New directions in synthetic solid state chemistry: chalcophosphate salt fluxes for discovery of new multinary solids

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There have been recent developments in the application of molten polychalcophosphate salt fluxes for the synthesis of complex, multinary metal thiophosphate and selenophosphate compounds. New methodologies, new solids and the potential of polychalcophosphate fluxes have been discovered.

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Current Opinion in Solid State & Materials Science 1997, 2:139–149

Electronic identifier: 1359-0286-002-00139

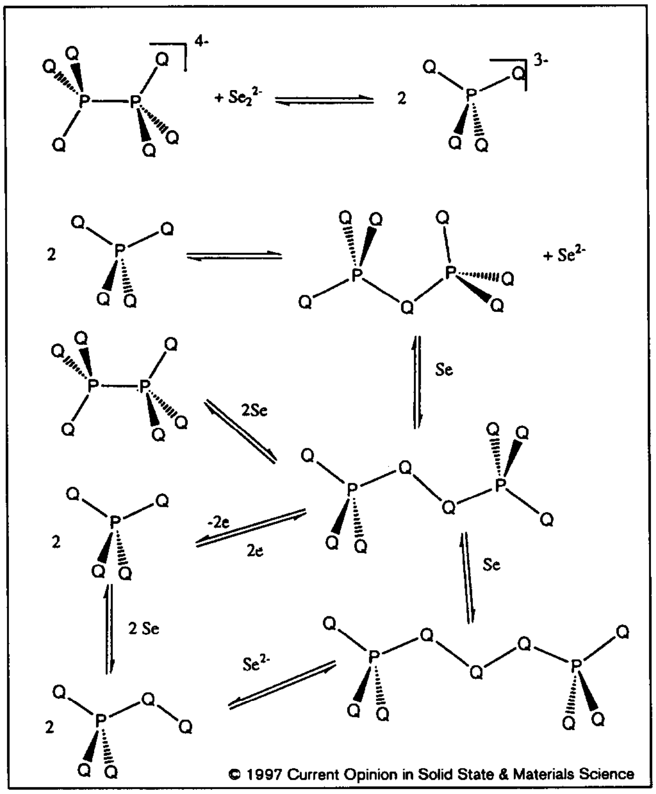
ISSN 1359-0286

Introduction

The application of salt fluxes to the synthesis of new solid state compounds has witnessed significant development in the last ten years. Particularly important has been the development of the molten polychalcogenide flux method in the exploratory synthesis of complex chalcogenides [1••,2]. This relatively new approach to the synthesis of chalcogenides has enabled access to low and intermediate temperatures (160–600°C) of formation and has contributed to the discovery of some very interesting materials [1••,2]. In many cases the compounds stabilized under polychalcogenide flux conditions are only kinetically stable and cannot be synthesized at higher temperatures; however, thermodynamic influences are not entirely avoided by this approach. Lower temperatures also make possible the use of molecular assemblies as building blocks for incorporation into solid state structures. It is this latter aspect which is the subject of this article, with emphasis being placed on the generation and diversity of new compounds, that result from the reactivity of flux-assembled $[P_yQ_z]^{n-}$ (Q = S,Se) anions with metal centers (using molten salts as the source of these metals).

The basis of coordination chemistry lies in the ability to design and use interesting ligands for coordination to metal ions. Monodentate, bidentate and multidentate anionic ligands, dissolved in water or organic solvents, are routinely used to assemble, at room temperature, a myriad of discrete molecular coordination compounds. If such entities were stable in a flux we would expect even larger molecules or infinite coordination solids to form. In the area of chalcogenides, of course such ligands would have to be thio- and seleno-anions. Such discrete anionic species, if stable in A_2Q_x (A = alkali metal) solutions, would be able to quickly diffuse and react with a second element in the flux. Alkali polychalcophosphates do not have to be the only media for $[P_yQ_z]^{n-}$ anions. Any other system which can meet the stability and solubility conditions necessary would do (e.g. alkali halides [3,4]). Polychalcophosphate fluxes are expected to be chemically different and thus yield results complementary to those of polychalcophosphates.

Figure 1



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Possible equilibria present in polychalcophosphate fluxes.

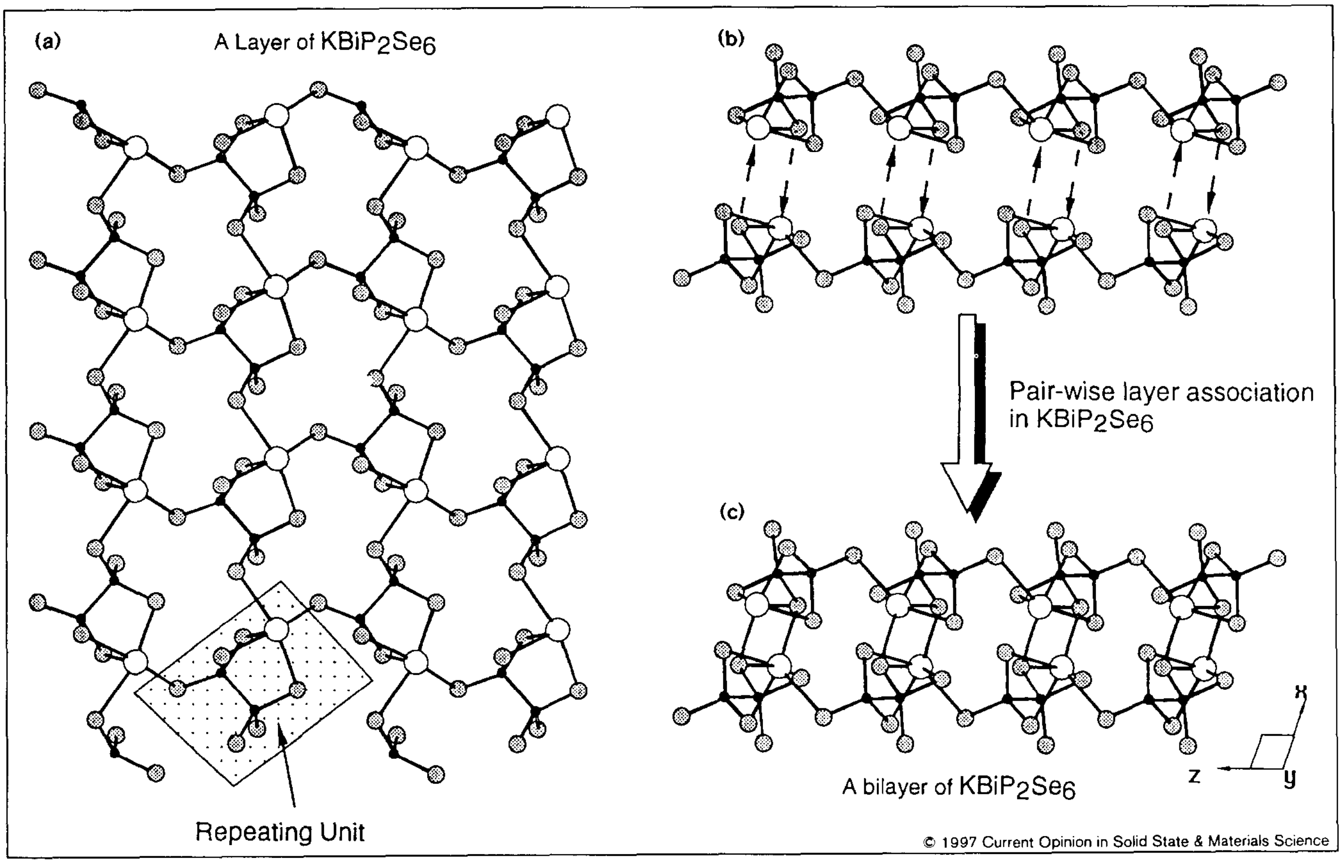
The concept of thio- and seleno-anionic ligands floating around in A_2Q_x fluxes provides an important foundation for exploratory synthesis by promoting species, other than polychalcogenides, which could be formed *in situ* and then used for coordination chemistry. In this context the molten polychalcogenide approach becomes less like a low temperature 'heat and beat' method and more like a bona fide solvent method in which, under appropriate conditions, various species can be stabilized and allowed to react preferentially, much like in a conventional synthetic coordination chemistry reaction. Therefore we can expect to form any chalcogenide-containing ligand *in situ* with the only limitation being that such ligands have the modest (in solid state terms) thermal stability necessary to remain viable within the flux. Species such as $[SnQ_4]^{4-}$, $[TeS_3]^{2-}$ and $[As_2Q_6]^{4-}$ have already demonstrated an appreciable stability under molten A_2Q_x salt conditions and been shown to act as ligands [5–8]. Investigations into such chemistry have led to several new heterometallic quaternary sulfides which will be discussed here. One related class of ligands are the chalcophosphates, $[P_yQ_z]^{n-}$ which produce a large family of chalcophosphate compounds.

