

Communications to the Editor

Stabilization of U⁵⁺ in Rb₄U₄P₄Se₂₆. An Actinide Compound with a Mixed Selenophosphate/Polyselenide Framework and Ion-Exchange Properties

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Received October 23, 1996

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* A₂Q_x and P₂Q₅ (Q = S, Se), which produces various [P₃Q₂]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 [PQ₄]³⁻, [PSe₅]³⁻, [P₂Q₆]⁴⁻, and [P₂Q₇]⁴⁻,^{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 ABiP₂S₇ (A = K, Rb),² A₃M(PS₄)₂ (A = Rb, Cs; M = Sb, Bi),³ Cs₃Bi₂(PS₄)₃,³ Na_{0.16}Bi_{1.28}P₂S₆,³ A₂MP₂Se₆ (A = K, Rb; M = Mn, Fe),¹ A₂M₂P₂Se₆ (A = K, Cs; M = Cu, Ag),¹ KMP₂Se₆ (M = Sb, Bi),⁴ Cs₈M₄(P₂Se₆)₅ (M = Sb, Bi),⁵ APbPSe₄,⁶ A₄M(PSe₄)₂ (A = Rb, Cs; M = Pb, Eu),⁶ Rb₄Ti₂(P₂Se₉)₂(P₂Se₇),⁷ KTiPSe₅,⁷ A₅Sn(PS₅)₃ (A = K, Rb),⁸ A₆Sn₂Se₄(PSe₅)₂ (A = Rb, Cs),⁸ A₂AuP₂Se₆ (A = K, Rb),⁹ A₃AuP₂Se₈ (A = K, Rb, Cs),¹⁰ A₂Au₂P₂Se₆ (A = K, Rb),¹⁰ A₂AuPS₄ (A = K, Rb, Cs),¹⁰ and AAuP₂S₇ (A = K, Rb).¹⁰ Extension of this chemistry to lanthanides and actinides yielded the K₄Eu(PSe₄)₂,^{6a} KEu(PSe₄),^{6b} and the first actinide selenophosphate K₂UP₃Se₉.¹¹ The latter is formally a U⁴⁺ compound with a complex layered structure that contains [P₂Se₆]⁴⁻ anions. The K(RE)P₂Se₆ (RE = Y, La, Ce, Pr, Gd) series has also been reported recently.¹² Here we report the Rb₄U₄P₄Se₂₆, a novel three-dimensional, ion-exchange material containing the rare U⁵⁺ ion. Pentavalent uranium compounds are relatively scarce because of uranium's strong tendency to disproportionate to U⁴⁺ and U⁶⁺. Therefore, they are of fundamental importance since

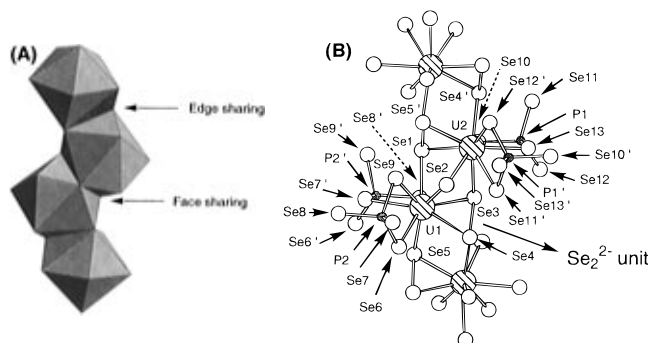
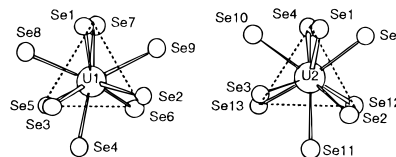


Figure 1. (A) Polyhedral representation of a (U₂Se₁₄)_n chain. (B) The U dimer in the chain with atomic labeling, including the [PSe₄]³⁻ groups. Selected distances (Å): U(1)–U(2) 4.071(1), U(1)–Se(1) 3.033(3), U(1)–Se(2) 3.033(3), U(1)–Se(3) 2.920(2), U(1)–Se(4) 2.952(3), U(1)–Se(5) 3.032(3), U(1)–Se(6) 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.

