# Synthesis and Structure of the Rubidium Uranium Selenophosphate $Rb_4U_2P_5Se_{17}$

## Brian J. Bellott[a,b] and James A. Ibers*[a]

**Abstract.** Black crystals of the rubidium uranium selenophosphate $Rb_4U_2P_5Se_{17}$ have been prepared by the solid-state reaction of uranium, $P_2Se_5$, and $Rb_2Se_3$ at 1023 K. The compound crystallizes with four formula units in the triclinic space group $P\bar{1}$ with cell constants at 100 K of $a = 10.0824(2)$, $b = 10.6905(2)$, $c = 15.7845(3)$ Å, $a = 84.678(1)$, $\beta = 76.125(1)$, $\gamma = 85.874(1)°$. Its complex three-dimensional structure displays four different types of ligands that bridge uranium atoms. Three are $P_2Se_6^{4-}$ anions in different bonding modes and the fourth is an asymmetric $Se_2^{2-}$ dianion. The compound may be written $Rb_4U_2(P_2Se_6)_{2.5}(Se_2)$ and is charge-balanced as a $U^{4+}$ compound.

## Introduction

The reactive flux method[1] has led to a vast array of interesting and unusual compounds. The application of this method to the actinides involving the use of polychalcogenide fluxes has been extensive.[2,3] The addition of phosphorus, either in elemental form or in combination with a chalcogen, has produced an array of chalcophosphates of thorium, uranium, neptunium, and plutonium of unexpected compositions and structures.[4–15] These complexes demonstrate the versatility that the chalcophosphate ligands have in their bonding modes.

Here we report the synthesis and structure of the new rubidium uranium selenophosphate compound $Rb_4U_2P_5Se_{17}$ that displays three different bonding modes to uranium of the $P_2Se_6^{2-}$ ligand in the same framework.

## Results and Discussion

Black crystals of the rubidium uranium selenophosphate $Rb_4U_2P_5Se_{17}$ were prepared in about 10 wt.-% yield by the solid-state reaction of uranium, $P_2Se_5$, and $Rb_2Se_3$ at 1023 K.

$Rb_4U_2P_5Se_{17}$ crystallizes with four formula units in the triclinic space group $P\bar{1}$. The asymmetric unit contains two crystallographically independent uranium, four rubidium, five phosphorus, and 17 selenium atoms, all in general positions.

The structure of $Rb_4U_2P_5Se_{17}$ displays four different types of bridging ligands. Three are $P_2Se_6^{4-}$ anions in different bonding modes and the fourth is an asymmetrically bound $Se_2^{2-}$

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dianion. The compound may be written $Rb_4U_2(P_2Se_6)_{2.5}(Se_2)$ and is charge-balanced as a $U^{4+}$ compound. The three bridging modes of the $P_2Se_6^{4-}$ ligand are shown in Figure 1. Mode A has one selenium per phosphorus atom bridging the uranium atoms and one selenium atom terminal on uranium. This bridging configuration is always accompanied by an asymmetrically bound $Se_2^{2-}$ ligand. The U1–U2 distance in this dimer is 4.376(1) Å. The second $P_2Se_6^{4-}$ bridging ligand (mode B) has two selenium atoms terminal on each uranium atom. The U1–U2 distance for this set of atoms is 5.793(1) Å. The final $P_2Se_6^{4-}$ ligand (mode C) bridges two sets of uranium dimers. The structure down the $a$ axis appears as ...U(mode A; $Se_2^{2-}$ ligand)U(mode B; mode C)U(mode A; $Se_2^{2-}$)... This infinite chain of uranium atoms is cross-linked via mode C to form a complicated three-dimensional network. The rubidium cations reside in the holes formed by mode C. A view of the unit cell approximately down the $b$ axis is shown in Figure 2.