The thio- and selenophosphate compounds as a class

Unlike the huge class of (oxo)phosphate compounds thio- and selenophosphates are still a relatively small group. There is a great divide between these two classes as their chemical, structural and physical properties differ substantially. Although more uses exist for the oxo-phosphates in the areas of catalysis, ceramics, glasses and molecular sieves, their thio and selenocounterparts include compounds which exhibit promising and unique properties. Several main group metal thiophosphates also have interesting physical properties. $InPS_4$ crystallizes in a noncentrosymmetric tetragonal space group (I-4) and has been found to have high nonlinear optical susceptibility [9], whereas $Sn_2P_2S_6$ crystallizes in the eccentric space group Pc and undergoes a second order, exothermic phase transition from ferroelectric (Pc) to paraelectric ($P2_1/c$) at 60°C [10]. This compound has been shown to be a promising ferroelectric material for use in memory devices [11].

To date it is mainly the ternary thiophosphate and selenophosphate compounds that have been seen to any significant extent in the literature; these are predominately the $M_2P_2Q_6$ (M = divalent metal) compounds [12,13] which contain the ethane-like $(P_2Q_6)^{4-}$ ligand, A_3PQ_4 [14] and MPQ_4 (M = trivalent metal) [15] ligands, but various other examples of $[P_yQ_z]^{n-}$ containing species also exist [16–18]. Recently, reports of some quaternary phases have begun to appear in the literature [19,20]. Typically, they are synthesized by direct combination of the elements at temperatures between 500 and 800°C, and under these conditions, complex acid/base equilibria have

Figure 2



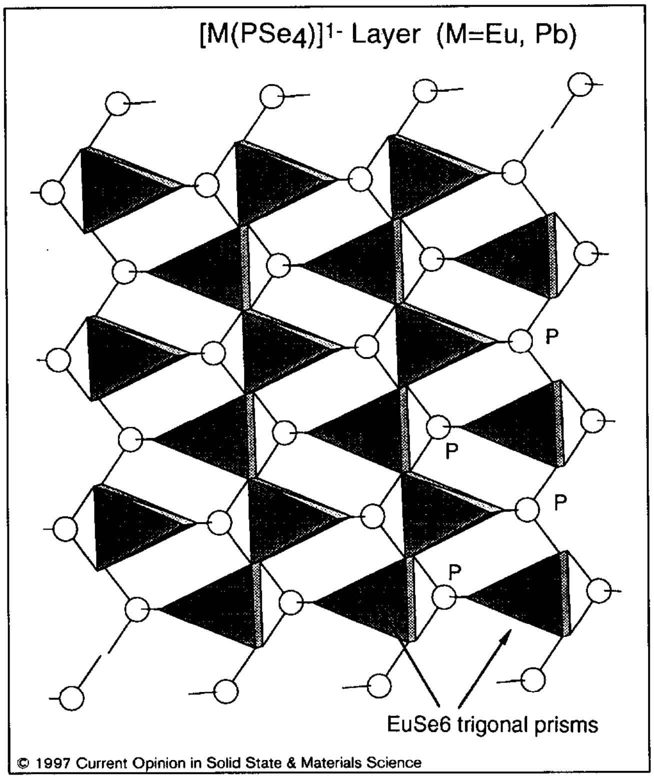
The structure of KMP_2Se_6 (M=Sb, Bi) is made of double layers. A single such layer is shown in **(a)**. Two such layers associate via interlayer M–Se bonds **(b)** to form a double layer **(c)**.

been observed between species such as $[P_2S_6]^{4-}$, $[P_2S_6]^{2-}$, $[P_2S_7]^{4-}$, and $[PS_4]^{3-}$.

$M_2P_2Q_6$ has been the most important family of compounds which contains the ethane-like $[P_2Q_6]^{4-}$ ligand. This family of compounds has been extensively studied because various members exhibit interesting intercalation chemistry and ion-exchange, magnetic and spectroscopic properties. The $M_2P_2S_6$ compounds have been examined extensively for use as cathode material for secondary lithium batteries [21]. A new interesting family of thiophosphates with Group 5 transition metals has been reported [22]. These compounds exhibit a wonderful structural diversity, derived from a large variety of anionic P/S ligands, and a tendency for low dimensionality. One could view them as a prelude to what could be expected in this, somewhat neglected, area of chemistry.

Because $[P_xQ_y]^{n-}$ containing solids are still few in number, and because, from a synthetic chemist's point of view, well-defined discrete anionic fragments are potential building blocks for new three-dimensional frameworks, methodologies which facilitate the production and usage of such synthons are particularly attractive. Thus, a general methodology by which new thiophosphate (or chalcophosphate) compounds can be consistently obtained would be very useful. In this article recent advances in the preparation of chalcophosphate compounds will be highlighted, particularly those taking advantage of the alkali metal polychalcophosphate fluxes.

Figure 3



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The structure of a $[M(PSe_4)]^{-}$ layer. Though not isostructural $CsPbPSe_4$ and $KEuPSe_4$ have the same layer structure where metals in trigonal prisms of Se atoms share edges. White circles are P atoms.

The polychalcophosphate flux

The polychalcophosphate fluxes are formed by simple *in situ* fusion of $A_2Q/P_2Q_5/Q$ in the same manner as has been used for A_2Q_x fluxes. Although the fluxes are conceptually $A_xP_yQ_z$, a more accurate description is probably that of $[P_yQ_z]^{n-}$ species solubilized in an excess of polychalcogenide flux, which also continues to serve as the oxidant to dissolve metallic elements into the flux. The inclusion of P in the fluxes renders them somewhat more basic than their all-chalcogenide counterparts (i.e. A_2Q_x), but the melting points of $A_xP_yQ_z$ are also in the intermediate temperature range (minimum melting points: 300–400°C) making possible the synthesis of metastable phases. In addition, the $[P_yQ_z]^{n-}$ species act as effective mineralizers, promoting large crystal growth.

