Inorg. Chem. **2002**, *41*, 640–642

Inorganic Chemistry

Communication

Solvothermal Synthesis and Structure of a New Selenium-Rich Selenophosphate $K_3PSe_4{\cdot}2Se_6$

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Received October 8, 2001

The compound $K_3PSe_4{\cdot}2Se_6$ was synthesized at 110 °C via solventothermal techniques from binary starting materials and Se in acetonitrile. The compound crystallizes in the space group $Fd\bar{3}$ of the cubic system with eight formula units in a cell with a dimension of $a = 16.415(2)$ Å at $T = 193$ K. The structure contains an unusual intermixing of ionic and uncharged species. The selenophosphate tetrahedral trianions PSe_4^{3-} are surrounded by potassium cations; other potassium cations in the structure are coordinated to 12 selenium atoms from four Se_6 rings in a tetrahedral arrangement. There are no short contacts between adjacent selenium rings. Heating the same reaction mixture to 160 °C results in the formation of only needles of trigonal selenium.

The synthesis of new transition-metal chalcogenophosphate compounds has been the focus of much research because of the myriad structures and chemical properties that have been exhibited by this class of compounds.[1−6] In the past decade, syntheses using phosphorus-containing fluxes at intermediate- (200−400 °C) and high-temperature regimes (400−1000 °C) have been successful in the preparation of many new compounds.[7−13] As recent efforts have pushed the synthetic envelope toward more gentle, or *chimie douce*, conditions, solvothermal synthesis has been used.[5,14−16] At higher temperatures, supercritical ethylenediamine has been used successfully in the synthesis of compounds such as $Cs_2Cu_2Sb_2Se_5$[17] and $[Ca(en)_4]As_2Se_7$.[5] Other arsenic and antimony selenide compounds including $AAsSe_2$ (A = K, Rb, Cs), $KSbSe_2$, and $K_2Sb_4Se_8$ can be prepared in methanol.[14] However, thiophosphate and selenophosphate compounds have not been made in the most commonly used oxygen-containing solvents (water and methanol) because of nucleophilic attack of oxygen on the phosphorus atoms. We avoided this problem through the use of acetonitrile as solvent. Here we present the first synthesis of a phosphorus-containing chalcogenide compound via a solvothermal approach. The new compound is a structural analogue of $Rb_3AsSe_4{\cdot}2Se_6$ that was prepared in methanol at 175 °C.[18]

The binary starting material K_2Se_3 was prepared from the elements in liquid ammonia; P_2Se_5 was prepared by heating a stoichiometric combination of the elements in a Pyrex tube at 450 °C for 24 h. A mixture of K_2Se_3 (122.2 mg), P_2Se_5 (57.0 mg), elemental Se (19.8 mg), and 1.0 mL of degassed acetonitrile was combined in a Teflon-lined reaction vessel, heated at 110 °C for 24 h, and cooled to ambient temperature at a rate of 7 °C/h. Octahedral crystals of $K_3PSe_4{\cdot}2Se_6$ suitable for X-ray structure determination[19] were manually selected from the amorphous byproducts and needles of

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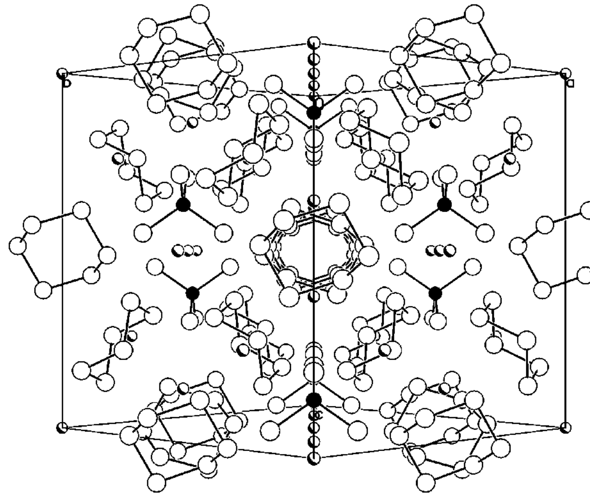

