)	0.0202(1)	0.6710(1)	4(1)
Th(2)	0.7845(1)	0.2475(1)	0.5802(1)	4(1)
Cs(1)	0.7903(1)	0.0232(1)	0.9414(1)	30(1)
Cs(2)	0.1985(1)	0.2905(1)	0.6864(1)	34(1)
Se(1)	0.7188(1)	0.0311(1)	0.7796(1)	8(1)
Se(2)	0.9624(1)	0.1266(1)	0.5296(1)	7(1)
Se(3)	0.9509(1)	0.1468(1)	0.7229(1)	6(1)
Se(4)	0.6839(1)	0.2152(1)	0.6776(1)	6(1)
Se(5)	0.9646(1)	-0.1016(1)	0.7104(1)	9(1)
Se(6)	0.6745(1)	-0.1679(1)	0.6799(1)	6(1)
Se(7)	0.5354(1)	0.2281(1)	0.5697(1)	8(1)
Se(8)	0.7267(1)	0.2430(1)	0.4701(1)	8(1)
Se(9)	0.6952(1)	0.0495(1)	0.5710(1)	6(1)
Se(10)	0.5342(1)	0.0179(1)	0.6756(1)	8(1)
Se(11)	0.8362(1)	-0.0675(1)	0.5728(1)	7(1)
Se(12)	0.9736(1)	0.1355(1)	0.6269(1)	8(1)
Se(13)	0.9672(1)	0.3731(1)	0.5487(1)	10(1)
P(1)	0.5444(3)	0.0196(2)	0.7567(1)	7(1)
P(2)	0.0494(3)	0.2585(2)	0.5112(1)	7(1)

<sup>a</sup> *U*(eq) is defined as one-third of the trace of the orthogonalized *U*<sub>ij</sub> tensor.

**Table 3.** Selected Bond Distances (Å) and Angles (Deg) for Cs<sub>4</sub>Th<sub>4</sub>P<sub>4</sub>Se<sub>26</sub>.

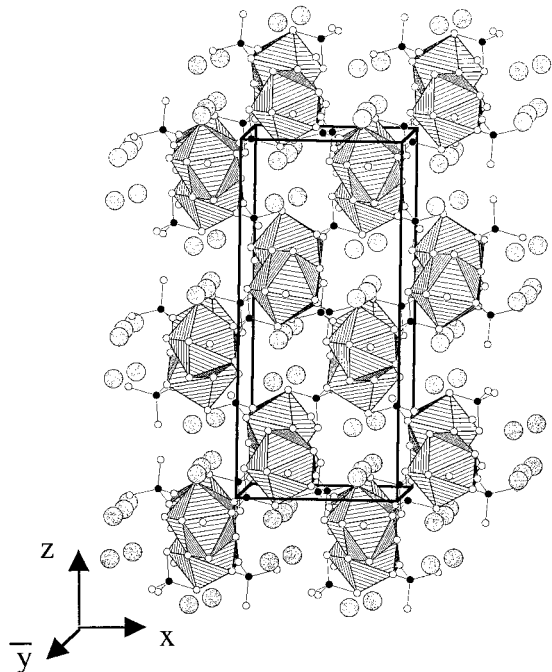
Th(1)–Se(9)	2.947(1)	Th(1)–Se(5)	2.997(1)
Th(1)–Se(10)	3.007(1)	Th(1)–Se(11)	3.020(1)
Th(1)–Se(6)	3.052(1)	Th(1)–Se(1)	3.054(1)
Th(1)–Se(3)	3.064(1)	Th(1)–Se(12)	3.070(1)
Th(1)–Se(4)	3.092(1)	Th(2)–Se(9)	3.088(1)
Th(2)–Se(4)	2.943(1)	Th(2)–Se(13)	2.983(1)
Th(2)–Se(6)	3.013(1)	Th(2)–Se(7)	3.019(1)
Th(2)–Se(8)	3.067(1)	Th(2)–Se(11)	3.067(1)
Th(2)–Se(12)	3.070(1)	Th(1)–Th(2)	4.1283(6)
Th(2)–Se(2)	3.090(1)	Se(2)–Se(12)	2.645(2)
Se(3)–Se(12)	2.624(2)	Se(4)–Se(6)	2.409(2)
Se(9)–Se(11)	2.404(2)	P(2)–Se(2)	2.246(3)
P(1)–Se(1)	2.192(3)	P(2)–Se(7)	2.209(3)
P(1)–Se(3)	2.238(3)	P(2)–Se(8)	2.190(3)
P(1)–Se(5)	2.199(3)	P(2)–Se(13)	2.192(3)
P(1)–Se(10)	2.203(3)		
Se(3)–Se(12)–Se(2)	171.07(6)		
Se(1)–P(1)–Se(5)	111.2(1)		
Se(1)–P(1)–Se(10)	109.7(1)		
Se(5)–P(1)–Se(10)	111.9(1)		
Se(1)–P(1)–Se(3)	110.2(1)		
Se(5)–P(1)–Se(3)	110.2(1)		
Se(10)–P(1)–Se(3)	103.3(1)		
Se(8)–P(2)–Se(13)	109.8(1)		
Se(8)–P(2)–Se(7)	107.8(1)		
Se(13)–P(2)–Se(7)	111.12(1)		
Se(8)–P(2)–Se(2)	113.1(1)		
Se(13)–P(2)–Se(2)	109.8(1)		
Se(7)–P(2)–Se(2)	105.2(1)		
P(1)–Se(3)–Se(12)	98.2(1)		
P(2)–Se(2)–Se(12)	99.01(9)		