The formation of alkali metal chalcophosphate fluxes results from the fusion of an alkali metal monochalcogenide, P_2Q_5, and an elemental chalcogen (see Eqn 1).

$$(x/2)A_2S + (y/2)P_2S_5 + zS \rightarrow A_x[P_yS_{x+y+z}] \qquad (1)$$

Notice that these compositions always have an excess of chalcogen, which is important in two ways. First, it helps to lower the melting point of the flux and second, it serves as an electron acceptor when the metal is dissolved in the flux. Less frequently, the excess chalcogen gets incorporated into the compound as Q^{2-} or Q_x^{2-} species. The acid/base characteristics of the $A_x[P_yS_z]$ fluxes are very different from those of the A_2S_x fluxes in that they tend to be more basic. The chemical properties of these melts can be controlled by varying the ratios of their constituent elements. The relatively good solubility properties of $A_x[P_yS_z]$ salts in water and organic solvents allow for easy isolation of products. The same considerations of course apply for the corresponding Se fluxes but the extent of chemical equilibria, nature of $[P_xSe_y]^{n-}$ anions and coordination behavior towards metal ions are very different. Based on the characterization of the compounds formed in these fluxes [1••], the equilibria, depicted in Figure 1, among the various $[P_xSe_y]^{n-}$ and Q or Q_x^{2-} anions can be speculated. Many other such species could be present whose concentration would depend on the precise flux composition under a particular set of reaction conditions. Probably, some of them have yet to be discovered. Because the extent of these equilibria will vary between the S and the Se system, even if all other conditions are equal, the final products from the flux reactions are often different. Physicochemical studies aimed at understanding the nature of these fluxes are scant. An interesting report dealing with ^{31}P and ^{7}Li NMR studies in the Li-P-S system confirmed that the equilibria (as shown in Fig. 1) are in effect [23]; however, more investigations are needed.

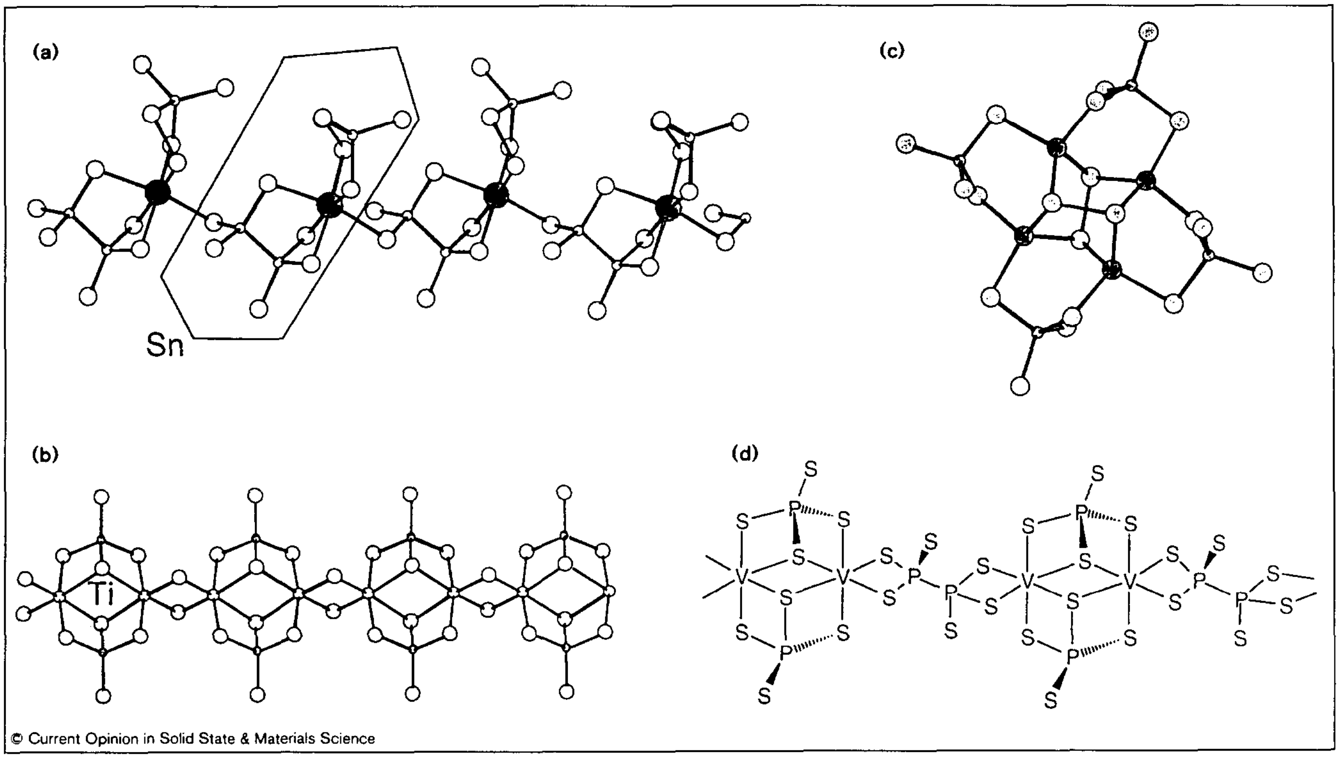
Reactivity of main group and late transition metals

Although early investigations concentrated on Bi there is no element (metal or metalloid) which does not react with these fluxes. The compounds $ABiP_2S_7$ (A = K,Rb), $A_3M[PS_4]_2$ (A = K,Rb,Cs; M = Sb,Bi), $Cs_3Bi_2[PS_4]_3$, and the nonstoichiometric $Na_{0.16}Bi_{1.28}P_2S_6$ were among the first to be made from fluxes [24,25]. As in the A_2Q_x fluxes, modest changes in the composition of the $A_xP_yQ_z$ flux can alter the equilibria between $[P_yQ_z]^{n-}$ species, changing which ligand is incorporated into the final product. Prior to the use of the flux method $BiPS_4$ was the only known Bi-P-S compound [26]. $KBiP_2S_7$ forms from a reaction of Bi with a flux of composition $K_4P_6S_{21}$, heated at 400–450°C [25] for 4 days, however, it was from a more basic flux, richer in S (e.g. $K_8P_6S_{26}$) that $K_3Bi[PS_4]_2$ was isolated [26]. In the structure of $K_3Bi[PS_4]_2$, the Bi electron lone pairs are apparently stereochemically active with two kinds of Bi coordination, a square pyramidal and a see-saw type. The Bi atoms are linked into zig-zag chains by $[PS_4]$ tetrahedra, with the lone electron pair of Bi^{3+} presumably active at the base of the pyramid. The two $(PS_4)^{3-}$ ligands each have a different bonding mode to the Bi atoms. In $ABiP_2S_7$ the 'pyrothiophosphate' $(P_2S_7)^{4-}$ anion acts as a multidentate ligand, bridging four different Bi^{3+} in four different modes. This leads to a complicated connectivity within the layer which has been described in detail [24,25].

The structural diversity in the Bi system ranges from the pseudo-helical one-dimensional noncentrosymmetric chains of $A_3Bi(PS_4)_2$ and the layered compounds, $ABiP_2S_7$ and $Cs_3Bi_2(PS_4)_2$, to the dense three-dimensional framework of $Na_{0.16}Bi_{1.28}P_2S_6$ [25]. This great multitude of coordination modes of chalcophosphate ligands gives rise to many possibilities for novel lattice construction.

