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Synthesis of the One-dimensional Compound $(Ph_4P)[In(P_2Se_6)]$ in a Ph_4P^+-Containing Selenophosphate Flux, and Structure of $[In(P_2Se_6)_2]^{5-}$ – a Discrete Molecular Fragment of the $[In(P_2Se_6)]_n^{n-}$ Chain

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Abstract. The reaction of one equivalent of In with a molten flux of $(Ph_4P)_2Se_5$ and P_2Se_5 (1:2), at 250 °C gave the $(Ph_4P)[In(P_2Se_6)]$ (**I**). Stoichiometric elemental synthesis at 750 °C produced the $Cs_5In(P_2Se_6)_2$ (**II**). The thin, yellow crystals of (**I**), and the irregular, dark orange crystals of (**II**), appear to be air- and water-stable. Compound (**I**) crystallizes in the monoclinic space group C2/c (no. 15) and at 23 °C: $a = 23.127(7)$ Å, $b = 6.564(1)$ Å, $c = 19.083(3)$ Å, $\beta = 97.42(2)°$, $V = 2873(1)$ Å^3, $Z = 4$, final $R/R_w = 4.4/5.2\%$. Compound (**II**) crystallizes in the tetragonal space group $P4_2/m$ (no. 84) and at 23 °C: $a = b = 13.886(1)$ Å, $c = 7.597(2)$ Å, $V = 1464.9(3)$ Å^3, $Z = 2$, final $R/R_w = 3.9/5.1\%$. Compound (**I**) contains infinite $[In(P_2Se_6)]_n^{n-}$ with a structure related to that of $K_2FeP_2Se_6$. Compound (**II**) contains the discrete $[In(P_2Se_6)_2]^{5-}$ which can be viewed as a fragment of the $[In(P_2Se_6)]_n^{n-}$ chain.

Keywords: Selenophosphates; indium; tetraphenylphosphonium compounds.

Synthese der eindimensionalen Verbindung $(Ph_4P)[In(P_2Se_6)]$ in einer Ph_4P^+-enthaltenden Selenophosphat-Schmelze und die Struktur von $[In(P_2Se_6)_2]^{5-}$ – ein isoliertes, molekulares Fragment der $[In(P_2Se_6)]_n^{n-}$-Kette

Inhaltsübersicht. Die Reaktion von einem Äquivalent In mit einer Schmelze von $(Ph_4P)_2Se_5$ und P_2Se_5 (1:2) bei 250 °C ergab $(Ph_4P)[In(P_2Se_6)]$ (**I**). Die Stöchiometrische Synthese mit elementarem Cs und In bei 750 °C ergab $Cs_5In(P_2Se_6)_2$ (**II**). Die dünnen, gelben Kristalle von (**I**) und die irregulären, dunkelorangen Kristalle von (**II**) sind in Luft und Wasser beständig. (**I**) kristallisiert in der monoklinen Raumgruppe *C*2/c (Nr. 15), bei 23 °C mit $a = 23{,}127(7)$ Å, $b = 6{,}564(1)$ Å, $c = 19{,}083(3)$ Å, $\beta = 97{,}42(2)°$, $V = 2873(1)$ Å^3, $Z = 4$, $R/R_w = 4{,}4/5{,}2\%$. (**II**) kristallisiert in der tetragonalen Raumgruppe $P4_2/m$ (Nr. 84) bei 23 °C mit $a = b = 13{,}886(1)$ Å, $c = 7{,}597(2)$ Å, $V = 1464{,}9(3)$ Å^3, $Z = 2$, $R/R_w = 3{,}9/5{,}1\%$. (**I**) enthält unendliche Einheiten von $[In(P_2Se_6)]_n^{n-}$ mit einer zu $K_2FeP_2Se_6$ ähnlichen Struktur. (**II**) enthält die isolierte Einheit $[In(P_2Se_6)_2]^{5-}$, die als ein Fragment der $[In(P_2Se_6)]_n^{n-}$-Kette betrachtet werden kann.

