K₄In₂(PSe₅)₂(P₂Se₆) and Rb₃Sn(PSe₅)(P₂Se₆): One-Dimensional Compounds with Mixed Selenophosphate Anions

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INTRODUCTION

Recent exploratory synthesis with the polychalcophosphate fluxes has yielded many novel quaternary thiophosphate and selenophosphate compounds (1). Many unusual compounds containing main group (2), transition metals (3), lanthanides, and actinides (2e, 2f, 4) have been reported. The basic building elements in these compounds are the negatively charged [P₅Qₓ]ⁿ⁻ (Q = S, Se) chalcophosphate units, which bind to the metal ions in an astonishing number of ways, forming extended covalent framework structures. The frameworks then incorporate alkali metal counterions according to their charge balancing needs. The great number of different [P₅Qₓ]ⁿ⁻ building blocks, along with their impressive bonding versatility, creates many possibilities for new structure types and compositions, most of which are unanticipated. The other important building block, the metal ion, also plays an important role in the stabilization of a specific structure, but this role is not fully understood yet. For example, in K₄Ru₅P₅Se₁₀ we observe a protagonistic role for the metal (Ru) in determining ligand formation and selection according to its coordination chemistry needs (3e). Herein we report the synthesis, structural characterization, optical, and thermal properties of the new quaternary selenophosphate compounds K₄In₂(PSe₅)₂(P₂Se₆) and Rb₃Sn(PSe₅)(P₂Se₆).

EXPERIMENTAL SECTION

Reagents

The reagents mentioned in this study were used as obtained unless noted otherwise: (i) red phosphorus powder, Morton Thiokol, Inc., ~100 mesh, Danvers, MA; (ii) rubidium metal, analytical reagent, Johnson Matthey/AESAR Group, Seabrook, NH; (iii) potassium metal, analytical reagent, Aldrich Chemical Co., Milwaukee, WI; (iv) selenium powder, 99.5 % purity ~100 mesh, Aldrich Chemical Co., Milwaukee, WI; (v) N,N-dimethylformamide (DMF) reagent grade, EM Science, Inc., Gibbstown, NJ; (vi) diethyl ether, ACS anhydrous, EM Science, Inc., Gibbstown, NJ.

Syntheses

A₄Se (A = K, Rb) were prepared by reacting stoichiometric amounts of the elements in liquid ammonia as described elsewhere (2).

The amorphous phosphorus selenide glass “P₂Se₅” was prepared by heating a stoichiometric ratio of the elements as described elsewhere (2).

Preparation of K₄In₂(PSe₅)₂(P₂Se₆)

A mixture of In (0.25 mmol), P₂Se₅ (0.5 mmol), K₂Se (0.5 mmol), and Se (2.5 mmol) was sealed under vacuum in...
a Pyrex tube and heated to 480°C for 3 days, followed by cooling to 150°C at 4°C h⁻¹. The excess K₃P₂Se₂ flux was removed by washing with DMF under N₂ atmosphere. The product was then washed with tri-n-butylphosphine to remove residual elemental Se and then ether to reveal analytically pure, brick-red needles (77% yield based on In). The crystals are air- and water-stable. Microprobe analysis carried out on several randomly selected crystals gave an average composition of K₁.₃InP₁.₉Se₈.₂.

Preparation of Rb₃Sn(PSe₅)(P₃Se₆)

A mixture of Sn (0.3 mmol), P₃Se₅ (0.3 mmol), Rb₂Se (0.3 mmol), and Se (2.0 mmol) was sealed under vacuum in a Pyrex tube and heated to 495°C for 4 days followed by cooling to 150°C at 4°C h⁻¹. The flux was removed as above to reveal a mixture of black plates of Rb₃Sn(PSe₅) (P₃Se₆) (70%) and black, irregular crystals of Rb₂Sn₅ (P₃Se₆)₃Se₂ (30%) (2e). The plate crystals were manually separated, and they are air- and water-stable. Microprobe analysis gave an average composition of Rb₂.₈SnP₂.₇Se₁.₃.

Powder X-ray Diffraction (XRD)

Analyses were performed using a calibrated Rigaku-Denki/RW400F2 (Rotaflex) rotating anode powder diffractometer controlled by an IBM computer, operating at 45 kV/100 mA with a 1°/min. scan rate, employing Ni-filtered Cu radiation. Powder patterns were calculated with the CERIUS² software (5). Calculated and observed XRD patterns are deposited with the Supplementary Material.

