Stabilization of U5+ in RbU6PSe26. An Actinide Compound with a Mixed Thiophosphate/Selenophosphate Framework and Ion-Exchange Properties

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The advancement of the polychalcophosphate flux technique in recent years has resulted in many novel quaternary thiophosphate and selenophosphate compounds.1 To form these fluxes, we fuse in situ A2Q3 and P2Q5 (Q = S, Se), which produces various [P2Q5]n− ligands (Q = S, Se). In the presence of metal ions, these highly anionic ligands bind in an astounding number of ways to the metals, forming new materials.1 The variation of the flux composition stabilizes different ligands such as [P2Q8−], [PSe4]2−, [P2Q6]4−, and [P2Q7]3−,1−12 which become the building blocks of various polymeric solid-state or even molecular structures.8 This chemistry gave rise to several unusual compounds such as AbIP5 (A = K,Rb),2 A2(P(pH)3)2 (A = Rb, Cs; M = Sb, Bi),3 Cs12Bi2(P2S6)3,4 Na16Bi2P2Se6,5 A3MP2Se6 (M = K, Rb; M = Mn, Fe),6 A4M2P2Se6 (M = K, Cs; M = Cu, Ag),7 KMP2Se6 (M = Sb, Bi),4 Cs15M(P2Se5)8 (M = Sb, Bi),3 APbPSe6,6 A2M(P2Se5)2 (A = Rb, Cs; M = Pb, Eu),6 Rb2Ti2P2Se7,7 A2Sn12P2Se7 (A = K, Rb),8 A5Sn2Se25 (A = K, Rb),9 A5Au2PSe6 (A = K, Rb, Cs),10 A2Au2PSe6 (A = K, Rb),10 A2AuP2S (A = K, Rb, Cs),10 and A2AuP2S (A = K, Rb).10 Extension of this chemistry to lanthanides and actinides yielded A2Au2P2Se6 (A = K, Rb).10 A2AuP2S (A = K, Rb, Cs),10 and A2AuP2S (A = K, Rb).10

Figure 1. (A) Polyhedral representation of a (U5+Se14) chain. (B) The U dimer in the chain with atomic labeling, including the [PSe4]2− groups. Selected distances (Å): U(1)−U(2) 4.071(1), U(1)−Se(1) 3.033(3), U(1)−Se(2) 3.033(3), U(1)−Se(3) 2.920(2), U(1)−Se(4) 2.952(3), U(1)−Se(5) 3.032(3), U(1)−Se(6) 2.966(3), U(1)−Se(7) 2.986(3), U(1)−Se(8) 2.990(3), U(1)−Se(9) 3.046(3); similar distances observed for U(2), Se(1)−Se(5) 2.411(4), Se(3)−Se(4) 2.413(4).

Chart 1

U5+ has the simplest 5f-electron configuration [Rn]5f1, and are useful in understanding the behavior of the f electrons of actinide ions. RbU6PSe26 has a three-dimensional framework with pentavalent U centers. It contains [PSe4]−, [Se2]2−, and (Se2)2− anions, and so it could be described as Rb2U2P2Se8([PSe4]3−, (Se2)2−,[Se2]2−)2−. The most unusual feature of the structure is the presence of pentavalent U. Some notable, structurally characterized examples with U5+ include Ph3ASUCl6,14 U(OR)5,14 and Ba(UO3)2.14 In RbU6PSe26 every U5+ atom is coordinated to two [PSe4]−, three Se2−, and one Se2− ligands. The structure contains two crystallographically independent uranium atoms, both displaying tricapped trigonal prismatic (TTP) geometry; see Chart 1. This coordination is unusual for uranium chalcogenides, and it has been observed for K3UP2Se8 as well.11 Other uranium chalcogenides exhibit bicapped trigonal prismatic geometry as in UMS3 (M = V, Cr, Co, Ni)15 and U2MS3 (M = Co, Fe).16 Two U TTPs share a triangular face (via atoms Se−

Figure 2. (A) Tunnel framework of Rb₄U₄P₄Se₂₆. Rb cations have been omitted for clarity. (B) Polyhedral representation down the [100] direction showing the intersecting narrower tunnels. The tunnels in this material are accessible to smaller cations via ion exchange.