There are two crystallographically independent uranium atoms in $Rb_4U_2P_5Se_{17}$. The arrangement around atom U1 may be viewed as a highly distorted capped square antiprism with atoms Se16, Se9, Se2, and Se13 making up one face and atoms Se5, Se6, Se14, and Se15 comprising the other. The second face is capped by atom Se1 (Figure 3) with a U1–Se1 distance of 2.8181(6) Å. The other U1–Se distances range from 2.9353(7) to 3.3422(7) Å. These may be compared to those for the nine-coordinate uranium atom in $\beta$-$USe_2$[16] of 2.850(4) to 3.250(3) Å. The arrangement about atom U2 can be viewed as a distorted bicapped trigonal bipyramid with atoms Se12, Se15, Se10 comprising one face and atoms Se11, Se9, and Se13 being the other face with capping atoms Se14 and Se10 (Figure 3). The U2–Se distances range from 2.8980(6) to 3.0396(7) Å. These may be compared to those for the eight-coordinate uranium atom in $USe_3$[17] of 2.896(1) to 2.967(1) Å The Se–Se bond length in $Rb_4U_2P_5Se_{17}$ is 2.353(1) Å, a normal Se–Se single bond. Selected interatomic distances are given in Table 1.
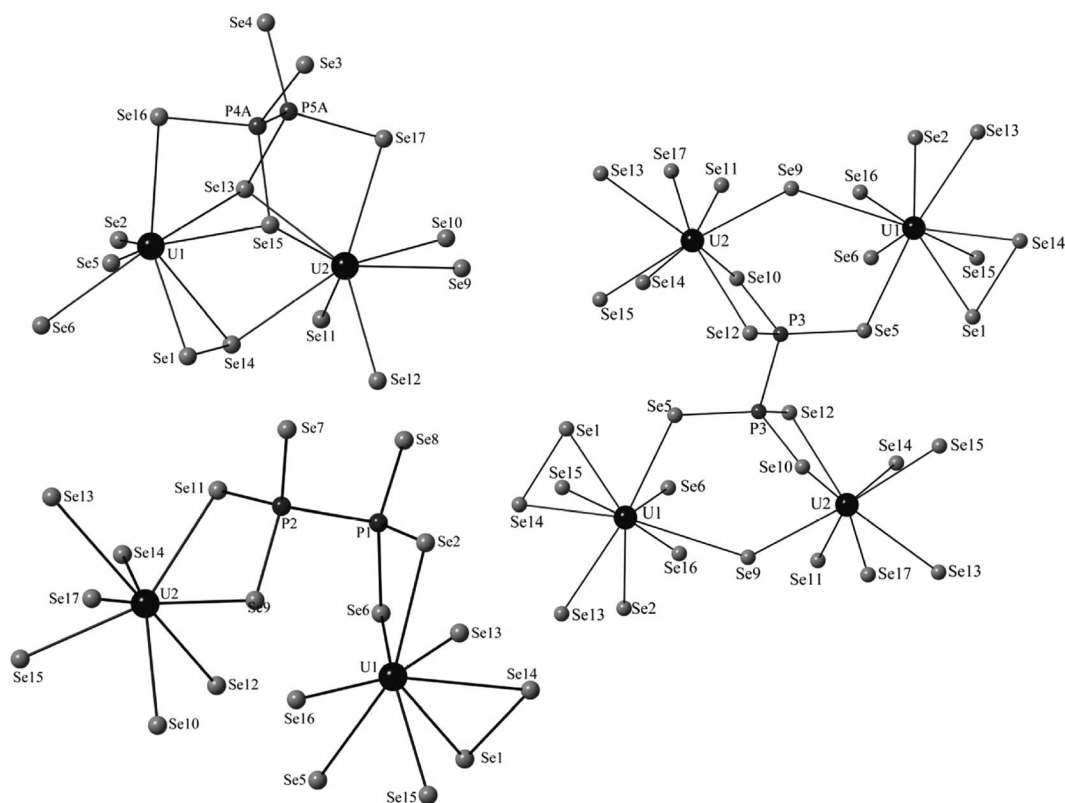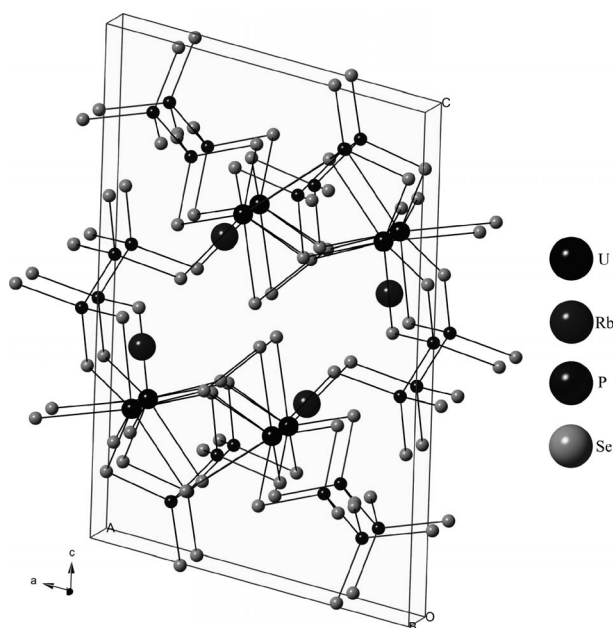
**Figure 1.** The ligand bridging modes in $Rb_4U_2P_5Se_{17}$.