Introduction

The broad synthetic scope of the molten polychalcophosphate flux technique [1] has been well demonstrated with the synthesis of several chalcophosphate compounds containing main group [2], transition metals [3], lanthanides and actinides [2e, 4, 5]. To extend this work and stabilize new compounds with novel structural frameworks we undertook a related synthetic approach, employing a $(Ph_4P)_xP_ySe_z$ flux. In an effort to stabilize open, anionic, metal-polyselenophosphate frameworks we attempted to use organic cations as templates. The flux method is well suited for such exploratory work because it could allow a complex reaction system to equilibrate at relatively low temperature, favoring kinetically stable phases. To overcome the instability of organic salts in a polyselenide environment, we used the Ph_4P^+ as the organic

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cation which is stable under flux conditions and this led to the two-dimensional framework compound $(Ph_4P)InSe_{12}$ [6]. Our attempts to extend the incorporation of Ph_4P^+ in other solid state compounds yielded the first example of an anionic, polymeric selenophosphate framework, stabilized by an organic countercation, namely $(Ph_4P)[In(P_2Se_6)]$ (**I**). The compound $Cs_5In(P_2Se_6)_2$ (**II**) is related to (**I**) because they share common structural elements and was prepared by direct stoichiometric reaction.

Experimental Section

Synthesis

Reagents. The reagents mentioned in this study were used as obtained unless noted otherwise: (i) In metal (99.99%) was acquired from Johnson Matthey/AESAR Group, Seabrook, NH. (ii) red phosphorus powder, Morton Thiokol, Inc., –100 mesh, Danvers, MA. (iii) cesium metal, analytical reagent, Johnson Matthey/AESAR Group, Seabrook, NH. (iv) selenium powder, 99.5+% purity, –100 mesh, Aldrich Chemical Co., Inc., Milwaukee, Wi. (v) N,N-Dimethylformamide (DMF) reagent grade, EM Science, Inc., Gibbstown, NJ. (vi) diethyl ether, ACS anhydrous, EM Science, Inc., Gibbstown, NJ.

Cs_2Se was prepared by reacting stoichiometric amounts of the elements in liquid ammonia as described elsewhere [3 a].

P_2Se_5 The amorphous phosphorus selenide glass "P_2Se_5", was prepared by heating a stoichiometric ratio of the elements as described elsewhere. [3 a]

Preparation of $(Ph_4P)[In(P_2Se_6)]$ (I). Compound (**I**) was synthesized from a mixture of In (0.35 mmol), $(Ph_4P)_2Se_5$ [6] (0.35 mmol), and P_2Se_5 (0.70 mmol) which was sealed under vacuum in a Pyrex tube and heated to 250 °C for 2 d, followed by cooling to 50 °C at 2.5 °C h^{-1}. The excess $(Ph_4P)_xP_ySe_z$ flux was removed with degassed DMF. Further washing with anhydrous ether revealed an intimate mixture of amorphous orange agglomerates and thin, yellow, crystals of $(Ph_4P)[In(P_2Se_6)]$ (~10%). The latter are air- and water-stable. Semiquantitative microprobe analysis on single crystals confirmed the presence of P, In and Se.

Preparation of $Cs_5In(P_2Se_6)_2$ (II). Compound (**II**) was synthesized from a mixture of In (0.4 mmol), Cs_2Se (1.00 mmol), P (1.60 mmol) and Se (3.80 mmol) which was sealed under vacuum in a quartz tube and heated to 750 °C for 2 d, followed by cooling to 150 °C at 25 °C h^{-1}. The product was washed with degassed DMF and anhydrous ether which revealed irregular, dark orange, crystals of $Cs_5In(P_2Se_6)_2$ (~85% based on In). The latter are air- and water-stable. Semiquantitative microprobe analysis gave a composition of $Cs_{4.7}In_{1.0}P_{4.3}Se_{13.1}$.

Physical Measurements

Powder X-ray diffraction. Analyses were performed using a calibrated Rigaku-Denki/RW400F2 (Rotaflex) rotating anode powder diffractometer controlled by an IBM computer, operating at 45 kV/100 mA and with a 1°/min scan rate, employing Ni-filtered Cu radiation. Powder patterns were calculated with the CERIUS2 software [7].

