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Structural Diversity by Mixing Chalcogen Atoms in the Chalcophosphate System K/In/P/Q (Q = S, Se)

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The new thiophosphate salt $K_4In_2(PS_4)_2(P_2S_6)$ (**1**), the selenophosphate salts $K_5In_3(\mu^3\text{-Se})(P_2Se_6)_3$ (**2**), $K_4In_4(\mu\text{-Se})_2(P_2Se_6)_3$ (**3**), and the mixed seleno-/thiophosphate salt $K_4In_4(\mu\text{-Se})(P_2S_{2.36}Se_{3.64})_3$ (**4**) are described. For the first time, a structurally different outcome of a chalcophosphate reaction was observed when sulfur and selenium are mixed, for example, by the use of K_2S/P_2Se_5/S/In instead of K_2Se/P_2Se_5/Se/In or K_2S/P_2S_5/S/In. In compounds **1**−**4** indium atoms exist in a variety coordination environments. While in **1**, indium is octahedrally coordinated, in **2**−**4** tetrahedral, trigonal-bipyramidal, and octahedral coordination environments are found for indium atoms. This remarkable structural diversity possibly is a reason, why particularly indium chalcophosphate flux reactions often produce a large variety of compounds at intermediate temperatures. In the mixed seleno-/thiophosphate salt $K_4In_4(\mu\text{-Se})(P_2S_{2.36}Se_{3.64})_3$ (**4**) most of the chalcogen sites around the tetrahedrally coordinated P atoms show mixed S/Se occupancy. There is, however, a preference for Se binding to In ions and S binding to potassium ions.

Introduction

A great deal of work has been carried out establishing chalcophosphate phases of almost all the metallic elements. In contrast to oxophosphate derivatives, where the anion is most of the time a discrete $[PO_4]^{3-}$ anion or a condensation product of *ortho*-phosphoric acid of the type $[O_3P{-}O{-}(PO_3)_n{-}PO_3]^{(n+4)-}$, chalcophosphate anions show great structural diversity because of the formation of P−P or chalcogen-chalcogen bonds.[1] From reactions of metals in molten salts prepared from mixtures of $A_2Q/P_2Q_5/Q$ (A = alkali metal, Q = group 16 element), many new chalcophosphate anions and phases can be prepared.[1] In the selenophosphate system, observed anions include $[PSe_4]^{3-}$,[2] $[P_2Se_6]^{4-}$,[3,4] $[P_2Se_9]^{4-}$,[5] $[P_8Se_{18}]^{6-}$,[6] and the polymeric anions $^1/_\infty[P_2Se_6^{\,2-}]$,[7] $^1/_\infty[PSe_6^{\,-}]$,[8] and $^1/_\infty[P_5Se_{10}^{\,5-}]$.[9] Little, however, is known about mixed chalcophosphate anion derivatives containing different heavier group 16 elements (S, Se, Te) as substituents on P atoms (without organic groups). Only recently it was found that in the system $APbPQ_4$ (A = alkali metal ion, Q = S, Se) all possible permutations of seleno-/thiophosphate ions $[PS_xSe_{4-x}]^{3-}$ ($x = 0{-}4$) are present and that the bandgap can be modified by changing the S/Se ratio in chalcophosphate anions.[10] Using mixtures of chemically similar elements from one group of the periodic table is a well-established method that has led to the discovery of new phases, for example, of Zr/Hf phosphides and mixed alkaline earth metal intermetallics of tin.[11,12] In the $APbPQ_4$-system the modification of the chalcogen ratio did not result in structural changes.[10] Such structure retention is a precondition when using chalcogen-mixing as a tool for the optimization of chalcophosphates with potential application, for example, as nonlinear optical materials.[7] In our effort to establish structural relationships between main group alkali metal chalcophosphates and mixed chalcophosphates we extended our studies to alkali metal indium chalcophosphates and report four new potassium salts with unusual structures that contain sulfur, selenium or a mix of sulfur and selenium.

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Table 1. Details of the X-ray Data Collection and Refinements for $K_2InPS_4(P_2S_6)_{0.5}$ (**1**), $K_5In_3(\mu^3\text{-}Se)(P_2Se_6)_3$ (**2**), $K_4In_4(\mu\text{-}Se)_2(P_2Se_6)_3$ (**3**), and $K_4In_4(\mu\text{-}Se)(P_2S_{2.36}Se_{3.64})_3$ (**4**)

	1	2	3	4
formula	$K_2InP_2S_7$	$K_5In_3P_6Se_{19}$	$K_4In_4P_6Se_{20}$	$K_4In_4P_6S_{7.87}Se_{12.13}$
formula weight	479.45	2226.02	2380.70	2011.60
T/K	100(2)	100(2)	100(2)	100(2)
crystal system	monoclinic	triclinic	monoclinic	triclinic
space group	$C2/m$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a/Å	14.114(3)	7.6603(10)	19.707(4)	7.7709(6)
b/Å	10.607(4)	13.1854(16)	7.7120(15)	13.007(11)
c/Å	8.5820(17)	18.378(3)	13.229(3)	18.9382(14)
α/deg	90	87.040(10)	90	105.382(6)
β/deg	109.01(3)	88.659(11)	106.42(3)	92.632(6)
γ/deg	90	82.025(10)	90	91.910(7)
V/Å^3	1214.7	1835.6(4)	1928.5(7)	1840.7(3)
Z	4	2	2	2
ρ/g·cm^{-1}	2.622	4.028	4.100	3.629
μ/mm^{-1}	4.042	21.540	21.921	15.632
$F(000)$	916	1956	2084	1801
reflections collected	3804	17370	17452	11346
unique data	1093	9090	5000	6005
R_{int}	0.1057	0.1075	0.0428	0.0722
parameters	63	298	154	262
$R_1{}^a$ $[I > 2\sigma(I)]$	0.0775	0.0756	0.0321	0.0673
$wR_2{}^b$ (all data)	0.1673	0.2093	0.0641	0.1441

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

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.

