

One-Dimensional Zinc Selenophosphates: A_2 **ZnP**₂**Se**₆ (A = K, **Rb**, **Cs**)

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Abstract. The new compounds $A_2 \text{ZnP}_2 \text{Se}_6$ (A = K, Rb, Cs) were synthesized via molten salt flux syntheses. The crystals feature one-dimensional $1/_{\infty}[\text{ZnP}_2\text{Se}_6]^{2-}$ chains charge balanced by alkali metal ions between the chains. K₂ZnP₂Se₆ crystallizes in the monoclinic space group $P2_1/c$; cell parameters a = 12.537(3) Å, b = 7.2742(14) Å, c = 14.164(3) Å, $\beta = 109.63(3)^\circ$, Z = 4, and V = 1216.7(4) Å³. Rb₂ZnP₂Se₆ and Cs₂ZnP₂Se₆ are isotypic, crystallizing in the triclinic space group

Introduction

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Selenophosphates are compounds containing selenium and phosphorus, typically conjoined molecular units of $[P_x Se_y]^{z-}$ as molecular species or coordinated ligands to metals. Selenophosphates have promising applications in nonlinear optics,^[1] ferroelectricity,^[2] magnetism,^[3] reversible phase-change transitions,^[4] γ -ray detection,^[5] and photoluminescence.^[4b,6] Generally, $[P_rSe_v]^{z-}$ units are made up of tetrahedral or pyramidal phosphorus and some have complex structures such as $^{1}/_{\infty}[P_{3}Se_{4}]^{-}, [7]$ $1/_{\infty}[PSe_{6}]^{-,[4a]}$ $1/_{\infty}[P_{2}Se_{6}^{2}]^{-,[8]}$ P_2Se_5 ,^[9] $[P_8Se_{18}]^{6-,[10]}$ $[P_2Se_{10}]^{4-,[11]}$ $[P_2Se_9]^{4-,[12]}$ $[P_5Se_{12}]^{5-,[6a]}$ $[P_6Se_{12}]^{4-,[6a,13]}$ and $[P_3Se_7]^{3-,[14]}$ The most prominent selenophosphate building block is $[P_2Se_6]^{4-.[15]}$ Its structure is analogous to ethane, where the phosphorus atoms are located where the carbon would be and the Se atoms are situated at the hydrogen positions.

A broad variety of ternary chalcophosphates containing $[P_2Se_6]^{4-}$ units have been discovered including the zero-dimensional (0D) $M_2P_2Se_6$ (M = Ba, Ca, Eu, Pb, Sn, Sr)^[16] and $M'_4P_2Se_6$ (M' = Ag, K, Na, Tl),^[12,17] all of which are composed of $[P_2Se_6]^{4-}$ molecular anions charge balanced by metal cations. There are also the two dimensional (2D), layered $M''_2P_2Se_6$ (M'' = Fe, Hg, Mg, Zn).^[18] Finally there are the one-dimensional (1D) $A_2P_2Se_6$ (A = K, Rb),^[19] with P_2Se_6 units condensing into $1/\infty[P_2Se_6]^{2-}$ helical chains with strong SHG responses and high transparency in the mid-IR region.^[19]

There is a plethora of quaternary materials containing the $[P_2Se_6]^{4-}$ unit. We will focus our discussion on quaternary al-

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 $P\overline{I}$. Rb₂ZnP₂Se₆ has cell parameters of a = 7.4944(15) Å, b = 7.6013(15) Å, c = 12.729(3) Å, $a = 96.57(3)^\circ$, $\beta = 105.52(3)^\circ$, $\gamma = 110.54(3)^\circ$, Z = 2, and V = 636.6(2) Å³. Cs₂ZnP₂Se₆ has cell parameters of a = 7.6543(6) Å, b = 7.7006(6) Å, c = 12.7373(11) Å, $a = 97.007(7)^\circ$, $\beta = 104.335(7)^\circ$, $\gamma = 109.241(6)^\circ$, Z = 2, and V = 669.54(10) Å³.

