

APSe₆ (A = K, Rb, and Cs): Polymeric Selenophosphates with Reversible Phase-Change Properties

In Chung, Junghwan Do, Christian G. Canlas, David P. Weliky,* and Mercouri G. Kanatzidis*

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824

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The ternary alkali selenophosphates KPSe₆ and RbPSe₆ crystallize in the polar orthorhombic space group *Pca*2₁ with *a* = 11.7764(17) Å, *b* = 6.8580(10) Å, *c* = 11.4596(16) Å, and *Z* = 4 for RbPSe₆. CsPSe₆ crystallizes in the monoclinic space group *P2*/*1**n* with *a* = 6.877(3) Å, *b* = 12.713(4) Å, *c* = 11.242(4) Å, *β* = 92.735(7)°, and *Z* = 4. All compounds feature the one-dimensional infinite chain of [PSe₂(Se)₄][−], where each P atom is connected with Se₄^{2−} bridge. These compounds show reversible glass–crystal transition, and ³¹P NMR data suggest that crystallization and infinite [PSe₆][−] chain formation are coupled processes.

Because complex metal chalcophosphates form readily in an alkali chalcogenide flux environment,¹ it is important to know more about what species are present during these reaction conditions. A number of free chalcophosphate anionic ligands [P_{*x*}Q_{*y*}]^{*n−*} (Q = S, Se) have been isolated and characterized as alkali metal salts, including [PQ₄]^{3−},² [PSe₄]^{3−}·2Se₆,³ [P₂S₆]^{2−},⁴ [P₂Q₆]^{4−},⁵ [P₂Se₉]^{2−},⁶ [P₈Se₁₈]^{6−},⁷ and [P₂S₁₀]^{4−}.⁸ They are all discrete molecular anions mainly as they do not coordinate to metals in the structure. Investigations of new [P_{*x*}Q_{*y*}]^{*n−*} building blocks could help us understand the stability ranges of these in the flux and how the observed solid-state structure motifs arise.⁹ The alkali salts of [P_{*x*}Q_{*y*}]^{*n−*} (Q = S, Se) can also be useful starting materials for solid-state reactions or coordination chemistry in solution.

Here we report on the isolation of a new polymeric [PSe₆][−] anion crystallized as alkali salts APSe₆ (A = K, Rb, and Cs). These materials undergo an interesting reversible crystal–glass transition.¹⁰

* To whom correspondence should be addressed. E-mail: kanatzid@cem.msu.edu (M.G.K.); weliky@cem.msu.edu (D.P.W.).

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KPSe₆ (**1**) and RbPSe₆ (**2**) are isostructural and adopt the polar space group *Pca*2₁. This discussion will concentrate mainly on the Rb⁺ salt¹¹ which consists of infinite one-dimensional chains of [∞][PSe₆][−] along the *a*-axis and separated by Rb⁺ ions, Figure 1a. The crystallographically unique anion has PSe₄ tetrahedra condensed with diselenide linkages to give the polymeric [∞][PSe₆][−] chain. The PSe₄ tetrahedron is only slightly distorted from the ideal one with the Se–P–Se angles ranging from 101.46(7)° to 119.79(8)°. The P–Se distances are normal at 2.1529(18)–2.2994(17) Å. The Se–Se distances range from 2.3534(10) to 2.3859(10) Å. The dihedral angles around the bonds Se(1)–Se(2), Se(2)–Se(3), and Se(3)–Se(4) are −93.53(5)°, 112.41(4)°, and 87.35(5)°. The largest deviation from 90° gives the longest internal Se(2)–Se(3) distance as reported for disulfides¹² and leads to a bond distance alternation in the Se₄^{2−} unit. This trend is generally shown in unligated Se₄^{2−} ions.¹³ Unusually short Se···Se nonbonding interactions between adjacent chains along the *c*-axis are observed at 3.217(1)–3.350(1) Å. Short intra- and interlayer Se···Se interactions, much shorter in distance than the van der Waals radii sum of 3.80 Å,¹⁴ play a crucial role in