anions that help to form the face of the dimer, as can be seen in Figure 2. Each of these diselenium anions are coordinated to both of the thorium atoms in a fashion similar to that seen in Cs<sub>4</sub>Th<sub>2</sub>P<sub>5</sub>Se<sub>17</sub>,<sup>8</sup> in that one of the anions is bound η<sup>1</sup> to one thorium atom and is bound η<sup>2</sup> to the other (Figure 2). Each dimer edge-shares two selenium atoms along the [010] direction to form kinked, zigzag chains, Figure 3, whose fundamental building blocks can be thought of as (Th<sub>2</sub>(P<sub>2</sub>Se<sub>9</sub>)(Se<sub>2</sub>)<sub>2</sub>)<sup>2-</sup> clusters. These chains are bound together in three directions by a [P<sub>2</sub>Se<sub>9</sub>] unit (vide infra). The thorium atoms are separated from each other in the dimer by a distance of 4.1283(6) Å. The nine-coordinate Cs countercations occupy the channels between the chains along the [010] direction as seen in Figure 1.

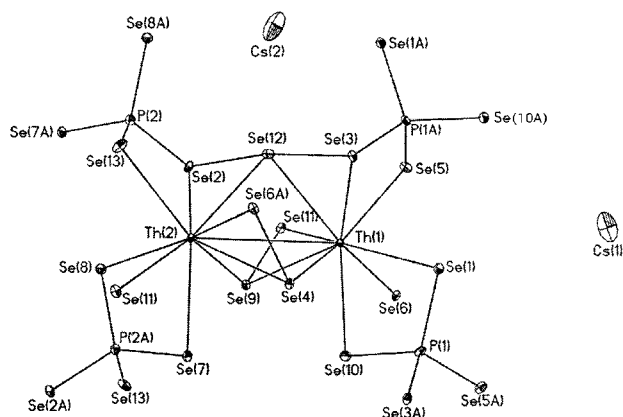
(10) Schoonover, J. R.; Weesner, F.; Havrilla, G. J.; Sparrow, M.; Treado, P. *Appl. Spectrosc.* **1998**, *52*, 1505.

(11) Sheldrick, G. M. *SHELXS-86*; Sheldrick, G. M., Kruger, C., Doddard, R., Eds.; Oxford University Press: Oxford, 1985; pp 175–189.