kali metal selenophosphates. Most discovered quaternary chalcophosphates with [P₂Se₆]⁴⁻ also have 1D chain structures composed of $[P_2Se_6]^{4-}$ units coordinated to a metal in an alternating pattern. Depending on the metal identity, $[P_2Se_6]^{4-}$ has been shown to accommodate tetrahedral, octahedral, seesaw, or square planar metal coordination. For example, A_2 HgP₂Se₆ $(A = K, Rb)^{[20]}$ have tetrahedral metal coordination, $A_2PdP_2Se_6$ $(A = K, Cs)^{[20,21]}$ have square planar metal coordination, Cs₂SnP₂Se₆ has see saw metal coordination,^[22] and A₂MP₂Se₆ $(A = K, Rb, Cs; M = Mn, Fe, Sn, Cd, Mg)^{[3a,18c,20]}$ have octahedral metal coordination. $A_2MP_2Se_6$ (A = K, Rb, Cs; M = Mn, Fe)^[3a] are interesting in that they have magnetic properties resulting from the high-spin Fe and Mn atoms coupling antiferromagnetically from 10-20 K. There are also many unique 1D structures containing $[P_2Se_6]^{4-}$, including $A_2M_2P_2Se_6$ (A = K, Cs; M = Cu, Ag, Au),^[3a,23] KInP₂Se₆,^[24] $K_4Sc_2(PSe_4)_2(P_2Se_6)$,^[25] $K_4In_2(PSe_5)_2(P_2Se_6)$,^[26] $Rb_3Sn(PSe_5)$ (P₂Se₆),^[26] K₅In₃P₆Se₁₉,^[27] K₄In₄P₆Se₂₀,^[27] and Rb₂MP₂Se₇ (M = Ce, Gd).^[28] 2D structures with [P₂Se₆]⁴⁻ include KMP_2Se_6 (M = Sb, Bi),^[29] NaCeP₂Se₆,^[30] K₂LaP₂Se₇,^[31] $A_{2}\text{ThP}_{3}\text{Se}_{9}$ (A = K, Rb),^[32] Cs₄ThP₅Se₁₇,^[32] and Rb₄Sn₅P₄Se₂₀.^[33] Three-dimensional structures include $K_{10}Sn_3(P_2Se_6)_4^{[22]}$ and $K(RE)P_2Se_6$ (RE = Y, La, Ce, Pr, Gd).^[3b] Many of these compounds have been isolated via the molten salt flux synthesis method,^[34] in which high melting reagents are dissolved in a lower-melting salt. In these conditions, products are able to form at lower temperatures than traditional solid state methods. Additionally, the acidity/basicity of the flux is easily tunable by varying the ratio of A_2 Se:Se (A = alkali metal). Therefore within the same system of elements, different products are stabilized with different flux ratios.

There are no known solved structures for quaternary selenophosphates containing both an alkali metal and zinc; hence, we performed exploratory synthesis experiments using the molten salt flux technique to uncover them. Herein we discuss the

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discovery of three new quaternary selenophosphates, $A_2 ZnP_2 Se_6 (A = K, Rb, Cs)$. These compounds resemble some of the aforementioned quaternary compounds in that the structures are comprised of $1/\infty [MP_2 Se_6]^{2-}$ chains. The zinc ions in $A_2 ZnP_2 Se_6$ are tetrahedrally coordinated to the $[P_2 Se_6]^{4-}$ units, and the alternation of Zn^{2+} and $[P_2 Se_6]^{4-}$ yields 1D chains. The potassium compound is monoclinic, whereas the rubidium and cesium compounds are triclinic, and all three compounds are centrosymmetric. The compounds were synthesized via the molten salt flux technique with stoichiometric and nonstoichiometric ratios of the starting materials. We describe the synthetic pathways utilized as well as the difficulties we encountered in attempts to synthesize pure samples of the compounds.