Synthesis of $K_4In_2(PS_4)_2(P_2S_6)$ (1). A mixture of 115 mg (1.04 mmol) of K_2S, 231 mg (1.04 mmol) of P_2S_5, 33.0 mg (1.04 mmol) of S, and 119 mg (1.04 mmol) of In was sealed in a quartz tube under vacuum. The mixture was heated to 550 °C over the course of 24 h and kept at this temperature for 3 d. Cooling to 250 °C (5 K/h) and to 50 °C (10 K/h) gave colorless **1** together with a mixture of an orange crystalline solid of similar composition and In_2S_3. The crystals were isolated by washing and sonicating the solid reaction products with *N*,*N*-dimethylformamide (DMF). DMF was decanted, and **1** was washed with Et_2O and dried in a nitrogen stream. **1** is not infinitely stable in DMF. Powdered reaction products dissolved and reacted with DMF (yield ca. 60% based on K_2S supplied; not all byproducts could be removed).

Synthesis of $K_5In_3(\mu^3\text{-}Se)(P_2Se_6)_3$ (2) and $K_4In_4(\mu\text{-}Se)_2(P_2Se_6)_3$ (3). A mixture of 66 mg (0.42 mmol) of K_2Se, 49 mg (0.62 mmol) of Se, 287 mg (0.62 mmol) of P_2Se_5, and 97 mg (0.84 mmol) of In 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 d. Cooling to 150 °C (4 K/h) and to room temperature (RT) gave orange (**2** and **3**) and yellow (**3**) crystalline solids that were covered in gray flux medium. The solid residue was washed with a mixture 20 mL of MeOH/0.5 mL of $P(nBu)_3$ placed in an ultrasound bath. The MeOH/$P(nBu)_3$ mixture was decanted, and crystals were washed with MeOH, Et_2O and dried in a stream of dinitrogen. There are several byproducts formed during the reaction. A black agglomerate of the approximate composition $In_2P_3Se_9$ was identified together with yellow crystalline $KInP_2Se_6$. Once isolated, **2** and **3** slowly decompose in ambient atmosphere releasing red selenium (yield ca. 60% of an orange glassy mixture of **2** and **3**; not all byproducts can be removed)

Synthesis of $K_4In_4(\mu\text{-}Se)(P_2S_{2.36}Se_{3.64})_3$ (4). A mixture of 49 mg (0.44 mmol) of K_2S, 28 mg (0.87 mmol) of S, 200 mg (0.44 mmol) of P_2Se_5, and 100 mg (0.87 mmol) of In 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 d. Cooling to 250 °C (5 K/h. The solid residue was washed with a mixture 20 mL of MeOH/0.5 mL of $P(nBu)_3$ placed in an ultrasound bath. The MeOH/ $P(nBu)_3$ mixture was decanted, and yellow crystals of **4** were washed with MeOH, Et_2O and dried in a stream of dinitrogen (yield ca. 7%). There are several byproducts formed during the reaction including a red glass of the composition $KInPS_2Se_3$.

Efforts were made to synthesize **1**−**4** by stoichiometric combination of starting materials. In all cases mixtures of products were obtained (Supporting Information).

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. **1**: Found: P, 17.1; S, 59.0; K, 15.4; In, 8.5; $K_2InP_2S_7$ requires P, 12.9; S, 46.8; K, 16.3; In, 23.9%. **2**: Found: P, 21.3; K, 16.0; Se, 52.0; In, 10.6; $K_5In_3P_6Se_{19}$ requires P, 8.4; K, 8.8; Se, 67.4; In, 15.5%. **3**: Found: P, 22.8; K, 11.0; Se, 54.5; In, 11.8; $K_4In_4P_6Se_{20}$ requires P, 7.8; K, 6.6; Se 66.3; In 19.3%. **4**: Found: P, 18.9; S, 27.2; K, 11.1; Se, 31.7; In, 11.2; $K_4In_4P_6S_{7.87}Se_{12.13}$ requires P, 9.4; S, 11.4; K, 7.9; Se, 48.0; In, 23.3%. In **4** the ratio of S/Se was determined by occupational refinement of the mixed chalcogen sites. Solid state absorption spectra were measured on a U-6000 microscopic FT spectrophotometer using single crystals suspended in paraffin oil. The DTA measurements were performed on a Shimadzu thermogravimetric analyzer in sealed quartz ampules. The Raman measurement was carried out at RT 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}).

X-ray Crystallographic Study

Data for **1**−**4** were collected on a Stoe Ipds 2T diffractometer using graphite-monochromated Mo-K_α 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.[13] All S atoms and all Se atoms were assigned common thermal parameters using the Eadp instruction.[13] Numerical absorption corrections were performed for **1**−**4**. A summary of crystal data and refinement

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parameters is given in Table 1. Crystal coordinates are listed in Table 2.

Results and Discussion

A new approach to mixed thio-/selenophosphates of indium involves flux reactions of $A_2Q/In/P_2Q5/Q$ (A = alkali metal, Q = S, Se). To probe if S/Se mixing can lead to the formation of new compounds that cannot be obtained using S or Se alone, three reactions in the system K/In/P/Q (Q = S, Se) were investigated where Q = 1. S, 2. Se and 3. S/Se (Scheme 1). At first a mixture of $In/K_2S/P_2S_5/S$ was heated to 550 °C for several days and after washing with DMF, colorless flakes of $K_4In_2(PS_4)_2(P_2S_6)$ (**1**) were isolated (Scheme 1).