The KMP_2Se_6 compounds (M = Sb, Bi) have been synthesized from mixtures of K_2Se, M, P_2Se_5, Se in a 2:1:3:8 ratio, heated at 410°C for four days when M = Bi and at 450°C for six days when M = Sb [27]. As can be inferred from the formula, the selenophosphate ligand manifested here is $[P_2Se_6]^{4-}$ and exhibits great multidenticity. There are bilayers of MP_2Se_6 in the structure which are made of single layers (see Fig. 2a) containing five coordinate metal atoms. Two single layers then associate side-by-side via cross-layer M–Se bonds which expand the metal coordination number to six, giving rise to a distorted octahedron (see Fig. 2b,c). $Cs_8M_4[P_2Se_6]_5$ (M = Sb,Bi) were synthesized by reacting BiSb in a molten mixture of

Figure 4



Unusual chalcophosphate compounds. **(a)** The chain structure of $Rb_4Sn(PSe_5)(P_2Se_6)$. Only one chain is shown. **(b)** The chain structure of $KTiPSe_5$. **(c)** The structure of the cluster $[M_4(Se_2)_2(PSe_4)_4]^{8-}$ (M=Cd, Hg). **(d)** A schematic structure of the chain found in $K_4V_2\ (PS_4)_2(P_2S_6)$.

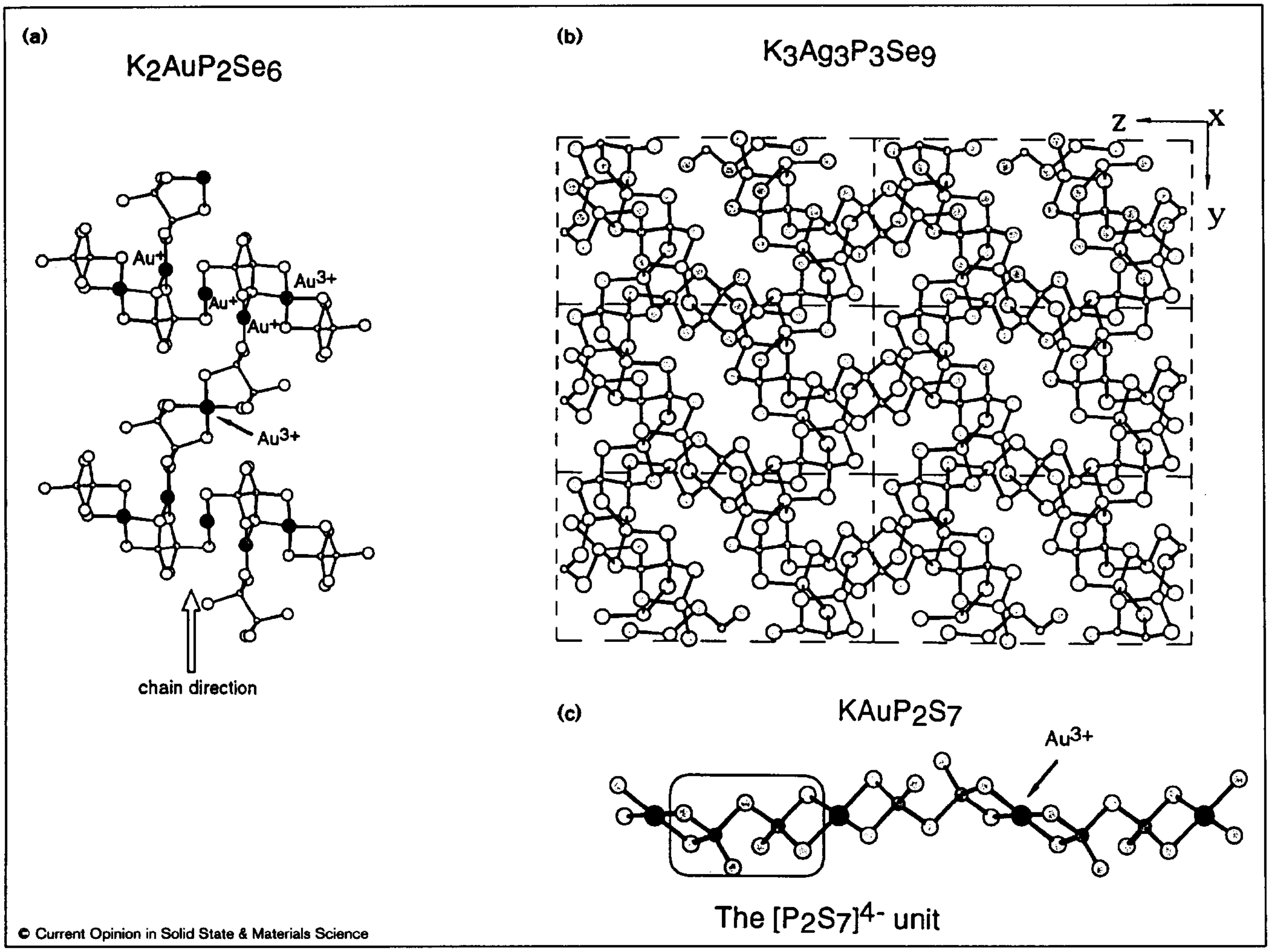
Cs_2Se, P_4Se_{10}, Se in a 2:1.5:4 ratio at 460°C. The structure is complicated and features weak M...M interactions and a $[P_2Se_6]^{4-}$ ligand in three unique bonding modes [28].

The $[P_2Se_6]^{4-}$ ligand again manifests itself in reactions involving Mn and Fe at 450°C [29]. The $A_2MP_2Se_6$ compounds were found for the K^+ and Cs^+ salts of both metals. The materials, all isostructural, possess one-dimensional anionic chains in which the M^{2+} are octahedrally coordinated and bridged by $[P_2Se_6]^{4-}$, making two tridentate chelations to two separate M atoms. If the center of the P–P bond in the ligand is taken as an atomic position, then the structure can simply be considered as a chain of face-sharing octahedra (TiI_3 structure type) [29].

An interesting homologous sequence was identified in the Pb system, namely $APbPSe_4$, $A_4Pb[PSe_4]_2$ (A = Rb,Cs) with a tetrahedral $[PSe_4]^{4-}$ unit [30]. Under similar conditions Sn behaves entirely differently than Pb, partly because it can undergo further oxidation to Sn^{4+}. A different selenophosphate species, $[PSe_5]^{4-}$, was also observed. Therefore, the structural and compositional possibilities increase, giving rise to the compounds α–, β-$A_5Sn(PSe_5)_3$ (A = K, Rb), and $A_6Se_2Se_4(PSe_5)_2$ (A = Rb, Cs) and $Rb_3Sn(PSe_5)(P_2Se_6)$.

$CsPbPSe_4$ has the two-dimensional layered structure shown in Figure 3. The $[PbPSe_4]_n^{n-}$ layers are separated by Cs^+ ions which have an irregular seven coordination. The layers are composed of $PbSe_6$ trigonal prisms and $[PSe_4]^{3-}$ tetrahedra. The trigonal prisms share rectangular edges in such a way that the trigonal faces of the prisms point alternative up and down, forming parallel chains

Figure 5



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Chalcophosphate compounds of the coinage metals. **(a)** A section of the elaborate chain found in $K_2AuP_2Se_6$. The different Au atoms in the chain are indicated. **(b)** The three-dimensional tunnel structure of $K_3Ag_3P_3Se_9$. Actually, the compound contains $[P_2Se_6]^{4-}$ units and not the $[P_3Se_4]^{6-}$ units implied by the formula. The K ions have been omitted for clarity. The $K_3Cu_3P_3Se_9$ is isostructural. **(c)** The chain structure of the chain found in $KAuP_2S_7$.Dark shaded circles are Se, small open circles are P and large open circles are Ag.

along the b-axis. These chains are then joined by $[PSe_4]^{3-}$ tetrahedra [30].

