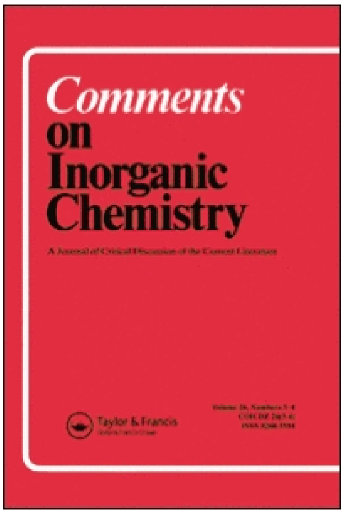

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# Soluble Polychalcogenides of the Late Transition and Main Group Elements

Mercouri G. Kanatzidis[a]
[a] Department of Chemistry and the Center for Fundamental Materials Research, Michigan State University, East Lansing, Michigan

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# Soluble Polychalcogenides of the Late Transition and Main Group Elements

MERCOURI G. KANATZIDIS
*Department of Chemistry*
*and the Center for Fundamental Materials Research,*
*Michigan State University,*
*East Lansing, Michigan 48824*

A review of the coordination chemistry of heavier polychalcogenide ligands with late transition and main group metals with a focus on recent developments in the author's laboratory is given. The complexes available thus far are mainly homoleptic anionic compounds of the general formula $[M(Q_x)_m]^{n-}$ ($x \geq 2$, Q = Se,Te), (M = late transition or main group metal) stabilized by large organic counterions. In most cases it was found that the structural types accessible by the heavier polychalcogenides are different from those of corresponding polysulfides. The complexity of polychalcogenide solutions in polar solvents currently makes *a priori* prediction of new complexes difficult. Results from thermolysis studies from these compounds are briefly presented.

**Key Words:** *polychalcogenide ligands, polyselenide ligands, polytelluride ligands, main group elements, metal-chalcogen compounds*

## 1. INTRODUCTION

Metal–chalcogen compounds can be divided into two groups: (i) those containing formally $Q^{2-}$ ions and (ii) those containing $Q_x^{2-}$ ions in which there are Q–Q bonds. The latter are referred

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to as polychalcogenides. The catenating ability of the chalcogen atoms, particularly S, Se and Te, is responsible for an exciting, diverse and useful class of inorganic molecules.[1,2] The last two decades witnessed the development of considerable synthetic chemistry of soluble transition metal polysulfide complexes. The interest in this area originated mainly from (a) the possible relevance of such ligands to the chemical nature of the surfaces of heterogeneous hydroprocessing catalysts,[3,4] (b) the importance of some M/S complexes in modeling of bioinorganic systems[5] and (c) the need to explore the coordination chemistry of the $S_x^{2-}$ ligands. The first two factors which motivated the exploration of polysulfide chemistry do not exist in the heavier chalcogens Se and Te, and thus similar developments did not keep apace. Perhaps a discouraging factor may have been the notion that the heavier chalcogens would exhibit analogous, and thus not new, chemistry to that of polysulfides. Although this can be true, more often it has been found that polyselenide and polytelluride chemistry is distinct and thus very interesting on its own. For example, the structures of the complexes $[Hg_2Te_5]^{2-}$[6], $[Hg_4Te_{12}]^{4-}$[6], $[V_2Se_{13}]^{2-}$[7], $[W_2Se_9]^{2-}$[8], $[Ni(Se_2)(WSe_4)]^{2-}$[9], $[Mo_4Te_{16}(en)_4]^{2-}$[10], $[NbTe_{10}]^{3-}$, $[Au_2(Te_2)_2]^{2-}$[12], $[KAu_9Te_7]^{4-}$[13], $[K_2Au_4Te_4(solv)_4]^{2-}$[13], $[Fe_2(Te_2)(Te)(CO)_6]^{2-}$[14], $[Cr(CO)_4(Te_4)]^{2-}$[15], and $[Cr_3(Q_4)_6]^{3-}$[16] ($Q$ = Se, Te) are not only intriguing but could not have been predicted, and do not find analogs in polysulfide chemistry. Our group has prepared a number of complexes, most of which do not bear sulfur analogs either (*vide infra*). The reason for this deviation probably lies in the significant size differences between sulfur and the heavier chalcogens, the difference in equilibria of the various $Q_x^{2-}$ species in polar solvents (*vide infra*), and the difference in redox potentials of the $Q/Q_x^{2-}$ couple.