Infrared spectroscopy. Infrared spectra, in the far-IR region (600–50 cm^{-1}), were recorded on a computer controlled Nicolet 750 Magna-IR Series II spectrophotometer equipped with a TGS/PE detector and silicon beam splitter in 4 cm^{-1} resolution. The samples were ground with dry CsI into a fine powder and pressed into translucent pellets.

Differential thermal analysis (DTA). DTA experiments were performed on a computer-controlled Shimadzu DTA-50 thermal analyzer. Typically a sample (~25 mg) of ground crystalline material was sealed in quartz ampoules under vacuum. A quartz ampoule of equal mass filled with Al_2O_3 was sealed and placed on the reference side of the detector. The samples were heated to the desired temperature at 10 °C/min, then isothermed for 10 minutes and finally cooled to 50 °C at the same rate. To evaluate congruent melting we compared the X-ray powder diffraction patterns before and after the DTA experiments. The stability/reproducibility of the samples were monitored by running multiple heating/cooling cycles.

Semiquantitative microprobe analyses. The analyses were performed using a JEOL JSM-6400V scanning electron microscope (SEM) equipped with a TN 5500 EDS detector. Data acquisition was performed with an accelerating voltage of 20 kV and 30 s accumulation time.

Single crystal optical transmission spectroscopy. Room temperature single crystal optical transmission spectra were obtained on a Hitachi U-6000 Microscopic FT Spectrophotometer mounted on an Olympus BH2-UMA metallurgical microscope over a range of 380 to 900 nm. Crystals lying on a glass slide were positioned over the light source and the transmitted light was detected from above.

Single crystal X-ray crystallography. Intensity data for both compounds were collected using a Rigaku AFC6S four-circle automated diffractometer equipped with a graphite

Table 1 Crystallographic data for $(Ph_4P)[In(P_2Se_6)]$ (**I**) and $Cs_5In(P_2Se_6)_2$ (**II**)

Formula	$(Ph_4P)[In(P_2Se_6)]$ (**I**)	$Cs_5In(P_2Se_6)_2$ (**II**)
FW	989.92	1850.76
Crystal dimensions (mm)	0.40×0.20×0.10	0.36×0.06×0.06
a, Å	23.127(7)	13.886(1)
b, Å	6.564(1)	13.886(1)
c, Å	19.083(3)	7.597(2)
α (deg)	90.00	90.00
β (deg)	97.42(2)	90.00
γ (deg)	90.00	90.00
Z, V(Å^3)	4; 2873(1)	2; 1464.9(3)
λ (Mo–Kα), Å	0.71069	0.71069
space group	C2/c (#15)	$P4_2/m$ (#84)
Dcalc, g/cm^3	2.289	4.196
μ(Mo–Kα), cm^{-1}	85.17	220.52
$2\theta_{max}$, deg	50	50
	0 < h < 28	0 < h < 17
Octants	0 < k < 8	0 < k < 17
	–23 < l < 23	0 < l < 9
Total data	2365	1516
Unique data	2305	1396
$F_o > 3\sigma(F_o)$	961	742
Variables	156	63
Abs. ratio (min/max)	0.453	0.810
Temp (°C)	23	23
Final R/Rw[a], %	4.4/5.2	3.9/5.1
G.O.F.	1.46	1.81
Largest residues	0.84/–0.83	1.20/–1.05

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $R_w = \{\Sigma_w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$.

