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Soft−Hard Acid−Base Interactions: Probing Coordination Preferences of Sulfur and Selenium in Mixed Chalcophosphates in the Family $APbPS_{4-x}Se_x$ (A = K, Rb, Cs; x = 0−4)

Alexander Rothenberger,[†] Collin Morris,[†] Hsien-Hau Wang,[‡] Duck Young Chung,[‡] and Mercouri G. Kanatzidis*[,†,‡]

[†] *Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, and*
[‡] *Materials Science Division (Bldg. 223), Argonne National Laboratory, 9700 S. Cass Ave., Argonne, Illinois 60439*

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The synthesis and structures of the three new compounds, $KPbPS_{1.84}Se_{2.16}$ (**1**), $RbPbPS_{1.56}Se_{2.43}$ (**2**), and $CsPbPS_{3.46}Se_{0.54}$ (**3**), are reported. The solid state structures of **1**−**3** consist of two-dimensional layers of $[PbP(S/Se)_4]$ separated by alkali metal ions. The structure of **1** was solved in the orthorhombic space group $Pna2_1$. Compounds **2** and **3** possess the $CsSmGeS_4$ structure type, crystallizing in the orthorhombic space group $P2_12_12_1$. All compounds were refined as racemic twins. All chalcogen sites around the tetrahedrally coordinated P atoms show mixed S/Se occupancy; however, there is a preference for Se binding to Pb ions and S binding to alkali ions. A ^{31}P magic angle spinning NMR study on **1** suggests that, in mixed seleno-/thiophosphates, all of the anions $[PS_xSe_{4-x}]^{3-}$ (x = 0, 1, 2, 3, 4) are present. The different amount of sulfur and selenium present in $KPbPS_{1.84}Se_{2.16}$ (**1**), $RbPbPS_{1.56}Se_{2.43}$ (**2**), and $CsPbPS_{3.46}Se_{0.54}$ (**3**) is reflected in the solid state absorption spectra from which bandgaps of 2.2 eV were determined for **1** and **2**, and a blue-shift to 2.5 eV was observed because of the higher sulfur-content in **3**. Thermogravimetric analysis experiments indicated that, upon heating, compound **1** decomposes forming PbSe and sulfur together with other unidentified products. A Raman spectrum of compound **1** showed more bands than are usually observed in seleno- or thiophosphate salts and is another indicator of the mixed seleno-/thiophosphate anions found in **1**.

Introduction

A great variety of selenophosphate anions have been synthesized, including the discrete anions $[PSe_4]^{3-}$,[1] $[P_2Se_6]^{4-}$,[2,3] $[P_2Se_9]^{4-}$,[4] and $[P_8Se_{18}]^{6-}$ [5] and the polymeric anions $^{1}/_{\infty}[P_2Se_6^{2-}]$,[6] $^{1}/_{\infty}[PSe_6^{-}]$,[7] and $^{1}/_{\infty}[P_5Se_{10}^{5-}]$.[8] In order to enhance the properties of metal selenophosphates for potential use in semiconducting devices,[9] as phase-change materials in read−write devices, and as nonlinear optical materials,[6] several new directions are pursued. A promising route involves the incorporation of heavy and polarizable p-block elements into selenophosphate coordination environments. In $Cs_5BiP_4Se_{12}$, for example, the complex anion $[Bi(P_2Se_6)_2]^{5-}$ is held together by weak Se···Se interactions, and the phase can be processed to transparent fibers. These are transparent in the near- and mid-IR ranges and were found to exhibit a nonlinear optical second harmonic generation response at 1 μm that is approximately twice that of the benchmark material $AgGaSe_2$.[10] Less established is the modification of the chalcophosphate anions, for example, by mixing group 16 elements Q in $[PQ_4]^{3-}$ anions or other chalcophosphate derivatives.[11,12] Whereas the thiophosphate anions $[PO_xS_{4-x}]^{3-}$ (x = 1−3) can be readily obtained by the treatment of P_4S_{10} or PCl_3 with aqueous NaOH solutions,[13−19] similar reactions of P_2Se_5 resulted in the

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*To whom correspondence should be addressed. Fax: +1-847-491-5937. E-mail: m-kanatzidis@northwestern.edu.