Experimental Section

Reagents

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All chemicals were used as obtained: potassium metal (98%, Sigma Aldrich, St. Louis, MO); rubidium metal (99.9+%, Strem Chemicals, Inc., Newburyport, MA); cesium metal (99.9+%, Strem Chemicals, Inc., Newburyport, MA); red phosphorus powder (99%, Sigma Aldrich, St. Louis, MO); selenium pellets (99.99%, Sigma Aldrich, St. Louis, MO); granular zinc (30 mesh, 99.8%, J.T. Baker Chemical Co., Phillipsburg, NJ); *N*,*N*-dimethylformamide (DMF) (99.8%, BDH, Radnor, PA); anhydrous ethyl ether (99%, Mallinckrodt Baker, Inc., Phillisburg, NJ); triethylphosphine (99%, Sigma Aldrich, St. Louis, MO). K₂Se, Rb₂Se₂ and Cs₂Se were synthesized by reacting stoichiometric ratios of phosphorus and selenium by traditional solid state methods; the synthesis is described elsewhere.^[3a]

Molten Salt Flux Synthesis

Starting materials were placed in 9 mm fused silica tubes in an inert nitrogen atmosphere contained within a glovebox. The tubes were evacuated to 10^{-4} mbar, flame sealed, and shaken to mix the contents. The reactions were heated to 500 °C, dwelled for 72 h, and cooled to room temperature in 48 h. The resulting material was placed in degassed, room-temperature DMF (50 mL) to dissolve the flux, and the DMF was changed after the solution had become a dark green or brown color. After the DMF solution remained clear, the samples were placed in diethyl ether (approx. 20 mL) and triethylphosphine (0.3 mL) was added to dissolve the excess selenium present. The products from these experiments were air and water sensitive and therefore stored in an evacuated desiccator.

K₂ZnP₂Se₆: A mixture of K₂Se (0.079 g, 0.5 mmol), Zn (0.016 g, 0.25 mmol), P₂Se₅ (0.228 g, 0.5 mmol), and Se (0.197 g, 2.5 mmol) in a 2:1:2:10 molar ratio of K₂Se:Zn:P₂Se₅:Se resulted in yellow rod crystals of K₂ZnP₂Se₆ (95%) and yellow block crystals of ZnSe (5%).

Rb₂ZnP₂Se₆: A mixture of Rb₂Se₂ (0.164 g, 0.5 mmol), Zn (0.016 g, 0.25 mmol), P₂Se₅ (0.228 g, 0.5 mmol), and Se (0.197 g, 2.5 mmol) in a 2:1:2:10 ratio of Rb₂Se₂:Zn:P₂Se₅:Se resulted in yellow rod crystals of Rb₂ZnP₂Se₆ (85%), orange rod crystals of RbPSe₆ (10%) and yellow block crystals of ZnSe (5%).

 $Cs_2ZnP_2Se_6$: A mixture of Cs_2Se (0.172 g, 0.5 mmol), Zn (0.016 g, 0.25 mmol), P_2Se_5 (0.228 g, 0.5 mmol), and Se (0.197 g, 2.5 mmol) in

a 2:1:2:10 ratio of Cs₂Se:Zn:P₂Se₅:Se resulted in yellow rod crystals of Cs₂ZnP₂Se₆ (50%) and orange rod crystals of β -CsPSe₆ (50%).

Direct Combination Synthesis

Stoichiometric amounts of the starting material were placed in 9 mm fused silica tubes in an inert nitrogen atmosphere contained within a glovebox. The tubes were evacuated to 10^{-4} mbar, flame sealed, and shaken to mix the contents. The tubes were heated to 500 °C in 5 h, dwelled for 10 h, and cooled to room temperature in 48 h. The products from these experiments were air and water sensitive and therefore stored in an evacuated desiccator.

K₂ZnP₂Se₆: A mixture of K₂Se (0.116 g, 0.736 mmol), Zn (0.048 g, 0.736 mmol), P (0.046 g, 1.47 mmol), and Se (0.291 g, 3.68 mmol) in a 1:1:2:5 molar ratio of K₂Se:Zn:P:Se resulted in a mixture of yellow rod crystals of K₂ZnP₂Se₆ (80%), orange rod crystals of K₂P₂Se₆ (10%), and yellow block crystals of ZnSe (10%).