Table 2 Positional parameters and B(eq)[a] for $(Ph_4P)[In(P_2Se_6)]$

Atom	Wyckoff position	X	Y	Z	B_{eq}[a)] Å^2
In(1)	*c*	1/4	1/4	0	2.3(1)
Se(1)	*f*	0.3453(1)	–0.0088(4)	0.0030(1)	2.47(8)
Se(2)	*f*	0.2986(1)	–0.4856(4)	–0.0925(1)	2.7(1)
Se(3)	*f*	0.2129(1)	–0.0086(4)	–0.1111(1)	2.41(9)
P(1)	*f*	0.2743(3)	–0.2039(8)	–0.0443(3)	2.0(2)
P(2)	*e*	0	0.159(1)	1/4	2.4(3)
C(1)	*f*	–0.008(1)	–0.003(4)	0.172(1)	3(1)
C(2)	*f*	–0.054(1)	0.032(4)	0.118(1)	3(1)
C(3)	*f*	–0.058(1)	–0.091(4)	0.058(1)	3(1)
C(4)	*f*	–0.014(1)	–0.228(5)	0.048(1)	5(1)
C(5)	*f*	0.030(1)	–0.260(4)	0.101(1)	4(1)
C(6)	*f*	0.034(1)	–0.138(3)	0.165(1)	3(1)
C(7)	*f*	0.0644(9)	0.313(3)	0.251(1)	1.9(8)
C(8)	*f*	0.101(1)	0.290(3)	0.201(1)	2(1)
C(9)	*f*	0.152(1)	0.409(5)	0.207(2)	5(2)
C(10)	*f*	0.164(1)	0.551(4)	0.258(1)	4(1)
C(11)	*f*	0.126(1)	0.583(4)	0.306(1)	4(1)
C(12)	*f*	0.075(1)	0.463(3)	0.302(1)	3(1)
H(1)	*f*	–0.0826	0.1391	0.1220	3.7
H(2)	*f*	–0.0920	–0.0785	0.0230	4.1
H(3)	*f*	–0.0163	–0.3032	0.0039	5.2
H(4)	*f*	0.0596	–0.3624	0.0947	5.1
H(5)	*f*	0.0673	–0.1546	0.2027	3.5
H(6)	*f*	0.0929	0.1941	0.1625	2.7
H(7)	*f*	0.1799	0.3867	0.1734	5.9
H(8)	*f*	0.1990	0.6321	0.2593	4.4
H(9)	*f*	0.1330	0.6886	0.3424	4.3
H(10)	*f*	0.0470	0.4849	0.3343	3.9

[a)] *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$

Table 3 Displacement parameters U_{ij}[a)] for $(Ph_4P)[In(P_2Se_6)]$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
In(1)	0.031(1)	0.025(1)	0.032(1)	0.001(1)	0.004(1)	–0.004(1)
Se(1)	0.025(1)	0.032(1)	0.036(1)	–0.001(1)	0.000(1)	–0.005(1)
Se(2)	0.042(1)	0.029(1)	0.035(1)	0.003(1)	0.015(1)	–0.006(1)
Se(3)	0.028(1)	0.033(1)	0.030(1)	0.002(1)	–0.001(1)	0.001(1)
P(1)	0.027(3)	0.030(3)	0.017(3)	–0.000(3)	0.004(3)	–0.003(2)
P(2)	0.019(5)	0.043(4)	0.027(5)	0	–0.001(4)	0
C(1)	0.04(1)	0.06(1)	0.02(1)	0.01(2)	–0.01(1)	0.00(1)
C(2)	0.04(1)	0.05(2)	0.02(1)	–0.01(1)	–0.01(1)	–0.01(1)
C(3)	0.03(2)	0.05(1)	0.04(2)	–0.02(1)	0.00(1)	0.00(1)
C(4)	0.05(2)	0.09(2)	0.03(1)	0.02(2)	–0.00(2)	–0.02(2)
C(5)	0.04(2)	0.04(1)	0.09(2)	0.01(2)	0.03(2)	–0.01(2)
C(6)	0.03(2)	0.04(1)	0.04(2)	0.01(1)	–0.00(1)	0.00(1)
C(7)	0.02(1)	0.02(1)	0.03(1)	0.00(1)	–0.01(1)	–0.00(1)
C(8)	0.04(1)	0.05(1)	0.01(1)	–0.03(1)	0.01(1)	–0.01(1)
C(9)	0.02(2)	0.10(2)	0.08(2)	–0.01(2)	0.03(2)	–0.01(2)
C(10)	0.03(1)	0.07(2)	0.04(2)	–0.01(1)	0.01(1)	0.01(1)
C(11)	0.04(2)	0.05(1)	0.05(2)	–0.00(1)	0.01(1)	–0.01(1)
C(12)	0.05(2)	0.03(1)	0.05(2)	–0.01(1)	0.03(1)	–0.01(1)
H(1)	0.0474					
H(2)	0.0523					
H(3)	0.0658					
H(4)	0.0641					
H(5)	0.0439					
H(6)	0.0344					
H(7)	0.0753					
H(8)	0.0555					
H(9)	0.0550					
H(10)	0.0489					