(1) Knaust, J. M.; Dorhout, P. K. *J. Chem. Crystallogr.* **2006**, *36*, 217–223.
(2) Francisco, R. H. P.; Tepe, T.; Eckert, H. *J. Solid State Chem.* **1993**, *107*, 452–459.
(3) (a) McCarthy, T. J.; Kanatzidis, M. G. *Inorg. Chem.* **1995**, *34*, 1257–1267. (b) McCarthy, T. J.; Kanatzidis, M. G. *Chem. Mater.* **1993**, *5*, 1061–1063.
(4) Chondroudis, K.; McCarthy, T. J.; Kanatzidis, M. G. *Inorg. Chem.* **1996**, *35*, 840–844.
(5) Chondroudis, K.; Kanatzidis, M. G. *Inorg. Chem.* **1998**, *37*, 2582–2584.
(6) Chung, I.; Malliakas, C. D.; Jang, J. I.; Canlas, C. G.; Weliky, D. P.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2007**, *129*, 14996–15006.
(7) Banerjee, S.; Malliakas, C. D.; Jang, J. I.; Ketterson, J. B.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2008**, *130*, 12270−12272.
(8) Chondroudis, K.; Kanatzidis, M. G. *Angew. Chem., Int. Ed.* **1997**, *36*, 1324–1326.
(9) Afzaal, M.; O'Brien, P. *J. Mater. Chem.* **2006**, *16*, 1597–1602.
(10) Chung, I.; Song, J.-H.; Jang, J. I.; Freeman, A. J.; Ketterson, J. B.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2009**, *131*, 2647–2656.
(11) Gagor, A.; Pietraszko, A.; Panko, V. V. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2008**, *64*, I33–I34.
(12) Evain, M.; Queignec, M.; Brec, R.; Sourisseau, C. *J. Solid State Chem.* **1988**, *75*, 413–431.
(13) Kubierschky, C. *J. Prakt. Chem.* **1885**, *31*, 93–111.
(14) Yasuda, S. K.; Lambert, J. L. *Inorg. Synth.* **1957**, *5*, 102–104.

formation of salts containing the water-stable anion $[P_2Se_6]^{4-}$.[20] These findings prompted the investigation of related mixed thio-/selenophosphate anions. We hypothesized that, in a mixed S/Se environment, a molten mixture containing soft Lewis acid metal ions such as Pb^{2+} and hard acids such as alkali metal ions, we would observe a coordination preference of the chalcogens in the $[PS_{4-x}Se_x]^{3-}$ ions consistent with the hard and soft acids and bases concept.[21] Namely, the softer Se^{2-} ions would exhibit predominantly Pb−Se bonding, whereas the less soft S^{2-} ions would be primarily engaged in A−S bonding. Although a strong entropically driven tendency for randomly mixed $[PS_{4-x}Se_x]^{3-}$ ions is expected, mixtures of $[PS_4]^{3-}$ and $[PSe_4]^{3-}$ ions may also be present. We describe here a case study of the system A/Pb/P/S/Se (A = K, Rb, Cs) addressing these issues and determine the nature of the mixed chalcophosphate anion by solid state NMR spectroscopy.

Experimental Section

P_2Se_5 was prepared by heating the stoichiometric mixture of P and Se in an evacuated sealed quartz tube at 460 °C for 24 h.

Compounds 1−3. A mixture of 0.45 mmol of alkali metal sulfide, 205 mg (0.45 mmol) of P_2Se_5, 28 mg (0.80 mmol) of S, and 186 mg (0.90 mmol) of Pb was sealed in a quartz tube under vacuum. The reaction was heated to 500 °C over the course of 24 h and kept at this temperature for 3 days. Cooling to 250 °C (5 K/h) and to 50 °C (10 K/h) gave orange (**1** and **2**) and yellow (**3**) crystalline solids that were covered in a gray flux medium. The solid residue was washed with a mixture of 20 mL MeHO and 0.5 mL of $P(n\mathrm{Bu})_3$ placed in an ultrasound bath. The $MeOH/P(n\mathrm{Bu})_3$ mixture was decanted, and crystals were washed with MeOH and Et_2O and dried in a stream of dinitrogen (yield 80% for **1**, 20% for **2** and **3**). The presence of metals, P, S, and Se was confirmed by semiquantitative energy dispersive X-ray analysis (EDS) on a Hitachi S-3400 scanning electron microscope (SEM) equipped with a PGT energy dispersive X-ray analyzer. Solid state absorption spectra were measured on a U-6000 microscopic FT spectrophotometer using single crystals suspended in parrafine oil. The TGA measurements were performed on a Shimadzu TGA-50 thermogravimetric analyzer in aluminum boats under a N_2 flow. The Raman measurements are carried out at room temperature with the use of a Raman microscope spectrometer (Renishaw, Ltd.) equipped with a HeNe laser (632.8 nm). The Raman spectrum is calibrated against a Si wafer standard (520 cm^{-1}). ^{31}P magic angle spinning (MAS) NMR spectra were recorded on a Varian Mercury 400 spectrometer and referenced to $NH_4H_2PO_4$ (δ 0.8). The delay time between scans was 60s.