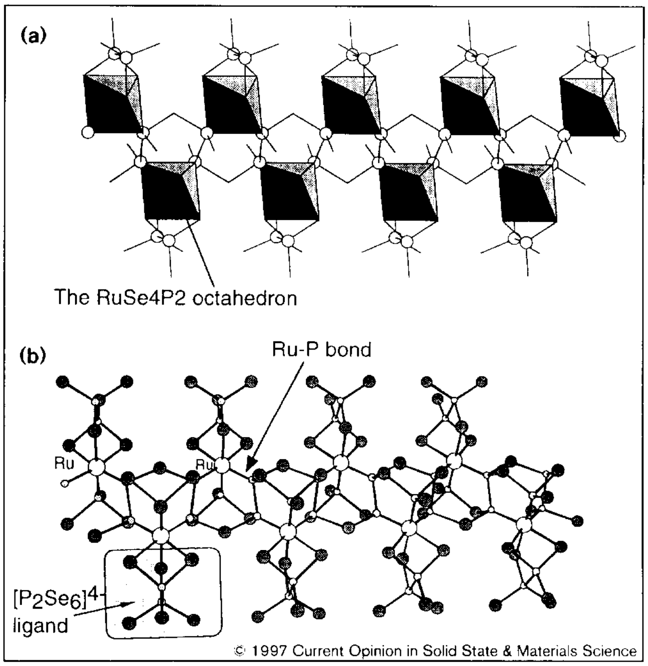
The α-, β-$A_5Sn(PSe_5)_3$ (A = K, Rb), and $A_6Sn_2Se_4(PSe_5)_2$ (A = Rb, Cs) compounds contain discrete molecular anions and have been discussed [31]. $Rb_3Sn(PSe_5)(P_2Se_6)$ is one dimensional with two different selenophosphate anions in an unusual ligation and octahedrally coordinated Sn^{4+} atoms; see Figure 4a. The stabilization of the chelating $[PSe_5]^{4-}$ ligand seems to be particularly favored in the Sn system. This most likely arises from the need to form an energetically relaxed five-membered chelating ring with the Sn center, and a plain $[PSe_4]^{4-}$ unit, unable to do so, can easily access an Se atom from the surrounding flux to form $[PSe_5]^{4-}$. Furthermore, the multidentate nature of the $[P_2Se_6]^{4-}$ ligand is beautifully demonstrated in this example. The tris-chelating mode caps a triangular face of the Sn octahedron while another Se atom anchors to another Sn atom to form the one-dimensional structure. Such diverse binding occurs very often in the chemistry described in this review.

The reaction of Cd or Hg with basic polychalcophosphate fluxes, $Rb_8P_4Se_{24}$ and $Rb_8P_2Se_{16}$ respectively leads to quaternary, mixed ligand, tetranuclear, cluster compounds $[M_4(Se_2)_2(PSe_4)_4]^{8-}$ (M = Cd, Hg) [32]. The compounds possess a stellane-like core which consists of four M^{2+} centers and two bridging Se_2^{2-} ligands. Four bidentate $[PSe_4]^{3-}$ ligands complete the tetrahedral coordination around M^{2+} (see Fig. 4b).

Coinage metals give rise to a large variety of structural types, the most interesting being $Cs_2M_2P_2Se_6$ (M = Cu, Ag) [29], $K_3M_3P_3Se_9$ (M = Cu [33], Ag [29]), $K_2Au_2P_2Se_6$ [34], A_2AuPS_4 (A = K, Rb, Cs) [31], $AAuP_2S_7$ (A = K, Rb) [34] and $A_2AuP_2Se_6$ [35], which is an unusual mixed-valency compound that can be written as $A_4Au^+Au^{3+}(P_2Se_6)_2$. The compound possesses a unique but complicated one-dimensional structure. The structure features the $[P_2Se_6]^{4-}$ group, which acts as a bridging multidentate ligand coordinating to the Au atoms. There are three types of these ligands in the structure. Each type coordinates to one, two and three metal centers respectively (see Fig. 5a). Another intriguing aspect of this odd compound is the presence of three different types of coordination for Au.

In the A-Ag-P-Se system a change in the alkali cation size at the Rb/K interface causes a transition from the one-dimensional to a three-dimensional structure. The $K_3Ag_3P_3Se_9$ compound and its isostructural $K_3Cu_3P_3Se_9$ analog have a unique, complicated three-dimensional tunnel framework made up of $AgSe_4$ tetrahedra linked by P_2Se_6 units (see Fig. 5b). The channels run along the crystallographic a-axis and are filled with K^+ ions. There are two types of $[P_2Se_6]^{4-}$ ligands in this structure.

Figure 6



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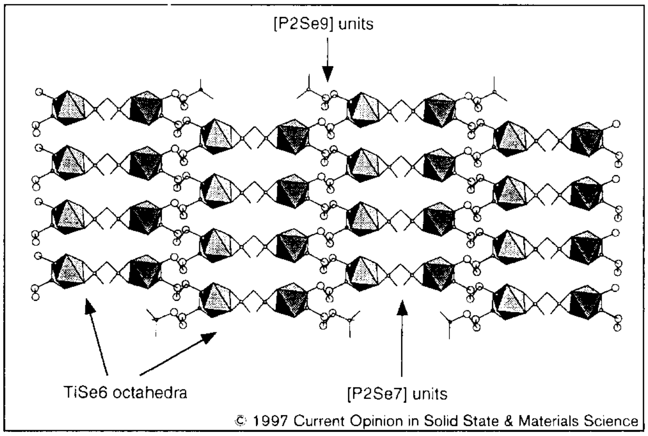
The first Ru chalcophosphate compound. **(a)** An infinite $[Ru(P_2Se_6)(P_3Se_4)]_n^{3n-}$ chain with the $RuSe_4P_2$ octahedra highlighted. **(b)** Ball and stick model of the chain showing the $[P_3Se_4]^-$ polymeric anion as the backbone on the structure and the $[P_2Se_6]^{4-}$ ligands acting as side groups.

Figure 7



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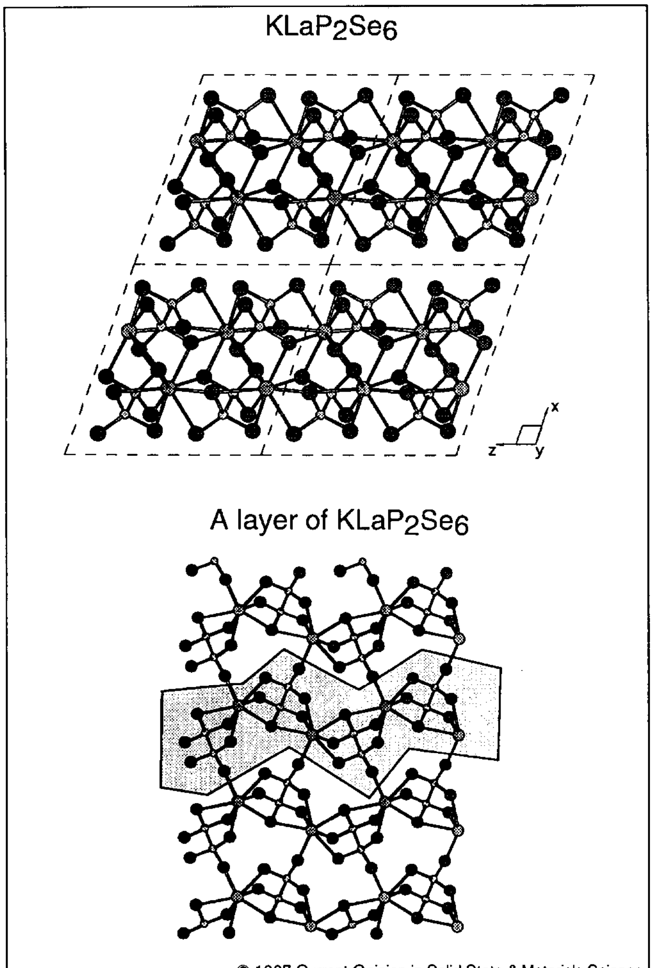
The layered structure of $Rb_4Ti_2(P_2Se_9)_2(P_2Se_7)$. The Rb atoms have been omitted for clarity.