[a)] $U_{ij} = \exp\{-2\pi^2(a^{*2}U_{11}h^2 + \ldots + 2b^*c^*U_{23}kl)\}$

crystal monochromator in an ω-2θ scan mode. An empirical absorption correction based on y scans was applied during initial stages of refinement. The space groups were determined from systematic absences and intensity. No crystal decay was detected in any of the compounds. The structures were solved by direct methods using SHELXS-86 software [8 a] and full matrix least squares refinement was performed using the TEXSAN software package [8 b]. For (**I**) phenyl H atoms were derived with the assumption of idealized geometries. All non-H atoms were refined anisotropically.

The data collection parameters are given in Table 1. The coordinates of all atoms, average temperature factors, displacement parameters and their estimated standard deviations are given in Tables 2 to 5.

Table 4 Positional parameters and B(eq) for $Cs_5In(P_2Se_6)_2$

Atom	Wyckoff position	X	Y	Z	B_{eq}[a)] Å^2
Cs(1)	*j*	0.3256(1)	0.0341(2)	0.0000	2.42(5)
Cs(2)	*j*	0.6738(2)	0.3402(2)	0.0000	3.48(6)
Cs(3)	α	0.0000	0.0000	0.0000	2.86(7)
In	*c*	0.5000	0.0000	0.5000	1.77(7)
Se(1)	*j*	0.6886(2)	–0.0355(2)	0.5000	1.86(7)
Se(2)	*k*	0.8193(1)	0.1498(2)	0.2603(3)	2.21(5)
Se(3)	*j*	0.6452(3)	0.3548(2)	0.5000	3.31(9)
Se(4)	*k*	0.5267(1)	0.1556(1)	0.7329(3)	1.95(4)
P(1)	*j*	0.7432(5)	0.1151(6)	0.5000	1.5(2)
P(2)	*j*	0.6079(5)	0.2057(5)	0.5000	1.7(2)

Table 5 Displacement parameters U_{ij} for $Cs_5In(P_2Se_6)_2$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cs(1)	0.026(1)	0.037(1)	0.029(1)	0.0044(9)	0.0000	0.0000
Cs(2)	0.056(2)	0.040(1)	0.036(1)	–0.016(1)	0.0000	0.0000
Cs(3)	0.038(2)	0.040(2)	0.031(2)	–0.009(2)	0.0000	0.0000
In	0.016(2)	0.020(2)	0.031(2)	–0.004(1)	0.0000	0.0000
Se(1)	0.017(2)	0.019(2)	0.034(2)	0.003(1)	0.0000	0.0000
Se(2)	0.023(1)	0.038(1)	0.023(1)	–0.0041(9)	0.005(1)	0.002(1)
Se(3)	0.064(3)	0.019(2)	0.043(2)	–0.011(2)	0.0000	0.0000
Se(4)	0.024(1)	0.026(1)	0.024(1)	–0.0027(9)	0.007(1)	–0.004(1)
P(1)	0.016(4)	0.022(4)	0.020(4)	–0.004(3)	0.0000	0.0000
P(2)	0.016(4)	0.019(4)	0.028(4)	–0.001(3)	0.0000	0.0000

Results and Discussion

$(Ph_4P)[In(P_2Se_6)]$ (**I**) is a one-dimensional compound containing infinite $[In(P_2Se_6)]_n^{n-}$ chains. These chains propagate along the [0 1 0] direction and are well separated by Ph_4P^+ cations, see Figure 1 A. Each $[In(P_2Se_6)]_n^{n-}$ chain consists of $InSe_6$ octahedra connected along the b-axis by hexadentate $[P_2Se_6]^{4-}$ groups. Every In^{3+} metal cation is coordinated by two $[P_2Se_6]^{4-}$ groups and every $[P_2Se_6]^{4-}$ group connects two In^{3+} octahedral centers (by supplying opposite trigonal faces of the octahedra), see Figure 1 B. The latter are fully eclipsed when viewed along the chain axis, see Figure 1 A. The chain is related to the $[MP_2Se_6]_n^{2n-}$ chain observed in the $A_2MP_2Se_6$ (A = alkali metal, M = divalent Mn, Fe, Pd, Zn, Cd, and Hg) family [3 a, 9 a]. In particular, the alignment of the MSe_6 octahedra along the chain axis, and the hexadentate nature of the $[P_2Se_6]^{4-}$ groups are observed for the Mn, Fe, Zn and Cd members [3 a, 9 a]. The Ph_4P^+ cations have a regular tetrahedral structure. Their arrangement in the cell is such that they form rectangular channels of approximate dimensions 5.6×6.4 Å, running down the [0 1 0] direction, see dashed box in Figure 1 A. These channels are occu-