Infrared Spectroscopy

Infrared spectra in the far-IR region (600–50 cm⁻¹) were recorded on a computer-controlled Nicolet 750 Magna-IR Series II spectrophotometer equipped with a TGS/PE detector and silicon beam splitter in 4 cm⁻¹ resolution. The samples were ground with dry CsI into a fine powder and pressed into translucent pellets.

Solid State UV/Vis Spectroscopy

Optical diffuse reflectance measurements were performed at room temperature using a Shimadzu UV-3101PC double-beam, double-monochromator spectrophotometer. The instrument is equipped with integrating sphere and controlled by a personal computer. BaSO₄ was used as a 100% reflectance standard for all materials. Samples are prepared by grinding them to a fine powder and spreading them on a compacted surface of the powdered standard material, preloaded into a sample holder. The reflectance versus wavelength data generated can be used to estimate a material’s band gap by converting reflectance to absorption data as described earlier (6).

Differential Thermal Analysis (DTA)

DTA experiments were performed on a computer-controlled Shimadzu DTA-50 thermal analyzer. Typically, a sample (~25 mg) of ground crystalline material was sealed in quartz ampoules under vacuum. A quartz ampoule of equal mass filled with Al₂O₃ was sealed and placed on the reference side of the detector. The samples were heated to the desired temperature at 10°C/min., then isothermed for 10 min., and finally cooled to 50°C at the same rate. Residues of the DTA experiments were examined by X-ray powder diffraction. To evaluate congruent melting, we compared the X-ray powder diffraction patterns before and after the DTA experiments. The stability and reproducibility of the samples were monitored by running multiple heating/cooling cycles.

Semi-quantitative Microprobe Analyses

The analyses were performed using a JEOL JSM-6400V scanning electron microscope (SEM) with a TN 5500 EDS detector. Data acquisition was performed with an accelerating voltage of 20 kV and 30 s accumulation time.

Single Crystal X-ray Crystallography

Intensity data for Rb₃Sn(PSe₅)(P₃Se₆) were collected using a Rigaku AFC6S four-circle automated diffractometer with a graphite crystal monochromator. Crystal stability was monitored with three standard reflections whose intensities were checked every 150 reflections, and no crystal decay was detected. An empirical absorption correction based on ψ scans was applied to all data during initial stages of refinement. An empirical DIFABS correction was applied after full isotropic refinement, as recommended (7), after which full anisotropic refinement was performed. A Siemens SMART Platform CCD diffractometer was used to collect data for K₃In₂(PSe₅)₂(P₃Se₆). An empirical absorption correction (8) was applied to the data. The space groups were determined from systematic absences and intensity statistics. To check for the correct enantiomorph for K₃In₂(PSe₅)₂(P₃Se₆), we refined the Flack parameter, which yielded the value of 0.0. Attempts at the other two possible space groups, C2/c and C2, were unsuccessful. The structures were solved by direct methods using SHELXS-86 software (9a), and full-matrix least-squares refinement was performed using the TEXSAN software package (9b).
The complete data collection parameters and details of the structure solution and refinement are given in Table 1. The coordinates of all atoms, average temperature factors, and their estimated standard deviations are given in Tables 2 and 3.

