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# $Rb_4Sn_2Ag_4(P_2Se_6)_3$: First Example of a Quinary Selenophosphate and an Unusual Sn−Ag $s^2$−$d^{10}$ Interaction

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In order to study the class of chalcophosphate compounds, we have developed the molten polychalcophosphate flux technique, the advantages of which are now well documented.[1−4] Many unusual compounds containing main group metals,[2] transition metals,[3] lanthanides, and actinides[4,5] have been discovered which demonstrably attest to the broad synthetic scope of this technique. The next question to be asked is how to access increasingly complex multinary phases, particularly those with more than one kind of metal in the framework, which are likely to feature new and novel characteristics. The flux method is well suited for such exploratory work because it could allow a complex reaction system to equilibrate at relatively low temperature, favoring kinetically stable phases. This twist for complexity tests the limits of the flux method in terms of its ability to deliver higher order multinary compounds, since the potential problem of phase separation has to be overcome. Both tin and silver have displayed a very fertile structural chemistry[1,2c,3a] and so we chose them in our attempts to increase complexity by introducing two different metals into the flux. Thus we obtained the first quinary selenophosphate: $Rb_4Sn_2Ag_4P_6Se_{18}$. In addition to its unique structure, an unforeseen feature of this new compound is the unusual $s^2$−$d^{10}$ interaction between Sn and Ag.

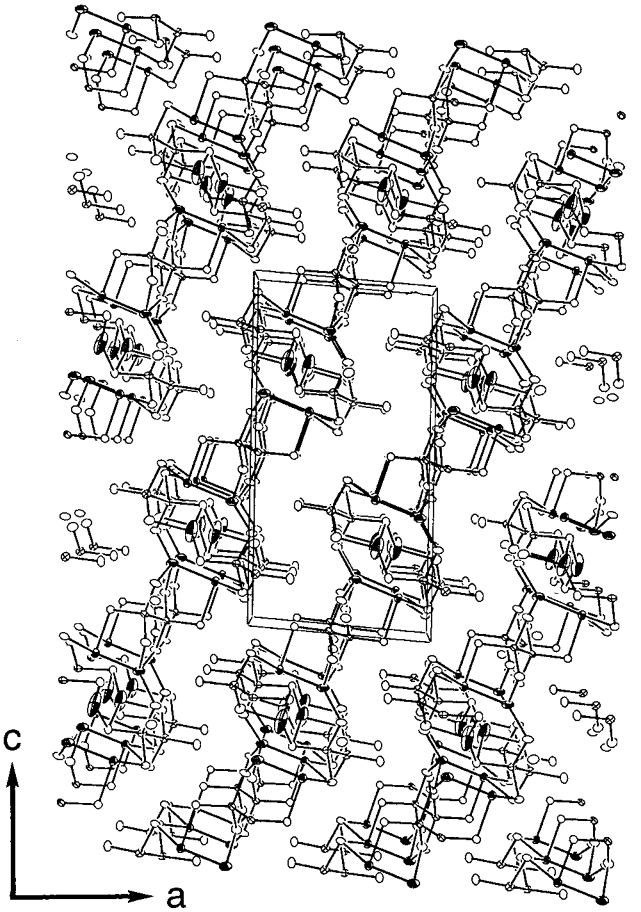

**Figure 1.** ORTEP representation of the unit cell of $Rb_4Sn_2Ag_4P_6Se_{18}$ viewed down the *b*-axis. $Rb^+$ cations have been omitted for clarity. Tin and silver atoms are shown as octant-shaped ellipses, selenium as open ellipses, and phosphorus as crossed ellipses with no shading (90% thermal ellipsoids).

$Rb_4Sn_2Ag_4P_6Se_{18}$[6] is an unusual two-dimensional compound with formally $Sn^{2+}$ and $Ag^+$ atoms held together by $[P_2Se_6]^{4-}$ units. The $[Sn_2Ag_4(P_2Se_6)_3]_n^{4n-}$ layers are separated by seven-coordinate $Rb^+$ cations [range of Rb−Se distances, 3.425(3)-3.845(3) Å; average 3.624 Å], see Figure 1. The layers form a perforated network which contains rings made of 8 $[P_2Se_6]^{4-}$ groups, 12 Ag atoms, and 6 Sn atoms (ring dimensions: 9.0 × 3.8 Å), Figure 2A. These layers stagger by being offset along the [1 0 1] direction by a 1/2 translation so that the rings do not form channels. Each layer consists of $[Sn_2Ag_4(P_2Se_6)_2]_x$ "chains" which propagate along the [0 1 0] direction, Figure 2A. These "chains" contain infinite zigzag $(AgSe_3)_x$ strands which consist of corner-sharing Ag(1) trigonal planes. The $(AgSe_3)_x$ fragments