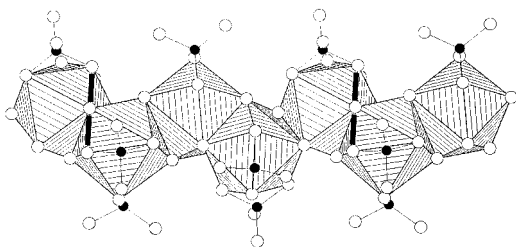
(12) Sheldrick, G. M. *SHELXL-93*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1994.



**Figure 1.** A view of Cs<sub>4</sub>Th<sub>4</sub>P<sub>4</sub>Se<sub>26</sub> down [010]. Polyhedra are thorium selenide, selenium atoms are open circles, phosphorus atoms are filled, cesium atoms are gray. The box represents the unit cell.



**Figure 2.** Thermal ellipsoid plot (50% ellipsoids) of the crystallographically unique portion of the structure.



**Figure 3.** Polyhedral view of the chains of thorium polyhedra. Highlighted bonds are long selenium contacts in the P<sub>2</sub>Se<sub>9</sub><sup>6-</sup>. Selenium atoms are open circles, phosphorus atoms are filled circles.

Selected bond distances and angles for Cs<sub>4</sub>Th<sub>4</sub>P<sub>4</sub>Se<sub>26</sub> can be found in Table 3. Th–Se bond distances range from 2.9831(13) to 3.0921(13) Å (av. 3.036 Å). This may be compared to an average Th–Se distance of 3.102 Å for K<sub>2</sub>ThP<sub>3</sub>Se<sub>9</sub> and 3.059 Å for Cs<sub>4</sub>Th<sub>2</sub>P<sub>5</sub>Se<sub>17</sub>.<sup>8</sup> The P–Se distances range from 2.190(3) to 2.246(3) Å (av. 2.209 Å). Phosphorus exists here as P(V) and is coordinated to four selenium atoms in a regular tetrahedral geometry. The cesium cations are nine-coordinate, and the Cs–Se bond distances range from 3.653 to 4.291 Å (av. 3.905 Å).

There are two distinct Se–Se distances, those in the (Se<sub>2</sub>)<sup>2-</sup> anions that may be described as single bonds are 2.404(2) and 2.409(2) Å, respectively, for an average single bond length of 2.406 Å. This value is slightly longer than that found for the (Se<sub>2</sub>)<sup>2-</sup> distance in Cs<sub>4</sub>Th<sub>2</sub>P<sub>5</sub>Se<sub>17</sub> (2.362 Å),<sup>8</sup> but is a reasonable value for a Se–Se bond. Two additional Se···Se distances are found in the [P<sub>2</sub>Se<sub>9</sub>] unit displaying lengths of 2.645(2) and 2.624(2) Å (av. 2.634 Å). While these distances are approximately 0.2–0.3 Å longer than a typical Se–Se single bond, they are significantly shorter than the van der Waals contact of two selenium atoms (3.80 Å). In addition to the unusual bond length, the Se–Se–Se angle that makes up the backbone of the selenophosphate anion is a surprisingly near linear, 171°. The (P<sub>2</sub>Se<sub>9</sub>)<sup>4-</sup> anion has been crystallographically characterized in Rb<sub>4</sub>Ti<sub>2</sub>(P<sub>2</sub>Se<sub>9</sub>)<sub>2</sub>(P<sub>2</sub>Se<sub>7</sub>) and Cs<sub>4</sub>P<sub>2</sub>Se<sub>9</sub>, with Se–Se bond distances of 2.333(6) and 2.340(2) Å and Se–Se–Se bond angles of 103.7(2) and 111.7(1)°, respectively.<sup>13,14</sup>