X-Ray Crystallographic Study. Data for **1−3** were collected on a Stoe IPDS 2T diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least-squares on F^2 (all data) using the SHELXTL program package.[22] All S atoms and all Se atoms were assigned common thermal parameters using the EADP instruction.[22] Numerical absorption corrections were performed for **1−3**. A summary of crystal data and refinement parameters is given in Table 1. Atomic coordinates are listed in Table 2.

Table 1. Details of the X-Ray Data Collection and Refinements for $KPbPS_{1.84}Se_{2.16}$ (**1**), $RbPbPS_{1.56}Se_{2.43}$ (**2**), and $CsPbPS_{3.46}Se_{0.54}$ (**3**)

compound	**1**	**2**	**3**
formula	$KPbPS_{1.84}Se_{2.16}$	$RbPbPS_{1.56}Se_{2.43}$	$CsPbPS_{3.46}Se_{0.54}$
fw	506.92	566.07	524.75
T/K	100(2)	100(2)	100(2)
cryst syst	orthorhombic	orthorhombic	orthorhombic
space group	$Pna2_1$	$P2_12_12_1$	$P2_12_12_1$
a/Å	17.0617(12)	6.6040(13)	6.3226(4)
b/Å	6.6134(6)	6.8560(14)	6.8060(3)
c/Å	6.7435(5)	17.594(4)	18.0909(10)
V/Å^3	760.91(10)	796.6(3)	778.48(7)
Z	4	4	4
ρ/g·cm^{-1}	4.425	4.720	4.477
μ/mm^{-1}	33.664	38.878	29.838
F(000)	876	967	903
reflns collected	6214	6621	7227
unique data	2011	2141	2105
R_{int}	0.0406	0.0491	0.0358
params	59	59	59
R_1[a] [$I > 2\sigma(I)$]	0.0338	0.0403	0.0247
wR$_2$[b] (all data)	0.0683	0.0737	0.0550
BASF param	0.493(10)	0.506(15)	0.494(7)

[a] $R_1 = \sum \| F_o| - |F_c\| / \sum |F_o|$. [b] $wR_2 = \{\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\}^{1/2}$.

Results and Discussion

Synthesis. Phases containing the element combinations A/Pb/P/S[23−26] and A/Pb/P/Se[27,28] (A = K, Rb, Cs) are prepared using reactive salt fluxes.[29] In order to obtain a mixed seleno/thiophosphate, a mixture of lead, alkali metal sulfide, elemental sulfur, and P_2Se_5 as the only potential selenium source was melted (ratio $Pb/A_2S/S/P_2Se_5$ = 1:1:2:2; A = K, Rb, Cs). In the course of the reaction, elemental selenium is formed, indicating that some of the Se atoms bound to phosphorus are substituted by sulfur atoms. At room temperature, the solidified melts were crushed, and byproducts were removed by washing with a solution of $P(n\text{-}\mathrm{Bu})_3$ in methanol under an ambient atmosphere (Scheme 1). Analogous reactions with the lighter alkali metal salts Li_2S and Na_2S were also performed. In the case of Li_2S, by EDS, only an amorphous aggolmerate consisting of Pb, P, S, and Se in the ratio 1:1:1:2 was detected (the presence of lithium cannot be detected by EDS). For the reaction with the alkali metal sulfide Na_2S (Scheme 1), PbSe and $PbPSe_3$[30] were the only crystalline compounds that were obtained. Modification of the reaction conditions may, however, result in the formation of compounds related

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(15) Pompetzki, M.; Jansen, M. *Monatsh. Chem.* **2002**, *133*, 975–986.

(16) Pompetzki, M.; Dinnebier, R. E.; Jansen, M. *Solid State Sci.* **2003**, *5*, 1439–1444.

(17) Pompetzki, M.; Jansen, M. *Z. Anorg. Allg. Chem.* **2003**, *629*, 1929–1933.

(18) Takas, N. J.; Aitken, J. A. *Inorg. Chem.* **2006**, *45*, 2779–2781.

(19) Gjikaj, M. *Z. Kristallogr., New Cryst. Struct.* **2008**, *223*, 1–2.

(20) Rothenberger, A.; Malliakas, C. D.; Kanatzidis, M. G. *Z. Anorg. Allg. Chem.* **2009**, *635*, DOI: 10.1002/zaac.200900184.

(21) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533–3539.

(22) Sheldrick, G. M. *SHELXTL*, v. 5.1; University of Göttingen: Göttingen, Germany, 1997.

(23) Belkyal, I.; El Azhari, M.; Wu, Y. D.; Bensch, W.; Hesse, K. F.; Depmeier, W. *Solid State Sci.* **2006**, *8*, 59–63.

