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Synthesis, Structure, and Spectroscopy of Two Ternary Uranium(IV) Thiophosphates: UP_2S_9 and UP_2S_7 Containing $P_2S_9{}^{2-}$ and $P_2S_7{}^{2-}$ Ligands

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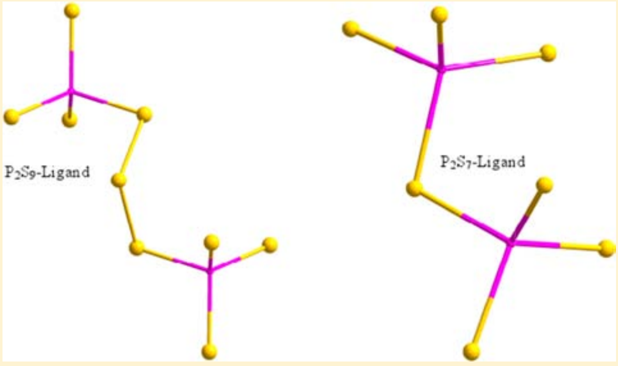
Ⓢ *Supporting Information*

ABSTRACT: The two ternary uranium thiophosphate compounds were isolated from polychalcogenide flux reactions. UP_2S_9 crystallizes in the tetragonal space group $P4_2/mcm$ with two formula units per unit cell, where $a = 7.762(1)$ and $c = 9.691(3)$ Å. UP_2S_7 crystallizes in the orthorhombic space group $Fddd$ with 16 formula units per unit cell, here $a = 8.919(3)$, $b = 15.198(4)$, and $c = 30.104(9)$ Å. Both compounds were characterized through single crystal X-ray, UV−vis−NIR, and Raman spectroscopy. The structures of the two compounds are formed from $[US_6]^{8-}$ chains connected to each other by either the tridentate-chelating $P_2S_9{}^{4-}$ in UP_2S_9 or the $P_2S_7{}^{4-}$ in UP_2S_7 resulting in 3D frameworks. These two ligands have different geometries, but they exhibit similar coordination modes, comparable to the ethane-like $P_2S_6{}^{4-}$. The uranium cations in both compounds can be assigned an unambiguous oxidation state of +4. The two compounds are semiconductors with nearly identical band-gaps of 1.41 eV.



INTRODUCTION

Thiophosphates are a remarkably rich group of compounds that can contain polysulfide linkages between the phosphorus atoms. These ligands include $P_2S_6{}^{4-}$, $P_2S_7{}^{4-}$, $P_3S_9{}^{3-}$, $P_3S_{10}{}^{4-}$, $P_4S_{10}{}^{4-}$, $P_3S_{12}{}^{4-}$, and $P_4S_{13}{}^{6-}$, and form from molten alkali metal chalcogenide fluxes that contain both d- and f-block metals.[1−10] In addition, these anions can form in ionic liquids as recently shown by Cody et al. where cyclic $P_2S_8{}^{4-}$, $P_3S_8{}^{3-}$, and $P_3S_9{}^{3-}$ anions were found.[11] P_2S_5 itself is low-melting (~290 °C), and can therefore be used as a reactive flux in relatively low temperature solid-state reactions. A testament to the complexity of these systems is that oxidation state assignment of the metals in these compounds is not always straightforward even with precise bonding metrics, and detailed spectroscopic measurements are often necessary. This is particularly true with actinide compounds where the oxidation state of the metal could vary from +3 to +6.[12]

Uranium thiophosphates represent a particularly rich system that includes both ternary and quaternary phases. UP_4S_{12}, an early example in this family, contains the $[P_2S_6]^{2-}$ anion, and possesses an interpenetrating diamond-like lattice.[4] More complex examples include, $A_{11}U_7(PS_4)_{13}$ (A = K, Rb), which displays interlocked helices.[13] The uranium also brings structural and electronic richness to this system in that the coordination chemistry of uranium is extremely flexible and coordination numbers of eight and nine are quite common. In addition, the oxidation state of uranium can be unusual in these compounds as found for $Rb_4U_4P_4Se_{26}$, which is a rare example of a U(V) compound.[14] Both UP_4S_{12} and $Cs_8U_5(P_3S_{10})(PS_4)_6$ contain multiple thiophosphate anions, and in the case of the latter the structure appears to be unique to uranium.[5]