**Figure 2.** A view approximately down *b* of the crystal structure of $Rb_4U_2P_5Se_{17}$.

The P–Se distances range from 2.116 (2) to 2.233(2) Å. These distances may be compared to those of 2.185(1) to 2.214(3) Å in the compounds $A_4P_2Se_6$ (A= Na, K).[18, 19] The three P–P bond lengths in $Rb_4U_2P_5Se_{17}$ of 2.206(3), 2.226(2), and 2.251(3) Å are consistent with those of 2.273(2) and 2.241(3) Å in the $A_4P_2Se_6$ compounds.

The structures of four other actinide selenophosphates have been reported, namely $Rb_4U_4P_4Se_{26}$,[7] $K_2ThP_3Se_9$,[8] $Rb_2ThP_3Se_9$,[8] and $Cs_2ThP_3Se_9$.[8] Although they share some features in common with the present compound, they differ in various respects. $Rb_4U_4P_4Se_{26}$ is described as a $U^{5+}$ compound that contains $PSe_4^{3-}$, $Se^{2-}$, and $Se_2^{2-}$ anions in a three-dimensional complex. The two crystallographically independent uranium atoms each display tricapped trigonal prismatic geometry. $K_2ThP_3Se_9$ and $Rb_2ThP_3Se_9$ are isostructural and contain tricapped trigonal prismatic $Th^{4+}$ atoms. Each contains $P_2Se_6^{4-}$ anions in the three bonding modes discussed above but no Se–Se bonds. $Cs_2ThP_3Se_9$ contains one eight-coordinate $Th^{4+}$ atom and one nine-coordinate $Th^{4+}$ atom. The structure comprises of infinite chains of $Th_2Se_{13}$ dimers linked by $P_2Se_6^{4-}$ anions. It contains a $Se_2^{2-}$ anion.

## Conclusions

The present compound $Rb_4U_2P_5Se_{17}$ augments the series of actinide chalcophosphates that have shown remarkable and diverse bonding patterns and complex three-dimensional structures. Among these, $Rb_4U_2P_5Se_{17}$ is unique in displaying three $P_2Se_6^{4-}$ anions in different bonding modes as well as an asymmetric $Se_2^{2-}$ dianion, all four of which bridge uranium atoms. The compound may be written $Rb_4U_2(P_2Se_6)_{2.5}(Se_2)$ and is charge-balanced as a $U^{4+}$ compound.