(24) Belkyal, I.; El Azhari, M.; Wu, Y. D.; Bensch, W.; Hesse, K. F.; Depmeier, W. *Z. Kristallogr., New Cryst. Struct.* **2005**, *220*, 127–128.

(25) Aitken, J. A.; Kanatzidis, M. G. *Inorg. Chem.* **2001**, *40*, 2938–2939.

(26) Yao, J.; Ibers, J. A. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2004**, *E60*, i108–i110.

(27) Aitken, J. A.; Marking, G. A.; Evain, M.; Iordanidis, L.; Kanatzidis, M. G. *J. Solid State Chem.* **2000**, *153*, 158–169.

(28) Canlas, C. G.; Kanatzidis, M. G.; Weliky, D. P. *Inorg. Chem.* **2003**, *42*, 3399–3405.

(29) Kanatzidis, M. G. *Curr. Opin. Solid State Mater. Sci.* **1997**, *2*, 139–149.

(30) Yun, H.; Ibers, J. A. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1987**, *C43*, 2002–2004.

Table 2. Wyckoff symbols, site occupancy factors (S. O. F.), atomic coordinates and displacement parameters (in Å^2) for $KPbPS_{1.84}Se_{2.16}$ (**1**), $RbPbPS_{1.56}Se_{2.43}$ (**2**), $CsPbPS_{3.46}Se_{0.54}$ (**3**)

$KPbPS_{1.84}Se_{2.16}$ (**1**)

atom	Wyck.	S. O. F.	*x*/*a*	*y*/*b*	*z*/*c*	U_{iso}
K1	4a	1	0.28706(12)	0.4801(4)	0.0074(4)	0.0209(5)
P1	4a	1	0.40088(13)	0.2785(4)	0.4956(3)	0.0071(4)
Pb1	4a	1	0.02212(2)	0.28393(5)	0.03110	0.0122(1)
S1	4a	0.154(9)	0.0267(12)	0.122(3)	0.439(3)	0.0064(8)
S2	4a	0.607(9)	0.1141(4)	0.5986(12)	0.2533(11)	0.0064(8)
S3	4a	0.464(7)	0.1756(4)	0.0287(11)	0.0000(15)	0.0064(8)
S4	4a	0.608(8)	0.3700(4)	0.1163(8)	0.2483(8)	0.0064(8)
Se1	4a	0.846(9)	0.02710(8)	0.1509(2)	0.47772(16)	0.0096(3)
Se2	4a	0.393(9)	0.1245(3)	0.6108(8)	0.2529(7)	0.0096(3)
Se3	4a	0.536(7)	0.16831(16)	0.0496(4)	0.0014(5)	0.0096(3)
Se4	4a	0.392(8)	0.3756(3)	0.0810(6)	0.2494(6)	0.0096(3)

$RbPbPS_{1.56}Se_{2.43}$ (**2**)

atom	Wyck.	S. O. F.	*x*/*a*	*y*/*b*	*z*/*c*	U_{iso}
P1	4a	1	0.2208(5)	0.0115(4)	0.34749(15)	0.0091(5)
Pb1	4a	1	0.28656(7)	0.47176(6)	0.22911(3)	0.0116(1)
Rb1	4a	1	0.0014(2)	0.00334(19)	0.03922(6)	0.0196(2)
S1	4a	0.446(8)	0.0622(16)	0.505(2)	0.0877(6)	0.0056(11)
S2	4a	0.186(9)	0.128(3)	0.072(3)	0.2249(12)	0.0056(11)
S3	4a	0.49(1)	0.3864(13)	0.2558(13)	0.3763(6)	0.0056(11)
S4	4a	0.49(2)	0.5920(17)	0.2542(16)	0.1369(6)	0.0056(11)
Se1	4a	0.554(8)	0.0439(6)	0.5050(8)	0.0830(2)	0.0107(4)
Se2	4a	0.814(9)	0.1508(2)	0.0324(2)	0.22553(11)	0.0107(4)
Se3	4a	0.51(1)	0.4164(6)	0.2576(6)	0.3734(3)	0.0107(4)
Se4	4a	0.51(2)	0.6109(8)	0.2525(7)	0.1307(3)	0.0107(4)