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- (10) Pure APSe₆ (A = K, Rb, and Cs) was achieved by a stoichiometric mixture of A₂Se/P₂Se₃/Se = 1/1/6 under vacuum in a silica tube at 350 °C for 10 days. Energy dispersive spectroscopy analysis of the crystals showed an average composition of “KPSe_{6.2}”, “Rb_{1.2}PSe_{6.1}”, and “CsPSe_{6.2}”, respectively, for the orange rod-type single crystals. The glassy phase of APSe₆ was prepared from a stoichiometric mixture of A₂Se/P₂Se₃/Se = 1/1/6 under vacuum in a quartz tube at 800–900 °C for 1–2 min and subsequent quenching to room temperature. All compounds are air-sensitive and begin to decompose in a week and are unstable under *N,N*-dimethylformamide and H₂O but relatively stable under acetonitrile.
- (11) Crystal data for RbPSe₆ at 293(2) K: Siemens SMART Platform CCD diffractometer, Mo Kα radiation (λ = 0.71073 Å), *Pca*2₁, *a* = 11.7764(17) Å, *b* = 6.8580(10) Å, *c* = 11.4596(16) Å, *V* = 925.5(2) Å³, *Z* = 4, *D_c* = 4.236 g/cm³, crystal dimensions 0.028 × 0.167 × 0.037 mm³, μ = 29.031 mm^{−1}, 2θ = 2.97–28.32°, 8770 total reflections, 2193 unique reflections with *R*(int) = 0.047, refinement on *F*², GOF = 0.977, 73 parameters, *R*₁ = 2.59%, *wR*₂ = 4.99% for *I* > 2σ(*I*). An empirical absorption correction was done using SADABS, and all atoms were refined anisotropically. Structure solution and refinement were performed with SHELXTL.
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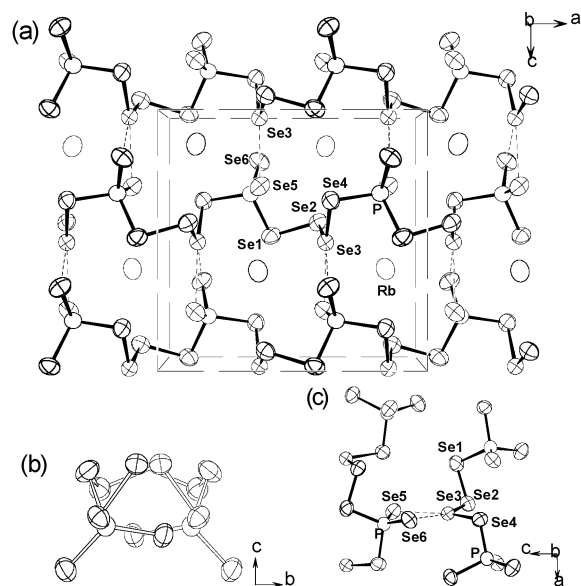


Figure 1. (a) Structure of RbPSe_6 viewed down the b -axis. The Rb^+ ions are coordinated by 12 Se atoms from four selenophosphate chains. Selected bond distances (Å): P–Se(1), 2.2994(17); P–Se(4), 2.2521(19); P–Se(5), 2.1529(18); P–Se(6), 2.1530(17); Se(1)–Se(2), 2.3473(10); Se(2)–Se(3), 2.3859(10); Se(3)–Se(4), 2.3534(10). Selected bond angles (deg): Se(1)–P–Se(4), 104.41(7); Se(1)–P–Se(5), 108.49(7); Se(1)–P–Se(6), 111.19(8); Se(4)–P–Se(5), 110.30(8); Se(4)–P–Se(6), 101.46(7); Se(5)–P–Se(6), 119.79(8); Se(1)–Se(2)–Se(3), 101.27(3); Se(2)–Se(3)–Se(4), 103.92(4). Dashed lines indicate weak Se...Se interactions (Å): Se(3)...Se(5), 3.350(1); Se(3)...Se(6), 3.217(1). (b) View of a $[\text{PSe}_6]^{3-}$ chain looking down the a -axis, clearly showing its polar character. (c) Segment of the $[\text{PSe}_6]^{3-}$ anion showing the short Se...Se interactions. The thermal ellipsoids with 90% probability are shown.

influencing the crystal structure. In fact, other low-dimensional compounds such as NbSe_3 with its charge density wave phenomenon exhibit similar Se...Se interactions of 3.30 Å.¹⁵ In K_2Se_5 ,¹⁶ short contacts between the Se_5^{2-} ions are also observed. The shorter Se...Se interactions in **2** affect the local geometry of the $[\text{PSe}_6]^{3-}$ chains to form pseudo-lamellar packing and relatively long Se–Se bonds due to the delocalization of electrons through short Se...Se contacts, Figure 1c.