An attempt to determine the crystal structure of **1** gave an orthorhombic cell of *a* = 10.697(2) Å, *b* = 18.344(3) Å,

Table 2. Atomic Coordinates and Displacement Parameters (in Å^2) for $K_2InPS_4(P_2S_6)_{0.5}$ (**1**), $K_5In_3(\mu^3\text{-}Se)(P_2Se_6)_3$ (**2**), $K_4In_4(\mu\text{-}Se)_2(P_2Se_6)_3$ (**3**), and $K_4In_4(\mu\text{-}Se)(P_2S_{2.36}Se_{3.64})_3$ (**4**)

$K_2InPS_4(P_2S_6)_{0.5}$ (**1**)

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}
In1	0	0.31120(12)	0.5	0.0287(4)
K1	0.1696(2)	0.2186(3)	0.1590(4)	0.0376(7)
P1	0.0610(3)	0	0.4419(6)	0.0302(11)
P2	0.1109(3)	0.5	0.8167(6)	0.0262(10)
S1	0.1453(2)	0.1572(3)	0.5364(4)	0.0293(7)
S2	0.0054(3)	0	0.1978(6)	0.0283(10)
S3	−0.0296(3)	0.3395(4)	0.1938(5)	0.0413(9)
S4	0.1412(3)	0.5	0.5936(6)	0.0286(10)
S5	0.2327(3)	0.5	1.0153(6)	0.0320(11)

$K_5In_3(\mu^3\text{-}Se)(P_2Se_6)_3$ (**2**)

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}
In1	0.49428(17)	0.90107(8)	0.67050(7)	0.0202(3)
In2	0.75495(17)	0.73573(7)	0.84110(7)	0.0200(3)
In3	0.81747(17)	0.56492(7)	0.67777(7)	0.0202(3)
K1	0.2678(6)	0.5933(3)	0.9245(3)	0.0279(9)
K2	0.0496(6)	0.8454(2)	0.5584(3)	0.0267(9)
K3	1.2495(6)	0.2161(2)	0.7947(3)	0.0263(9)
K4	0.4274(6)	0.3525(3)	0.6089(3)	0.0285(9)
K5	0.7621(6)	0.1147(3)	0.9106(3)	0.0292(10)
P1	0.3607(6)	0.9408(3)	0.8683(3)	0.0183(9)
P2	0.1376(6)	0.9004(3)	0.8044(3)	0.0187(9)
P3	0.8770(6)	0.4303(3)	0.8582(3)	0.0188(9)
P4	0.6258(6)	0.3924(3)	0.8133(3)	0.0202(10)
P5	1.0903(6)	0.5612(3)	0.4936(3)	0.0167(9)
P6	0.4969(6)	1.0661(3)	0.5351(3)	0.0193(9)
Se1	0.7881(2)	0.76072(10)	0.70407(10)	0.0190(4)
Se2	0.4842(2)	0.79516(11)	0.92279(11)	0.0208(4)
Se3	0.2601(3)	1.05050(11)	0.94530(11)	0.0222(4)
Se4	0.2614(2)	0.78523(10)	0.72846(11)	0.0194(4)
Se5	0.0002(2)	0.82869(11)	0.89679(11)	0.0211(4)
Se6	−0.0031(2)	1.03555(11)	0.75355(11)	0.0214(4)
Se7	0.8201(3)	0.56695(11)	0.92494(11)	0.0230(4)
Se8	1.0528(2)	0.46528(11)	0.76517(11)	0.0213(4)
Se9	0.9915(2)	0.30569(11)	0.92845(10)	0.0204(4)
Se10	0.5208(2)	0.54046(11)	0.75742(11)	0.0217(4)
Se11	0.6949(3)	0.26821(11)	0.74274(11)	0.0237(4)
Se12	0.4658(3)	0.35868(11)	0.90644(11)	0.0236(4)
Se13	1.1597(2)	0.58776(11)	0.60483(11)	0.0210(4)
Se14	0.9772(3)	0.69190(11)	0.42957(11)	0.0231(4)
Se15	1.3257(2)	0.47346(11)	0.44221(11)	0.0205(4)
Se16	0.7269(2)	1.03457(11)	0.60573(11)	0.0205(4)
Se17	0.2639(2)	1.06081(11)	0.60766(11)	0.0213(4)
Se18	0.4914(3)	1.19967(11)	0.46060(11)	0.0222(4)
Se19	0.5439(2)	1.00127(11)	0.78962(11)	0.0213(4)

$K_4In_4(\mu\text{-}Se)_2(P_2Se_6)_3$ (**3**)

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}
In1	0.17633(2)	0.02887(5)	0.03192(3)	0.0087(1)
In2	0.68826(2)	0.14451(4)	0.10199(3)	0.0084(1)
K1	0.08052(8)	0.54946(18)	0.17961(11)	0.0260(3)
K2	0.42686(7)	0.35475(15)	0.09723(9)	0.0143(2)

Table 2. Continued

$K_4In_4(\mu\text{-}Se)_2(P_2Se_6)_3$ (**3**)

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}
P1	0.02007(7)	0.11429(17)	0.05187(10)	0.0084(2)
P2	0.33555(7)	0.06295(16)	0.27443(10)	0.0075(2)
P3	0.65209(7)	0.32451(16)	0.31622(10)	0.0070(2)
Se1	0.07175(3)	0.28183(7)	−0.03826(4)	0.0111(1)
Se2	0.07187(3)	0.72804(7)	0.41512(4)	0.0110(1)
Se3	0.10390(3)	0.01585(7)	0.18552(4)	0.0105(1)
Se4	0.21789(3)	0.41871(6)	0.36469(4)	0.0085(1)
Se5	0.24299(3)	0.72250(6)	0.10478(4)	0.0084(1)
Se6	0.27622(3)	0.24140(6)	0.15397(4)	0.0083(1)
Se7	0.44006(3)	0.16153(7)	0.34763(4)	0.0093(1)
Se8	0.58858(3)	0.40040(7)	0.42164(4)	0.0088(1)
Se9	0.59142(3)	0.13011(6)	0.20566(4)	0.0085(1)
Se10	0.72316(3)	0.47169(6)	0.11416(4)	0.0092(1)