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(6) (a) $Rb_4Sn_2Ag_4(P_2Se_6)_3$ was synthesized from a mixture of Sn (0.60 mmol), Ag (0.30 mmol), $P_2Se_5$ (0.60 mmol), $Rb_2Se$ (0.30 mmol), and Se (3.00 mmol) which was sealed under vacuum in a Pyrex tube and heated to 515 °C for 4 days, followed by cooling to 150 °C at 4 °C $h^{-1}$. The excess $Rb_xP_ySe_z$ flux was removed with degassed DMF, and the product was washed with tri-*n*-butylphosphine to remove elemental Se, to give black hexagonal crystals of $Ag_2SnP_3Se_9$ (∼50% yield)[7] and red irregular-shaped crystals of $Rb_4Sn_2Ag_4(P_2Se_6)_3$ (∼50%). The latter are air- and water-stable. Semiquantitative microprobe analysis on single crystals gave $Rb_{3.9}Sn_{2.0}Ag_4P_{6.1}Se_{18}$. (b) Data were collected with a Rigaku AFC6S diffractometer using Mo Kα ($\lambda = 0.710\ 69$ Å) radiation from a crystal of 0.924 × 0.112 × 0.084 mm dimensions in an $\omega-2\theta$ scan mode. The structure was solved with SHELXS-86[8a] and refined with full-matrix least-squares techniques using TEXSAN.[8b] Crystal data at −125 °C: $a = 11.189(2)$ Å, $b = 7.688(2)$ Å, $c = 21.850(3)$ Å, $\beta = 94.31(1)°$, $V = 1874.2(5)$ Å$^3$, $Z = 2$, $D_c = 4.639$ g cm$^{-3}$, space group $P2_1/n$ (No. 14), $\mu$(Mo Kα) = 262.50 cm$^{-1}$, $2\theta_{max} = 50.0°$, octants collected $0 < h < 13$, $0 < k < 9$, $-26 < l < 26$; total data, 3774; unique data, 3579 ($R_{int} = 0.068$); data with $F_o^2 > 3\sigma(F_o^2)$, 1930. Number of variables: 154. An empirical absorption correction based on $\psi$ scans was applied to the data; all atoms were refined anisotropically. $R/R_w = 0.041/0.038$.

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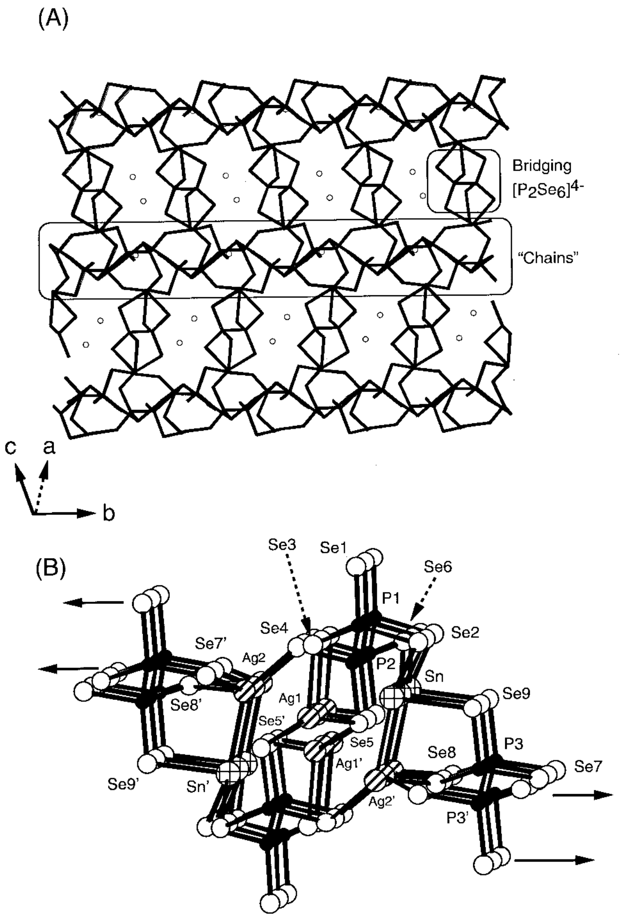