$CsPbPS_{3.46}Se_{0.54}$ (**3**)

atom	Wyck.	S. O. F.	*x*/*a*	*y*/*b*	*z*/*c*	U_{iso}
Cs1	4a	1	0.06060(8)	0.49471(7)	0.45474(3)	0.0180(1)
P1	4a	1	0.7827(3)	0.9841(3)	0.34670(9)	0.0063(3)
Pb1	4a	1	0.70699(4)	0.53079(4)	0.23397(1)	0.0087(1)
S1	4a	0.863(6)	0.5932(7)	0.7440(6)	0.3731(3)	0.0095(6)
S2	4a	0.866(6)	0.3876(9)	0.7402(8)	0.1327(3)	0.0095(6)
S3	4a	0.781(6)	0.8465(7)	0.9504(6)	0.2332(3)	0.0095(6)
S4	4a	0.936(6)	0.9436(7)	0.4938(9)	0.0946(3)	0.0095(6)
Se1	4a	0.137(6)	0.6166(14)	0.7386(14)	0.3777(6)	0.0059(13)
Se2	4a	0.134(6)	0.393(2)	0.7338(18)	0.1399(6)	0.0059(13)
Se3	4a	0.219(6)	0.8374(9)	0.9728(7)	0.2303(4)	0.0059(13)
Se4	4a	0.064(6)	0.926(4)	0.490(5)	0.0954(16)	0.0059(13)

Scheme 1. Synthesis of **1**−**3** [A = K (**1**), Rb (**2**), Cs (**3**)]

$$A_2S+2S+2P_2Se_5+Pb \xrightarrow{550\ ^\circ C} KPbPS_{1.84}Se_{2.16}\ (\mathbf{1})/RbPbPS_{1.56}Se_{2.43}\ (\mathbf{2})/CsPbPS_{3.46}Se_{0.54}\ (\mathbf{3})$$

to $Na_6Pb_3(PS_4)_4$.[25] For the more basic A_2S (A = K, Rb, Cs), the mixed seleno-/thiophosphate salts $KPbPS_{1.84}Se_{2.16}$ (**1**), $RbPbPS_{1.56}Se_{2.43}$ (**2**), and $CsPbPS_{3.46}Se_{0.54}$ (**3**) were obtained (Scheme 1).

$KPbPS_{1.84}Se_{2.16}$ (**1**) crystallizes as a racemic twin in the orthorhombic space group *Pna*2$_1$. Examination of the resultant atomic coordinates with the program Addsym in the Platon suite of programs did not reveal additional symmetry.[31] Refinement in the centrosymmetric space group *Pnma* was attempted, but the Se/S mixed occupancy could not be modeled and the refinement did not converge. On the basis of EDS results (Supporting Information), which showed a S/Se ratio of ca. 1:1, the four chalcogen sites around P(1) were refined as split S/Se positions. Each mixed site was refined in different parts using free variables determining the ratio of S/Se. In the solid state, the structure of **1** is structurally related to $RbPbPS_4$ and consists of [PbP(S/Se)$_4$] layers that are separated by the potassium ions (Figures 1b and 2, Table 3).[26] Each potassium ion is coordinated by a distorted trigonal bicapped prism of eight chalcogen atoms, and the P atoms are coordinated by a tetrahedron of four chalcogen atoms (Figure 1a). Each Pb atom is chelated by two chalcogen atoms of three chalcophosphate anions and one S/Se atom of another chalcophosphate anion, resulting in a trigonal monocapped prismatic coordination environment around the lead atoms (Figure 1a). The chalcogen atoms Se(1,2,4) and

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(31) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7–13.

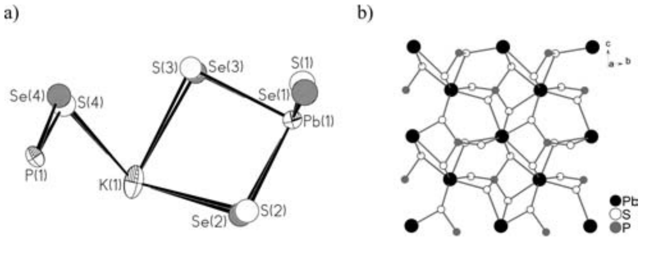

Figure 1. (a) Representation of the asymmetric unit in the mixed seleno-/thiophosphate **1** (ellipsoids for Pb, K, and P at 90% probability level). (b) Section of a [PbP(S/Se)$_4$] layer. Selenium atoms were omitted for clarity.