For the assignment of relative oxidation states of thorium, consider the following hypotheses: if the [P<sub>2</sub>Se<sub>9</sub>] unit in our [Cs<sub>2</sub>Th<sub>2</sub>(P<sub>2</sub>Se<sub>9</sub>)(Se<sub>2</sub>)<sub>2</sub>]<sub>2</sub> carries the standard 4– charge, as seen in Rb<sub>4</sub>Ti<sub>2</sub>(P<sub>2</sub>Se<sub>9</sub>)<sub>2</sub>(P<sub>2</sub>Se<sub>7</sub>),<sup>13,14</sup> and the oxidation states are assigned as Cs(I) and (Se<sub>2</sub>)<sup>2-</sup>, then thorium may be assigned as having a formal oxidation state of 3+. Conversely, if the central selenium atom of the Se–Se–Se backbone in the [P<sub>2</sub>Se<sub>9</sub>] unit is an isolated Se<sup>2-</sup> anion, as is described for Rb<sub>4</sub>U<sub>4</sub>P<sub>4</sub>Se<sub>26</sub>,<sup>5</sup> then thorium may be assigned a formal oxidation state of 5+, as was assigned to the uranium atom in Rb<sub>4</sub>U<sub>4</sub>P<sub>4</sub>Se<sub>26</sub>.

The compound [(η<sup>5</sup>-Cp<sup>''</sup>)<sub>3</sub>Th], a Th(III) species prepared by reduction of [(η<sup>5</sup>-Cp<sup>''</sup>)<sub>2</sub>ThCl<sub>2</sub>] in toluene, has an intense, dark-blue color that can be attributed to the presence of the lone electron on the metal center.<sup>15,16</sup> As Cs<sub>4</sub>Th<sub>4</sub>P<sub>4</sub>Se<sub>26</sub> has no intense color associated with it, but has instead a translucent orange color closely resembling its Th(IV) quaternary selenophosphate relatives such as Cs<sub>4</sub>Th<sub>2</sub>P<sub>5</sub>Se<sub>17</sub>,<sup>8</sup> it is reasonable to conclude that the oxidation state of thorium present in Cs<sub>4</sub>Th<sub>4</sub>P<sub>4</sub>Se<sub>26</sub> is not 3+. Likewise, the possibility of oxidizing thorium from its noble gas configuration in 4+ to the 5+ oxidation state is highly unlikely. To determine if unpaired electrons were present in the structure, a magnetic susceptibility measurement was made.

The magnetic susceptibility of Cs<sub>4</sub>Th<sub>4</sub>P<sub>4</sub>Se<sub>26</sub> was measured at 1 T. No perceptible paramagnetic moments were observed that would indicate any unpaired electron density. Measurements were comparable to those observed for a Th(IV), diamagnetic compound such as K<sub>2</sub>ThP<sub>3</sub>Se<sub>9</sub>.<sup>8</sup> A weak transition (~10<sup>-9</sup> emu/mole) was measured around 200K and was initially thought to be a structural transition. Determination of the crystal structure above and below this transition temperature was performed, and no structural differences were observed. Since the extra electrons necessary to balance the charge on the compound are clearly not localized on the central thorium atoms in the dimers, they must be located elsewhere in the structure, and thorium must be assigned as Th(IV).

In the case of the earlier-reported uranium compound, Rb<sub>4</sub>U<sub>4</sub>P<sub>4</sub>Se<sub>29</sub>,<sup>5</sup> two U(V) atoms, two PSe<sub>4</sub><sup>3-</sup> units, and one isolated Se<sup>2-</sup> anion were postulated to comprise the dimeric uranium cluster unit. Indeed, the long Se···Se interactions observed in our thorium compound are also present in the

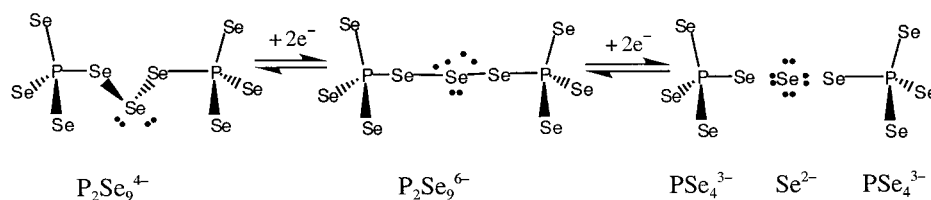
(13) Tremel, W.; Kleinke, H.; Derstroff, V.; Reisner, C. *J. Alloys Compd.* **1995**, *219*, 73–82.