Rb₂ZnP₂Se₆: A mixture of Rb₂Se₂ (0.223 g, 0.648 mmol), P (0.040 g, 1.30 mmol), Zn (0.042 g, 0.648 mmol), and Se (0.194 g, 2.46 mmol) in a 1:1:2:3.8 molar ratio of Rb₂Se₂:Zn:P:Se resulted in a mixture of yellow rod crystals of Rb₂ZnP₂Se₆ (95%) and yellow block crystals of ZnSe (5%).

Cs₂ZnP₂Se₆: A mixture of Cs₂Se (0.199 g, 0.577 mmol), Zn (0.038 g, 0.577 mmol), P (0.036 g, 1.15 mmol), and Se (0.228 g, 2.88 mmol) in a 1:1:2:5 molar ratio of Cs₂Se:Zn:P:Se resulted in a mixture of yellow rod crystals of Cs₂ZnP₂Se₆ (80%) and orange rod crystals of β -CsPSe₆ (20%).

Powder X-ray Diffraction (PXRD)

PXRD patterns were collected with a computer-controlled Rigaku Miniflex 600 powder diffractometer with Cu- K_{α} radiation operating at 40 kV and 15 mA and a high-speed silicon strip detector. Calculated PXRD patterns for A_2 ZnP₂Se₆ (A = K, Rb, Cs) were generated with CIFs through the Visualizer program in FINDIT.

Single Crystal X-ray Diffraction

Single crystals of $K_2ZnP_2Se_6$ (0.19×0.07×0.04 mm³), $Rb_2ZnP_2Se_6$ $(0.16 \times 0.10 \times 0.01 \text{ mm}^3)$, and $Cs_2ZnP_2Se_6$ $(0.04 \times 0.02 \times 0.01 \text{ mm}^3)$ were glued to the tip of a glass fiber. Both the Rb2ZnP2Se6 and Cs₂ZnP₂Se₆ crystals were twinned, and numerous attempts to find untwined crystals were unsuccessful. Measurements were collected with a STOE IPDS II single crystal diffractometer. The diffractometer operated at 50 kV and 40 mA with graphite-monochromatized Mo- K_{α} radiation ($\lambda = 0.71073$ Å) at room temperature. The detector comprised of a 34 cm diameter imaging plate, and the crystal had ω rotation during collection. X-Area software was used for data collection, integration was performed with X-RED and numerical absorption correction was executed with X-SHAPE. The crystal structures were solved using SHELXT in OLEX2.^[36] The K and Rb analogues were refined in the OLEX2 program and the Cs analogue was refined in Jana2006 due to twinning.^[37] Details on refining twinning are listed in the Supporting Information.

Scanning Electron Microscopy

Semi-quantitative microprobe analyses and energy dispersive spectroscopy (EDS) were conducted with a Hitachi S-3400 scanning electron microscope with a PGT energy-dispersive X-ray analyzer. The EDS spectra were collected at 25 kV accelerating voltage, 60 mA probe current, and with 60 s acquisition time. SEM-EDS analysis of multiple single crystals gave an average composition of $K_{2,2}Zn_{1,0}P_{2,0}Se_{6,2}$, $Rb_{2,1}Zn_{1,0}P_{2,2}Se_{6,2}$, and $Cs_{2,0}Zn_{1,0}P_{2,0}Se_{5,5}$.

Differential Thermal Analysis (DTA)

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Approximately 50–80 mg of each sample was placed in a silica ampoule and α -Al₂O₃, the reference, was placed in a separate ampoule. The ampoules were evacuated to 10⁻⁴ mbar and flame sealed. A Shimadzu DTA-50 thermal analyzer collected data with a rate of ± 5 K·min⁻¹ from room temperature to 700 °C. The temperature at the maxima of crystallizing peaks and minima of melting peaks are the reported crystallization and melting temperatures, respectively.

Supporting Information (see footnote on the first page of this article): X-ray crystallographic data in CIF format, atomic coordinates and displacement parameters, PXRD patterns of direct combination syntheses, SEM images, and EDS spectra.