Table 3. Selected Geometric Parameters in **1** (Å, deg)^a

P(1)−S(1)$^{\mathrm{iii}}$	2.28(2)	Pb(1)−S(2)$^{\mathrm{viii}}$	3.084(7)
P(1)−S(2)$^{\mathrm{i}}$	2.121(8)	Pb(1)−S(3)	3.123(6)
P(1)−S(3)$^{\mathrm{ii}}$	2.108(9)	Pb(1)−Se(3)	2.943(2)
P(1)−S(4)	2.051(6)	Pb(1)−Se(1)$^{\mathrm{vi}}$	3.0175(14)
P(1)−Se(1)$^{\mathrm{iii}}$	2.207(3)	Pb(1)−Se(4)$^{\mathrm{vii}}$	3.036(4)
P(1)−Se(2)$^{\mathrm{i}}$	2.104(5)	Pb(1)−Se(1)	3.1388(12)
P(1)−Se(3)$^{\mathrm{ii}}$	2.147(4)	Pb(1)−Se(2)	3.157(5)
P(1)−Se(4)	2.156(4)	Pb(1)−Se(2)$^{\mathrm{viii}}$	3.204(5)
K(1)−S(4)	3.229(6)	S(4)−P(1)−Se(2)$^{\mathrm{i}}$	110.0(2)
K(1)−S(4)$^{\mathrm{iv}}$	3.324(6)	S(4)−P(1)−S(3)$^{\mathrm{ii}}$	105.2(3)
K(1)−S(1)$^{\mathrm{iv}}$	3.35(2)	Se(2)$^{\mathrm{i}}$−P(1)−S(3)$^{\mathrm{ii}}$	105.9(3)
K(1)−S(3)$^{\mathrm{ii}}$	3.397(10)	S(4)−P(1)−S(2)$^{\mathrm{i}}$	110.0(3)
K(1)−S(2)	3.475(7)	S(3)$^{\mathrm{ii}}$−P(1)−S(2)$^{\mathrm{i}}$	110.7(3)
K(1)−S(2)$^{\mathrm{v}}$	3.485(7)	S(4)−P(1)−Se(3)$^{\mathrm{ii}}$	108.1(2)
K(1)−Se(4)$^{\mathrm{iv}}$	3.343(5)	Se(2)$^{\mathrm{i}}$−P(1)−Se(3)$^{\mathrm{ii}}$	108.18(18)
K(1)−Se(2)	3.343(5)	S(2)$^{\mathrm{i}}$−P(1)−Se(3)$^{\mathrm{ii}}$	112.8(2)
K(1)−Se(1)$^{\mathrm{iv}}$	3.372(3)	Se(2)$^{\mathrm{i}}$−P(1)−Se(4)	105.9(2)
K(1)−Se(3)$^{\mathrm{ii}}$	3.448(4)	S(3)$^{\mathrm{ii}}$−P(1)−Se(4)	111.3(3)
K(1)−Se(4)	3.452(5)	S(2)$^{\mathrm{i}}$−P(1)−Se(4)	105.5(2)
Pb(1)−S(1)$^{\mathrm{vi}}$	2.879(19)	Se(3)$^{\mathrm{ii}}$−P(1)−Se(4)	114.21(17)
Pb(1)−S(1)	2.951(17)	S(4)−P(1)−Se(1)$^{\mathrm{iii}}$	108.5(2)
Pb(1)−S(2)	3.006(7)	Se(2)$^{\mathrm{i}}$−P(1)−Se(1)$^{\mathrm{iii}}$	110.94(15)
Pb(1)−S(4)$^{\mathrm{vii}}$	3.052(6)		

^{a} Symmetry codes: (i) $x+1/2, y-1/2, z+1/2$; (ii) $-x+1/2, y+1/2, z+1/2$; (iii) $x+1/2, -y+1/2, z$; (iv) $-x+1/2, y+1/2, z-1/2$; (v) $-x+1/2, y-1/2, z-1/2$; (vi) $-x, -y, z-1/2$; (vii) $x-1/2, -y+1/2, z$; (viii) $-x, -y+1, z-1/2$.

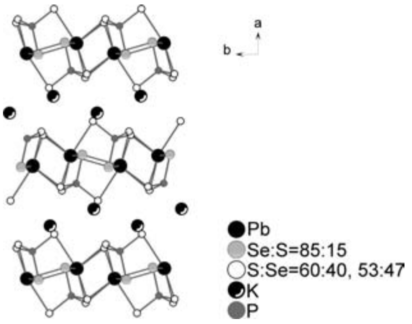

Figure 2. The structure of KPbPS$_{1.84}$Se$_{2.16}$ (**1**) viewed down [001]. The [PbP(S/Se)$_4$] layer-embedded chalcogen positions are predominantly occupied with selenium.