CsPSe_6 (**3**)¹⁷ is a centrosymmetric compound also with $[\text{PSe}_6]^{3-}$ chains but of a different conformation than in the K^+ and Rb^+ analogues, Figure 2a. The differences in conformation are seen clearly in projection of the two chains in Figure 1b and 2b. Adjacent $[\text{PSe}_6]^{3-}$ chains along b -axis are related by a 2-fold symmetry operation along the a -axis. P–Se distances range from 2.135(2) to 2.262(2) Å. The Se–Se distances with alteration are similar to the Rb^+ analogue at 2.3549(16)–2.3798(15) Å. The dihedral angle around the Se(2)–Se(3) bond of $-121.06(1)^\circ$ contributes to its longer distance than the external ones. Short Se...Se interactions are observed at 3.160(2)–3.280(7) Å, even shorter than those of **2**. Interchain interactions generate

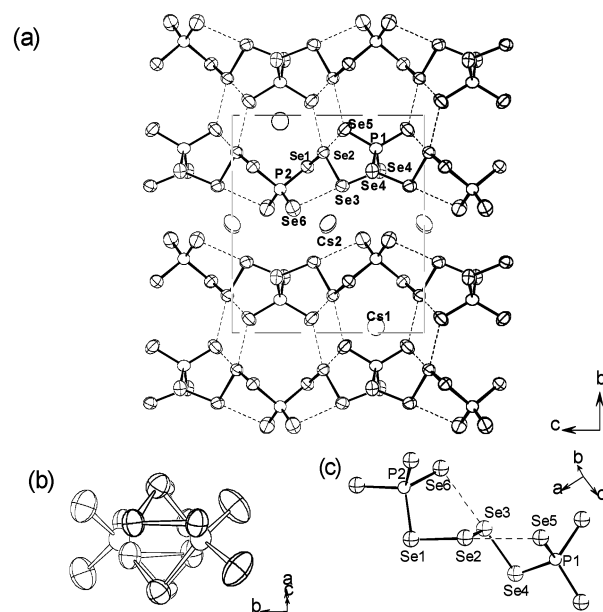


Figure 2. (a) Structure of CsPSe_6 viewed down the a -axis. Both Cs(1) and Cs(2) are surrounded by four different $[\text{PSe}_6]^{3-}$ chains. Selected bond distances (Å): P(1)–Se(4), 2.240(2); P(1)–Se(5), 2.135(2); P(2)–Se(1), 2.262(2); P(2)–Se(6), 2.138(2); Se(1)–Se(2), 2.3549(16); Se(2)–Se(3), 2.3798(15); Se(3)–Se(4), 2.3558(16). Selected bond angles (deg): Se(4)–P(1)–Se(4), 108.43(15); Se(5)–P(1)–Se(5), 117.54(17); Se(1)–P(2)–Se(6), 102.95(5); Se(6)–P(2)–Se(6), 117.92(17); Se(1)–Se(2)–Se(3), 100.20(5); Se(2)–Se(3)–Se(4), 98.20(5); P(1)–Se(4)–Se(3), 98.56(5); P(2)–Se(1)–Se(2), 97.81(6). Dashed lines indicate weak Se...Se interactions (Å): Se(2)...Se(5), 3.280(7); Se(3)...Se(6), 3.160(2); Se(2)...Se(5), 3.248(2). (b) View of a $[\text{PSe}_6]^{3-}$ chain looking down $[10\bar{1}]$ axis. (c) Local geometry of the $[\text{PSe}_6]^{3-}$ anion in CsPSe_6 showing the short Se...Se interactions. The thermal ellipsoids with 90% probability are shown.

a pseudo-lamellar packing and influence the conformation of the Se_4^{2-} linkage to form straight lines of Se(1)–Se(2)...Se(5) and Se(4)–Se(3)...Se(6) connections and possibly maximize the $p\pi$ orbital overlap, Figure 2c.

