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$Ag_5U(PS_4)_3$: A Transition-Metal Actinide Phosphochalcogenide

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ABSTRACT: The structure of $Ag_5U(PS_4)_3$ is unique as in the literature there are no other structures of the type MAnPQ (M = transition metal, An = actinide, Q = S, Se, or Te). The compound has been synthesized at 1123 K by standard solid-state methods and its single-crystal X-ray structure has been determined at 100(2) K. $Ag_5U(PS_4)_3$ crystallizes in a remarkable new structure type in space group $P3_221$ of the trigonal system with three formula units in a hexagonal cell of dimensions $a = b = 9.6635(2)$ Å, $c = 17.1834(4)$ Å, and $\gamma = 120°$. In the structure each U atom is coordinated to eight S atoms in a bicapped trigonal prismatic manner. Each P atom is tetrahedrally coordinated to four S atoms. Two of the three unique Ag atoms are connected to four S atoms in a distorted tetrahedral manner whereas the third unique Ag atom forms a Ag_2S_6 species. The overall structure consists of U polyhedra connected to each other via PS_4 tetrahedra through edge-sharing in a zig-zag fashion along the *c* axis to form infinite layers. PS_4 groups and the Ag atoms pack these layers.

From DFT calculations $Ag_5U(PS_4)_3$ is found to have finite spin polarization in the crystal cell: the magnetic moments of two of the U atoms are parallel, whereas the magnetic moment of the third U atom is antiparallel.

INTRODUCTION

The search for new actinide chalcogenides (An = Th, U, Np; Q = S, Se, Te) has been widely conducted through the use of solid-state methods involving a flux method or direct combination of elements.[1-5] The phosphochalcogens offer structural flexibility that often leads to a variety of exciting new structures. The greater diversity of stoichiometries among the phosphochalcogens arises from their ability to form Q−Q bonds that leads to polymeric substructures such as PQ_3, P_2Q_6, P_2Q_{10}, P_4Q_{13}, P_6Q_{12}, and PQ_6.[6-10] Known phosphosulfides include ternaries such as $UP_{1-x}S_x$,[11] UPS,[12] ThP_2S_6,[13] UP_2S_6,[14] $U(P_2S_6)_2$,[14] UP_2S_7,[14, 15] UP_2S_9,[15] and $U_3(PS_4)_4$;[14] quaternaries such as $A_{11}U_7(PS_4)_{13}$ (A = K, Rb),[16] $CsLiU(PS_4)_2$,[17] $Cs_8U_5(P_3S_{10})_2(PS_4)_6$,[8] $A_5An(PS_4)_3$ (A = K, Rb, Cs; An = U, Th),[8] $AkAn(PS_4)_2$ (Ak = Sr, Ba; An = Th, U),[18] and $Cs_4Th_2P_6S_{18}$;[19] and the quintaries or greater such as $A_6U_3Sb_2P_8S_{32}$,[20] $Cs_5Na_6[U(PS_4)_4](PS_4)$,[21] $Rb_5Na_3[U(PS_4)_4]$,[21] $CsNa[U(PS_4)_2]$,[21] $Cs_{1.67}Na_{0.52}I_{0.19}[U(PS_4)_2]$,[21] $Cs_{1.033}Na_{1.343}I_{0.376}[U(PS_4)_2]$,[21] and $Rb_{1.35}Na_{0.93}I_{0.28}[U(PS_4)_2]$.[21] But there are also examples of phosphoselenides and less so of phosphotellurides. These include AnPSe (An = U, Th),[22, 23] $K_2U(P_3Se_9)$,[24] $Rb_4U_2(P_2Se_6)_{2.5}(Se_2)$,[25] $Cs_2An_2(P_2Se_9)(Se_2)_2$ (An = U, Th),[26, 27] $Rb_7Th_2(PSe_4)_3(P_2Se_6)_{1.5}$,[19] $A_2Th(P_3Se_9)$ (A = K, Rb),[28] $Cs_4Th_2P_5Se_{17}$[28] for the selenides and only AnPTe (An = U, Th) for tellurides.[29]

In the present paper, we report the synthesis, crystal structure, and electronic structure of the compound $Ag_5U(PS_4)_3$. Its structure is the first example of an actinide transition-metal phosphochalcogenide.