Results and Discussion

Synthesis

The title compounds were synthesized via the molten salt flux synthesis technique using excess A_2 Se (A = K, Rb, Cs), P_2 Se₅, and Se to form the flux. The potassium and rubidium analogues yield a persistent ZnSe phase regardless of the flux composition or alkali metal (Figure 1a and b). Most flux syntheses of the cesium analogue additionally resulted in β -CsPSe₆ as a second phase (Figure 1c), but one particular flux synthesis, in which the ratios of the reagents Cs:Zn:P:Se were 2:1:3:8, yielded only very little amounts of ZnSe as a second



Figure 1. PXRD patterns of A_2 ZnP₂Se₆ (A = K, Rb, Cs) made with molten salt flux syntheses: (a) K_2 ZnP₂Se₆ showing ZnSe as a second phase; (b) Rb₂ZnP₂Se₆ showing RbPSe₆ and ZnSe as additional phases; (c) Cs₂ZnP₂Se₆ showing β -CsPSe₆ as a second phase; (d) Cs₂ZnP₂Se₆ synthesized via the 2:1:3:8 flux composition showing ZnSe as a slight second phase. Zoomed-in versions of these PXRD patterns in Figures S1–S4 (Supporting Information).

phase (Figure 1d). This demonstrates the benefits of molten salt flux syntheses in its ability to preferentially stabilize phases.

We also attempted to form the materials using stoichiometric amounts of the starting materials, which we call the direct combination method. These syntheses of the potassium analogue yields K₂ZnP₂Se₆ as the major phase, but it also contains K₂P₂Se₆^[19] and ZnSe^[38] as additional phases (Figure S5, Supporting Information). Direct combination reaction of the rubidium analogue results in Rb₂ZnP₂Se₆ as the major phase with ZnSe as a second phase (Figure S6). Direct combination of the cesium analogue consistently yields β -CsPSe₆^[39] as a second phase (Figure S7).

Attempts to make the glassy phases of the compounds were conducted by heating the direct combination stoichiometry of starting materials to temperatures ranging from 700–1100 °C then water quenching the reactions. All samples were a melt at the quenching temperatures used, but the resulting product was always crystalline and contained the second phases seen for other direct combination syntheses.

Crystal Structures

The new cesium and rubidium compounds crystallize in the triclinic space group $P\overline{1}$, and the potassium analogue crystallizes in the monoclinic space group $P2_1/c$ (Table 1). Even though the space groups are different, all three structures are similar. They contain parallel $1/\infty$ [ZnP₂Se₆]^{2–} chains comprised of alternating units of tetrahedrally coordinated Zn²⁺ ions to the ethane-like [P₂Se₆]^{4–} units (Figure 2). The chains are separated by charge-balancing alkali metal ions to make up the unit cell. In all three compounds, there is an inversion center, which causes adjacent ZnSe₄ tetrahedra within the same chain to face opposite directions, giving centrosymmetric chain conformation. In the cesium and rubidium structures, this is the only symmetry and therefore there are two asymmetric units in the unit cell (Figure 3).



Figure 2. Structure of $1/\infty [ZnP_2Se_6]^{2-}$ chains in $A_2ZnP_2Se_6$ with ellipsoids set to 90% probability; (a) along the chain; (b) down the chain. Color scheme: selenium (red), zinc (cyan), and phosphorus (black).

Table 1. Crystal data and structure refinement for A₂ZnP₂Se₆.