(14) Chondroudis, K.; Kanatzidis, M. G. *Inorg. Chem.* **1995**, *34*, 5401–5402.

(15) Blake, P. C.; Lappert, M. F.; Atwood, J. L.; Zhang, H. *J. Chem. Soc., Chem. Commun.* **1986**, 1148.

(16) Blake, P. C.; Lappert, M. F.; Taylor, R. G.; Atwood, J. L.; Zhang, H. *Inorg. Chim. Acta* **1987**, *139*, 13–20.

## Scheme 1

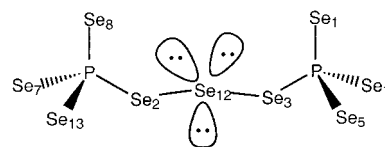


uranium compound at 2.628 and 2.655 Å, an average of 2.642 Å, distances that are statistically equal to our bond distances. Only the electronic spectra discussed for  $\text{Rb}_4\text{U}_4\text{P}_4\text{Se}_{29}$ , magnetic and optical reflectance data, suggest that the oxidation state for uranium is U(V); however, the data reported therein is ambiguous. It was reported that the uranium compound displayed a  $1.85 \mu_B$  moment based on the  $1/\chi$  versus  $T$  data collected from room temperature to 70 K, and a peak appeared in the reflectance data at  $3900 \text{ cm}^{-1}$ . This assignment of U(V) is not unambiguous for magnetic data for uranium  $f^1$  assignments or for the optical data reported.<sup>17,18</sup> It would seem that the oxidizing power of the flux, rubidium polyselenide, may support the elusive pentavalent uranium. However, our studies in strongly oxidizing polysulfide salts have only yielded U(IV) and Pu(III) compounds such as  $\text{K}_5\text{U}(\text{PS}_4)_3$ ,  $\text{Cs}_8\text{U}_5(\text{P}_3\text{S}_{10})_2(\text{PS}_4)_6$ , and  $\text{KPuP}_2\text{S}_7$ .<sup>19,20</sup>

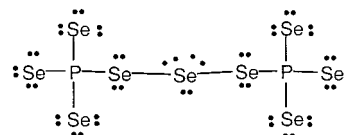
Yet another consideration may be applied to our hypotheses that delocalizes the electron density on the  $[\text{P}_2\text{Se}_9]$  unit rather than on either the Th atom (i.e., Th(III)) or on a selenide (i.e.,  $\text{Se}^{2-}$ ). The  $\text{ATH}_2\text{Q}_6$  and  $\text{AETH}_2\text{Q}_5$  series of compounds (A = K, Cs, Cu; AE = Sr; Q = Se, Te)<sup>17,21</sup> exhibit structures wherein networks of chalcogen anions are separated by distances too long for Q–Q single bonds but are also shorter than their van der Waals contacts. If all of the Q atoms in  $\text{ATH}_2\text{Q}_6$  exist as  $\text{Q}^{2-}$  anions, as they do for the electron-precise Th(IV) compound,  $\text{SrTh}_2\text{Se}_5$ ,<sup>7</sup> thorium in  $\text{ATH}_2\text{Q}_6$  might be assigned a formal oxidation state of 5.5+, clearly not a viable option in their thorium compounds. Instead, Ibers described the chains of Q atoms with shorter interatomic distances (2.81 Å) than van der Waals contacts as  $[\text{Q}^{-(1+\delta)}]$ , allowing for partial oxidation of the  $\text{Q}^{2-}$  anions to form quasi-infinite chains having holes in the selenium valence band. Nevertheless, this description did not allow for a formal oxidation state assignment of the thorium atoms in all cases.<sup>21</sup> In our  $\text{Cs}_4\text{Th}_4\text{P}_4\text{Se}_{26}$ , assigning partial positive charges to the Se–Se–Se portion of  $[\text{P}_2\text{Se}_9]$  will account for a charge balanced structure, unless the selenium portion of the anion carries a higher partial negative charge with respect to the  $\text{Se}^-$  ion, as was described in Ibers' compounds. While we do not have infinite selenide chains, we do find that partial reduction of the selenide linkage can account for different geometry for the  $[\text{P}_2\text{Se}_9]$  unit than was previously reported for the titanium compound,  $\text{Rb}_4\text{Ti}_2(\text{P}_2\text{Se}_9)_2(\text{P}_2\text{Se}_7)$ .<sup>13,14</sup>