Recently reported ternary and quaternary thiophosphates moieties have proven to contain structural features that are reminiscent of saturated hydrocarbons. The structural relationships between $P_2S_7{}^{4-}$ and $P_2S_8{}^{4-}$ thiophosphate are good examples of this.[5,8] Cyclic structures are also known that incorporate polysulfide linkages, such as the S_3 group in $P_2S_8{}^{4-}$.[1,8] Compounds containing multiple types of thiophosphates have also been found and these include $A_4Ti_2(P_2Q_9)_2(P_2Q_7)$ (A = K, Rb; Q = S, Se)[10] and $Cs_8U_5(P_3S_{10})_2(PS_4)_6$.[5] While there are more than two dozen of quaternary actinide thiophosphate representatives,[3,5,6,13,15] very few ternary phases are known.[1,2,4]

Here we present the synthesis and characterization of two ternary U(IV) thiophosphates, UP_2S_9 and UP_2S_7, that both

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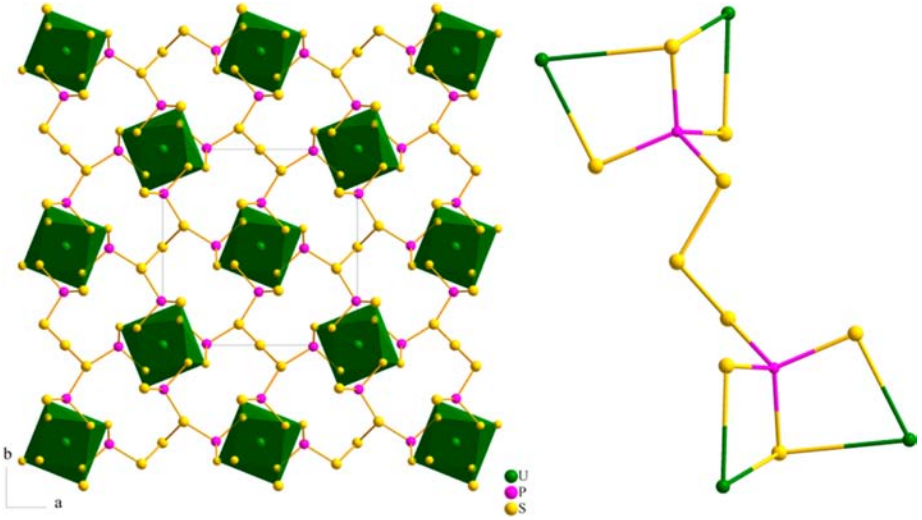

Figure 1. View of the UP_2S_9 crystal structure down the *c*-axis (*left*) with the coordination mode of P_2S_9 ligand (*right*).

possess framework structures that exclusively contain $P_2S_9^{4-}$ and $P_2S_7^{4-}$ thiophosphate ligands, respectively. Other members of this family include UP_2S_6 and $An(P_2S_6)_2$ (An = U, Np).[1,2,4] This contribution adds to the complex nature of 5f metal chalcogenides and the chalcophosphate chemistry with the formation of complex thiophosphate ligands.

■ EXPERIMENTAL SECTION

Synthesis. UP_2S_9 was synthesized by reacting 917 mg of BaS/U/P_2S_5/S in 1:1:2:1 stoichiometric ratio in an evacuated silica glass tube with an outer diameter of 10 mm. This was then slowly heated to 500 °C over 24 h, held there for 5 days, and then slowly cooled to room temperature at the rate of 6°/h. Dark red lath-shaped crystals formed on the walls of the tube and were hand-picked for further analyses. A yellowish poorly crystalline phase was found at the bottom of the tube, and was determined to be $Ba_2(P_2S_6)$ according to observed unit cell as previously reported.[16] Any attempt to increase the amount of sulfur to match the stoichiometric with the latter byproduct led to lower yield and a glassy-phase at the bottom of the tube. Whereas attempts at using A_2S_x (A = Rb, Cs; x = 3 and 4) in the absence of elemental sulfur resulted in the formation of either $Rb_{11}U_7(PS_4)_{13}$[13] or, in the of case of cesium, only an unknown orange red-colored glassy-phase. Dark red irregular shaped crystals of UP_2S_7 were synthesized via the same experiments as described above, but with the presence of elemental antimony (one equivalent) or via the reaction of 794 mg of Li_2S/U/P_2S_5/S in 1:1:2:1 stoichiometric ratio in the presence of silicon (one equivalent). The EDX analysis of both UP_2S_9 and UP_2S_7 shows the presence neither of barium nor antimony/silicon. However, we were unable to synthesize in our reaction conditions those compounds without these elements being present in the reaction.