RESULTS AND DISCUSSION

Description of Structures

The structure of $K_4\text{In}_2(\text{PSe}_3)_2(\text{P}_2\text{Se}_6)$ is shown in Fig. 1. The compound has one-dimensional infinite chains of $[\text{In}_2(\text{PSe}_3)_2(\text{P}_2\text{Se}_6)]^{n\text{-}}$ that contain $\text{In}_2(\text{PSe}_3)_2$ dimers. Each dimer is formed by two edge-sharing InSe$_6$ octahedra that are bridged via tridentate $[\text{PSe}_3]^{3\text{-}}$ ligands (Fig. 1b). Every $[\text{PSe}_3]^{3\text{-}}$ ligand employs two monoselenides to coordinate to the In atoms [e.g., Se(7), Se(9)] and one Se atom from the diselenide “arm” that is shared by both In atoms [e.g., Se(11)]. Two such ligands cap the dimer from above and below, yielding an In–In distance of 4.036(2) Å. The dimers are then linked along the $a$-axis by tetradentate $[\text{P}_2\text{Se}_6]^{4\text{-}}$ ligands to form the chain. The $[\text{P}_2\text{Se}_6]^{4\text{-}}$ unit adopts the staggered conformation and employs two Se atoms from each $\text{P}$ [e.g., Se(1), Se(2) from $\text{P}(1)$] to bridge the neighboring dimers, while the third Se is noncoordinating. A similar chain structure exists in $K_2\text{M}_2\text{P}_2S_8$ ($M = \text{V}, \text{Cr}$), which contain $[\text{M}_2(\text{PS}_4)_2(\text{P}_2\text{Se}_6)]^{n\text{-}}$ chains (10). In these chains $M_2(\text{PS}_4)_2$ dimers are linked by tetradentate $[\text{P}_2\text{Se}_6]^{4\text{-}}$ ligands in a different coordination mode than those of $\ldots$
FIG. 1. (A) Unit cell of $K_4\text{In}_2(\text{PSe}_5)_2(\text{P}_2\text{Se}_6)$ viewed down the $a$-axis. In the infinite part of the structure, indium is shown as octant shaded ellipses, selenium as open ellipses, and phosphorus as crossed ellipses. The $K^+$ ions located between the chains are shown as open ellipses. (B) An isolated $[\text{In}_2(\text{PSe}_5)_2(\text{P}_2\text{Se}_6)]^{4-}$ chain with labeling.

In $K_4\text{In}_2(\text{PSe}_5)_2(\text{P}_2\text{Se}_6)$, there are two sets of In–Se distances: the first set of long distances averages 2.80(2) Å, and the second set of short distances averages at 2.74(2) Å. For comparison, the repeating units of the $K_4\text{In}_2(\text{PSe}_5)_2(\text{P}_2\text{Se}_6)$ and $K_2\text{MP}_2\text{S}_7$ are shown in Scheme 1A and 1B, respectively.
Similar distances have been observed in \( \text{In}_4(\text{P}_2\text{Se}_6)_3 \) (11). The \( \text{In}_2(\text{P}_2\text{Se}_6)_3 \) chains are separated by \( \text{K}^+ \) ions located in four different sites. \( \text{K}(1) \) is coordinated by seven \( \text{Se} \) atoms [range of \( \text{K}(1)-\text{Se} \) distances, 3.367(6)–3.769(7) Å, avg. 3.552 Å], \( \text{K}(2) \) is eight-coordinated [3.295(6)–3.744(7) Å, avg. 3.502 Å], \( \text{K}(3) \) is eight-coordinated [3.366(6)–3.815(6) Å, avg. 3.546 Å], and \( \text{K}(4) \) is also eight-coordinated [3.384(6)–3.685(6) Å, avg. 3.538 Å]. Selected distances and angles for \( \text{K}_4\text{In}_2(\text{P}_2\text{Se}_6)_2(\text{P}_2\text{Se}_6) \) are given in Table 4.

The structure of \( \text{Rb}_3\text{Sn}(\text{P}_2\text{Se}_6) \) is shown in Fig. 2. The compound features one-dimensional infinite chains of \( \text{Sn}(\text{P}_2\text{Se}_6)(\text{P}_2\text{Se}_6) \) consisting of \( \text{Sn}(\text{P}_2\text{Se}_6) \) units stacked parallel to the \( a \) axis. The \( \text{P}_2\text{Se}_6 \) ligands are bidentate and use one monoselenide and the diselenide “arm” to chelate to an octahedral \( \text{Sn} \) atom. The tetradeinate \( \text{P}_2\text{Se}_6 \) unit plays a bridging role as in the indium compound. It uses three \( \text{Se} \) atoms to cap a triangular face of one octahedron [e.g., \( \text{Se}(6), \text{Se}(7), \) and \( \text{Se}(9) \)] and employs another \( \text{Se} \) [e.g., \( \text{Se}(10) \)] to share a corner with a neighboring octahedron (Fig. 2b). There are two sets of \( \text{Sn}–\text{Se} \) distances: the first set of long distances is between \( \text{Sn} \) and \( \text{Se}(6), \text{Se}(7), \text{Se}(9), \) and \( \text{Se}(10), \) with an average distance of 2.75(4) Å, and the second set of short distances is between \( \text{Sn} \) and \( \text{Se}(1) \) and \( \text{Se}(5), \) with an average distance of 2.63(5) Å. The same \( \text{Sn} \) coordination has been observed in the molecular compounds \( \text{A}_2\text{Sn}(\text{P}_2\text{Se}_6)_3 \) (\( \text{A} = \text{K}, \text{Rb} \)) (2g), with average \( \text{Sn}–\text{Se} \) distances of 2.76(2) Å and 2.66(1) Å for long and short set, respectively. The \( \text{Sn}(\text{P}_2\text{Se}_6)(\text{P}_2\text{Se}_6) \) chains are separated by \( \text{Rb}^+ \) ions located in three different sites. \( \text{Rb}(1) \) is coordinated by eight \( \text{Se} \) atoms [range of \( \text{Rb}(1)–\text{Se} \) distances, 3.537(2)–3.881(2) Å; avg. 3.710 Å] and one \( \text{P} \) atom at 3.785(4) Å, \( \text{Rb}(2) \) is eight-coordinated [3.613(3)–3.800(2) Å; avg. 3.699 Å], and \( \text{Rb}(3) \) is eight-coordinated [3.511(3)–3.864(2) Å; avg. 3.694 Å]. Selected distances and angles for \( \text{Rb}_3\text{Sn}(\text{P}_2\text{Se}_6) \) are given in Table 5.