EXPERIMENTAL METHODS

Synthesis and Analyses. ***Caution!*** *Depleted U is an α-emitting radioisotope and as such is considered a health risk. Experiments using radioisotopes require appropriate infrastructure and personnel trained in the handling of radioactive materials.*

The following reactants were used as supplied: Ba (Johnson Matthey, 99.5%), P_2S_5 (Aldrich, 99%), S (Mallinckrodt 99.6%), and Ag (Aldrich, 99.99%). Depleted U powder was obtained after hydridization of U chips (IBI Laboratories) in a modification[30] of previous procedure.[31]

Synthesis of $Ag_5U(PS_4)_3$. In attempts to prepare a possible quintary compound containing Ba, Ag, U, P, and S black blocks what turned out to be $Ag_5U(PS_4)_3$ were obtained in a reaction of U (20.23 mg, 0.085 mmol), Ag (18.32 mg, 0.17 mmol), Ba (35.01 mg, 0.255 mmol), P_2S_5 (56.61 mg, 0.255 mmol), and S (16.35 mg, 0.510 mmol). The reactants were weighed and transferred into a 6 mm carbon-coated fused-silica tube inside an Ar-filled dry box. The silica tube containing the mixture was then evacuated to 10^{-4} Torr, flame sealed, and heated to 1123 K in a computer-controlled furnace, held at that temperature for 96 h, and then cooled at a rate of 2.5 Kh^{-1} to 673 K, and finally the furnace was turned off. The reaction produced single-crystal black blocks of different sizes. Semi-quantitative analyses of these were obtained via EDX with the use of a Hitachi S-3400 SEM. Small blocks of a size suitable for single-crystal structure determination showed a composition Ag:U:P:S ≈ 5:1:3:12. Some of the larger crystals analyzed consistent with UP_2S_6.[14]

Structure Determination. Single-crystal X-Ray diffraction data for $Ag_5U(PS_4)_3$ were collected at 100(2) K using a Bruker APEX2 Kappa diffractometer equipped with the Cu$K\alpha$ (λ = 1.54178 Å) radiation. By the use of the algorithm COSMO in APEX2[32] the data collection comprised a combination of ω and φ scans with steps of 0.3° and counting time of 10 s/frame. Recorded data were indexed, refined, and integrated by SAINT in the APEX2 package.[32] The crystal-to-detector-distance was 40 mm. Face-indexed absorption, incident beam, and decay corrections were performed with the use of the program SADABS.[33] Precession images constructed from the data set showed no indication of super cells or modulation. The structure was difficult to solve. Ultimately, the program XT[34] provided a solution that could be refined with the use of programs in the SHELXTL 2014 package.[33, 35] The asymmetric unit contains one U, three Ag, two P, and 6 S atoms, with atoms U1 and P2 having .2. symmetry. The anisotropic refinement of the atoms suggests some disorder in the Ag2 atoms. The occupancy of the Ag1 site was not constrained by symmetry and ultimately refined to 0.503(3). Consequently, this occupancy was set to 0.5 to give the formula $Ag_5UP_3S_{12}$, which is consistent with the EDX results. Further details are provided in Table 1and in Supporting Information.

Theoretical Calculations. These have been conducted with density functional theory[36, 37] using the projector augmented wave method[38] as implemented in the VASP (Vienna ab Initio Simulation Package)[39, 40] code. The generalized gradient approximation of Perdew, Burke and Ernzerhof[41] in its spin polarized version was used as the exchange and correlation potential. The parameters of the cell and the positions of the atoms were taken from the experiment, but because the experimental structure contains one Ag site that is half occupied we have created several models consistent with the chemical formula $Ag_{15}U_3P_9S_{36}$ in the following way: all the equivalent positions of this site were generated and then models were produced after populating half the Ag1 atoms while keeping the remaining unoccupied. This can be done in different ways, and we have retained the one with the lowest total energy for our analysis. The criterion for the convergence of the total energy was set to 10^{-6} eV To obtain a sufficient convergence, a 2 × 2 × 1 mesh was used for the Brillouin zone. The default value was used for the cut-off of the plane wave part of the wave function.

RESULTS

Synthesis. The reaction of Ba, Ag, U, P_2S_5, and S at 1123 K resulted in the formation of black blocks of $Ag_5U(PS_4)_3$ in a yield of about 50 wt% yield based on the U content. Side products included UP_2S_6 and BaS. The isolated crystals of $Ag_5U(PS_4)_3$ were stable in oil for a few weeks. Unfortunately, by the time we knew the composition and the nature of the structure, the isolated crystals had decomposed.

Structure. A search of the ICSD data base failed to reveal any structures of the type MAnPQ (M = transition metal, An = actinide, Q = S, Se, or Te); however, it did display the isostructural compounds $AgLn(P_2Se_6)$ (Ln = rare earth = Sc, Er, Tm).[42] The structure of these isostructural compounds is layered and very different from that of $Ag_5U(PS_4)_3$. $Ag_5U(PS_4)_3$ crystallizes in a remarkable new structure type in space group $P3_221$ of the trigonal system with three formula units in a hexagonal cell of dimensions $a = b = 9.6635(2)$ Å, $c = 17.1834(4)$ Å, and $\gamma = 120°$. The asymmetric unit contains one U, three Ag, two P, and six S atoms. All are in general positions except atoms U1 and P2, which have .2. site symmetry.