$K_4In_4(\mu\text{-}Se)(P_2S_{2.36}Se_{3.64})_3$ (**4**)

atom	*x*/*a*	*y*/*b*	*z*/*c*	$U_{eq/iso}$
In1	0.29278(16)	0.76811(9)	0.46480(7)	0.0128(3)
In2	0.24517(16)	0.95838(9)	0.65220(7)	0.0127(3)
In3	0.16687(16)	1.22614(9)	0.97717(7)	0.0133(3)
In4	0.15290(17)	1.43307(9)	1.15949(7)	0.0170(3)
K1	0.3533(6)	0.8162(3)	0.9402(3)	0.0290(11)
K2	0.7112(6)	0.4377(3)	0.4117(3)	0.0238(9)
K3	−0.2576(6)	0.8404(4)	0.7305(2)	0.027(1)
K4	0.1960(7)	1.3082(4)	0.7382(3)	0.0377(12)
P1	0.1186(6)	1.0320(3)	0.4802(2)	0.0098(9)
P2	0.3745(6)	0.5554(3)	0.3060(2)	0.014(1)
P3	0.1758(6)	0.4882(3)	0.3638(3)	0.014(1)
P4	0.1889(6)	1.0021(3)	0.8242(2)	0.0147(10)
P5	0.4485(6)	1.0863(3)	0.8405(3)	0.0121(9)
P6	−0.1247(6)	1.4548(3)	1.0005(2)	0.0124(9)
S1	0.182(4)	0.893(2)	0.3901(17)	0.0124(6)
S2	0.2965(16)	1.0906(10)	0.5742(7)	0.0098(8)
S3	0.033(3)	1.1569(15)	0.4255(10)	0.0151(8)
S4	0.5201(14)	0.6691(9)	0.3842(6)	0.0143(9)
S6	0.530(2)	0.4239(13)	0.2563(9)	0.0293(10)
S7	0.060(3)	0.6157(15)	0.4445(12)	0.0134(6)
S8	0.2789(10)	0.3983(6)	0.4194(4)	0.0213(13)
S9	−0.0091(10)	0.4092(6)	0.2753(4)	0.0107(8)
S10	0.021(3)	1.0916(19)	0.7512(13)	0.0173(7)
S11	0.2016(12)	0.8493(7)	0.7649(5)	0.0157(9)
S12	0.1100(17)	1.0116(10)	0.9348(7)	0.0145(8)
S13	0.6214(14)	1.0152(9)	0.8949(7)	0.0176(10)
S14	0.502(2)	1.0920(14)	0.7268(10)	0.0121(7)
S15	0.391(3)	1.2617(17)	0.8793(13)	0.0092(5)
S16	−0.084(4)	1.300(2)	0.9121(18)	0.0124(5)
S17	−0.145(2)	1.4517(16)	1.1154(12)	0.0138(7)
S18	−0.3032(11)	1.5328(7)	0.9613(5)	0.0119(10)
Se1	0.2147(3)	0.9047(2)	0.39493(18)	0.0124(6)
Se2	0.2788(9)	1.0991(6)	0.5707(4)	0.0098(8)
Se2′	0.2281(7)	1.2381(3)	1.1108(2)	0.0095(11)
Se3	0.0396(9)	1.1509(5)	0.4332(3)	0.0151(8)
Se4	0.5408(9)	0.6599(6)	0.3900(4)	0.0143(9)
Se5	0.2396(3)	0.63322(17)	0.23249(12)	0.0286(5)
Se6	0.5057(7)	0.4328(4)	0.2443(3)	0.0293(10)
Se7	0.0393(3)	0.6257(2)	0.42674(14)	0.0134(6)
Se8	0.3043(18)	0.4073(11)	0.4324(8)	0.0213(13)
Se9	0.0146(6)	0.3860(4)	0.2832(3)	0.0107(8)
Se10	0.0320(4)	1.0667(2)	0.75164(18)	0.0173(7)
Se11	0.2359(7)	0.8408(4)	0.7729(3)	0.0157(9)
Se12	0.0889(6)	1.0241(4)	0.9280(3)	0.0145(8)
Se13	0.5968(16)	1.011(1)	0.8996(8)	0.0176(10)
Se14	0.5262(4)	1.0776(3)	0.73238(19)	0.0121(7)
Se15	0.4116(3)	1.25561(18)	0.89749(12)	0.0092(5)
Se16	−0.1120(3)	1.2944(2)	0.92775(13)	0.0124(5)
Se17	−0.1771(4)	1.4579(3)	1.1111(2)	0.0138(7)
Se18	−0.3299(12)	1.5339(8)	0.9537(5)	0.0119(10)
Se19	0.4368(2)	0.80746(13)	0.58974(10)	0.0147(4)
Se20	0.1774(7)	1.2317(3)	1.1103(3)	0.0135(12)