As can be seen at the [010] view in Figure 2A. The Se₂⁻ chains cross-linked at four sides by [PSe₄]³⁻ and [Se²⁻]₆ ligands, as can be seen at the [010] view in Figure 2A. The Se₂⁻ ligands [e.g., Se(3)−Se(4), Se(1)−Se(5)'] have an average distance of 2.412(2) Å and play an important role in the structure since they bridge the dimers, leading to the formation of the chains. It is interesting that the compound shares many structural features with the layered K₃UP₃Se₉. Both structures are formed by interstitched (U₂Se₁₄)ₙ chains despite the fact that they contain different selenophosphates ([P₂Se₆]⁴⁻ versus [PSe₄]³⁻) and different oxidation states of U (U⁴⁺ versus U⁵⁺). The (U₂Se₁₄)ₙ chains are made by face-sharing U dimers in both compounds, but in K₃UP₃Se₉, the U−U distance is 0.530(2) Å longer. On the other hand, the dimers join by sharing corners in K₃UP₃Se₉, whereas in Rb₄U₄P₄Se₂₆ they share edges. The structure possesses Rb⁺⁻filled interconnected channels which run in both the [100] and [010] directions. The largest size channels have a rectangular cross-section with dimensions 6.95 Å × 5.34 Å and run in the [010] direction; see Figure 2. The Rb⁺ size (1.52 Å) is relatively small for the cavity, and both crystallographically independent Rb⁺ cations seem to “rattle”, trying to occupy more cavity space, as indicated by their anisotropic displacement parameters (Supporting Information). This suggests possible ion-exchange properties for this material, which we have tested. The Rb⁺ cations exchange readily with other smaller cations such as Li⁺. The extent of ion exchange exceeds 90%.

The valency of U atoms in chalcogenide compounds can be postulated by considering the mean U−Q (Q = S, Se) distances in the structure. The values for Rb₄U₄P₄Se₂₆ (2.99 Å) and K₃UP₃Se₉ (3.06 Å) are consistent with U⁴⁺ and U⁵⁺, respectively. There are two crystallographically independent, five-coordinate Rb cations with an average Rb−Se distance of 3.692 Å.

Diffuse reflectance mid-IR spectroscopy reveals one well-defined, broad peak at ~3900 cm⁻¹ (0.48 eV), which is associated with an f−f transition and the f⁴ configuration of U⁵⁺. By comparison, K₃UP₃Se₉ displays two such f−f transitions, at ~3725 cm⁻¹ (0.46 eV) and ~5856 cm⁻¹ (0.72 eV). Rb₄U₄P₄Se₂₆ melts incongruently at 597 °C, yielding amorphous Rb₄P₄Se₂₆, and the known binary USe₂ phases. Since K₃UP₃Se₉ melts congruently, it is tempting to attribute the instability of Rb₄U₄P₄Se₂₆ on melting to the tendency of U⁵⁺ to disproportionate. Above 70 K the magnetic susceptibility of Rb₄U₄P₄Se₂₆ shows Curie−Weiss law with a Θ of ~42.6 K. The μₜeff of 1.85 μB calculated from the slope of the straight line in the data (1/μm vs T) is consistent with an f⁴ configuration.

The stabilization of U⁵⁺ in a magnetically and optically “inert” Rb−PSe₄/Se₆ three-dimensional framework provides an interesting and unequivocal example of an air stable f⁴ actinide for magnetic and spectroscopic studies. The three-dimensional framework is amenable to “soft-chemistry” modifications such as ion exchange.

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Supporting Information Available: Tables of fractional atomic coordinates of all atoms, anisotropic and isotropic thermal parameters of all atoms, interatomic distances and angles, calculated and observed X-ray powder patterns, and graphs of magnetic susceptibility data (23 pages). See any current masthead page for ordering and Internet access instructions.

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