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	$K_2ZnP_2Se_6$	$Rb_2ZnP_2Se_6$	$Cs_2ZnP_2Se_6$
Formula weight	679.27	772.01	866.9
Temperature /K	293(2)	293(2)	293(2)
Wavelength /Å	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
Unit cell lengths and angles	-		
a /Å	12.537(3)	7.4944(15)	7.6543(6)
b /Å	7.2742(15)	7.6013(15)	7.7006(6)
c /Å	14.164(3)	12.729(3)	12.7373(11)
a /°	90.00	96.57(3)	97.007(7)
β/°	109.63(3)	105.52(3)	104.335(7)
γ /°	90.00	110.54(3)	109.241(6)
Volume /Å ³	1216.7(4)	636.6(2)	669.54(10)
Z	4	2	2
Calculated $\rho / \text{g·cm}^{-3}$	3.708	4.028	4.2986
μ / mm^{-1}	20.857	26.874	23.688
F(000)	1208	676	748
θ range for data collection	1.72 to 29.14°	1.71 to 25.00°	3.39 to 34.34°
Index ranges	$-17 \le h \le 17$	$-8 \le h \le 8$	$-12 \le h \le 11$
	$-9 \le k \le 9$	$-9 \le k \le 9$	$-12 \le k \le 12$
	$-19 \le l \le 18$	$-15 \le l \le 13$	$-20 \le l \le 20$
Reflections collected	11290	8129	18911
Independent reflections	3265	2232	2410
R _{int}	0.0589	0.0724	0.0575
Completeness to $\theta = 25^{\circ}$	99.90%	99.90%	99.90%
Refinement method		Full-matrix least-squares on F^2	
Data / restraints / parameters	3265 / 0 / 100	2232 / 0 / 100	2410 / 0 / 101
Goodness-of-fit	0.988	1.333	5.61
Final <i>R</i> indices ^{a)} [> $2\sigma(I)$]	$R_{\rm obs} = 0.0356$	$R_{\rm obs} = 0.0397$	$R_{\rm obs} = 0.0590$
	$wR_{\rm obs} = 0.0565$	$wR_{\rm obs} = 0.0831$	$wR_{\rm obs} = 0.1792$
R indices ^{a)} [all data]	$R_{\rm all} = 0.0603$	$R_{\rm all} = 0.0447$	$R_{\rm all} = 0.0658$
	$wR_{\rm all} = 0.0612$	$wR_{\rm all} = 0.0845$	$wR_{\rm all} = 0.1817$

a) $R = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$; $wR = \{\Sigma [w(|F_0|^2 - |F_c|^2)^2] / \Sigma [w(|F_0|^4)] \}^{1/2}$ and calcd $w = 1 / [\sigma^2 (F_0^2) + (0.0234 \text{P})^2 + 0.0000\text{P}]$, where $\text{P} = (F_0^2 + 2F_c^2) / 3$.



Figure 3. Crystal structure of $Cs_2ZnP_2Se_6$ and $Rb_2ZnP_2Se_6$ as viewed down the *b* axis with ellipsoids set to 90% probability. Color scheme: cesium or rubidium (green), selenium (red), zinc (cyan), and phosphorus (black).

The potassium phase has other symmetry in addition to the inversion center, namely a 2_1 screw axis about the *b* axis normal to a *c*-glide plane (Figure 4). This creates two additional asymmetric units in the potassium unit cell, resulting in a vol-



Figure 4. Crystal structure of $K_2ZnP_2Se_6$ as viewed down the *c* axis with ellipsoids set to 90% probability. Color scheme: potassium (blue), selenium (red), zinc (cyan), and phosphorus (black).

ume that is about twice that of the rubidium and cesium compound unit cells: 1216.7(4) Å³ for K₂ZnP₂Se₆, and 636.6(2) Å³ and 669.54(10) Å³ for Rb₂ZnP₂Se₆ and Cs₂ZnP₂Se₆, respectively. The compositional phase transition from monoclinic to triclinic going from K to Rb and Cs also reflects on the coordination of the alkali metal. In monoclinic K₂ZnP₂Se₆, there are 4 and 6 contacts, respectively, by the two crystallographically



	$K_2ZnP_2Se_6$	$Rb_2ZnP_2Se_6$	$Cs_2ZnP_2Se_6$	
Zn–Se	2.383(1)-2.489(1)	2.473(1)-2.492(1)	2.468(3)-2.498(3)	
P–P	2.239(2)-2.245(2)	2.253(1)-2.255(1)	2.247(6)-2.260(7)	
P-Se(bridging)	2.206(2)-2.215(2)	2.201(1)-2.205(1)	2.199(7)-2.210(7)	
P-Se(terminal)	2.139(2)-2.141(2)	2.128(1)-2.145(1)	2.134(6)-2.145(6)	
Se–Zn–Se	103.99(3)-114.25(3)	100.99(1)-121.68(2)	100.79(11)-123.13(12)	