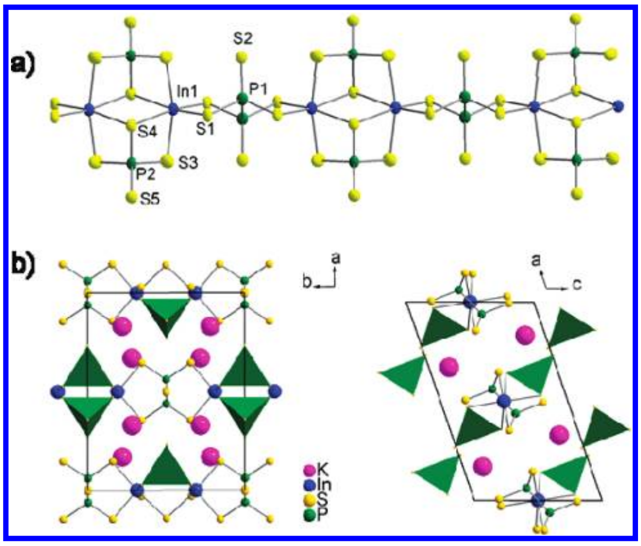
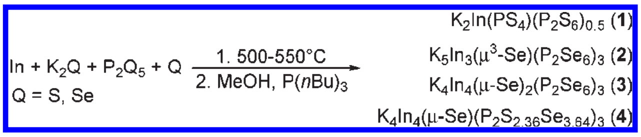


Figure 1. (a) Section of the 1D-polymeric anion $[In_2(PS_4)_2(P_2S_6)]_n^{4n-}$ in **1** (ellipsoids at 50% probability level); (b) Arrangement of the $[P_2S_6]^{4-}$ and $[PS_4]^{3-}$ (green tetrahedra) in the unit cell of **1**. Selected bond lengths [Å] and angles [deg.]: In(1)−S(1) 2.560(3), In(1)−S(3) 2.541(4), S(1)−P(1) 2.056(4), S(2)−P(1) 1.983(7), S(4)−P(2) 2.093(7), S(5)−P(2) 1.987(6), K−S about 3.2−3.6, S(3)−In(1)−S(1) 93.26(11), S(3)−In(1)−S(4) 94.31(14), S(1)−In(1)−S(4) 87.34(9), P(1)−S(1)−In(1) 97.55(15), P(2)−S(4)−In(1) 85.58(14), S(2)−P(1)−S(1) 113.3(2), S(5)−P(2)−S(4) 114.0(3).

Scheme 1. Synthesis of **1**−**4**



$$\text{In} + K_2Q + P_2Q_5 + Q \xrightarrow[\text{2. MeOH, P}(n\text{Bu})_3]{\text{1. 500-550°C}} \begin{array}{r} K_2In(PS_4)(P_2S_6)_{0.5}\ (\mathbf{1}) \\ K_5In_3(\mu^3\text{-Se})(P_2Se_6)_3\ (\mathbf{2}) \\ K_4In_4(\mu\text{-Se})_2(P_2Se_6)_3\ (\mathbf{3}) \\ K_4In_4(\mu\text{-Se})(P_2S_{2.36}Se_{3.64})_3\ (\mathbf{4}) \end{array}$$

$$Q = S, Se$$

c = 24.854(5) Å, similar to the cell dimensions of the new compound $Rb_4In_2(PS_4)_2(P_2S_6)$ [$Fdd2$, no. 43, a = 18.6367(8) Å, b = 25.3369(16) Å, c = 10.7576(5)] which will be reported in a subsequent paper. Efforts at solving the structure of **1** initially failed because of the poor quality of the data. Having established the basic composition of **1** by semiquantitative energy-dispersive X-ray analysis (EDS), single crystals of **1** were obtained by a direct combination reaction of K_2S/P/In/S. In the solid state **1** consists of a one-dimensional (1D) polymeric arrangement of centrosymmetric $[In_2\{(\mu\text{-S})PS_3\}_2]$ units that are connected by chelating $[P_2S_6]^{4-}$ ions. The 1D polymeric strands are separated by the potassium ions (Figure 1).

The bond lengths and angles in the anions are in the range of what is commonly observed in compounds containing $[PS_4]^{3-}$ and $[P_2S_6]^{4-}$ anions.[14−16] These usually contain rare earth cations with a higher coordination number than the indium cation in **1** and form layered compounds. In $K_4Sm_2(PS_4)_2(P_2S_6)$, for example, 1D arrangements similar to the one found in **1** (Figure 1) are connected by bridging thiophosphate groups to give a two-dimensional (2D) assembly.[15]

The second reaction we investigated for comparison with the mixed seleno/thiophosphate to be described later was the selenium-only mixture of In/K_2Se/P_2Se_5/Se in the ratio of 4:2:3:3, heated to 500 °C and slowly cooled to RT. Orange crystals of $K_5In_3(\mu^3\text{-Se})(P_2Se_6)_3$ (**2**) and $K_4In_4(\mu\text{-Se})_2(P_2Se_6)_3$ (**3**) form in a flux and were isolated by dissolving the excess flux in a mixture of MeOH/P(nBu)$_3$. Compound **2** crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit in **2** consists of an assembly of three indium atoms that are bridged by one Se atom and coordinated by Se atoms of $[P_2Se_6]^{4-}$ anions (Figure 2).