**Comparison of structures.** The most important difference between the two compounds reported here is the oxidation state of the metal center. In the \( \text{Sn}(\text{P}_2\text{Se}_6)(\text{P}_2\text{Se}_6) \) chain we find one \( \text{P}_2\text{Se}_6 \) chain and one \( \text{P}_2\text{Se}_6 \) chain equivalent per \( \text{Sn}^{2+} \) metal center. On the other hand, the \( \text{In}_2(\text{P}_2\text{Se}_6) \) chain contains one \( \text{P}_2\text{Se}_6 \) chain and half \( \text{P}_2\text{Se}_6 \) chain per metal center for the lower charged \( \text{In}^{3+} \). The rare \( \text{P}_2\text{Se}_6 \) ligand can be derived from the tetrahedral \( \text{P}_2\text{Se}_6 \) by substitution of an \( \text{Se}_2\text{Se} \) ion for a monoselenide. Known examples of compounds containing this group include \( \text{[PPh}_4]_2[\text{Fe}_2\text{CO}_4(\text{P}_2\text{Se}_6)] \) (12), \( \text{A}_2\text{Sn}(\text{P}_2\text{Se}_6) \) (2g), \( \text{A} = \text{K, Rb} \) and \( \text{A}_2\text{Sn}(\text{P}_2\text{Se}_6) \) (\( \text{A} = \text{Rb, Cs} \)), all of which contain finite molecular anions (2g). In the present study, the

**TABLE 4**

| Selected Distances (Å) and Angles (°) for \( \text{K}_4\text{In}_2(\text{P}_2\text{Se}_6)_2(\text{P}_2\text{Se}_6) \) with Standard Deviations in Parentheses |
|-----------------|-----------------|-----------------|-----------------|
| \( \text{In}(1)-\text{Se}(1) \) | 2.757(3) | \( \text{P}(3)-\text{Se}(7) \) | 2.209(6) |
| \( \text{In}(1)-\text{Se}(6) \) | 2.746(3) | \( \text{P}(3)-\text{Se}(8) \) | 2.164(6) |
| \( \text{In}(1)-\text{Se}(7) \) | 2.799(3) | \( \text{P}(3)-\text{Se}(9) \) | 2.184(6) |
| \( \text{In}(1)-\text{Se}(11) \) | 2.828(3) | \( \text{P}(3)-\text{Se}(10) \) | 2.243(6) |
| \( \text{P}(1)-\text{Se}(2) \) | 2.192(6) | \( \text{P}(1)-\text{P}(2) \) | 2.247(7) |
| \( \text{P}(1)-\text{Se}(2) \) | 2.244(6) | \( \text{P}(1)-\text{P}(2) \) | 2.247(7) |
| \( \text{In}(1)-\text{In}(2) \) | 4.036(2) | \( \text{Se}(7)-\text{P}(3)-\text{Se}(9) \) | 114.2(3) |
| \( \text{P}(2)-\text{Se}(2) \) | 2.136(6) | \( \text{Se}(7)-\text{P}(3)-\text{Se}(9) \) | 114.2(3) |
| \( \text{P}(2)-\text{Se}(2) \) | 2.239(5) | \( \text{P}(1)-\text{P}(2) \) | 107.3(3) |
| \( \text{P}(2)-\text{Se}(6) \) | 2.193(6) | \( \text{P}(1)-\text{P}(2) \) | 107.3(3) |