Crystal Structure Determination. The crystal data collections were performed at room temperature on a Bruker APEXII CCD X-ray diffractometer using graphite-monochromatized MoKα radiation. SAINT software[17] was used for data integration including Lorentz and polarization corrections. The absorption corrections were done using the SADABS program. The structure solutions and refinements were performed with the aid of the SHELXTL package of crystallographic programs.[18]

Solid-State UV−vis Spectroscopy. The absorption spectra of the title compounds were collected from single crystals at room temperature using a Craic Technologies UV−vis−NIR microspectrometer in the 200−1500 nm region. This enabled us to confirm the oxidation state of the uranium.

Elemental Analysis. Semiquantitative elemental analyses were measured using a field emission scanning electron microprobe (LEO EVO 50) equipped with an Oxford INCA Energy Dispersive X-ray Spectrometer (EDX). EDX data were collected from several crystals of the same compound and only the presence of U, S, and P were detected in the samples.

Raman Spectroscopy. Raman spectra were collected on single crystals of UP_2S_9 and UP_2S_7 using a Bruker Sentinel system linked via fiber optics to a video-assisted Raman probe in a microscope mount. The laser wavelength was 750 nm with a power of 400mW, while the collection was made between 100 and 700 cm^{-1}. The instrument is equipped with a high-sensitivity, TE-cooled 1024 × 255 CCD array.

■ RESULTS AND DISCUSSION

Synthesis. The successful synthesis of UP_2S_9 was accomplished only by using a mixture of BaS/S in the reaction. Our motivation here was based on the fact that phase diagram studies of barium sulfide and sulfur show the formation of BaS_3 (our S_3^{2-} source), and this compound was also found as a byproduct in some of our reactions at 500 °C. The synthesis of quaternary actinide thiophosphate with alkaline earth metal is apparently quite difficult compare to lanthanides. The synthesis and characterization of UP_2S_7 have already been reported in the C. Gieck dissertation,[19] but we rediscuss its synthesis, structure, and the Raman spectroscopy here to enable and facilitate its comparison with UP_2S_9. The crystals of both compounds are stable in moist air with yields around 40% based on uranium.

Crystal Structures. UP_2S_9 crystallizes in the tetragonal $P4_2/mcm$ with two formula units per unit cell, where a = 7.762(1), c = 9.691(3) Å, and V_m = 175.80 cm^3. In this space group there are fully occupied crystallographic positions for U and P and four half-occupied positions for S. An attempt to solve the same structure in the lower monoclinic $P2/c$ space group with the same data set again gives one fully occupied crystallographic position for U and P as well and nine for S which are all still half-occupied. The R_1/wR_2 solutions parameters are 0.014/0.026 and 0.02/0.037, respectively, for tetragonal and monoclinic solution. In these two solutions, the uranium and phosphorus cations are apparently surrounded by 16 and 8 S anions but, because of the half occupancy of the sulfide positions, they are actually 8 and 4, respectively. Moreover, many of the S−S interactions are between 1.946(4) and 2.534(2) Å, which suggest the presence of homolytic bonds between sulfur atoms; several possibilities can be postulated. Both solutions seem good, but their crystal structure representations are not simple or comprehensible. To have a