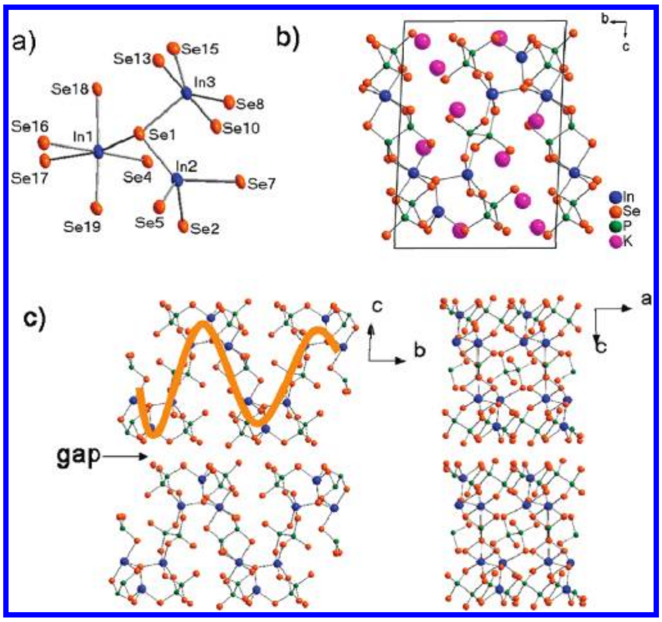


Figure 2. (a) Coordination of the indium atoms in **2** (ellipsoids at 80% probability level); (b) Representation of the unit cell in **2**; (c) Section of two corrugated anionic $[In_3(\mu^3\text{-Se})(P_2Se_6)_3]_n^{5n-}$ layers in **2** viewed down [100] and [010] (without K atoms; the corrugated shape of a layer is indicated by the orange line). The "gap" between layers corresponds to interlayer K−Se distances of about 3.8 Å. Selected bond lengths [Å] and angles [deg.]: In(1)−Se(1) 2.768(2), In(2)−Se(1) 2.534(2), In(3)−Se(1) 2.6291(18), In−Se 2.587(2)-2.962(2), K−Se about 3.4−3.8, P−Se 2.128-(4)−2.222(5), P−P 2.234(7), 2.240(7), Se(1)−In(1)−Se(17) 163.95(8), Se(4)−In(1)−Se(1) 95.20(6), Se(4)−In(1)−Se(17) 99.57(7), Se(4)−In-(1)−Se(19) 97.66(7), Se(19)−In(1)−Se(1) 89.77(7), Se(19)−In(1)−Se(17) 94.40(6), Se(4)−In(1)−Se(16) 176.55(7), Se(1)−In(2)−Se(2) 128.28(8), Se(1)−In(2)−Se(7) 129.47(7).

Compound **2** is composed of corrugated layers of $[In_3(\mu^3\text{-Se})(P_2Se_6)_3]_n^{5n-}$ that are held together by electrostatic interactions between exposed Se atoms of one layer and K^+ ions embedded in an adjacent layer (Figure 2). The thickness of the layer corresponds to the c-axis of the unit cell and the distance between layers (referred to as "gap" in Figure 2c) corresponds to interlayer K−Se distances of about 3.8 Å . The structural motif $[(\mu^3\text{-Se})In_3]$ has been observed in compounds where In atoms have a tetrahedral coordination environment.[17−23] In **2**, however, indium atoms are surrounded by Se atoms in tetrahedral, trigonal-bipyramidal

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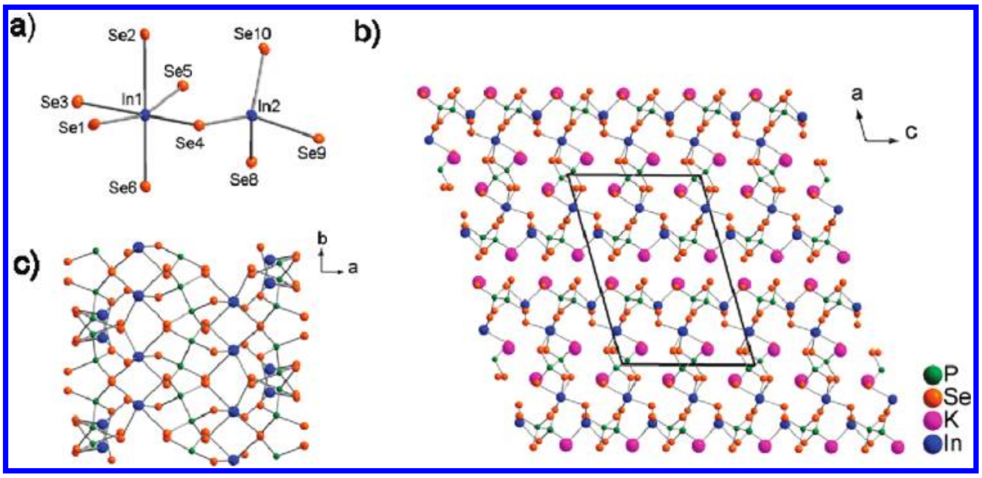

Figure 3. (a) Coordination of the indium atoms in **3** (ellipsoids at 80% probability level); (b) Packing of the porous anions $[In_4(\mu\text{-}Se)_2(P_2Se_6)_3]_n^{4n-}$ and potassium ions in **3** viewed down [010]; (c) Section of the anionic 2D framework viewed down [010]. Selected bond lengths [Å] and angles [deg.]: In(1)−Se(1) 2.7988(8), In(1)−Se(2) 2.9585(9), In(1)−Se(3) 2.7956(9), In(1)−Se(4) 2.5987(8), In(1)−Se(5) 2.7425(8), In(1)−Se(6) 2.7150(9), In(2)−Se(4) 2.4871(7), In(2)−Se(8) 2.6499(11), In(2)−Se(9) 2.6487(9), In(2)−Se(10) 2.6082(8), P−Se 2.1516(15)-2.2002(15), K−Se about 3.3−3.8, Se(1)−In(1)−Se(3) 77.69(2), Se(1)−In(1)−Se(6) 96.81(3), Se(2)−In(1)−Se(6) 174.49(2), Se(3)−In(1)−Se(6) 91.30(2).

and octahedral fashion. Compound **3** crystallizes in the monoclinic space group $P2_1/c$ (Figure 3).