If we take into consideration the linearity of the selenium link in  $[\text{P}_2\text{Se}_9]$  and the two “missing” electrons, one for each thorium 4+ atom in each dimer, we may postulate what we believe to be the  $(\text{P}_2\text{Se}_9)^{6-}$  anion, which is versatile enough to

## Scheme 2



## Scheme 3



accommodate extra electrons within its selenium backbone and possibly exist in a continuum from the oxidized  $(\text{P}_2\text{Se}_9)^{4-}$  found in the titanium compound,<sup>13,14</sup> to a straight selenium chain, to the fully reduced separated model comprising two  $\text{PSe}_4^{3-}$  and one isolated  $\text{Se}^{2-}$  anion, shown in Scheme 1.

In our thorium example, the two extra electrons may be accounted for if they are placed on the central selenium atom, as shown in Scheme 2, where the numbers refer to crystallographic atomic labels. From a simple VSEPR view, this would demand that the central selenium atom assume a trigonal bipyramidal geometry, yielding a linear Se–Se–Se chain. The lengthening in the Se–Se bonds may be attributed to either an “allylic” interaction in which these electrons are delocalized over the structure, or the electrons can occupy an additional lone pair on the central selenium and lone pair–lone pair interactions lead to a lengthening of the Se–Se bonds.

The latter model above can be rationalized by formulating an analogy to the telluride networks, that are known to form distorted square networks, that comprise linear and bent tellurium segments.<sup>22</sup> Hypervalent telluride building blocks are found in  $\text{Cs}_2\text{Te}_5$  within  $\text{Te}_5^{2-}$  units<sup>23</sup> and in extended structures such as  $\text{TlTe}$ , as explained by Hoffmann.<sup>22</sup> It is likely that, in our case, the selenide bridge between selenophosphate units in this structure comprises a hypervalent central selenium atom.

This model can be supported using the Parthé valence electron concentration (VEC) rules for tetrahedral building blocks.<sup>24</sup> Using the VEC constructs, we can easily describe a simple Lewis dot picture of the  $\text{P}_2\text{Se}_9^{6-}$  unit, as shown in Scheme 3. It may also be possible to construct two resonance structures for this anion using two other tetrahedral building blocks,  $\text{PSe}_4^{3-}$  and  $\text{PSe}_5^{3-}$ , as shown in Scheme 4.

For Scheme 3, the VEC' (electrons per anion) for 70 anion valence electrons suggests that we should find a building block that has one anion–anion bond per tetrahedral unit and 25 Lewis-dot-type lone pairs of electrons localized on the nine

(17) Fournier, J. M. In *Actinides – Chemistry and Physical Properties*; Manes, L., Ed.; Springer-Verlag: Berlin, 1985; pp 129–196.

(18) Miyake, C.; Kawasaki, O.; Gotoh, K.; Nakatani, A. *J. Alloys Compd.* **1993**, *200*, 187–190.

(19) Hess, R. F.; Abney, K. D.; Burris, J. L.; Hochheimer, H. D.; Dorhout, P. K. *Inorg. Chem.* **2001**, *40*, 2851–2859.

(20) Hess, R. F.; Abney, K. D.; Dorhout, P. K. *J. Am. Chem. Soc.* **2001**, submitted.

(21) Wu, E. J.; Pell, M. A.; Ibers, J. A. *J. Alloys Compd.* **1997**, *255*, 106–109.

(22) Papoian, G. A.; Hoffmann, R. *Angew. Chem., Int. Ed.* **2000**, *39*, 2408–2448.

(23) Böttcher, P.; Kretschmann, U. *Z. Anorg. Allg. Chem.* **1982**, *491*, 39–43.

(24) Parthé, E. *Elements of Inorganic Structural Chemistry*, 2nd ed.; K. Sutter Parthé: Petit-Lancy, Switzerland, 1996.