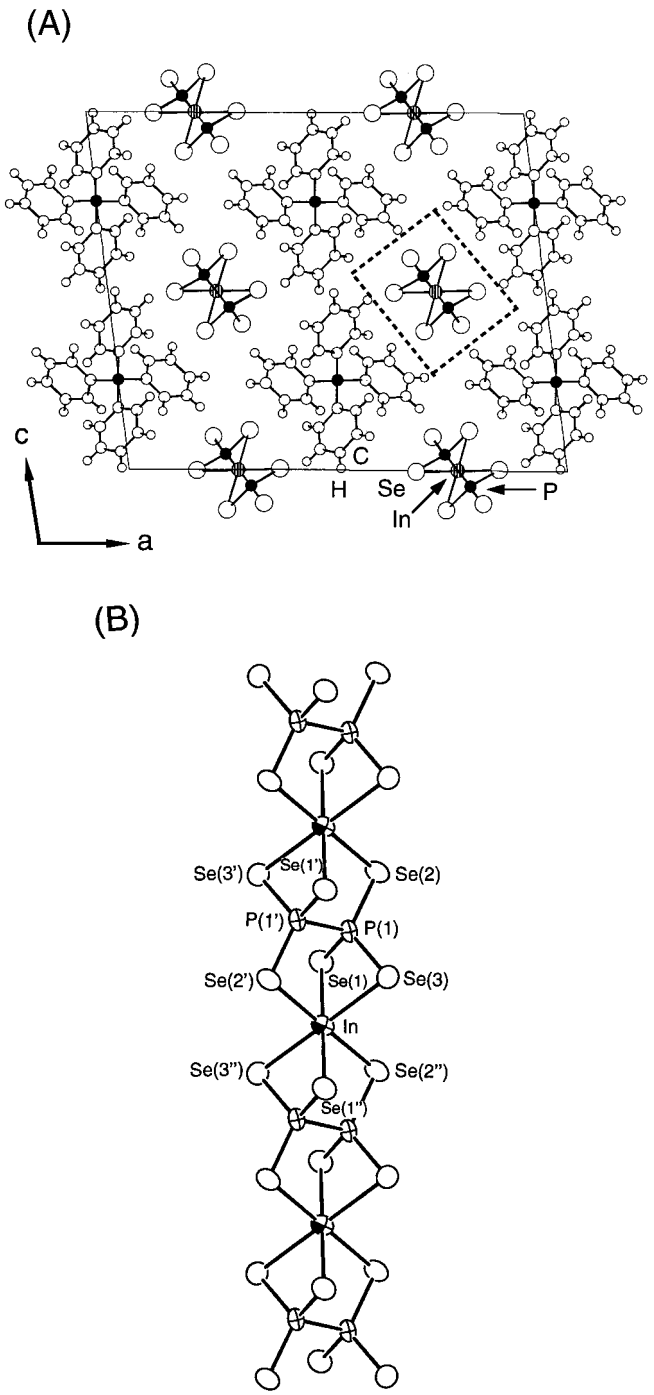

Fig. 1 (A) The unit cell of $(Ph_4P)[In(P_2Se_6)]$ viewed down the b-axis. Dashed box indicates the channels formed by the packing of the Ph_4P^+ cations. (B) A single $[In(P_2Se_6)]_n^{n-}$ chain with labeling (ORTEP view, 75% ellipsoids).

pied by the $[In(P_2Se_6)]_n^{n-}$ chains which are an exact fit for this free space. Therefore, the organic cations can be viewed as templates for the stabilization of the chain structure.