In many cases a thiophosphate flux is a completely different medium from its selenium analog and does not yield just isostructural analogs to the Se counterpart; for example, $KAuP_2S_7$ is a unique compound with no Se analog. The structure features one-dimensional chains with alternating $[P_2S_7]^{4-}$ units and square planar Au^{3+} cations (see Fig. 5c). The Au^{3+} atom adopts a square planar

Figure 8



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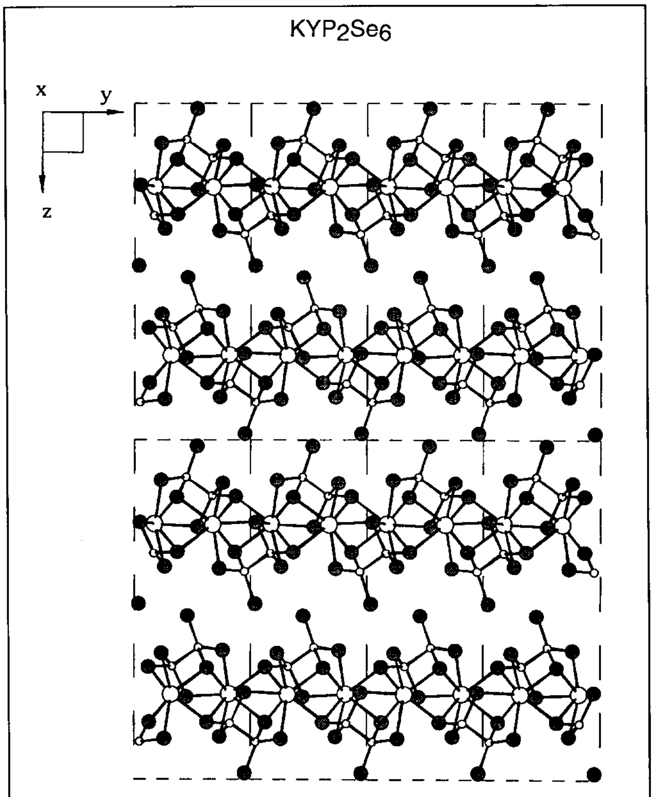
The structure of $KLaP_2Se_6$. The K atoms have been omitted. The shaded portion of the structure represents the one-dimensional chain motif from which the layer is made. Dark shaded circles are Se atoms.

coordination environment. Cs_2AuPS_4 and Cs_2AuPS_4 have straight chains of $[AuPS_4]_2{}^{n-}$ and are separated by alkali cations. The Au atoms are linearly coordinated [34].

An inspection of the entire class of chalcophosphate compounds reveals a conspicuous absence of any Ru containing members, even though several Fe compounds are known. Furthermore, in all compounds the metal atoms form exclusively M–Q bonds. The highly reactive polychalcogenide fluxes serve as an excellent tool to access Ru chemistry. $K_3RuP_5Se_{10}$ shows a significant departure from the chemistry of any other metal studied in the P/Q systems and adds a new perspective in the coordination chemistry of $[P_yQ_z]^{n-}$ anions. $K_3RuP_5Se_{10}$ has a one-dimensional structure with Ru in the 2+ oxidation state (see Fig. 6). It contains $[P_2Se_6]^{4-}$ and $[P_3Se_4]_n{}^{n-}$ anions and so it can be described as $K_3{}^+Ru^{2+}(P_2Se_6)^{4-}(P_3Se_4)^-$. There are two unprecedented features in this compound: first the mixed P/Se coordination of the Ru centers, and second, the stabilization of a novel polymeric $[P_3Se_4]_n{}^{n-}$ anion with P atoms in two different oxidation states (P^{2+}, P^{3+}). The anion binds the Ru^{2+} exclusively via P atoms. To date, in polychalcophosphate chemistry, all the $[P_yQ_z]^{n-}$ units coordinate to the metal centers via the Q atoms (Q=S, Se) which are negatively charged. In $K_3RuP_5Se_{10}$, for the first time, we observe bonding between the metal center and the P atoms of a $[P_yQ_z]^{n-}$ unit. The strong preference of Ru^{2+} for binding to P is reminiscent to that of phosphine (R_3P) coordination and organometallic complexes. The selection of P in a sea of selenide anions for bonding is remarkable.

Figure 9



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The layered compound KYP_2Se_6. The K atoms have been omitted. Dark shaded circles are Se atoms.

Reactivity of early transition metals, rare earths and actinides

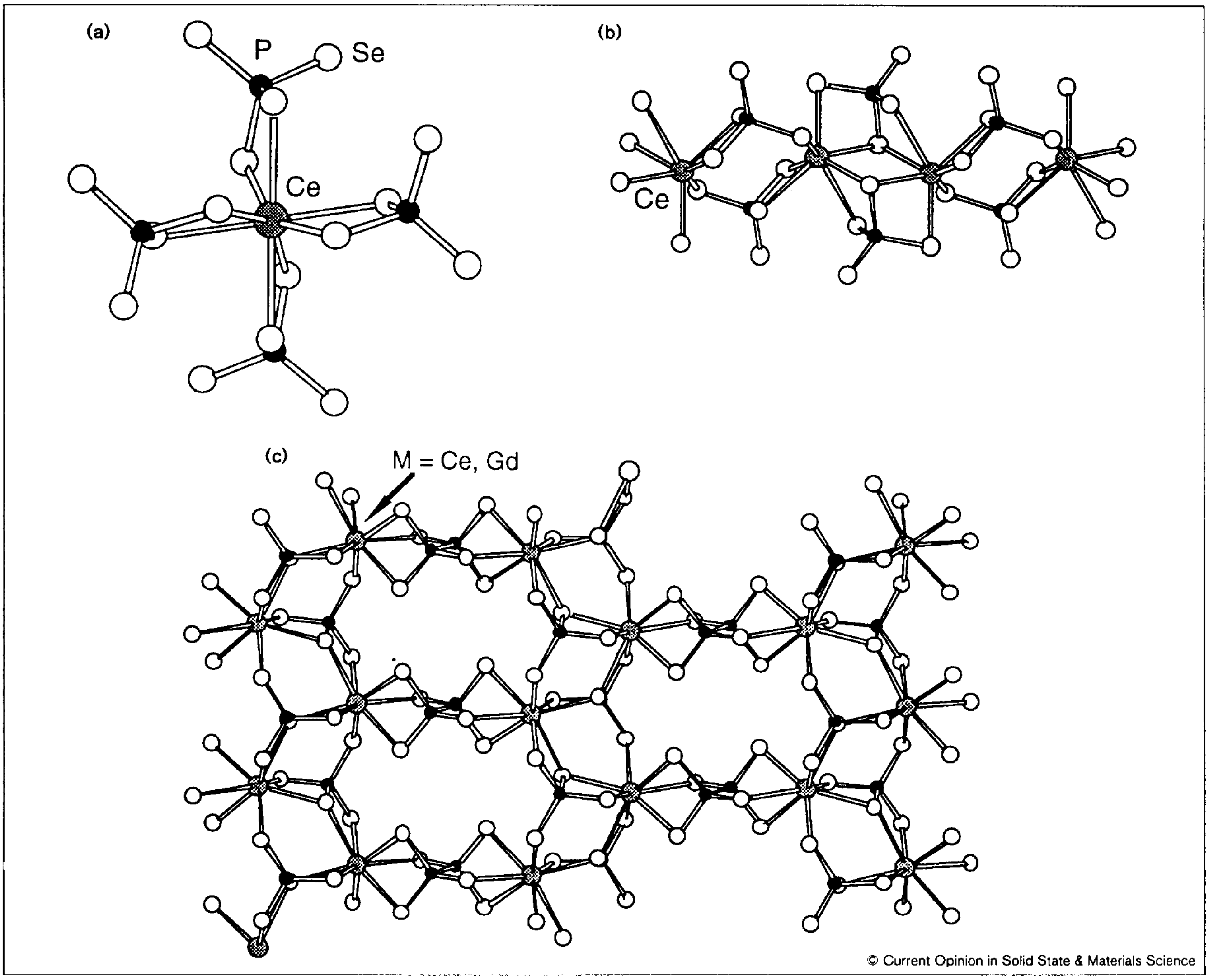
As the size of elements gets larger (towards the left of the periodic table) the structural types produced become more complex and more elaborate as the highly coordinated metals and $[P_xSe_y]^{n-}$ ligands try to achieve low energy arrangements.