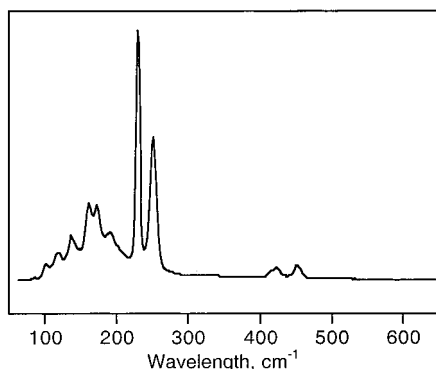


Figure 4. Raman spectrum of Cs<sub>4</sub>Th<sub>4</sub>P<sub>4</sub>Se<sub>26</sub>.

#### Scheme 4

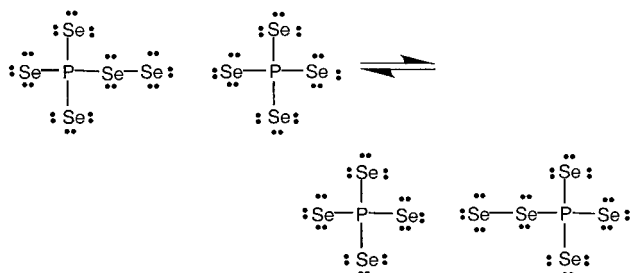


Table 4. Raman Data for Cs<sub>4</sub>Th<sub>4</sub>P<sub>4</sub>Se<sub>26</sub>.

band assignment (T <sub>d</sub> )	Cs <sub>4</sub> Th <sub>4</sub> P <sub>4</sub> Se <sub>26</sub>	K <sub>3</sub> La(PSe <sub>4</sub> ) <sub>2</sub> (ref 25)	
ν <sub>2</sub> (E)	102 vw	103 w	
	118 w		
	ν <sub>4</sub> (T <sub>2</sub> )	134 w	145 w
		162 m	163 m
		174 m	
191 w			
ν <sub>1</sub> (A <sub>1</sub> )	228 vs	237 vs	
Q–Q stretch	253 s		
ν <sub>3</sub> (T <sub>2</sub> )	423 vw	443 vw	
	452 vw		

selenium atoms. For Scheme 4, the 70 valence electrons are spread over two different, isolated tetrahedra. This scheme suggests that 26 lone pairs of electrons are localized on the nine selenium atoms, 12 on PSe<sub>4</sub><sup>3-</sup> and 13 on PSe<sub>5</sub><sup>3-</sup>, and that there is only one anion–anion bond per two tetrahedra. In the second scheme, the “central” selenium atom is not hypervalent but is rather part of a normal diselenide bound to a phosphorus atom. If we examine the thermal ellipsoid of the central Se(12) atom in the chain, see Figure 2, there is no evidence of thermal disorder. Equally careful analysis of the diffraction data does not suggest any superstructure ordering. These observations are consistent with the description of most resonance structures in the absence of hydrogen bonding.

Since there are two possible, indistinguishable, yet reasonable models, we proposed that the Raman vibrational analysis could possibly reveal significant differences between Se···Se interactions that would develop in either Scheme 3 or 4. The Raman data for Cs<sub>4</sub>Th<sub>4</sub>P<sub>4</sub>Se<sub>26</sub> is shown in Figure 4. The most notable features are its similarities to other compounds containing the [PSe<sub>4</sub>] unit. The tetrahedral anion has four stretching modes, all of which are Raman active. A list of these bands and tentative assignments based on our recent rare-earth selenophosphates<sup>25</sup> are given in Table 4. Splittings within groups of similar resonances are due to the different coordination environments where the [PSe<sub>4</sub>] units exist. Also of interest is the broad peak

seen at approximately 252 cm<sup>-1</sup>, which is assigned to Se–Se stretching. The broadness of this peak is most likely due to the fact that there are two different types of Se–Se interaction, and they probably overlap. The Se–Se stretch seen here for Cs<sub>4</sub>Th<sub>4</sub>P<sub>4</sub>Se<sub>26</sub> is notably less than that for Cs<sub>4</sub>Th<sub>2</sub>P<sub>5</sub>Se<sub>17</sub> (283 cm<sup>-1</sup>),<sup>8</sup> reflecting the longer bond distances in P<sub>2</sub>Se<sub>9</sub><sup>6-</sup> and a subsequently weaker bond. Nevertheless, the Raman spectrum does not reveal which model, Scheme 3 or Scheme 4, is the more accurate picture of this anion.