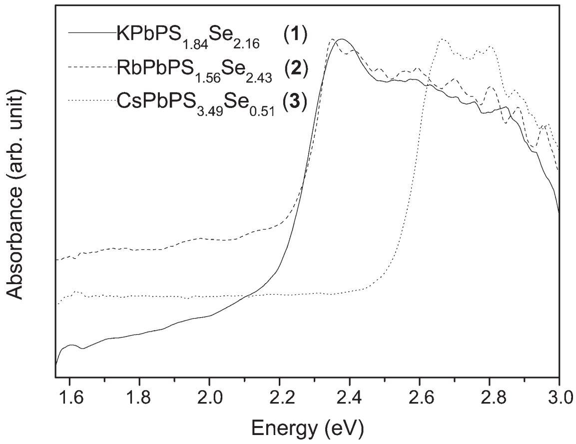

Figure 3. Solid-state UV−vis optical absorption spectra of single crystals of **1**−**3**. The band gaps for **1** and **2** are ca. 2.2 eV. The band gap of **3** is ca. 2.5 eV.

S(1,2,4) all coordinate Pb atoms in the bridging mode and show refined S/Se ratios of S(1)/Se(1) = 15:85 and 60:40 for the remaining S/Se split positions. It is noteworthy that the chalcogen positions S/Se(1) are embedded in the 2D slabs of [PbPS$_4$]$^-$, and that there is a marked preference for selenium over sulfur at this Pb-binding site (Figure 2). P−S bond distances found in **1** are ca. 0.1 Å longer than P−S distances found in KPbPS$_4$, whereas P−Se bond distances are within what is commonly observed in salts containing [PSe$_4$]$^{3-}$ anions.[23,32]

Compounds **2** and **3** are isostructural to RbPbPS$_4$, and they were refined as racemic twins in the space group $P2_12_12_1$.[26] In the rubidium salt **2**, both sulfur and selenium are present, and a preference for selenium (Se/S = 80:20) is observed at the layer-embedded chalcogen site which binds to Pb. Other positions that were refined with free variables indicate a 50% occupancy of sulfur and selenium (Figure 2).

In the cesium salt CsPbPS$_{3.46}$Se$_{0.54}$ (**3**), only a small fraction of selenium was incorporated. The increased ionic radius of Cs$^+$, together with a more effective packing of the [PbP(S/Se)$_4$]$^-$ layers when smaller S donor atoms are coordinating Cs$^+$ ions, may play a role in the formation of **3**.

Spectroscopy. The lower amount of selenium that is incorporated in **3** is also reflected in the solid state absorption spectra of **1**−**3**, from which the bandgaps of **1**−**3** were determined (Figure 3).

Measured bandgaps on single crystals of **1** and **2** are ca. 2.2 eV. The highest occupied molecular orbital−lowest unoccupied molecular orbital separation in **3** is in comparison increased remarkably to ca. 2.5 eV. In agreement with EDS analysis, this result confirms that the lighter group 16 element sulfur is preferably incorporated into chalcophosphate anions of **3**.

Having established the basic composition of **1**−**3**, a question to answer is that of the true nature of the anions giving rise to the mixed seleno-/thiophosphates **1**−**3**. Because of the near 1:1 ratio of selenium and sulfur, **1** was chosen as a model compound for further characterizations. In order to investigate whether the approximate 1:1 ratio of S/Se in **1** is the result of cocrystallizing anions [PSe$_4$]$^{3-}$ and [PS$_4$]$^{3-}$, a ^{31}P MAS NMR investigation was carried out showing that, in **1**, all possible permutations of [PS$_x$Se$_{4-x}$]$^{3-}$ (x = 0−4) anions are present (Figure 4). The ^{31}P MAS NMR experiments were performed at different spinning rates to clearly identify spinning sidebands, and for reference a ^{31}P MAS NMR spectrum of KPbPS$_4$[23] was recorded, showing one resonance at δ 93 (Supporting Information).

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(32) Evenson, C. R., IV; Dorhout, P. K. *Inorg. Chem.* **2001**, *40*, 2875–2883.

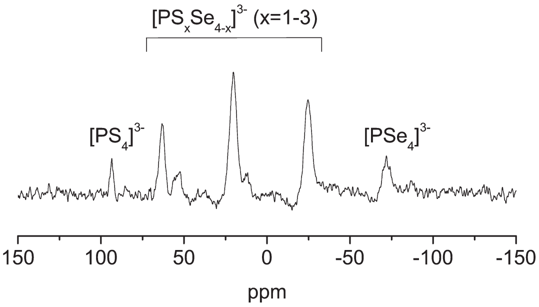

Figure 4. ^{31}P MAS NMR of $KPbPS_{1.84}Se_{2.16}$ (**1**). All five possible chalcophosphate ions $[PS_xSe_{4-x}]$ ($x = 0-4$) are present in **1**.