Figure 1. The unit cell of $K_3PSe_4{\cdot}2Se_6$ viewed down [110]. The K atoms are shaded circles, the P atoms are small circles, the Se atoms are large open circles. Atom sizes are arbitrary.

trigonal selenium.[20] The overall yield of the product was low (~20%), but the uniform crystal size (0.2−0.3 mm edge length) and shape enabled facile separation. Semiquantitative elemental analyses of several crystals were made with an energy dispersive spectrometry (EDS) equipped Hitachi S-3500 scanning electron microscope: the average K:P:Se ratio is 2.2:1:15. When the same reaction mixture is heated at temperatures greater than 110 °C, the products are predominantly needles of trigonal selenium[20] and small amounts of amorphous phosphorus-selenide glasses. The presence of K_2Se_3 is essential for the formation of trigonal selenium: without it no needles of Se are obtained; needles are formed even when the only reactant is K_2Se_3. If the more strongly reducing reactant K_2Se is used in the reaction mixture in place of K_2Se_3, significant amounts of kyanmethin (2,6-dimethyl-4-pyrimidinamine) are obtained from trimerization of the solvent.

The structure of $K_3PSe_4{\cdot}2Se_6$ consists of tetrahedral PSe_4^{3-} anions, isolated neutral Se_6 rings, and potassium cations (Figure 1). The selenophosphate anions are almost perfectly tetrahedral with Se−P−Se angles of 109.47−109.5° (Figure 2). The shape of each Se_6 ring resembles the chair conformation of cyclohexane; Se_8 "crowns" are found in the α-monoclinic elemental form of selenium.[20] The selenium distances in the rings are consistent with the Se−Se distances found in the α-monoclinic[20] and trigonal[21] forms of Se (Table 1).

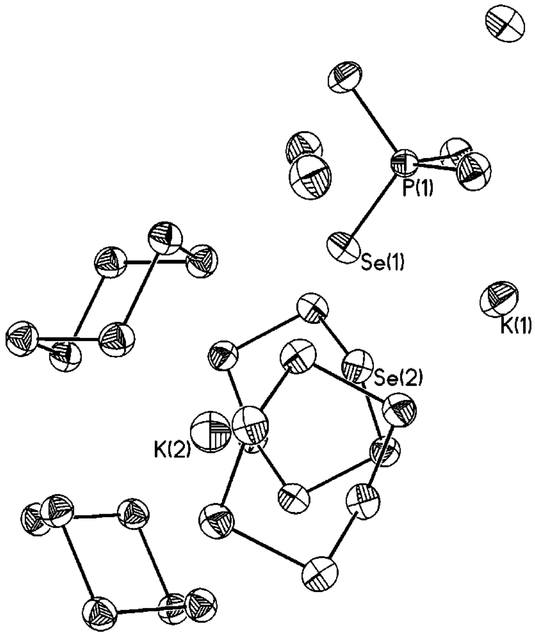

Figure 2. A view of the coordination environments for the potassium and selenophosphate ions in $K_3PSe_4{\cdot}2Se_6$. Thermal ellipsoids are presented at the 90% level.

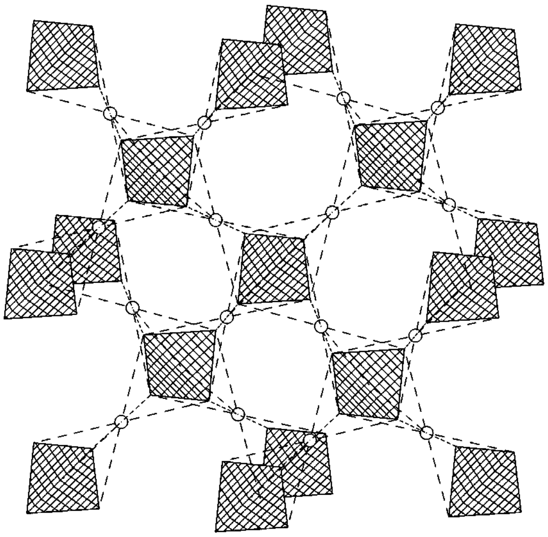

Figure 3. A polyhedral representation of the subnet formed of PSe_4^{3-} tetrahedra and bridging K(1) atoms. Dotted lines show K⋯Se interactions. The Se_6 rings and K(2) atoms in the structure have been omitted for clarity.