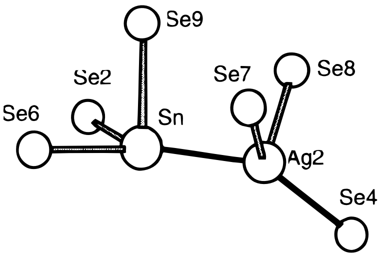
**Figure 2.** (A) View perpendicular to a single $[Sn_2Ag_4P_6Se_{18}]_n^{4n-}$ layer showing the rings (stick model). (B) A section of the layer with labeling. Solid arrows indicate connectivity to the rest of the layer. Selected distances (Å) are as follows: Sn−Se(2) 2.866(2), average Sn−Se 2.74(5), average Ag(1)−Se 2.61(3), average Ag(2)−Se 2.64(4), P(1)−Se(1) 2.132(6), P(1)−Se(2) 2.247(6), P(1)−Se(3) 2.176(6), similar distances exist for the rest of the P−Se bonds, P(1)−P(2) 2.269(7), P(3)−P(3) 2.26(1). Selected angles (deg) are as follows: Se(2)−Sn−Se(6) 90.55(7), Se(2)−Sn−Se(9) 81.35(7), Se(2)−Sn−Ag(2′) 134.87(9), Se(3)−Ag(1)−Se(5) 104.29(9), Se(3)−Ag(1)−Se(5′) 102.7(1), Se(4)−Ag(2)−Se(7′) 127.0(1), Se(4)−Ag(2)−Se(8′) 97.04(9), Se(7′)−Ag(2)−Se(8′) 101.97(8), Se(4)−Ag(2)−Sn′ 135.09(9), Se(1)−P(1)−Se(2) 112.9(2), Se(1)−P(1)−Se(3) 115.8(3), Se(1)−P(1)−P(2) 107.3(3), similar angles exist around P(2) and P(3).

are capped by pentadentate $[P_2Se_6]^{4-}$ groups [P(1)−P(2)] which also bind to the $Ag(2)^+$ and $Sn^{2+}$ cations to form the $[Sn_2Ag_4(P_2Se_6)_2]_x$ "chains", Figure 2B. These "chains" are connected along the [0 0 1] direction by bridging $[P_2Se_6]^{4-}$ groups [P(3)−P′(3)] to form the layer, Figure 2A.

A unique feature of the structure is the presence of $Sn^{2+}-Ag^+$ interactions involving Sn and Ag(2) [2.866(2) Å], Chart 1. Both metal ions have a closed shell yielding an $s^2-d^{10}$ interaction[9] (sum of van der Waals radii: 3.90 Å).

The coordination of Sn resembles a trigonal bipyramid which is missing an empty axial position. Assuming that the lone pair is stereochemically active, it would occupy the empty axial position to form a trigonal bipyramid (tpb). Tpb geometry has been observed for several four-coordinate $Sn^{2+}$ compounds.[10] On the other hand, the lone pair could also be used as a donor to Ag,

**Chart 1**



as is the case for $SnCl_3^-$ in compounds with a Sn−M bond.[11] The bonding nature of this interaction is also supported from the following observations: (a) The Sn−Ag bond [2.866(2) Å] is only slightly longer than the Sn−Se bonds [average 2.74(4) Å]; (b) the coordination of Ag(2) significantly deviates from trigonal planar, and it can better be described as tetrahedral with a corner occupied by Sn. To our knowledge, there are no other compounds with a Sn−Ag interaction. In fact, $s^2-d^{10}$ interactions have been attributed to relativistic effects.[12,13] They are rare, with those observed in $AuTl[Ph_2P(CH_2)S]_2$[12,13] and $Au_2Pb[Ph_2P(CH_2)S]_4$[13] being exemplary. Atom Ag(1) is in a trigonal planar coordination and has a relatively high thermal parameter; see Supporting Information. This is a common feature in silver-containing and other $d^{10}$ selenophosphates and has been attributed to anharmonic thermal vibrations of these atoms.[3a,14] Selected distances and angles are given in the Figure 2 caption.

Single-crystal optical transmission spectroscopy shows a sharp optical gap of 2.15 eV. The infrared spectrum displays absorptions at ca. 500, 474, 462, 439, 430, 298, 190, 175, and ∼166 $cm^{-1}$. The peaks at ca. 500, 474, and 462 $cm^{-1}$ can be attributed to $PSe_3$ stretching modes, whereas the one at 298 $cm^{-1}$ can be attributed to an out-of-phase $PSe_3$ mode.[3a,c] The absorptions below 200 $cm^{-1}$ are most probably due to M−Se vibrations.[3] By differential thermal analysis (DTA) $Rb_4Sn_2Ag_4P_6Se_{18}$ melts congruently at ca. 568 °C.

The synthesis of a quinary selenophosphate has been achieved in a polyselenophosphate $A_x[P_ySe_z]$ flux. As the level of complexity in a flux reaction system goes up, by introducing different kinds of metals, the risk of phase separation and formation of mixtures also increases. The successful outcome reported here may be due to various factors, the most intriguing one being the ability of Sn and Ag to associate via $s^2-d^{10}$ bonding. This is apparently enough to hold the two elements in the crystal and avoid the alternative of forming a mixture of Rb/Sn/P/Se and Rb/Ag/P/Se phases. The unexpected observation of this Sn−Ag interaction suggests that new chemistry can be learned by exploring selenophosphates with more complex compositions.

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**Supporting Information Available:** Table of crystallographic details, fractional atomic coordinates, anisotropic and isotropic thermal parameters, and interatomic distances and angles (25 pages). Ordering information is given on any current masthead page.

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