In (**I**), there are two sets of In–Se distances; the first set of long distances averages at 2.812(2) Å and the second set of short distances averages at 2.771(7) Å. Similar distances have been observed in $K_4In_2(PSe_5)_2(P_2Se_6)$ [9 b] and $In_4(P_2Se_6)_3$ [10]. The P–Se distances range from 2.172(6) to 2.195(6) Å. Other selected distances and angles are given in Table 6.

Table 6 Selected Distances (Å) and Angles (deg) for $(Ph_4P)[In(P_2Se_6)]$ with Standard Deviations in Parentheses

In–Se(1)	2.777(2)	Se(1)–In-Se(1″)	180.00
In–Se(2′)	2.812(2)	Se(1)–In–Se(2′)	89.43(7)
In–Se(3)	2.764(2)	Se(1)–In–Se(2″)	90.57(7)
P(1)–Se(1)	2.183(6)	Se(1)–In–Se(3)	78.89(7)
P(1)–Se(2)	2.172(6)	Se(1)–In–Se(3″)	101.11(7)
P(1)–Se(3)	2.195(6)	Se(1)–P(1)–Se(2)	116.9(3)
P(1)–P(1′)	2.23(1)	Se(1)–P(1)–Se(3)	107.0(2)
		Se(1)–P(1)–P(1′)	105.7(4)
		P(1)–Se(1)–In	78.4(2)
		P(1)–Se(3)–In	78.5(2)
		P(1′)–Se(2′)–In	96.5(2)

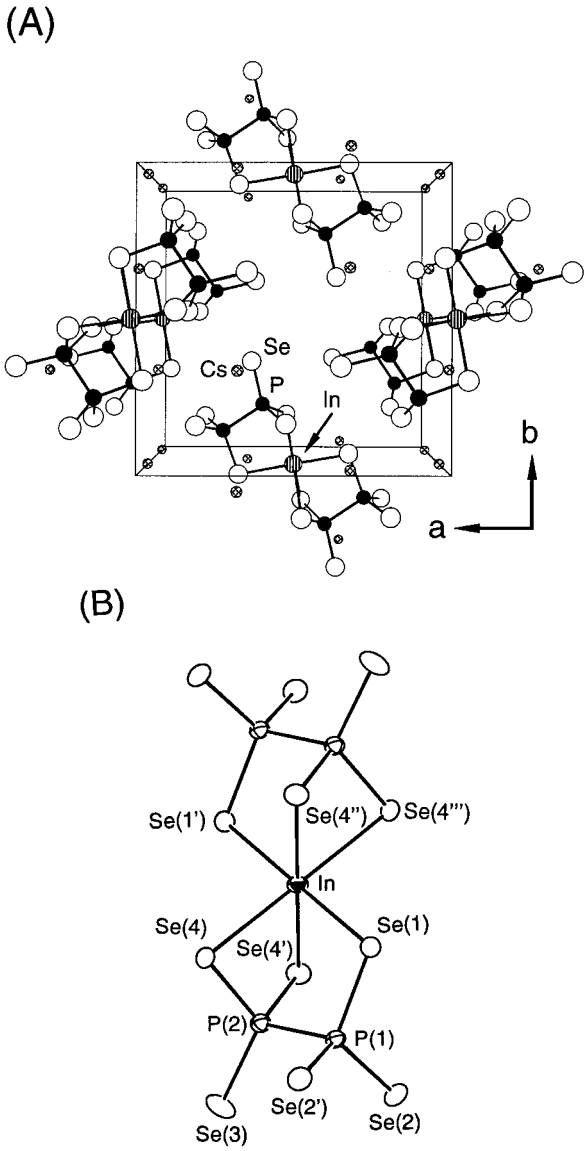

Fig. 2 (A) The unit cell of $Cs_5In(P_2Se_6)_2$ viewed down the c-axis. (B) A single $[In(P_2Se_6)_2]^{5-}$ molecule with labeling (ORTEP view, 50% ellipsoids).