In soluble polychalcogenide chemistry it is nearly impossible to predict the structures of the proposed complexes or elucidate their structures with spectroscopic techniques. Therefore, all compounds must be structurally characterized by X-ray crystallography. Most complexes, however, can be routinely examined and characterized by $^{77}Se$ and $^{125}Te$ NMR spectroscopy which is a useful and unique characterization tool (not applicable to polysulfides) for the investigation of the solution behavior of the heavier polychalcogenides.[2]

Work in polychalcogenide chemistry is of fundamental interest and will lead to a better understanding of the chemistry of not only heavier chalcogens, but also of polysulfides themselves. For instance, it is possible that several stable structural arrangements in heavier polychalcogenide chemistry may serve as models for reactive, metastable and difficult to isolate polysulfide species important in catalysis. Furthermore, once new soluble polyselenide and polytelluride complexes are available, they may have practical uses in materials chemistry as suitable low temperature precursor compounds to either new metastable or "old" but useful electronic solids.[17,18] Due to our interest in the latter prospect as well, and since a variety of useful semiconductors involve late transition and main group metals, we focused our efforts on the chemistry of such metals. In this article I will provide a midcourse report on progress made in this area, primarily in our laboratory, since the state of the art in this expanding field has already been reviewed.[2]

## 2. THE NATURE OF THE POLYCHALCOGENIDE SOLUTIONS

It is generally accepted that the nature of polychalcogenide solutions in polar solvents is complex. In $NH_3$ and DMF solutions of $S_x^{2-}$ it is fairly well established that dissociation to $S_x^{-}\cdot$ radicals occurs, giving rise to blue and green solutions, depending on concentration and the value of $x$.[21] Fast equilibria dominate such solutions.[20] A UV/vis absorption band at ca. 610–650 nm in these solvents has been attributed to $S_x^{-}\cdot$ radical anions. Water and alcohols form yellow solutions which do not show low energy absorptions indicating the absence of $S_x^{-}\cdot$ radical anions. The solution behavior of $Se_x^{2-}$ ($x > 2$) species is not very well studied but appears analogous to that of polysulfides. Solutions of $Se_x^{2-}\cdot$ in $NH_3$ and DMF are dark green with two absorptions in the visible spectrum at ca. 610 and 440 nm.[22] Water and alcohol solutions are dark red with a UV/vis absorption at ~460 nm as shown in Fig. 1. The presence of the ~610 nm band is probably due to paramagnetic $Se_x^{-}\cdot$ radical anions. Consistent with this interpretation is the absence of any $^{77}Se$ NMR signals in DMF solutions. In water, however, a $^{77}Se$ NMR signal is observed (e.g., from either $Na_2Se_4$

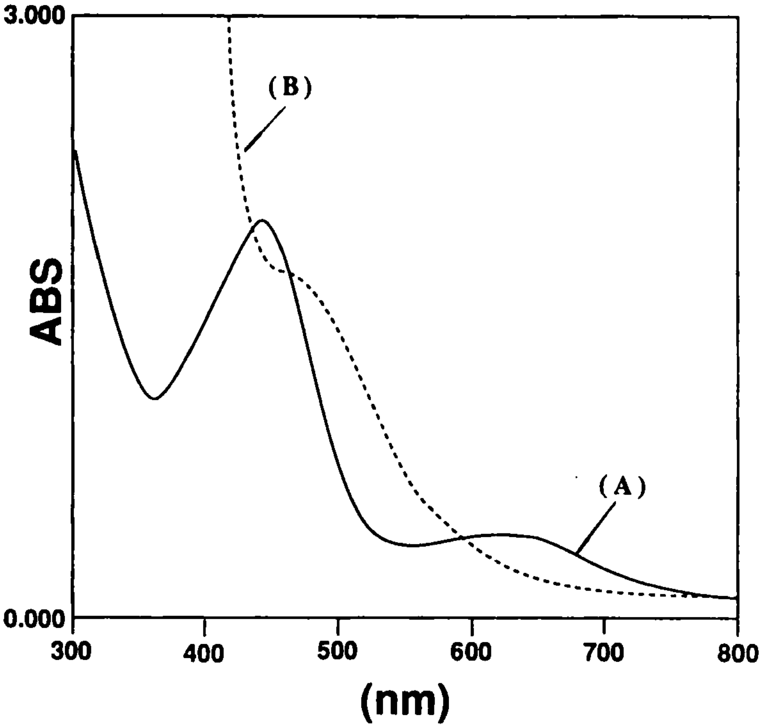
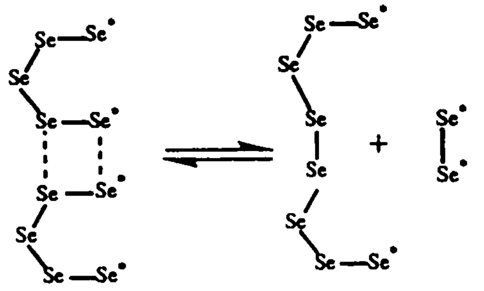