The reactivity of Ti and V has already been investigated. The compounds $Rb_4Ti_2(P_2Q_9)_2(P_2Q_7)$ [Q = S,Se] [36•,37], $KTiPSe_5$ [36•] and $K_4V_2(PS_4)_2(P_2S_6)$ [37] have been reported. $Rb_4Ti_2(P_2Se_9)_2(P_2Se_7)$ [36•] has the layered structure shown in Figure 7. The $[Ti_2(P_2Se_9)_2(P_2Se_7)]^{4-}$

layers form a perforated network made of $TiSe_6$ octahedra linked in two dimensions by $[P_2Se_7]^{4-}$ and $[P_2Se_9]^{4-}$ anions. The latter is a rare ligand with a Se-Se-Se chain linking two P atoms. These layers contain very large 44-membered rings, consisting of six Ti atoms, two $[P_2Se_7]^{4-}$, and four $[P_2Se_9]^{4-}$ units (ring dimensions: 26.61 Å, a-axis; 6.57 Å, c-axis). $KTiPSe_5$ [36•] has the one-dimensional structure shown in Figure 4b. The chains consist of centrosymmetric $Ti_2(PSe_4)_2$ dimeric cores which are bridged by two μ_2-Se^{2-} ions. In these cores two $[PSe_4]^{3-}$ ligands bridge two Ti atoms employing three Se atoms each. The fourth Se remains nonbonding. The Ti atoms are in a distorted octahedral environment. The structure of $K_4V_2(PS_4)_2(P_2S_6)$ is somewhat related with centrosymmetric chains made of $[V(PS_4)_2]$ units linked by $[P_2S_6]^{4-}$ ligands (see Fig. 4c) [37].

The chemistry of rare-earth and actinide elements is also very rich. Studies have thus far revealed some very interesting materials, including the family $KLnP_2S_6$ (M = Y, La, Ce, Pr, Gd) [38,39•], $K_4Eu(PSe_4)_2$ [30], $K_2UP_3Se_9$ [40••], $KEu(PSe_4)$ and $Rb_4U_4P_4Se_{26}$ [41]. The latter is a novel three-dimensional, ion-exchange material containing the rare U^{5+} ion. The layers in $KEu(PSe_4)$ have the same structure as those in the $CsPb(PSe_4)$ compound mentioned in this review (see Fig. 3).

Figure 10



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Two Ce^{3+} selenophosphate compounds. **(a)** The discrete molecular anion $[Ce(PSe_4)_4]^{9-}$. **(b)** A fragment from the one-dimensional chain in $Rb_3Ce(PSe_4)_2$. **(c)** A layer in $Rb_4Ce_2(PSe_4)_2(P_2Se_6)$ which is assembled with two different kinds of selenophosphate anions.

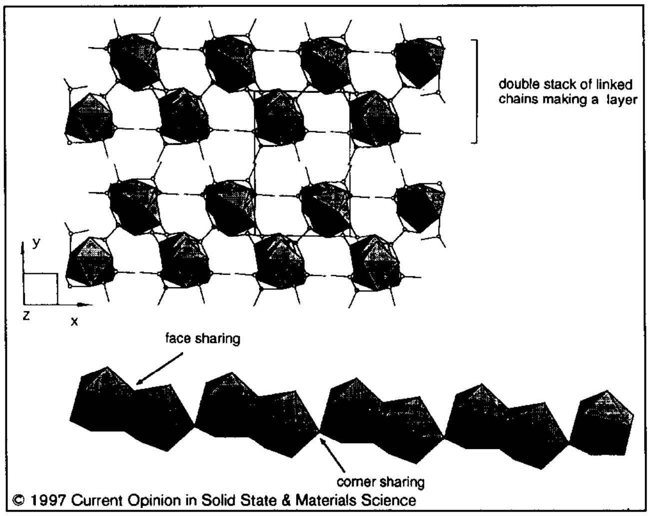
The novel $KLaP_2Se_6$ structure forms when La reacts with a polyselenophosphate flux at 700°C [38]. Its two-dimensional structure resembles that of $KBiP_2Se_6$ with double layers of La, but it has additional intricacies arising from the larger coordination sphere of La, which is a distorted, bicapped pentagonal bipyramid of nine Se atoms (see Fig. 8). The $[P_2Se_6]$ unit has a unique coordination mode where it brings together four La atoms and serves as a cap to one of the triangular faces of the bicapped pentagonal bipyramidal $LaSe_9$ units. The structure of $KLaP_2Se_6$ can be derived from the structure of the layered $M_2P_2Se_6$ by pairwise condensation of such layers by allowing the M to expand its coordination sphere from six to nine and deleting one half of the metal atoms. The Ce, Pr analogs can be prepared similarly and are isostructural.

The compound KYP_2Se_6 on the other hand, prepared similarly to the La^{3+} compound at 750°C, has a different two-dimensional structure with single layers of Y which is found here in eight-coordination, see Figure 9 [39•]. The layers in this structure can be related to the one-dimensional structure of $[FeP_2S_6]^{2-}$ [42], because they can be derived from it by the association of the chains into layers via coordination expansion of the metal from six to eight. The $KGdP_2Se_6$ is isostructural.

The effect of temperature on the equilibrium distribution of $[P_xSe_y]^{n-}$ species in the flux is beautifully demonstrated in Ce and Gd systems. When the temperature is lowered from 750°C to 490°C the compounds $Rb_9Ce(PSe_4)_4$ and $Rb_3Ce(PSe_4)_2$ contain $[PSe_4]^{3-}$, suggesting that the tetrahedral $[PSe_4]^{3-}$ unit is unstable at elevated temperatures. $Rb_4Ce_2(PSe_4)_2(P_2Se_6)$ and isostructural $Cs_4Gd_2(PSe_4)_2(P_2Se_6)$ can be isolated from lower synthesis temperatures and contain both $[PSe_4]^{3-}$ and $[P_2Se_6]^{4-}$ anions in the lattice. $Rb_9Ce(PSe_4)_4$ contains a discrete molecular complex, $Rb_3Ce(PSe_4)_2$ is one-dimensional while $Rb_4Ce_2(PSe_4)_2(P_2Se_6)$ is two-dimensional; see Figure 10. The effect of temperature on the outcome of these reactions is currently under active investigation in our laboratory.