The packing in the structure of **3** is similar to the arrangement of **2**. The asymmetric unit in **3** may have been constructed from the one found in **2** by disconnecting the In(3)−Se(1) bond (Figure 2a), incorporation of another μ-Se atom, and a slight variation of the In/K ratio to balance the charge. As a consequence of these slight structural changes, the corrugated layer structure in **2** is connected at the peaks to give a porous anionic layer of $[In_4(\mu\text{-}Se)_2(P_2Se_6)_3]_n^{4n-}$ in **3** (Figure 3). Potassium ions are located within the pores and on the surface of layers. Like in **2**, layers are stacked so that electrostatic interactions of layer-embedded K^+ ions and exposed selenium atoms of adjacent layers are possible. Both **2** and **3** represent new phases in the system K/In/P/Se. Their formation is surprising because the previously reported $K_4In_2(PSe_5)_2(P_2Se_6)$ and $KInP_2Se_6$ were synthesized under similar conditions with the only difference being the large excess selenium.[24,25] Because **2** and **3** could not be separated manually, their synthesis was attempted by direct combination of the appropriate amounts of K_2Se/In/P_2Se_5/Se on a 2 g scale. Powder diffraction studies on samples from these attempts, however, showed a mix of products that could not be identified unequivocally (Supporting Information). By EDS, among other byproducts, a black agglomerate of the approximate composition $In_2P_3Se_9$ was identified together with yellow crystalline $KInP_2Se_6$.[25]

The differential thermal analysis (DTA) of a stoichiometric reaction that should give rise to the formation of **2** showed a broad endothermic peak at about 390 and 480 °C and a broad single exothermic peak at 430 °C. This melting behavior is similar to the one reported for $K_4In_2(PSe_5)_2(P_2Se_6)$, which decomposes to In_2Se_3 and an amorphous glass and recombines at lower temperature.[24] The DTA of the stoichiometric reaction that should give rise to **3** only shows a broad endothermic peak at about 480 °C and no exothermic peak. Although further modifications of the reaction conditions may result in even more phases in the system K/In/P/Se, the flexible coordination of the indium atoms in **2** and **3** together with the structural complexity of selenophosphate fluxes suggests that product mixtures will be favored.

Having obtained compounds **1**−**3** from flux reactions involving the element combinations K/In/P/S and K/In/P/Se, finally, the influence of the presence of both S and Se in an otherwise analogous flux reaction was studied. This approach has recently been used for the preparation of the family $APbPS_{4-x}Se_x$ (A = K, Rb, Cs, $x = 0-4$) and is currently used for the synthesis of a broader variety of mixed calcophosphates.[10]

For the synthesis of **4**, a mixture of In/P_2Se_5/S/K_2S in the ratio 2:1:2:1 was reacted at 500 °C and slowly cooled to 250 °C and RT. It was hoped that by choosing P_2Se_5 as electrophile and *in situ* formed K_2S_3 as both nucleophile and oxidant (K_2S_3 can also oxidize In), mixed-chalcogen sites within a chalcophosphate anion derivative would form. An energy dispersive X-ray analysis of yellow crystals of **4** confirmed the presence of the elements K/In/P/S/Se. Single crystals of $K_4In_4(\mu\text{-}Se)(P_2S_{2.36}Se_{3.64})_3$ (**4**) formed in low yield together with a mix of products, including a red glass of the composition $KInPS_2Se_3$, which was identified by EDS (Supporting Information). In the solid state, the mixed chalcophosphate **4** shows structural elements of both the chalcophosphate **1** and the selenophosphate salts **2** and **3** (Figure 4).

Similar to compound **1**, a 1D arrangement is found in **4** that is possibly a result of the shorter metal-S bond distances favoring a less extended structure. Similar to compounds **2** and **3**, a cyclic arrangement of chalcophosphate anions and indium atoms in different coordination environments is found in **4**. The chalcogen sites in **4** were refined as split S/Se positions. Each mixed site was refined using free variables to determine the ratio of S/Se. Because only nine free variables were used for all chalcogen positions, S/Se ratios were initially kept 1:1 according to EDS results. In the refinement cycles, free variables were assigned to different chalcogen position to give rerefined S/Se ratios. This procedure was repeated several times until the refinement became

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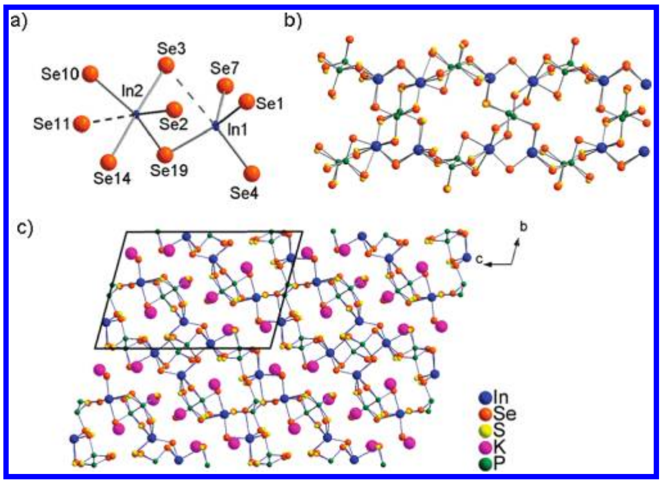

Figure 4. (a) Coordination of the indium atoms in **4** (ellipsoids for In at 80% probability level; In···Se contacts are longer than 3 Å), (b) Section of the 1D anionic ribbon $[In_4(\mu\text{-}Se)_2(P_2Q_6)_3]_n^{4n-}$ (Q = S/Se in the ratio 7.87:12.13) in **4** (K atoms were omitted for clarity); (c) Packing diagram of **4**. Selected bond lengths [Å]: In(1)−Se(1) 2.553(3), In(1)−Se(4) 2.660(8), In(1)−Se(7) 2.597(3), In(1)−Se(19) 2.488(2), In(2)−Se(2) 2.703(8), In(2)−Se(10) 2.703(3), In(2)−Se(14) 2.775(4), In(2)−Se(19) 2.567(2), In(2)−Se(3A) 2.788(7), In(2)−Se(11) 3.070(6), In(1)−S(1) 2.56(3), In(1)−S(4) 2.543(12), In(1)−S(7) 2.58(2), In(2)−S(2) 2.580(13), In(2)−S(14) 2.684(17), In(2)−S(11) 2.885(10), In(2)−S(10) 2.89(3), P−Se 2.019(13)−2.214(5).