FIGURE 1 UV/vis spectra of $Na_2Se_5$ in (A) DMF and (B) aqueous solution.

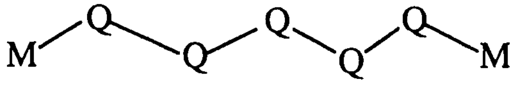
or $Na_2Se_5$).[22] This coupled with the absence of a 610 nm band suggests that $Se_x^{-}\cdot$ radical anions do not dominate aqueous polyselenide solutions. Fast equilibria, however, do occur as evidenced by the single NMR peak at 420 ppm, indicating that all Se atoms are equivalent in this time scale. Some possible but not unique equilibria that explain the equivalence of terminal and internal atoms in the chain are shown in Eq. (1) and Eq. (2):

(1)



The corresponding $Te_x^{2-}$ solutions also show (see Fig. 2) solvent dependent UV/vis spectral variations, similar to $S_x^{2-}$ and $Se_x^{2-}$ solutions. As is the case for the polyselenides, literature data on such solutions are scant.[23] In DMF two peaks are observed at 531 nm and 742 nm while in water only one peak at 493 nm is observed. An analogous situation involving $Te_x^{-}\cdot$ radical anions may be envisioned for polytelluride solutions as well.

When a metal ion is added to polychalcogenide solutions the aforementioned equilibria are affected dramatically due to coordination. The circumstantial evidence available thus far suggests that the preference of a metal ion for a particular $Q_x^{2-}$ ligand drives all existing equilibria towards formation of that ligand. For $M^{n+}$ ions (with $n \geq 2$) these equilibria are completely suppressed upon coordination, as stable $MQ_x$ metallacycle rings are formed. This can be seen clearly from $^{77}$Se and $^{125}$Te NMR data of such polychalcogenide complexes. The stability of the $MQ_x$ rings depends not only on the metal ionic charge but also on ring size and geometry and thus, since Q–Q bonds vary significantly from chalcogen to chalcogen, on the nature of the $Q_x^{2-}$ ligands. This accounts in part for the differences in chemistry observed between the various polychalcogenides and the fact that control over the final products often cannot be exerted. If monovalent ions are involved (e.g., Ag, Cu), or the $Q_x^{2-}$ ligands bridge two different metal centers as shown below,



. (2)

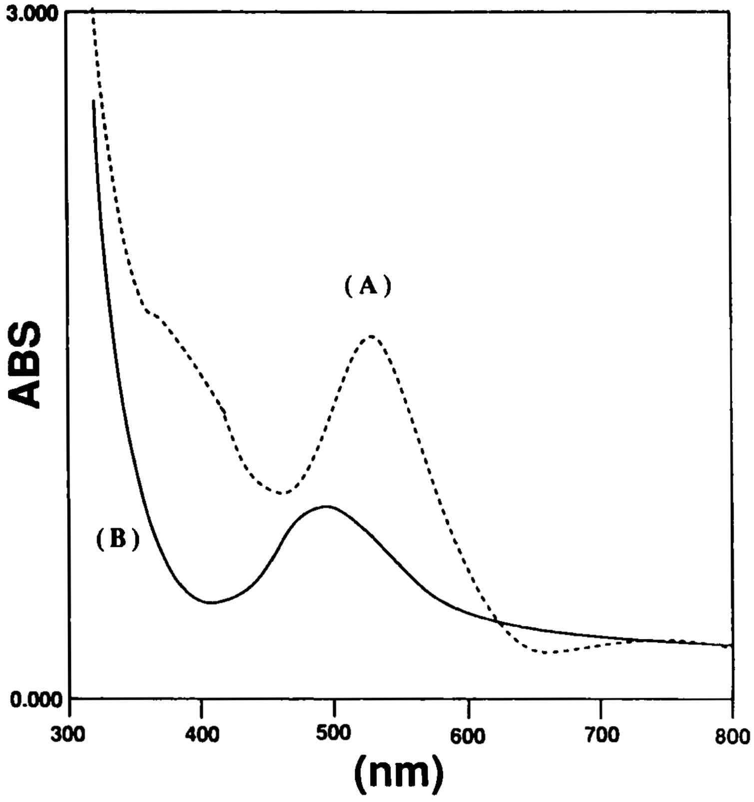


FIGURE 2 UV/vis spectra of $K_2Te_4$ in (A) DMF and (B) aqueous solution.

then dissociation may occur in polar solvents such as DMF, to resume the complex equilibria.