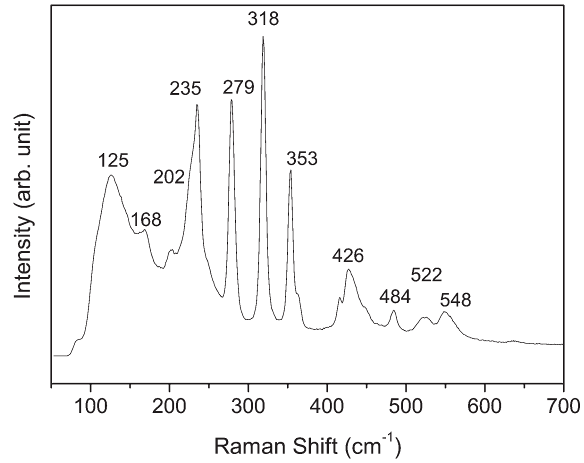

Figure 5. Raman spectrum of **1**.

The ^{31}P MAS NMR of $KPbPSe_4$ has been reported showing the resonance at δ −71 that is also observed in **1**.[28] The remaining three major peaks can be tentatively assigned to $[PSSe_3]^{3-}$, $[PS_2Se_2]^{3-}$, and $[PS_3Se]^{3-}$. The shift to a lower field with increasing sulfur content is in good agreement with the higher electronegativity of sulfur in comparison to selenium. In the Raman spectrum of a single crystal of **1**, the various resonances between 230 and 370 cm^{-1} point toward different P-chalcogen symmetric stretching modes in the mixed anion system (Figure 5).

In the Raman spectra of selenophosphate anions, these are commonly observed at 230 cm^{-1}, while the P−S stretching modes are observed at ca. 350 cm^{-1}.[32−35] Bands below 200 cm^{-1} can be assigned to the bending vibrations and those > 450 cm^{-1} to asymmetric P-chalcogen stretching modes in the chalcophosphate units $[PS_xSe_{4-x}]^{3-}$ ($x = 0-4$) present in **1**.[32] The thermogravimetric analysis of **1** showed a weight loss of ca. 10% between 250 and 550 °C (Figure 6). This weight loss is probably caused by the evaporation of sulfur, which represents ca. 10% of $KPbPS_{1.84}Se_{2.16}$ (**1**).

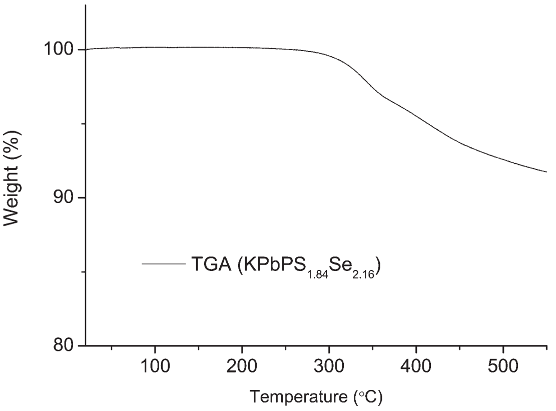

Figure 6. Thermogravimetric analysis of **1** showing a weight loss of ca. 10%, which corresponds to the weight of sulfur in **1** (heating rate: 5 K/min, N_2 flow).

Besides amorphous byproducts, black cubic crystals of PbSe were formed during thermogravimetric analysis (see the Supporting Information for energy dispersive X-ray analysis). The formation of the very stable PbSe is possibly a reason why there are only few examples of phases with the composition A/Pb/P/Se (A = alkali metal).

Concluding Remarks

For the future preparation of new chalcophosphate phases, it can be concluded that, in the case of mixed seleno-/thiophosphates, one is very likely to obtain a mixture of all possible anions. Although the softer donor atom selenium does preferably go into the soft coordination sites, all chalcogen sites are likely to show mixed S/Se occupancy. Present work focuses on the exploratory synthesis of mixed seleno-/thiophosphates with the aim of discovering chemically different outcomes of reactions when mixed chalcophosphates are prepared as opposed to the well-established routes to nonmixed seleno- and thiophosphates.

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Supporting Information Available: Powder diffraction patterns, SEM, DTA, ^{31}P MAS NMR spectra at different rotation speeds, and crystallographic information files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(33) Aitken, J. A.; Brown, S.; Chondroudis, K.; Jobic, S.; Brec, R.; Kanatzidis, M. G. *Inorg. Chem.* **1999**, *38*, 4795–4800.

(34) Chondroudis, K.; Hanko, J. A.; Kanatzidis, M. G. *Inorg. Chem.* **1997**, *36*, 2623–2632.

(35) (a) Chondroudis, K.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1997**, *119*, 2574–2575. (b) McCarthy, T. J.; Kanatzidis, M. G. *J. Alloys Compd.* **1996**, *236*, 70–85.