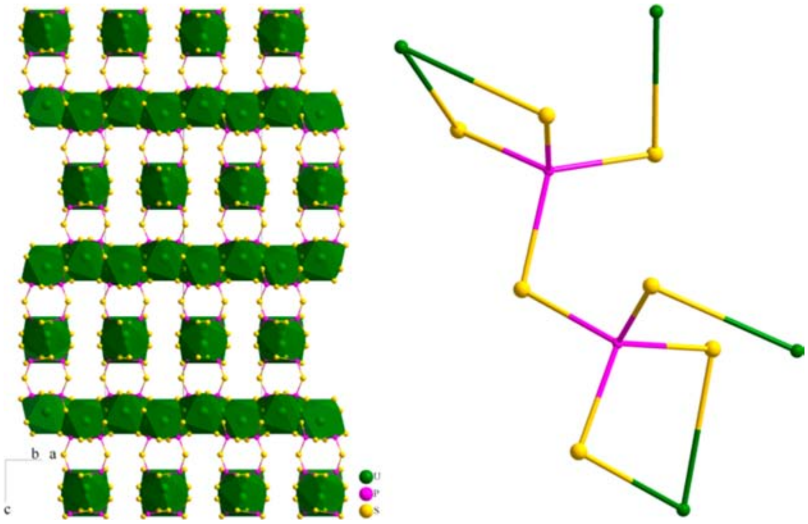

Figure 2. Crystal structure of UP_2S_7 depicting connectivity of the $[US_6]^{8-}$ chains along the *c*-axis (*left*) with the coordination mode of P_2S_7 ligand (*right*).

clearer view, we decided to remove some symmetry elements and attempt to solve it in the triclinic setting, which will double the volume of the cell: $a' = 10.976(3)$, $c' = 9.689(2)$; $Z = 4$, $V_m = 175.65$ cm^3. The triclinic and the tetragonal cell parameters have the following relations: $a\sqrt{2} = a'$ and $c = c'$. The solution in the $P\overline{1}$ space group gives 0.0296/0.0552 for R_1/wR_2. Now the two U and two P crystallographic positions are fully occupied together with 20 other positions for S. Among those S positions only four are half occupied; however, all U and P cations are surrounded by 8 and 4 S anions, respectively, all from the fully occupied positions. We found that the half-occupancy S positions are exclusively those of the sulfur atoms bridging two neighboring PS_4^{3-} groups. Thus, each U atom is now surrounded by four $[PS_4{-}S{-}PS_4]^{4-}$ chelating moieties. From this “super cell” structural solution of the UP_2S_9, the crystal structure can be clearly projected and indicates the tetragonal model is in fact the best solution refinement. In the $P4_2/mcm$ space group, U^{4+} cations are sitting at a specific position with symmetry $\overline{4}2m$. Each of those cations is coordinated by four PS_4^{4-} groups from four different $P_2S_9^{4-}$ ligands in the tetrahedral environment which was also found in triclinic system. Within this high symmetry environment sulfur atoms generate dumbbells. The only real S−S interactions are between the bridging sulfur (S4) atoms and those directly linked to phosphorus (S2), as found in triclinic solution. Each PS_4^{3-} group of the $P_2S_9^{4-}$ ligand chelates two U centers (Figure 1-*right*) resulting in a three-dimensional framework structure. This can be seen as a defect diamond structure of U and P if S atoms are omitted. All solutions were tested in the PLATON program,[20] which confirmed the tetragonal crystal system. Similar challenging structure has also been reported by Fragnaud et al.[9]

The coordination environment of U is a distorted square antiprism formed from sulfide anions, while P is tetrahedrally coordinated by sulfide. The U−S distances range between 2.733(2) and 2.986(1) Å in good agreement with those of 2.812(1)−2.879(1) Å found in $U(P_2S_6)_2$ or those of 2.725(4)−2.980(4) Å in $Cs_8U_5(P_3S_{10})_2(PS_4)_6$. Each $[US_8]^{12-}$ polyhedron shares two edges with two others to form $[US_6]^{8-}$ chains extending down the *c*-axis. The P−S values are between 1.969(2)−2. 185(3) Å and are consistent with these from 1.931(2) to 2.195(2) Å reported in refs 1,21−23. The shorter P−S distances are attributed the terminal S (S1, S3) while the longer is assigned to S2 that is further connected to bridging S4. The S2−S4 contact at 2.101(2) Å is the only true sulfur−sulfur interaction in this structure, despite many similar distances found but these are derived from the disordered sulfurs. The P−S2−S4 and S2−S4−S2 angles of 98.96(1) and 106.04(1)° found in this structure are consistent with those of 101.32(9) and 111.70(10)° reported for $Cs_4P_2Se_9$, respectively. This structure can also be presented as $[US_6]^{8-}$ chains linked to each other by the $P_2S_9^{4-}$ rod-like building units as viewed on the Figure 1-*left*, built from the triclinic solution.