## 3. SYNTHESIS OF $[M(Q_x)_y]^{m-}$ ANIONS

The synthesis of soluble $[M(Q_x)_y]^{m-}$ species is usually carried out via metathetical reactions of metal salts with alkali metal polychalcogenides in the general reaction shown below:

$$MCl_n + yNa_2Q_x \longrightarrow [M(Q_x)_y]^{m-} + NaCl \qquad (3)$$

These anionic complexes are stabilized, in the solid state, with large organic cations such as $R_4N^+$ and $R_4P^+$. Less common methods such as the reaction of low valent metal carbonyls with a polychalcogenide source have also been used.[14,15] In general polytellurides are more difficult to crystallize than polyselenides and they are characterized by lower solubilities and a propensity to deposit Te films on the reactor walls.

### 3.1. Group 9 and 10 Chemistry

The absence of homoleptic anionic $Ru/Q_x$ ($Q = S, Se, Te$) complexes is probably due to their instability with respect to internal redox processes. In this process electron transfer between $Ru^{n+}$ and $Q_x^{2-}$ can result in mixtures of species from which pure materials are difficult to isolate. The choice of starting material and solvent in this system is extremely important if crystallization of compounds is to be successful. The Ru/Q system has proven rather recalcitrant in this respect, providing only ill defined powders. $Ru_3(CO)_{12}$ has given the most promising results thus far. $Ru_3(CO)_{12}$ reacts with $Na_2Se_5$ in acetone in the presence of $Et_4N^+$ to yield red orange $(Et_4N)_{1.5}Na_{0.50}[Ru(CO)_2(Se_4)_2]$ (**I**) in excellent yield.[24] The $Na^+$ ion is important in the crystallization of (I). The use of $K_2Se_5$ as a reagent in the synthesis of this complex results only in a poorly crystalline powder which did not contain $K^+$.

The crystal structure of $(Et_4N)_{1.5}Na_{0.50}[Ru(CO)_2(Se_4)_2]$ consists of non-interacting $Et_4N^+$ cations and interacting $Na^+$ and $[Ru(CO)_2(Se_4)_2]^{2-}$ ions. The $Na^+$ ion is found in a crystallographic center of symmetry and it is coordinated by two centrosymmetrically disposed $[Ru(CO)_2(Se_4)_2]^{2-}$ anions through the Se(2), Se(4) and Se(8) atoms, as shown in Fig. 3. The Se atoms create an excellent octahedral pocket for $Na^+$. The Na–Se distances range from 2.921(1) Å to 3.148(1) Å. The $[Ru(CO)_2(Se_4)_2]^{2-}$ adopts an octahedral geometry with two *cis* CO groups and two chelating $Se_4^{2-}$ ligands, as shown in Fig. 4. The molecule possesses a noncrystallographic two-fold axis which bisects the C(1)–Ru–C(2) and Se(4)–Ru–Se(8) angles. The Ru–C(1) and Ru-C(2) bond distances are 1.858(7) Å and 1.846(7) Å, respectively, with a C(1)–Ru–C(2) angle of 95.0(2)°. The Ru–Se bonds are divided into two sets of short and long bonds. The Ru–Se(1) and Ru–Se(5)