Rb₄U₄P₄Se₂₆¹³ has a three-dimensional framework with pentavalent U centers. It contains [PSe₄]³⁻, Se²⁻, and (Se₂)²⁻ anions, and so it could be described as Rb₄⁺U₄⁵⁺(PSe₄)₄³⁻(Se₂)₂²⁻(Se₂)₄²⁻. The most unusual feature of the structure is the presence of pentavalent U. Some notable, structurally characterized examples with U⁵⁺ include Ph₄AsUCl₆,¹⁴ U(OR)₅,¹⁴ and Ba(UO₃)₂.¹⁴ In Rb₄U₄P₄Se₂₆ every U⁵⁺ atom is coordinated to two [PSe₄]³⁻, 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 K₂UP₃Se₉ as well.¹¹ Other uranium chalcogenides exhibit *bicapped* trigonal prismatic geometry as in UMS₃ (M = V, Cr, Co, Ni)¹⁵ and U₂MS₅ (M = Co, Fe).¹⁶ Two U TPPs share a triangular face [via atoms Se-

(13) (a) Rb₄U₄P₄Se₂₆ was synthesized from a mixture of U (0.60 mmol), P₂Se₅ (0.3 mmol), Rb₂Se (0.60 mmol), and Se (6 mmol) that was sealed under vacuum in a Pyrex tube and heated to 500 °C for 4 d followed by cooling to 50 °C at -2 °C h⁻¹. The excess Rb₄P₃Se₂ flux was removed with DMF under a N₂ atmosphere. The product was then washed with tri-*n*-butylphosphine and ether. Metallic gray, irregular, rodlike crystals were obtained (81% yield based on U). The crystals appear air and water stable. (b) A Siemens SMART Platform CCD diffractometer was used to collect data from a crystal of 0.225 × 0.013 × 0.013 mm dimensions and Mo Kα (λ = 0.710 73 Å) radiation. An empirical absorption correction^{13c} was applied to the data. Crystal data at 23 °C: a = 11.9979(1) Å, b = 14.4874(1) Å, c = 27.1377(2) Å; V = 4709.17(6) Å³; Z = 4; D_c = 4.895 g cm⁻³; space group *Pbca* (no. 61); μ(Mo Kα) = 380.63 cm⁻¹; index ranges -13 ≤ h ≤ 13, -16 ≤ k ≤ 16, -21 ≤ l ≤ 30; total data, 21 432; unique data, 4150 (R_{int} = 0.089); data with F_o² > 3σ(F_o²), 2211; no. of variables, 163; final R/Rw = 0.047/0.057; GOF = 2.84. (c) Blessing, R. H. *Acta Crystallogr.* **1995**, A51, 33–38. (d) Far-IR vibrational modes of the [PSe₄]³⁻ group are at ~453, ~444, ~416, ~278, and ~270 cm⁻¹.

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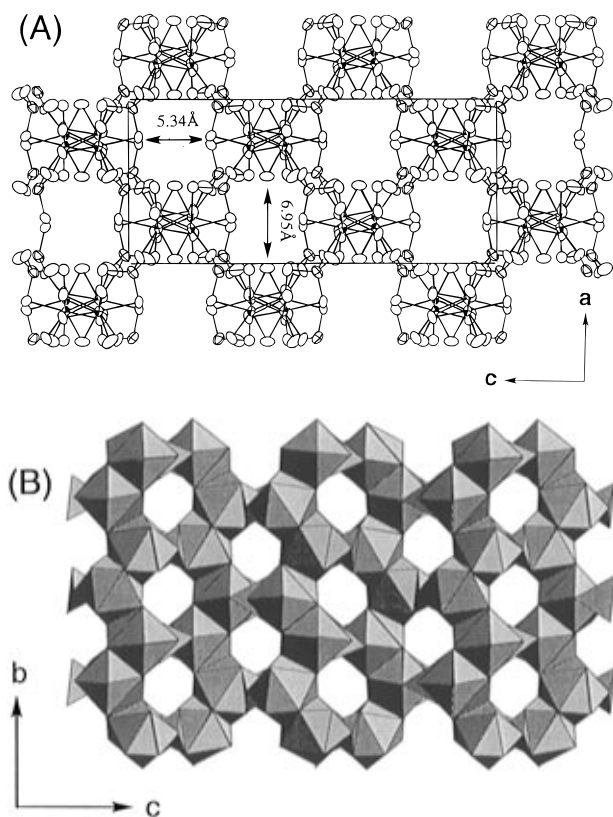


Figure 2. (A) Tunnel framework of $\text{Rb}_4\text{U}_4\text{P}_4\text{Se}_{26}$. Rb cations have been omitted for clarity. (B) Polyhedral representation down the [100] direction showing the intersecting narrower tunnels. The tunnels in this material are accessible to smaller cations via ion exchange.