The $[\text{PSe}_2(\text{Se}_4)]^-$ anion is a rare example of a free-standing polymeric chalcophosphate with no coordinating metals. The only other reported polymeric anion is the $[\text{P}_3\text{Se}_4]^-$ ion which was found bound to Ru or Os atoms in $\text{K}_3\text{RuP}_5\text{Se}_{10}$,¹⁸ $\text{Rb}_3\text{RuP}_5\text{Se}_{10}$, $\text{A}_3\text{OsP}_5\text{Se}_{10}$ ($\text{A} = \text{K}, \text{Rb}$).¹⁹

According to differential thermal analysis (DTA) performed at a rate of 10 °C/min, RbPSe_6 (**2**)²⁰ and CsPSe_6 (**3**) melt congruently at 315 and 303 °C, respectively, (Figure

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(17) Crystal data for CsPSe_6 at 296(2) K: Siemens SMART CCD diffractometer, Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å), $P2_1/n$, $a = 6.877(3)$ Å, $b = 12.713(4)$ Å, $c = 11.242(4)$ Å, $\beta = 92.735(7)^\circ$, $V = 981.8(6)$ Å³, $Z = 4$, $D_c = 4.236$ g/cm³, crystal dimensions $0.139 \times 0.014 \times 0.014$ mm³, $\mu = 26.095$ mm⁻¹, $2\theta = 1.60$ – 28.32° , 5747 total reflections, 2260 unique reflections with $R(\text{int}) = 0.0535$, refinement on F^2 , GOF = 1.024, 79 parameters, $R_1 = 3.81\%$, $wR_2 = 8.74\%$ for $I > 2\sigma(I)$. Cs(2) was originally assigned to special position (0, 0.5, -0.5), but because of a large x -axis atomic displacement parameter (U_{11}, U_{22}, U_{33}) = (0.1015, 0.0487, 0.0208), it was allowed into a general position. This refined to (-0.972682, 0.494929, -0.501068) with reasonable displacement parameters of (U_{11}, U_{22}, U_{33}) = (0.0559, 0.0489, 0.0211). Cs(2), however, still exhibited disorder near its refined position leading to relatively high standard deviation of bond lengths between Cs(2) and P and Se atoms. An empirical absorption correction was done using SADABS, and all atoms were refined anisotropically.

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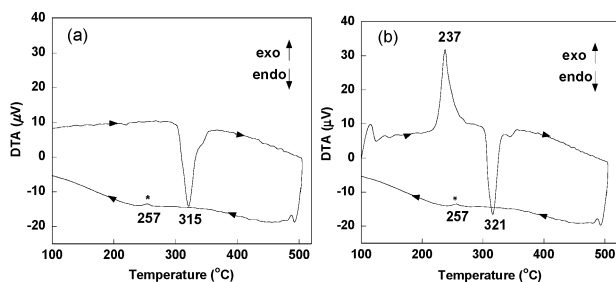


Figure 3. Differential thermal analysis diagrams of RbPSe₆ representing (a) melting in the first cycle with no crystallization upon cooling and (b) subsequent recrystallization and complete melting upon heating in the second cycle. Asterisks indicate the vitrification upon cooling.

3) and form dark red glasses rather than crystals upon cooling.²¹ Crystallization is only achieved on heating. The glasses recrystallize exothermically at 237 °C for **2** and 206 °C for **3** upon subsequent heating followed by melting at 321 and 310 °C for **2** and for **3**, respectively. RbPSe₆ showed vitrification at 257 °C on cooling to room temperature. The XRD patterns after recrystallization are the same as those of pristine **2** and **3** indicating full recovery of the original crystal structure. Recrystallization and vitrification are reversible as they were repeatedly observed by repeating the DTA cycles. We may speculate that the facile crystallization of these glasses suggests that the glass structure is somewhat related to the crystal structure, and given the polar character of the Rb salt, we may expect a similar polar nature for the precursor glass.

The solid-state diffuse reflectance UV–vis spectra of both crystalline and glassy APSe₆ (A = K, Rb, and Cs) reveal sharp absorption edges. The band gaps of crystalline phases **1**, **2**, and **3** revealed 2.16, 2.18, and 2.16 eV values while those of glassy counterparts **4**, **5**, and **6** showed 1.82, 1.91, and 1.71 eV values, respectively, which are consistent with their respective orange and dark red colors. It is noteworthy that red shifts in the absorption edge are typical in glassy phases. Glass formation in compounds with extended solid-state structures generally produces massive defects and mid-gap states, which leads to lower band gaps than corresponding crystalline phases.²² This phenomenon is a key aspect of optical storage systems based on phase-change materials.²³ Furthermore, the polar K⁺ and Rb⁺ salts enable them to be explored for nonlinear optical properties.