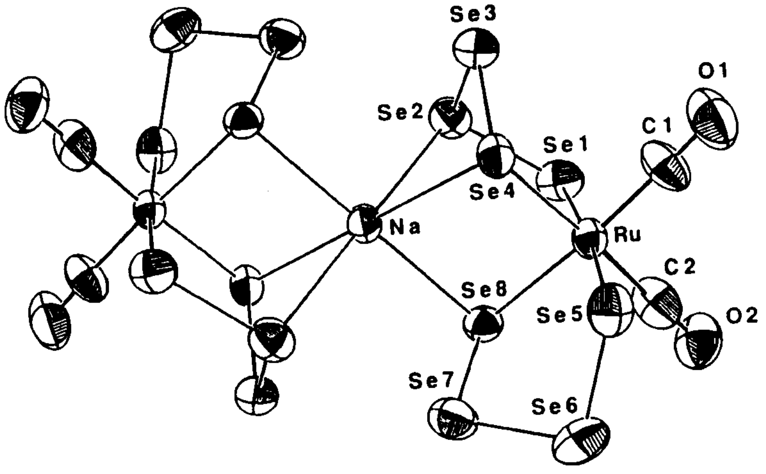


FIGURE 3 Representation of the $[Na\{(Ru(CO)_2(Se_4)_2)\}_2]^{3-}$ portion of the structure showing the coordination environment of the $Na^+$ by two $[Ru(CO)_2(Se_4)_2]^{2-}$ ions.

bonds are *trans* to each other at 2.517(1) Å and 2.513(1) Å, and are shorter than the corresponding *cis* Ru–Se(4) and Ru–Se(8) bonds at 2.566(1) Å and 2.588(1) Å, respectively. The lengthening of the Ru–Se bonds which are disposed *trans* to the carbonyl groups reflects the effective competition between the CO and the

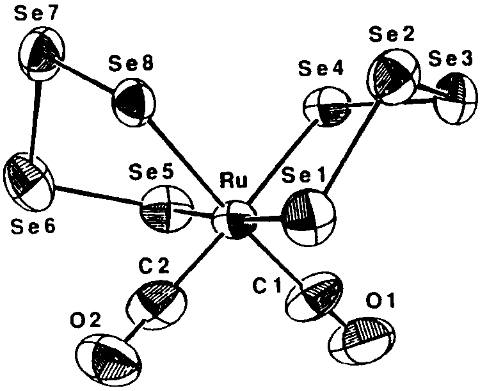


FIGURE 4 The structure of $[Ru(CO)_2(Se_4)_2]^{2-}$.

$Se_4^{2-}$ ligands for both σ (*xy* orbital) and to a lesser extend π (*xz* and *yz* orbitals) bonding to the metal center. The $Se_4^{2-}$ ligands adopt both half-boat (Se(1)/Se(2)/Se(3)/Se(4)) and envelop (Se(5)/Se(6)/Se(7)/Se(8)) conformations. In both $Se_4^{2-}$ ligands there is a bond alternation of long $Se_{(external)}-Se_{(internal)}$ average 2.352(11) Å and short $Se_{(internal)}-Se_{(internal)}$ average of 2.319(4) Å. This structural feature has been seen in $[(Me_2PCH_2CH_2PMe_2)Ir(Se_4)]Cl$[25] and metal polysulfides containing $MQ_4$ units in which the metal ions have partially filled shells (e.g., Mo, Ni, W).[26] This bond alternation has been attributed to $p_\pi$-$d_\pi$ M–Q bonding. SCF Xα-SW calculations on the $IrSe_4$ complex suggest that the internal Se–Se bond has a bond order of ca. 1.15 and is stronger than the external Se–Se bonds.

In solution the diamagnetic $[Ru(CO)_2(Se_4)_2]^{2-}$ maintains its integrity but it is no longer associated with the $Na^+$ ion. The $^{13}C$ NMR spectrum of $[Ru(CO)_2(Se_4)_2]^{2-}$ in DMSO-$d_6$ shows one resonance at 199 ppm assigned to the carbonyl carbon atom as expected for a species of $C_2$ symmetry. In the IR spectrum of (I) the symmetric and antisymmetric CO stretching vibrations occur at 1992 and 1927 $cm^{-1}$, respectively. Consistent with the $C_2$ point-group symmetry, four resonances are observed in the $^{77}Se$ NMR spectrum, respectively, at 717, 650, 630, 395 ppm (vs $Me_2Se$). The selenium atoms within the equivalent $Se_4^{2-}$ ligands are in chemically different environments, regarding their positions relative to the CO ligands.

We also have been able to prepare the analogous $[Ru(CO)_2(Te_4)_2]^{2-}$ and $[Fe(CO)_2(Se_4)_2]^{2-}$ complexes, but no complete structural characterization is as yet available.