#### Conclusions

Like the series of ternary and quaternary uranium and thorium chalcogenides before this report,<sup>1–8</sup> it becomes clear with the synthesis of Cs<sub>4</sub>Th<sub>4</sub>P<sub>4</sub>Se<sub>26</sub> that actinide chemists cannot depend only on magnetic data or An–Q bond lengths to give an accurate measure of oxidation state and must be careful in making absolute assignments unless the supporting data is completely conclusive. And so, it may be left to the redox chemistry of the actinide element to determine the electron configuration within a very versatile chalcogenide building block. Indeed, in the example of uranium in Rb<sub>4</sub>U<sub>4</sub>P<sub>4</sub>Se<sub>26</sub>, a higher oxidation state can exist for uranium, but in Cs<sub>4</sub>Th<sub>4</sub>P<sub>4</sub>Se<sub>26</sub>, only Th(IV) is possible. The average Th–Se bond lengths, while not identical between K<sub>2</sub>ThP<sub>3</sub>Se<sub>9</sub>, Cs<sub>4</sub>Th<sub>2</sub>P<sub>5</sub>Se<sub>17</sub>, and Cs<sub>4</sub>Th<sub>4</sub>P<sub>4</sub>Se<sub>26</sub>, are not significantly different to argue that thorium in Cs<sub>4</sub>Th<sub>4</sub>P<sub>4</sub>Se<sub>26</sub> is anything but Th(IV). Moreover, based on the magnetic data, weak color, and structural properties of Cs<sub>4</sub>Th<sub>4</sub>P<sub>4</sub>Se<sub>26</sub>, the oxidation state of thorium is *most likely* 4+. Given that Cs<sub>4</sub>Th<sub>4</sub>P<sub>4</sub>Se<sub>26</sub> and Rb<sub>4</sub>U<sub>4</sub>P<sub>4</sub>Se<sub>26</sub> are isostructural and both contain the unique [P<sub>2</sub>Se<sub>9</sub>]<sup>6-</sup> anion, we can conclude that the oxidation state of the actinide in both compounds should be described as An(IV). While the versatile nature of the selenophosphate building block has also been confirmed, the geometry of the bridging selenide chain will depend on the electron-donating ability of the metals to which this building block is associated.

Of particular future interest here is the relative effect of the mole percent selenium content and oxidizing power of the flux found in these types of reactions. For identical A:Th:P:Se molar ratios (A = Rb, Cs) run under identical reaction conditions, two discrete phases were found, Rb<sub>2</sub>ThP<sub>3</sub>Se<sub>9</sub> and Cs<sub>4</sub>Th<sub>4</sub>P<sub>4</sub>Se<sub>26</sub>. Similar results have been observed for Rb<sub>2</sub>ThP<sub>3</sub>Se<sub>9</sub> and Cs<sub>4</sub>Th<sub>2</sub>P<sub>5</sub>Se<sub>17</sub>.<sup>8</sup> Reactions run with cesium as the alkali metal appear to support the formation of (Se<sub>2</sub>)<sup>2-</sup> anions and selenophosphate anions, whereas potassium and rubidium have thus far produced the (P<sub>2</sub>Se<sub>6</sub>)<sup>4-</sup> anion exclusively. Current experiments that explore the role of the alkali metal and the effect of mole percent selenium content within these reactions is ongoing and may assist in the rational design of materials possessing specific anion building blocks.

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**Supporting Information Available:** Additional crystallographic details, tables of all bond distances and angles, and anisotropic thermal parameters are available. This information is free of charge via the Internet at <http://pubs.acs.org>.