A projection down the [110] direction of the $Ag_5U(PS_4)_3$ crystal structure is shown in Figure 1. Each U1 atom is coordinated to eight S atoms in a bicapped trigonal prismatic manner.

Each P atom is tetrahedrally coordinated to four S atoms. Each of the Ag1 and Ag3 atoms is connected to four S atoms in a distorted tetrahedral manner. In contrast, the Ag2 atoms exhibit a Ag2−Ag2 short distance of 2.774(5) Å and form a Ag_2S_6 species. The Ag–S network is presented in Figure 2. The overall structure consists of U polyhedra connected to each other via $P2S_4$ tetrahedra through edge-sharing in a zig-zag fashion along the *c* axis to form infinite layers. The $P1S_4$ and the Ag atoms pack these layers.

The U1–S distances in the structure of $Ag_5U(PS_4)_3$ range from 2.784(5) to 2.851(5) Å, these values are typical for U^{4+} coordinated to eight S atoms, as in the structures of $K_5U(PS_4)_3$[8] (2.802(2) to 3.021(2) Å); $CsLiU(PS_4)_2$[17] (2.768(1) to 2.884(1) Å); $K_{11}U_7(PS_4)_{13}$[16] (2.772(4) to 2.942(4) Å); $Ba_2U(S_2)_2S_2$[43] (2.7337(2) to 2.8199(7) Å); $K_{0.92}U_{1.79}S_6$[44] (2.761(2) to 2.846(2) Å); $Rb_{0.85}U_{1.74}S_6$[45] (2.775(3) to 2.847(2) Å); and $RbSbU_2S_8$[46] (2.752(3) to 2.854(1) Å). The Ag–S distances in the structure of $Ag_5U(PS_4)_3$ range from 2.429(6) to 2.917(6) Å. These distances may be compared with those in structures having Ag^+ in similar coordination as in $Ba_9Ag_{10}U_4S_{24}$[47] (2.526(2) to 2.852(4) Å); Ag_2CdGeS_4[48] (2.522(1) to 2.570(1) Å); $CsAgSb_4S_7$[49] (2.502(1) to 2.864(1) Å); $KAg(SCN)_2$[50] (2.577(6) to2.7262(5) Å); and $La_4Ag_2In_4S_{13}$[51] (2.659(1) to 2.933(1) Å). The P–S distances in the structure of $Ag_5U(PS_4)_3$ range from 2.008(7) to 2.064(7) Å. These are typical for P^{5+} in tetrahedral coordination as in the structures of $K_5U(PS_4)_3)$[8] (2.005(2) to 2.083(2) Å); $CsLiU(PS_4)_2$[17] (2.024(2) to 2.047(2) Å); and $SrU(PS_4)_2$ and $BaU(PS_4)_2$ with the values of 2.000(1) to 2.063(1) Å and 1.996(2) to 2.059(2) Å, respectively.[18]

The Ag2−Ag2 short distance of 2.774(5) Å is not atypical, as there are many examples in the CCDC database. Two examples are 2.772 Å in $[Ag_2(obpy)_2]_2{\cdot}14.5\ H_2O$[52], where obpy =2,2'bipyridinyl-6-one and 2.773 Å in $Ag_2C_2{\cdot}2AgCF_3CO_2{\cdot}2Ag_2PhPO_3{\cdot}Ag_3[(PhPO_3)_2H]$[53].

The crystal structure of the $Ag_5U(PS_4)_3$ has no S–S short distances and thus the assignment of formal oxidation states is straightforward: 5 × Ag^+, 1 × U^{4+}, 3 × P^{5+}, 12 × S^{2-}.

DFT Calculations. $Ag_5U(PS_4)_3$ is found to have finite spin polarization in the crystal cell: the magnetic moments of two of the U atoms are parallel, whereas the magnetic moment of the third U atom is antiparallel. This is seen in Figure 3 where the total density of states (top plot) is asymmetric with respect to spin. The partial density of states for each inequivalent atom in the cell is also presented in Figure 3. Most of the magnetic moment is carried by the U atoms which induces a small magnetization on the neighboring atoms. Also, the states at the Fermi level mostly arise from the U.