Table 2. Selected bond lengths /Å and angles /° in A_2 ZnP₂Se₆.

distinct K atoms to Se within the sum of their ionic radii.^[40] On the other hand, in triclinic $Rb_2ZnP_2Se_6$ and $Cs_2ZnP_2Se_6$, there are 6 contacts between each Rb or Cs atom to Se within the sum of their ionic radii. This shows that the Rb and Cs analogues tend to adopt a higher coordination number than the K analogue. This behavior follows the general trend of increasing coordination number with increasing atomic radii and is responsible for the observed structural transition.

In all three materials, all of the Zn–Se bond lengths are normal, and Zn has slightly distorted tetrahedral coordination, as evidenced by the Se–Zn–Se bond angles (Table 2). The P–P bonds are normal for $[P_2Se_6]^{4-}$ units, and as expected, the P– Se bridging bonds are slightly longer than the P–Se terminal bonds (Table 2).

The A_2 ZnP₂Se₆ structure is analogous to other materials with 1D chains of $1/_{\infty}[MP_2Se_6]^{2-}$. The metal coordination has been shown to be octahedral $[A_2MP_2Se_6 (A = K, Rb, Cs; M =$ Mn, Fe, Sn, Cd, Mg)], $[^{3a,18c,20,22]}$ square planar $[A_2PdP_2Se_6 (A + A_2PdP_2Se_6)]$ = K, Cs)],^[20,21] or tetrahedral $[A_2HgP_2Se_6 (A = K, Rb)]$,^[20] depending on the coordination preferences of the metal. This shows the versatility of the $[P_2Se_6]^{4-}$ unit in exploratory synthesis. In the title compounds, we found the Zn²⁺ is tetrahedrally coordinated to [P₂Se₆]⁴⁻, as expected. This is a difference from the prediction of octahedral coordination made in a previous article from our group,^[20] where it was reported that microcrystals were found of K₂ZnP₂Se₆ but were too small for single-crystal X-ray diffraction. K₂ZnP₂Se₆ was expected to be isostructural with A_2 CdP₂Se₆ (A = K, Rb, Cs)^[20] and therefore have octahedrally coordinated Zn. Due to similar PXRD patterns between the Zn²⁺ and Cd²⁺ quaternaries, we initially assumed that Zn²⁺ also had octahedral coordination in the quaternary compound. Our work shows this assumption was incorrect, and the Zn^{2+} is actually tetrahedrally coordinated.

Thermal Properties

Differential thermal analysis experiments showed that all three materials with ZnSe as a second phase (melting point: $1522 \,^{\circ}C$)^[41] melt incongruently with the final melting peak at 620 $^{\circ}C$ for K₂ZnP₂Se₆, 656 $^{\circ}C$ for Rb₂ZnP₂Se₆, and 674 $^{\circ}C$ for Cs₂ZnP₂Se₆. The phases recrystallize at 578 $^{\circ}C$ for K₂ZnP₂Se₆, 640 $^{\circ}C$ for Rb₂ZnP₂Se₆, and 661 $^{\circ}C$ for Cs₂ZnP₂Se₆.

Conclusions

All three A_2 ZnP₂Se₆ (A = K, Rb, Cs) are centrosymmetric and comprised of 1D $\frac{1}{\infty}$ [ZnP₂Se₆]²⁻ chains charge balanced by alkali metal ions. $1/\infty$ [ZnP₂Se₆]²⁻ has tetrahedrally coordinated Zn²⁺ to the adaptable [P₂Se₆]⁴⁻ ligand. Thus far, direct combination syntheses led to K₂P₂Se₆, RbPSe₆, β -CsPSe₆, and ZnSe as additional phases while nonstoichiometric flux syntheses successfully eliminated all additional phases except for ZnSe. Further work should be conducted on this system to obtain the pure phases so additional characterization can be performed.

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One-Dimensional Zinc Selenophosphates: A_2 ZnP₂Se₆ (A = K, Rb, Cs)