stable. It is noteworthy that all S/Se positions around indium atoms show a higher percentage of selenium. In particular the indium-bridging atom positions can only be refined as Se atoms. The chalcogen positions located at the edges of the polymeric strand coordinate harder alkali metal atoms and show a refined S/Se ratio of 3:1. This observation is in agreement with the HSAB principle and with recently reported results for the family $APbPS_{4-x}Se_x$ (A = K, Rb, Cs, x = 0−4) where softer selenium atoms preferentially coordinate lead atoms.[10,26] The coordination environment of the indium atoms in **4** is tetrahedral (In1) and octahedral (In2). The octahedral coordination environment is distorted with one long In−Se distance of about 3.1 Å that is significantly longer than distances of about 2.8 Å observed in compounds containing the structural motif $[In(Se)_6]$.[27,28]

Spectroscopy. The fraction of selenium that incorporated in **2**−**4** is reflected in the solid state absorption spectra of **2**−**4** from which the bandgaps were determined (Figure 5).

Measured bandgaps on single crystals of **2** and **3** are about 2.2 eV. The HOMO−LUMO separation in **4** is in comparison increased to about 2.5 eV. In agreement with EDS analysis, this result confirms that the lighter group 16 element sulfur is incorporated in the chalcophosphate anions of **4**.

In the Raman spectrum of a single crystal of **4**, the resonances between 230 and 370 cm^{-1} are poorly resolved but point toward different P-chalcogen symmetric stretching modes in the mixed anion system (Figure 6).

In the Raman spectra of selenophosphate anions, these are commonly observed at 230 cm^{-1} while the P−S stretching modes are observed at about 350 cm^{-1}.[28−30] Bands below 200 cm^{-1} can be assigned to the bending vibrations. Asymmetric P-chalcogen stretching modes in the chalcophosphate units $[P_2S_xSe_{6-x}]^{4-}$ (x = 0−6) present in **4** would be expected >450 cm^{-1} but are not observed.[10,31]

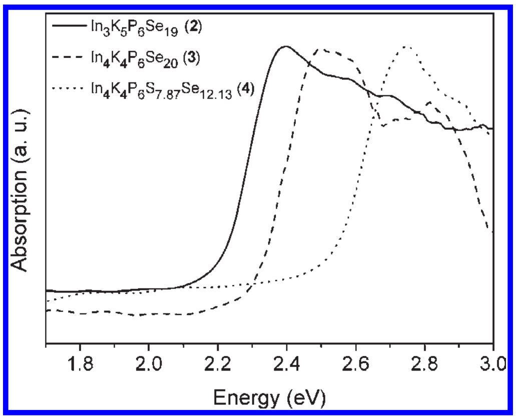

Figure 5. Solid-state UV−vis optical absorption spectra of single crystals of **2**−**4**. The band gaps for **2** and **3** are about 2.2−2.3 eV. The band gap of **4** is about 2.5 eV.

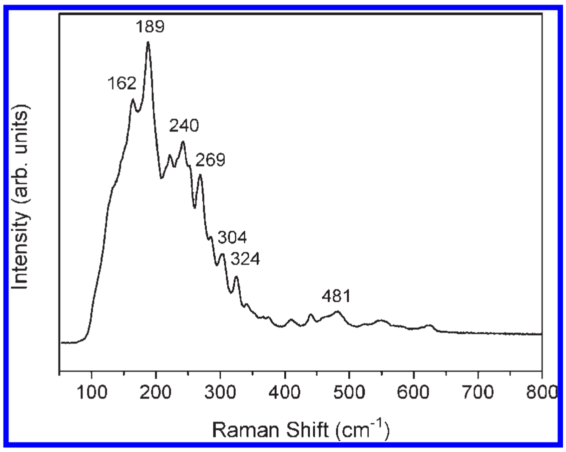

Figure 6. Raman spectrum of **4**.

Concluding Remarks

The synthesis and structures of the thiophosphate salt $K_4In_2(PS_4)_2(P_2S_6)$ (**1**), the selenophosphate salts $K_5In_3(\mu^3\text{-}Se)(P_2Se_6)_3$ (**2**), $K_4In_4(\mu\text{-}Se)_2(P_2Se_6)_3$ (**3**), and the mixed seleno-/thiophosphate salt $K_4In_4(\mu\text{-}Se)(P_2S_{2.36}Se_{3.64})_3$ (**4**) were described. For the first time, a structurally different outcome of a chalcophosphate reaction was observed when sulfur and selenium is mixed, for example, by the use of $K_2S/P_2Se_5/S/In$ instead of $K_2Se/P_2Se_5/Se/In$ or $K_2S/P_2S_5/S/In$. All the reactions described here, however, form mixtures of products. Therefore more work in this area is required before it can be claimed that the potassium indium chalcophosphate structure of **4** is only formed when a mixture of chalcogen atoms is present. In the mixed

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seleno/thiophosphate $K_4In_4(\mu\text{-}Se)(P_2S_{2.36}Se_{3.64})_3$ (**4**) almost all chalcogen positions were refined as partially occupied by both selenium and sulfur. The preferential coordination of selenium to the softer indium atoms and of sulfur to harder potassium ions was observed.

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Supporting Information Available: Powder diffraction patterns, SEM, DTA, crystallographic information files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.