Table 7 Selected Distances (Å) and Angles (deg) for $Cs_5In(P_2Se_6)_2$ with Standard Deviations in Parentheses

In–Se(1)	2.665(3)	Se(1)–In–Se(1′)	180.00
In–Se(4)	2.817(2)	Se(1)–In–Se(4)	90.72(7)
P(1)–Se(1)	2.224(8)	Se(1)–In–Se(4′)	90.72(7)
P(1)–Se(2)	2.160(5)	Se(1)–In–Se(4″)	89.28(7)
P(2)–Se(3)	2.133(8)	Se(1)–In–Se(4‴)	89.28(7)
P(2)–Se(4)	2.211(5)	Se(1)–P(1)–Se(2)	112.1(2)
P(1)–P(2)	2.26(1)	Se(1)–P(1)–Se(3)	112.1(2)
		Se(1)–P(1)–P(2)	103.9(4)
		P(1)–Se(1)–In	99.3(2)
		P(2)–Se(4)–In	78.8(2)
		P(2)–Se(4′)–In	78.8(2)

The discrete $[In(P_2Se_6)_2]^{5-}$ (**II**) anion features a trivalent indium center coordinated by two chelating $[P_2Se_6]^{4-}$ ligands, Figure 2. The six donor Se atoms around the In adopt an octahedral geometry. The In center is situated on a 2/m crystallographic site. The tridentate $[P_2Se_6]^{4-}$ ligands cap two opposite faces of the $InSe_6$ octahedron. By linking these complexes with the coordination of additional indium centers on the free sites of the $[P_2Se_6]^{4-}$ ligands, one can obtain the $[In(P_2Se_6)]_n^{n-}$ chains of (**I**). In this respect (**II**) can be considered as a building block of the anionic framework of (**I**).

In (**II**), there are also two sets of In–Se distances; the first set of long distances averages at 2.817(2) Å and the second set of short distances averages at 2.665(3) Å slightly shorter than the ones observed for (**I**). The P–Se distances range from 2.133(8) to 2.224(8) Å with the non-coordinating Se atoms exhibiting the shorter ones. Other selected distances and angles are given in Table 7.

It was not possible to perform physical measurements for (**I**) due to the large amount of impurities. Single crystal optical transmission spectroscopy performed on (**II**) shows a sharp optical gap Eg, of 2.25 eV, Figure 3. The infrared spectrum of (**II**) displays absorptions at *ca*. 507(s), 480(vs), 440(vs), 404(w), 377(w), 310(vs), 224(w), 206(m), 177(m) and 156(w) cm^{-1}. The vibrations at *ca*. 507, 480, 440, 404 and 377 cm^{-1} can be attributed to PSe_3 stretching modes whereas the one at 310 cm^{-1} can be ascribed to an out-of-phase PSe_3 mode [3 a, 3 c, 3 f, 4 a]. The absorptions at 224 cm^{-1} and below are most probably due to M–Se vibrations [3]. Differential thermal analysis (DTA) shows that (**II**) melts congruently at *ca*. 632 °C whereas (**I**) decomposes at *ca*. 290 °C.

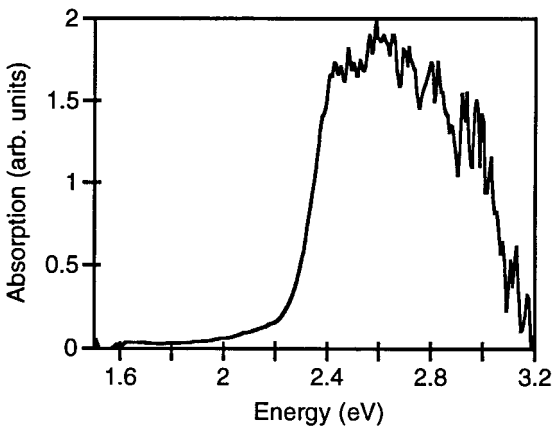

Fig. 3 Single-crystal absorption spectrum of $Cs_5In(P_2Se_6)_2$.

The synthesis of the first example of a selenophosphate framework, stabilized by an organic countercation has been achieved in a $(Ph_4P)_xP_ySe_z$ flux. The incorporation of organic countercations in fluxes warrants further exploration. The large organic cations could serve as templates for interesting structures with the only limitation being that they have the thermal stability necessary to remain viable within the flux. By optimizing the reaction parameters, construction of open-framework structures as in $(Ph_4P)InSe_{12}$ [6] might be feasible.

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