Table 1. Comparison of Se−Se Distances (Å) in Neutral Selenium Moieties

			Se	
	$K_3PSe_4{\cdot}2Se_6$	$Rb_3AsSe_4{\cdot}2Se_6$[18]	α-monoclinic[20]	trigonal[21]
Se−Se	2.3733(4)	2.367(2)	2.336(6) (av)	2.373(5)

The relationship of the different structural features in the compound can be described as two interpenetrating tetrahedral networks. The first network is formed from the selenophosphate anions and bridging K(1) atoms. Each face of the selenophosphate anions is capped by a potassium cation. Each capping K atom bridges two neighboring selenophosphate groups in a linear fashion (Figure 3). The second network comprises the Se_6 rings and K(2) atoms. Four Se_6 rings surround each K atom in approximate tetrahedral arrangement (Figure 2). This configuration gives the K atoms a coordination number of 12, and the arrangement of the neartest-neighbor Se atoms is approximately icosahedral.

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(19) Crystallographic information. Crystal data for $K_3PSe_4{\cdot}2Se_6$: fw, 1411.63; cubic, space group $Fd\bar{3}$; cell dimensions $a = 16.4151(19)$ Å, $V = 4423.1(9)$ Å^3, $Z = 8$, $D_c = 4.240$ g cm^{-3}, $\mu = 27.007$ mm^{-1}, $T = 193(2)$ K. Reflections collected, 10487; independent reflections, 467 [R(int) = 0.0376]. Final R indices [$I > 2\sigma(I)$]: R1 = 0.0156, wR2 = 0.0420.

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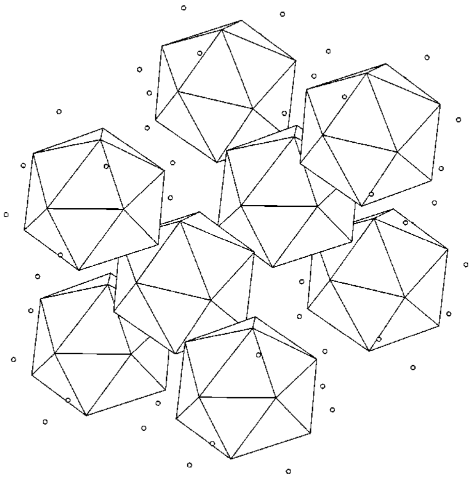

Figure 4. A polyhedral representation of the subnet formed of K-atom centered Se icosahedra. Since the bridging Se_6 units assume approximate tetrahedral arrangement around the K(2) atoms, each icosahedron is surrounded by four others. The PSe_4^{3-} tetrahedra and K(1) atoms have been omitted for clarity.

Each Se_6 ring forms a triangular face of two adjacent K-centered icosahedra, thus bridging two neighboring K atoms. This bridging arrangement extends in three dimensions and is shown in Figure 4.

The preparation of $K_3PSe_4{\cdot}2Se_6$ demostrates the utility of acetonitrile in very low temperature solvothermal techniques for the preparation of new selenophosphate compounds. Further exploration of the synthesis of phosphorus compounds in acetonitrile and other nonprotic solvents is currently underway.

Acknowledgment. Financial support of this work was provided by the Camille and Henry Dreyfus Foundation (Grant SU-97-062), Research Corporation (Grant CC4981), and the Petroleum Research Fund of the American Chemical Society (Grant 34739-GB3). Use was made of the Materials Research Center at Northwestern University (NSF Grant DMR 0076097). Single-crystal X-ray studies were performed at the Center for X-ray Diffraction at Auburn University.

Supporting Information Available: Crystallographic tables and crystallographic information files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

IC015602D