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**SCHEME 1**
[PSe$_5$]$^{3-}$ unit, with a different coordination mode in each case, is not involved in the chain propagation in both compounds. The torsion angle around the Se–Se bond in the [PSe$_5$]$^{3-}$ unit is quite different between the two compounds. For example, the angle for P(3)–Se(10)–Se(11)–In(2) is 47.0(0)$^\circ$, whereas for P(1)–Se(4)–Se(5)–Sn the angle is 58.6(1)$^\circ$ (a torsion angle of 63.3(1)$^\circ$ has been observed for $A_3$Sn(PSe$_3$)$_3$ ($A = \text{K, Rb}$)). The [P$_2$Se$_6$]$^{4-}$
The far-IR spectrum of K₄In₂(PSe₅)₂(P₂Se₆) displays absorptions at approximately 486, 469, 451, 427, 304, 225, 184, 150, and 135 cm⁻¹, whereas Rb₂Sn(PSe₅)(P₂Se₆) displays absorptions at approximately, 516, 490, 458, 425, 402, 389, 299, 225, 203, 186, 166, and 144 cm⁻¹. The absorptions above 200 cm⁻¹ are assigned to P–Se vibrations of the [P₂Se₆]₄⁻ and [PSe₅]₃⁻ units, with the characteristic Se–Se vibration appearing at approximately 225 cm⁻¹ (2g, 3a). The absorptions below 200 cm⁻¹ are probably due to M–Se vibrations (M = In, Sn) (2, 3).

Differential thermal analysis (DTA) data, followed by careful XRD analysis of the residues, show that Rb₂Sn(PSe₅)(P₂Se₆) melts incongruently at 426°C, yielding mainly SnSe₂. The DTA of K₄In₂(PSe₅)₂(P₂Se₆) displays more interesting behavior. The first cycle (Fig. 4a) shows a single endothermic peak at about 420°C, but no exothermic peaks appear on cooling. Examination of the residue with XRD analysis reveals only the presence of In₂Se₃. On subsequent heating, an exothermic peak is observed at about 300°C (Fig. 4b), indicating crystallization. Further heating results in the same endothermic peak at about 418°C. If the heating in the above experiment is terminated at 350°C, the XRD pattern of the residue matches that of K₂In₂(PSe₅)₂(P₂Se₆). We attribute this behavior to a phase transformation of K₂In₂(PSe₅)₂(P₂Se₆) to In₂Se₃ and an amorphous glass of nominal composition “K₄P₄Se₁₃” at 420°C, according to the reaction

\[\text{K}_4\text{In}_4\text{PSe}_5\text{P}_2\text{Se}_6 \rightarrow 420°C \rightarrow \text{In}_2\text{Se}_3 + \text{K}_4\text{P}_4\text{Se}_{13}.\] [1]

Upon reheating, In₂Se₃ and “K₄P₄Se₁₃” recombine, exothermically, to form the starting compound K₄In₂(PSe₅)₂(P₂Se₆) at 300°C. The decomposition of selenophosphate frameworks to simpler binary compounds and amorphous
glass has been observed previously in other compounds (3b, 3e, 4b), but this is the first case in which we observe reversibility of the decomposition reaction on reheating the decomposed byproducts. It is noteworthy that (Ph₄P) [In(Se₆)] displays a similar thermal behavior (14).

One of the appealing features of the chalcophosphate flux method is the possibility to obtain different [P₅O₄]⁻⁻ groups to coexisting in the same compound. In this type of chemistry, the metal is given the freedom to choose its own ligands suitable for lattice construction. Although we have developed a working knowledge as to which type of [P₅O₄]⁻⁻ groups (i.e., P⁴⁺ or P⁵⁺) are likely to be stable in certain flux compositions, the prediction of the exact ligands, especially when two different ones are involved in the same compound, is very difficult. It is hoped that further work, already in progress, will shed some light on the role of the metal center in the complex acid-base equilibria of these reactions.

Supporting information available includes tables of anisotropic thermal parameters of all atoms, interatomic distances and angles, calculated and observed X-ray powder patterns (55 pages).

FIG. 4. DTA diagram for K₄In₂(PSe₅)₂(P₂Se₇). (A) First cycle, (B) second cycle.

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