(1), Se(2), and Se(3)] to form “dimers” of $(\text{U}_2\text{Se}_{14})_x$ with a U–U distance of 4.071(2) Å; see Figure 1. These dimers then join by sharing edges [Se(4), Se(5)], forming chains of $(\text{U}_2\text{Se}_{14})_x$ that propagate along the [100] direction. The intricate three-dimensional structure is formed by the side-by-side arrangement of these chains cross-linked at four sides by $[\text{PSe}_4]^{3-}$ ligands, as can be seen at the [010] view in Figure 2A. The Se_2^{2-} 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 $\text{K}_2\text{UP}_3\text{Se}_9$.¹¹ Both structures are formed by interstitched $(\text{U}_2\text{Se}_{14})_x$ chains despite the fact that they contain different selenophosphates ($[\text{P}_2\text{Se}_6]^{4-}$ versus $[\text{PSe}_4]^{3-}$) and different oxidation states of U (U^{4+} versus U^{5+}). The $(\text{U}_2\text{Se}_{14})_x$ chains are made by face-sharing U dimers in both compounds, but in $\text{K}_2\text{UP}_3\text{Se}_9$ the U–U distance is 0.530(2) Å longer. On the other hand, the dimers join by sharing corners in $\text{K}_2\text{UP}_3\text{Se}_9$, whereas in $\text{Rb}_4\text{U}_4\text{P}_4\text{Se}_{26}$ 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)¹⁷ 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%.¹⁸

The valency of U atoms in chalcogenide compounds can be postulated by considering the mean U–Q (Q = S, Se) distances in the structure.¹⁹ The values for $\text{Rb}_4\text{U}_4\text{P}_4\text{Se}_{26}$ (2.99 Å) and $\text{K}_2\text{UP}_3\text{Se}_9$ (3.06 Å) are consistent with U^{5+} and U^{4+} , 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 $\sim 3900\text{ cm}^{-1}$ (0.48 eV), which is associated with an f–f transition and the f^1 configuration of U^{5+} . By comparison, $\text{K}_2\text{UP}_3\text{Se}_9$ displays two such f–f transitions, at $\sim 3725\text{ cm}^{-1}$ (0.46 eV) and $\sim 5856\text{ cm}^{-1}$ (0.72 eV). $\text{Rb}_4\text{U}_4\text{P}_4\text{Se}_{26}$ melts incongruently at 597 °C, yielding amorphous $\text{Rb}_3\text{P}_3\text{Se}_z$ and the known binary USe_x phases. Since $\text{K}_2\text{UP}_3\text{Se}_9$ melts congruently, it is tempting to attribute the instability of $\text{Rb}_4\text{U}_4\text{P}_4\text{Se}_{26}$ on melting to the tendency of U^{5+} to disproportionate. Above 70 K the magnetic susceptibility of $\text{Rb}_4\text{U}_4\text{P}_4\text{Se}_{26}$ shows Curie–Weiss law with a Θ of –42.6 K. The μ_{eff} of $1.85\ \mu_{\text{B}}$ calculated from the slope of the straight line in the data ($1/\chi_{\text{m}}$ vs T) is consistent with an f^1 configuration.^{14,20}

The stabilization of U^{5+} in a magnetically and optically “inert” $\text{Rb–PSe}_4/\text{Se}_x$ three-dimensional framework provides an interesting and unequivocal example of an air stable f^1 actinide for magnetic and spectroscopic studies. The three-dimensional framework is amenable to “soft-chemistry” modifications such as ion exchange.

Acknowledgment. Financial support from the National Science Foundation (Grant DMR-9527347) is gratefully acknowledged. The authors are grateful to the X-ray Crystallographic Laboratory of the University of Minnesota and to Dr. Victor G. Young, Jr., for collecting the single-crystal X-ray data sets.

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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