CONCLUSIONS

$Ag_5U(PS_4)_3$ has a unique structure as there appear to be no other known structures of the type MAnPQ (M = transition metal, An = actinide, Q = S, Se, or Te). $Ag_5U(PS_4)_3$ crystallizes in a remarkable new structure type in space group $P3_221$ of the trigonal system with three formula units in a hexagonal cell of dimensions $a = b =$ 9.6635(2) Å, c = 17.1834(4) Å, and γ = 120°. The asymmetric unit contains one U, three Ag, two P, and six S atoms. All are in general positions except atoms U1 and P2, which have .2. site symmetry. In the structure each U atom is coordinated to eight S atoms in a bicapped trigonal prismatic manner. Each P atom is tetrahedrally coordinated to four S atoms. Two of the three unique Ag atoms are connected to four S atoms in a distorted tetrahedral manner whereas the third Ag atom forms a Ag_2S_6 species. The overall structure consists of U polyhedra connected to each other via PS_4 tetrahedra through edge-sharing in a zig-zag fashion along the c axis to form infinite layers. PS_4 groups and the Ag atoms pack these layers. The crystal structure of the $Ag_5U(PS_4)_3$ has no S–S short distances and thus the assignment of formal oxidation states is straightforward: 5 × Ag^+, 1 × U^{4+}, 3 × P^{5+}, 12 × S^{2-}.

From DFT calculations $Ag_5U(PS_4)_3$ is found to have finite spin polarization in the crystal cell: the magnetic moments of two of the U atoms are parallel, whereas the magnetic moment of the third U atom is antiparallel.

ASSOCIATED CONTENT

Supporting Information

The crystallographic CIF file for $Ag_5U(PS_4)_3$ has been deposited with CCDC (https://www.ccdc.cam.ac.uk) as entry CCDC1866631.

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Notes

The authors declare no competing financial interest.

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Table 1. Crystallographic Data and Structure Refinement Details for $Ag_5U(PS_4)_3$.

Compound	$Ag_5U(PS_4)_3$
Space group	$P3_221$
fw ($g.mol^{-1}$)	1255.01
a (Å)	9.6635(2)
c (Å)	17.1834(4)
V ($Å^3$)	1389.66(7)
Z	3
T (K)	100(2)
λ (Å)	1.54178
ρ ($g\ cm^{-3}$)	4.499
μ (mm^{-1})	80.8
$R(F)$[b]	0.04
$R_w(F_o^2)$[c]	0.12

[b] $R(F) = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ for $F_o^2 > 2\sigma(F_o^2)$.

[c] $R_w(F_o^2) = \{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma wF_o^4\}^{1/2}$. For $F_o^2 < 0$, $w^{-1} = \sigma^2(F_o^2)$; for $F_o^2 \geq 0$, $w^{-1} = \sigma^2(F_o^2) + (qF_o^2)^2$ where $q = 0.0321$.

Table 2. Interatomic Lengths (Å) in $Ag_5U(PS_4)_3$.

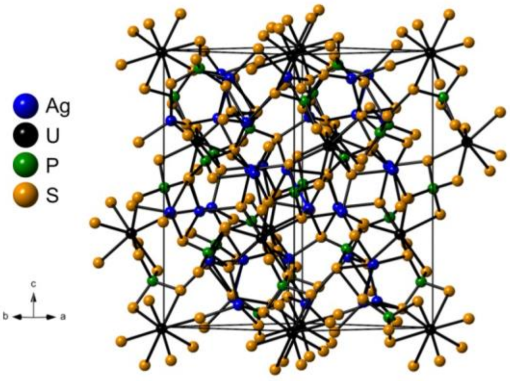
Atom–Atom	Distance (Å)	Atom–Atom	Distance (Å)
U1–S4	2 × 2.784(5)	Ag3–S6	2.510(6)
U1–S3	2 × 2.786(5)	Ag3–S5	2.595(5)
U1–S2	2 × 2.830(5)	Ag3–S4	2.602(7)
U1–S5	2 × 2.851(5)	Ag3–S1	2.917(6)
		Ag3–Ag3	3.341(6)
Ag1–S6	2.429(6)		
Ag1–S4	2.430(6)	P1–S1	2.008(7)
Ag1–S3	2.540(5)	P1–S3	2.037(7)
Ag1–S2	2.562(6)	P1–S6	2.062(7)
Ag1–Ag2	3.017(4)	P1–S4	2.064(7)
Ag2–S6	2.590(6)	P2–S5	2 × 2.032(6)
Ag2–S2	2.597(6)	P2–S2	2 × 2.056(6)
Ag2–S1	2.681(6)		
Ag2–S1	2.799(7)		
Ag2–Ag2	2.774(5)		

Figure Legends

Figure 1. A projection down the [110] direction of the $Ag_5U(PS_4)_3$ crystal structure.

Figure 2. The Ag−S network of the $Ag_5U(PS_4)_3$ crystal structure.

Figure 3. Total (upper plot) and partial density of states (lower plots) of $Ag_5U(PS_4)_3$.



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TOCLegend. A projection down the [110] direction of the $Ag_5U(PS_4)_3$ cryst