The UP_2S_7 crystallizes in the orthorhombic *Fddd* space group with 16 formula units per unit cell $a = 8.919(3)$, $b = 15.198(4)$, $c = 30.104(9)$ Å with $V_m = 153.62$ cm^3. Six crystallographic positions are found in this unit cell which are all fully occupied by one U, one P, and four S. U cations are surrounded by 8 S, while P cations are tetrahedrally surrounded by 4 S anions. Two nearest PS_4^{3-} groups share a common S atom to form the thiopyrophosphate $P_2S_7^{4-}$ ligand. Each PS_4^{3-} functional-group of the latter ligand chelates one U center meanwhile sharing a vertex with another U atom, generating the formation of a three-dimensional UP_2S_7 structure. The $P_2S_7^{4-}$ depicts four different P−S distances with the longer for the bridging S and the shorter for one S terminal. Each $[US_8]^{12-}$ polyhedron shares two edges with two direct neighbors to form infinite $[US_6]^{8-}$ chains similar to those describe above. The latter are arranged parallel to each other to form layers that are perpendicular to the [001] direction. Furthermore, the latter are alternatingly twisted then shifted for 60 and 120° as they are stacking along the *c*-axis resulting in an ABCD packing (Figure 2-*left*). The ligands are thus used to attach only chains of one layer to those of the next layer creating two different void shapes when viewed along [−1−10] direction. If S atoms are omitted in the structure, it can be seen as a super diamond structure made of U and P−P units.

The U environment here is the same as in the above structure with U−S distances ranging from 2.786(1) and 2.918(1) Å. The P−S bond lengths are found between 2.004(2) and 2.106(2) Å, with a P−S1−P angle of 106.196(9)° comparable to that of 106.57(4) reported in ZrP_2S_7.[24] Except for the P−S distance for the bridging S, the terminal ones are almost identical. The fact that UP_2S_7 and ZrP_2S_7 crystallize in two different space groups *Fddd* and *C2/c*, respectively, can be supported by the difference in their tetravalent ionic radii (r_{U+4} = 1.03 and r_{Zr+4} = 0.72 Å).[25]

■ DISCUSSION

Both reported framework structures are formed from $[US_6]^{8-}$ chains further linked to each other by either $P_2S_9^{4-}$ or $P_2S_7^{4-}$, respectively. Each of the two ligands possesses two PS_4^{3-} groups that display different coordination modes with U^{4+} cations. The replacement of the bridging S in $P_2S_7^{4-}$ by S_3 to generate $P_2S_9^{4-}$ resulted in small density changes (see Table 1), but rather made the $P_2S_9^{4-}$ connection to $[US_6]^{8-}$ chains more flexible, contrary to the observed unidirectionality for $P_2S_7^{4-}$ (Figure 2-*left*). The geometry of $P_2S_9^{4-}$ and that of $P_2Se_9^{6-}$ reported in $Cs_2Th_2(P_2Se_9)(Se_2)$ are different with an almost linear Se−Se−Se bond (171.07(6) °) contrary to the clear V-shape S−S−S bond (106.06(1)○). The reported synthesis and characterization of the latter thorium compound justified its ligand charge and suggested the +4 oxidation state for U in the isotypical $Cs_2U_2(P_2Se_9)(Se_2)_2$.[14] However, the shape of the titled $P_2S_9^{4-}$ is close to that of $P_2Se_9^{4-}$ found in $A_4Ti_2(P_2Se_9)_2(P_2Se_7)$ (*A* = K, Rb) and in $Cs_4P_2Se_9$,[10] in complete agreement with the ligands and cations charges. While the almost ecliptical $P_2S_7^{4-}$ ligand favors ABCD stacking arrangement, $P_2S_9^{4-}$ adopts the simple AB pilling also found in UP_2S_6 and $Cs_2An_2(P_2Se_9)(Se_2)_2$ (*An* = K, Rb) structures. This may be due to the nonlinear S_3 moiety twisting the two PS_4^{3-} functional groups. The uranium chalco-phosphate chemistry produces similar compounds to that of zirconium (such as tetragonal ZrP_2S_6 vs UP_2S_6), but ZrP_2S_9 representative remains unknown and there is no lanthanide representative either.