The far IR spectra of RbPSe₆ display absorption peaks at 482(s), 424(s), 386(s), 356(m), 247(m), 228(w), and 164(w) cm⁻¹. The peaks at 247 cm⁻¹ are attributed to Se–Se stretching.^{5,24} Those at higher energies are diagnostic of P–Se vibrations.²⁵ The far IR spectra of glassy RbPSe₆ display much broader and weaker peaks at 507(w), 420(w), 385–

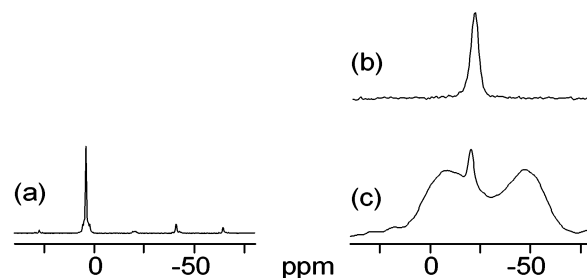


Figure 4. ³¹P NMR spectra of RbPSe₆ taken at 161.5 MHz Larmor frequency. Spectra a and c are for the crystalline and glassy materials, respectively, and were obtained at ambient temperature and with MAS frequency of ~11 kHz. Spectrum b is for the melt at 350 °C and was obtained under static conditions. For glassy RbPSe₆, *m* = ±1 spinning sidebands are seen in a spectrum with a larger range of displayed shifts.

(sh), and 252(sh) cm⁻¹. A comparison with crystalline RbPSe₆ suggests that the building block [PSe₆⁻] unit is substantially intact in the glass but lacks long-range order. The bridging Se₄²⁻ chains seem to be severely disordered in the glassy phase according to the very weak and broad Se–Se stretching vibrations.

³¹P NMR provided further insight into bonding and structure (Figure 4). For crystalline RbPSe₆ under magic angle spinning (MAS), the major peak has an isotropic chemical shift of 4.3 ppm and a full-width at half-maximum (FWHM) line width of 0.5 ppm. This shift is ~40 ppm higher than a typical shift of [P₂Se₉]⁴⁻, a comparable discrete unit with bridging Se.⁹ In addition, for discrete selenophosphate units, the δ₁₁–δ₃₃ chemical shift anisotropy (CSA) principal value difference correlates inversely with the degree of local symmetry about P, with ~65 ppm values observed for discrete tetrahedral [PSe₄]³⁻ units and ~200 ppm values observed for [P₂Se₉]⁴⁻ units.⁹ The ~115 ppm CSA value observed for RbPSe₆ fits within this correlation, with the pseudo-C₂ symmetry of P in [∞][PSe₆⁻] chains intermediate between the high and low symmetries of P in [PSe₄]³⁻ and [P₂Se₉]⁴⁻ anions, respectively.

In a 350 °C melt, the static ³¹P spectrum has a single resonance with -21 ppm peak chemical shift and 4 ppm fwhm line width. The shift is typical of PSe₄-type bonding,⁹ and the narrow line width is diagnostic of rapidly tumbling small molecular species such as [PSe₆]_{*m*}⁻ ring-based molecules which would result from depolymerization of [∞][PSe₆⁻] chains. In the RbPSe₆ glassy phase, there is a broad ³¹P MAS signal centered at -25 ppm. The similarity of the average shifts of the melt and glass spectra and the broad width of the glass spectrum are consistent with a frozen melt model for the glass with associated conformational, packing, and possibly molecular heterogeneity. Overall, the NMR, crystallographic, and DTA data suggest that crystallization and [∞][PSe₆⁻] chain formation are coupled processes.

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Supporting Information Available: X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(20) The thermal behavior of KPSe₆ showed the same patterns as that of RbPSe₆.

(21) The powder X-ray diffraction (XRD) patterns after each DTA cycle showed that amorphous glasses had formed.

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