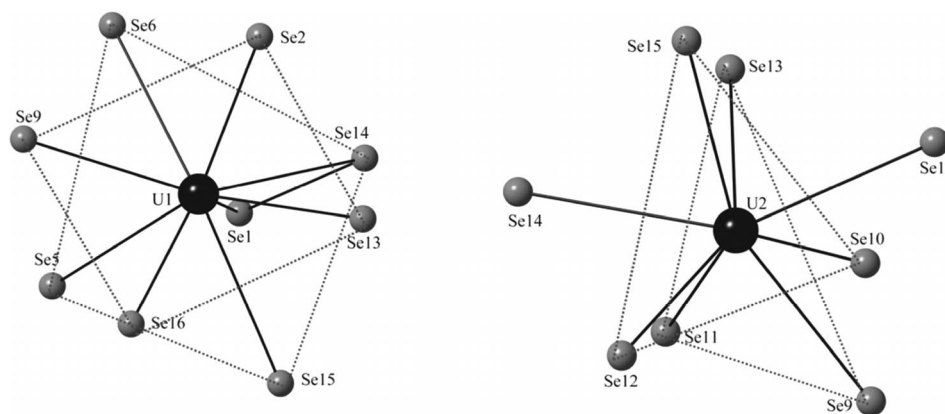**Figure 3.** View of the coordination environment about each uranium atom.

**Table 1.** Interatomic distances /Å in Rb4U2P5Se17.

| | | | |
|---|---|---|---|
| U1–Se1 | 2.8181(6) | U2–Se9 | 2.9517(7) |
| U1–Se2 | 2.9353(7) | U2–Se10 | 2.9574(7) |
| U1–Se14 | 2.9515(7) | U2–Se15 | 3.0030(7) |
| U1–Se16 | 2.9837(9) | U2–Se13 | 3.0105(6) |
| U1–Se6 | 3.0209(7) | U2–Se14 | 3.0396(7) |
| U1–Se5 | 3.0523(7) | P1–Se8 | 2.133(2) |
| U1–Se15 | 3.0792(7) | P1–P2 | 2.226(2) |
| U1–Se13 | 3.1247(7) | P3–P3 | 2.251(3) |
| U1–Se9 | 3.3422(7) | P4A–P5A | 2.206(3) |
| U2–Se12 | 2.8980(6) | U1–U2 | 4.376(1) |
| U2–Se11 | 2.9263(7) | U1–U2 | 5.793(1) |
| U2–Se17 | 2.9348(8) | Se1–Se14 | 2.3527(9) |

## Experimental Section

Uranium powder (25 mg, 0.105 mmol), $P_2Se_5$ (96 mg, 0.210 mmol), and $Rb_2Se_3$ (86 mg, 0.210 mmol) were combined in a carbon-coated fused-silica tube in an argon-filled glove box and flame sealed at $10^{-4}$ Torr. The tube was placed in a computer-controlled furnace and heated to 1023 K in 24 h, maintained there for 100 h, cooled at 5 K·h$^{-1}$ to 426 K, and then the furnace was turned off. The reaction produced about a 10 wt.-% yield of black Rb4U2P5Se17 crystals along with amorphous products. The crystals were separated manually from the reaction mixture and surface impurities were removed in oil. These crystals are air and moisture sensitive, but they remain stable for more than a year under heavy mineral oil.

EDS analysis on several single crystals using an Hitachi S-3400 SEM provided an approximate atomic ratio of 4:2:5:17 for Rb:U:P:Se respectfully.

Single-crystal X-ray diffraction data for Rb4U2P5Se17 were collected with the use of graphite-monochromatized Cu-$K_\alpha$ radiation at 100 K with a Bruker APEX2 diffractometer.[20] The crystal-to-detector distance was 4 cm. An algorithm in COSMO[20] comprising several $\phi$ and $\omega$ scans was used. Crystal decay was monitored by recollecting a 360° $\phi$ scan at the beginning and end of the data collection; there was no decay. The exposure time was 10 sec/frame. Cell refinement and data reduction were carried out with the use of the program APEX2.[20] A Leitz microscope equipped with a calibrated traveling micrometer eyepiece was employed to measure accurately the crystal dimensions. Face-indexed absorption corrections were performed with the use of the program XPREP.[21]