Table 1. Crystallographic Data for UP_2S_9 and UP_2S_7

compound	UP_2S_9	UP_2S_7
crystal system	tetragonal	orthorhombic
space group	$P4_2/mcm$ (no. 132)	*Fddd* (no. 70)
unit cell parameters		
a/Å	7.762(1)	8.921(3)
b/Å		15.198(4)
c/Å	9.691(3)	30.104(9)
formula unit per unit cell (Z)	2	16
calculated density (D_x in g/cm^3)	3.35	3.41
molar volume (V_m in cm^3/mol)	175.80	153.62
index range ($\pm h_{max}/\pm k_{max}/\pm l_{max}$)	10/10/12	11/19/38
$2\theta_{max}$ (in deg)	55.26	55.02
$F(000)$	738.0	3744.0
absorption coefficient (μ in mm^{-1})	42.38	17.58
collected reflections	4749	11973
unique reflections	401	1183
R_{int}/R_σ	0.052/0.020	0.063/0.031
reflections with $\lvert F_o \rvert \geq 4\sigma(F_o)$	346	1016
R_1/R_1 with $\lvert F_o \rvert \geq 4\sigma(F_o)$	0.021/0.014	0.030/0.022
wR_2 (for all reflections)	0.026	0.038
goodness of fit (GoF)	1.100	1.044
residual electron density (max./min.) (ρ in e$^-\cdot 10^6$ pm^{-3})	0.656/−0.666	0.840/−1.076

Raman Spectroscopy. The Raman spectra were collected on the selected crystals of the title compounds in the range of 100 and 700 cm^{-1} (Figure 3). It is difficult to unambiguously assign all the Raman peaks because the S−S and P−S vibrations overlap in certain regions of the spectrum. But having two compounds, each made with only one type of ligand, produced spectra that are easier to interpret and compare. The main symmetric stretching mode of the PS_4^{3-} is represented by strong peaks around 400 cm^{-1} which slightly varied according to the environment. Thus the UP_2S_7 spectrum depicts two different PS_4^{3-} environments while that of UP_2S_9 only shows one. The replacement of S by S_3^{2-} brings more freedom to the PS_4^{3-} function groups in $P_2S_9^{4-}$ than in $P_2S_7^{4-}$. The medium peaks at 275 and 510 cm^{-1} present on the UP_2S_9 spectrum and absent on the UP_2S_7 spectrum may be assigned to the S−S stretching modes.[10,11,14]

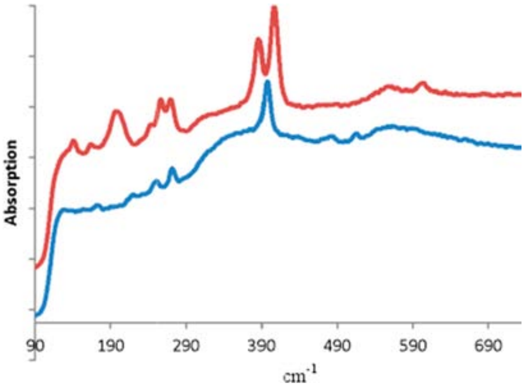

Figure 3. Raman spectrum of UP_2S_7 (*top*), and that of UP_2S_9 (*bottom*).