$K_2UP_3Se_9$ is formally a U^{4+} compound and has a complicated layered structure [40••]. The layers run perpendicular to the crystallographic b-axis (see Fig 11). The compound contains only $[P_2Se_6]^{4-}$ anions and so a more descriptive formula, which provides the formal oxidation states, would be $K^+{}_4U^{4+}{}_2[P_2Se_6]^{4-}{}_3$. The U atoms display tricapped trigonal prism (TTP) geometry, bound to four $[P_2Se_6]^{4-}$ ligands, which themselves engage in three different binding modes. This is the first time this coordination geometry has been observed for uranium chalcogenides. The closest relevant compound to the one reported here is UP_2S_6 in which the U atoms are eight-coordinate with a dodecahedral geometry [43]. Two such TTPs share a triangular face to form dimers of U_2Se_{14} with a U-U distance of 4.601(2) Å (see Fig. 11). These U dimers then join by sharing a Se atom to form chains of $(U_2Se_{14})_x$. The complicated intralayer structure is formed by the side-by-side arrangement of the $(U_2Se_{14})_x$ chains which propagate along the [001] direction to form what are essentially pleated layers. The chains are then cross-linked in two dimensions by $[P_2Se_6]^{4-}$ ligands.

Figure 11



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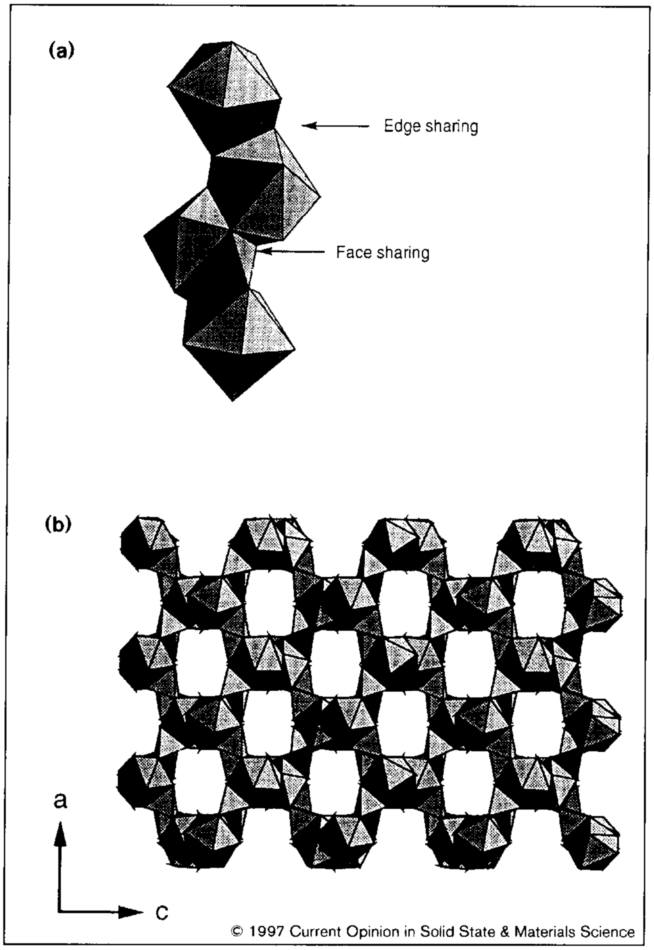
The formation of (U_2Se_{14}) dimers which join by sharing a Se atom to form chains of $(U_2Se_{a14})_x$. These chains form double pleated layers via side-by-side arrangement and linking with $[P_2Se_6]^{4-}$ ligands.

An even more unusual result has been found in $Rb_4U_4P_4Se_{26}$, a compound with a three-dimensional framework and pentavalent U centers. It contains $[PSe_4]^{3-}$, Se^{2-} and $(Se_2)^{2-}$ anions and so it could be described as $Rb^{4+}U_4{}^{5+}(PSe_4)_4{}^{3-}(Se)_2{}^{2-}(Se_2)_4{}^{2-}$ [41]. The most unusual feature of the structure is the presence of pentavalent U. The two crystallographically independent U atoms have a tricapped trigonal prism (TTP) geometry as in $K_2UP_3Se_9$.

The coordination polyhedron around U is a triangular decatetrahedron. Two of the latter share a triangular face to form 'dimers' of U_2Se_{14} with a U–U distance of 4.071(2) Å. These dimers then join by sharing edges, forming chains of $(U_2Se_{14})_x$ which propagate along the [100] direction. The intricate three dimensional structure is formed by the side-by-side arrangement of these chains cross-linked at four sides by $[PSe_4]^{3-}$ ligands. The $Se_2{}^{2-}$ ligands play an important role in the structure by bridging the dimers to form chains. It is interesting that the compound shares many structural features with the layered $K_2UP_3Se_9$. Both structures are formed by interstitched $(U_2Se_{14})_x$ chains despite the fact that they contain different selenophosphates ($[P_2Se_6]^{4-}$ versus $[PSe_4]^{3-}$), and different oxidation states of U (U^{4+} versus U^{5+}) [40••,41].

Figure 12



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A polyhedral representation of the three-dimensional structure of $Rb_4U_4P_4Se_26$. The Rb atoms are omitted for clarity.

The structure possesses Rb^+ filled interconnected channels which run in both the [100] and [010] directions. The largest size channels have a rectangular cross-section with dimensions 6.95 Å × 5.34 Å and run in the [010] direction, see Figure 12. A smaller set of tunnels runs along the [100] direction. The Rb^+ size is relatively small for the cavity and exchanges readily with other smaller cations such as Li^+. The extent of ion exchange exceeds 90%.

Conclusions and outlook

Only the most recent developments in this area have been touched here. Given the success of the flux method approach discussed here a number of important issues acquire increased relevance and urgency. First, what is the distribution of $[P_xQ_y]^{n-}$ anions in the flux as a function of temperature and composition? Second, is this distribution reflected in the structure of the final product? Third, what are important metal intermediates which lead to the solid state products? And fourth, what is the relative importance of flux composition vis-a-vis the nature of the metal in determining which $[P_xQ_y]^{n-}$ anions will be incorporated in the product? To shed some light on the nature of these fluxes, detailed studies with a wide variety of experimental techniques and over a wide range of temperatures are needed. The most attractive technique seems to be NMR spectroscopy focusing on the P and Se nuclei in the flux, but other bulk probing techniques such as *in situ* Raman spectroscopy and diffraction using X-ray or synchrontron radiation hold great promise.

The development of molten $A_2P_xQ_z$ fluxes as a reaction medium presents the greatest opportunity to date to expand the relatively small class of thiophosphate and selenophosphate compounds. The need to push for even more novel systems remains and so the complexity of the reactions will steadily increase from the bases outlined in this article. I anticipate that research activity in this area of solid state chemistry will grow substantially. Undoubtedly, the flux route to thio- and selenophosphate compounds is general with almost no exceptions with regard to any metal in the periodic table.

Acknowledgement

Financial support for the author's work on chalcophosphates comes from the National Science Foundation. I am a Camille and Henry Dreyfus Teacher-Scholar 1993–1998.

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