The structure was solved using direct-methods in the SHELXS program and refined with the least-squares SHELXL program.[21] The structure refined well to values of $R_1$ and $wR(F^2)$ of 0.0399 and 0.1143, respectively. However, there was some residual electron density in the vicinity of atoms P4A, P5A, Se16, and Se17; these comprise a "cap". These atoms were divided into parts 1 (P4A, P5A, Se16, Se17) and 2 (P4B, P5B, Se26, and Se27) and a free variable $q$ was assigned so that the occupancies of the atoms in part 1 were $q$ and those of the atoms in part 2 were $1–q$. The atoms in part 2 were restricted to isotropic displacements. The ensuing refinement converged to $R_1$ and $wR(F^2)$ values of 0.0273 and 0.0660, respectively, and to a value of $q$ of 0.858(4). The atoms in part 2, the minor component, are rotated from the atoms in part 1, the major component, by approximately 30° (Figure 4). The STRUCTURE TIDY program[22] in PLATON[23] was employed to standardize the positional parameters. Additional experimental details are given in Table 2 and in the CIF file, which has been deposited.[24]
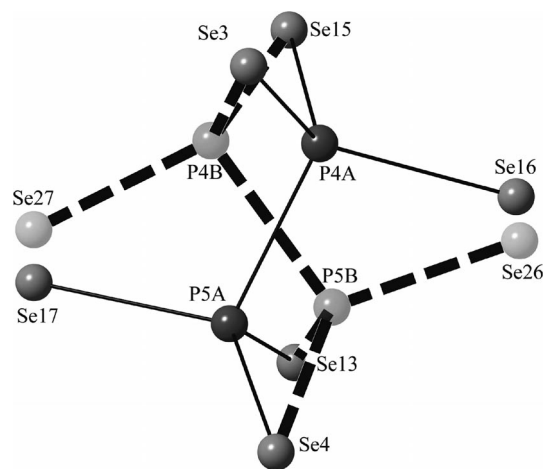


**Figure 4.** A sketch of the major (A) and minor (B) components of the disordered P4, P5, Se16, and Se17 cap.

## Acknowledgment

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**Table 2.** Crystallographic data and structure refinement for $Rb_4U_2P_5Se_{17}$.

| | |
|---|---|
| Temperature /K | 100 |
| Space group, Z | $P\bar{1}$, 4 |
| Formula mass | 1157.55 |
| Lattice constants /Å, deg | $a = 10.0824(2)$ |
| | $b = 10.6095(2)$ |
| | $c = 15.7845(3)$ |
| | $\alpha = 84.678(1)$ |
| | $\beta = 76.125(1)$ |
| | $\gamma = 85.874(1)$ |
| Volume /Å$^3$ | 1629.96(5) |
| Density (calculated) /g cm$^{-3}$ | 4.717 |
| Crystal size /mm | $0.23 \times 0.10 \times 0.01$ |
| Diffractometer | Bruker APEX2 CCD |
| X-ray radiation, $\lambda$ /Å | Cu-$K_\alpha$, 1.54178 |
| Monochromator | graphite |
| Absorption coefficient $\mu$ /mm$^{-1}$ | 59.032 |
| Index range | $-11 \leq h \leq 11$ |
| | $-12 \leq k \leq 12$ |
| | $-13 \leq l \leq 18$ |
| Independent reflections | 5511 |
| Transmission $t_{min}$, $t_{max}$ | 0.0264, 0.6186 |
| No. of parameters | 270 |
| $R_1[F^2 > 2\sigma(F^2)]$, $wR(F^2)$ | 0.0273, 0.0660 |
| $\Delta\rho_{min}$, $\Delta\rho_{max}$ /e·Å$^{-3}$ | $-1.26$, 1.71 |

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[24] The crystallographic file in CIF format for $Rb_4U_2P_5Se_{17}$ has been deposited with FIZ Karlsruhe as CSD number 424894. It may be obtained free of charge by contacting FIZ Karlsruhe at +49-7247-808-666 (Fax:) or crysdata@fiz-karlsruhe.de.

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