UV−vis Spectroscopy. Contrary to the uranium oxides' spectroscopy which shows clear differences between +3 and +4 oxidation states for U, these attributes are much less clear with softer ligands like sulfide. The data collected here rather are mostly used to determine the compounds' band gaps. The single crystal optical transmission measurements done on UP_2S_9 and UP_2S_7 crystals lead to the same sharp band gap of 1.41 eV. Both compounds are thus semiconductors, and the broad absorption peak observed around 1.0 eV on the two spectra (Figure 4) can be attributed to the f-f transition since the uranium cations here are $5f^2$, meanwhile similar peaks have been observed in many $4f^1$ and $5f^1$ compounds.[26−29]

■ CONCLUSIONS

The two presented compounds are thus far the only ternary structures containing exclusively an actinide and a larger

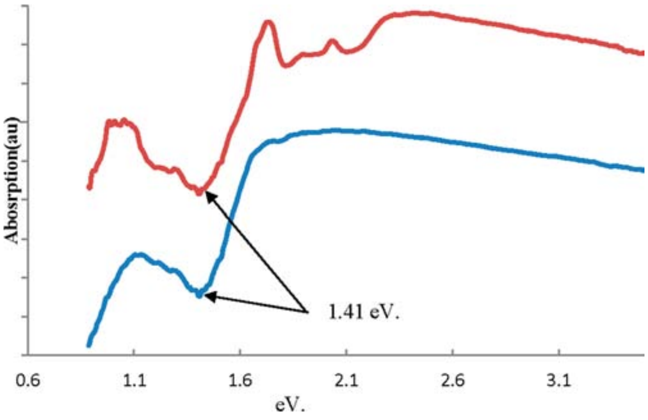

Figure 4. Solid state optical absorption spectrum of UP_2S_9 (*top*), and that of UP_2S_7 (*bottom*).

tridentate-chelating ligand beside AnP_2S_6 (An = Th, U)[3,28] with bidentate $P_2S_6^{2-}$. Both compounds adopt 3D structures (Tables 2 and 3). $P_2S_9^{4-}$ thiophosphate shows the same chelating-mode and staggered conformation as ethane-like $P_2S_6^{4-}$, while $P_2S_7^{4-}$ contains a different connection mode with an ecliptic conformation. The geometry of the reported thiophosphate $P_2S_9^{4-}$ ligand unlike that of $P_2Se_9^{6-}$ in $Cs_2Th_2(P_2Se_9)(Se_2)_2$ reinforces the assignment on the +4 oxidation state of actinide elements in $Cs_2An_2(P_2Se_9)(Se_2)_2$ (An = Th, U). It is difficult to synthesize $P_2S_9^{4-}$ by starting only with alkali metal polychalcogenides that already contain the S_3 moiety. Those formed in situ by mixing BaQ/Q or A_2Q/S (Q = S, Se) for example, can lead to an easy and reproducible synthetic approach for the chalco-phosphate $P_2Q_9^{4-}$ ligands. Only the geometry of the $P_2S_9^{4-}$ group in the presence of a high symmetry U-environment may somehow justify the complexity of the structural solution encountered in UP_2S_9. Flux reactions remain a successful approach for the synthesis of 3D inorganic materials in thiophosphate chemistry. The development of larger chalco-phosphate groups through infiltration of some S–S bounds has not been very successful. However, our next step will be the insertion of a chalcophilic main-group element such as Ga, Sn, or Ge between chalco-phosphate moieties.

Table 2. Selected Bond Distances (Å) and Angles (deg) in UP_2S_9

U–S1(4×)	2.734(2)	P–S1(2×)	1.969(2)
U–S3(4×)	2.985(1)	P–S2	2.185(3)
		P–S3	2.093(2)
S2–S4(2×)	2.101(2)		
S2–S4–S2	106.04(1)		
torsion angle around S2–S4: 97.700(10)		P–S2–S4	98.955(1)

Table 3. Selected Bond Distances (Å) and Angles (deg) in UP_2S_7

U–S2(2×)	2.868(1)	P–S1	2.106(2)
U–S2′(2×)	2.918(1)	P–S2	2.049(2)
U–S3(2×)	2.810(1)	P–S3	2.016(2)
U–S4(2×)	2.786(1)	P–S4	2.004(2)
		P–S2–P	106.196(9)

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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