The complex $(Ph_4P)_2Pd(Te_4)_2$ (**II**) was reported in two different crystalline modifications independently by Haushalter *et al.*[27] (triclinic, P-1, α-form) and ourselves (orthorhombic P bca, β-form), respectively. In both cases the complex was prepared from $PdCl_2$ and $K_2Te_4$ in DMF. However, the α-form was precipitated from ethylenediamine, while the β-form was obtained from ether. The structure of the $[Pd(Te_4)_2]^{2-}$ anion as determined in the orthorhomibic modification is shown in Fig. 5. It features a nearly square planar Pd center chelated by two $Te_4^{2-}$ ligands. This structure is similar to those of $[Ni(Se_4)_2]^{2-}$ [28] and $[Ni(S_4)_2]^{2-}$.[26] The $PdTe_4$

five-membered rings are puckered, forming an envelop conformation. The average Pd–Te distance is 2.587(2) Å in excellent agreement with that of the triclinic modification at 2.59(2) Å. As in (I) and α-$(Ph_4P)_2Pd(Te_4)_2$, a significant distance variation exists in the Te–Te bonds of the two $Te_4^{2-}$ ligands. The two external Te–Te bonds in the $Te_4^{2-}$ ligands are longer (average 2.762(5) Å) than the corresponding internal Te–Te bonds (average 2.700(5) Å). Other polytellurides showing a similar bond length alternation are $[MO(Te_4)_2]^{2-}$ (M = Mo, W).[29] Individual distances for β-(II) are shown in Fig. 5.

We have also prepared large crystals of $[(Ph_3P)_2N]_2[Pd(Se_4)_2]$ **(III)**, but to date we have not obtained an accurate X-ray structure determination due to disorder.[30] The $[Pd(Se_4)_2]^{2-}$ anion is situated on a 222 site in the crystal and features a square planar Pd center similar to (II). The $^{77}$Se NMR spectrum of $[Pd(Se_4)_2]^{2-}$ in DMF shows two resonances at 905 ppm and 780 ppm (vs $Me_2Se$) as expected.

Curiously $[Pt(Se_4)_2]^{2-}$ could not be made.[31] Attempts to prepare $[Pt(Se_4)_2]^{2-}$ were unsuccessful and yielded $[Pt(Se_4)_3]^{2-}$, a $Pt^{4+}$ complex. Such redox chemistry is known in the $Pt^{2+/4+}/S_x^{2-}$ system[32] and in other M/polyselenide systems as well *(vide infra)*.

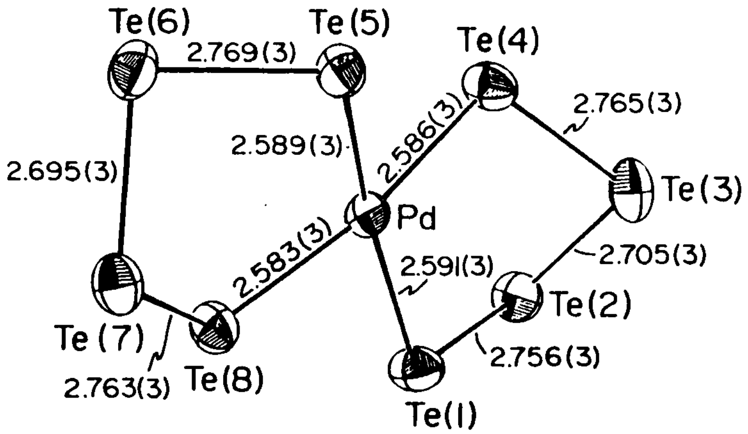


FIGURE 5 The structure of $[Pd(Te_4)_2]^{2-}$.

### 3.2. Group 11 Chemistry

Polyselenide chemistry with the coinage metals has proven to be the most versatile by far. In the $Ag^+/Se_x^{2-}$ system, we have been able to grow single crystals of polymeric low-dimensional as well as molecular cluster compounds stabilized by various organic counterions. These are $\{(Ph_4P)[Ag(Se_4)]\}_n$ **(IV)**[33] and $\{(Me_4N)[Ag(Se_5)]\}_n$ **(V)**[34], $[(Et_4N)Ag(Se_4)]_4$, **(VI)**[34] and $[(Pr_4N)_2[Ag_4(Se_4)_3]$ **(VII)**.[34] The first three belong to the general family $[M(Q_x)]_n^{n-}$. To date (IV), (VI) and (VII) do not enjoy corresponding sulfur analogs.

These compounds can be obtained upon reaction of $AgNO_3$ and $R_4NCl$ (R = Et, Me) (or $Ph_4PCl$) with $Na_2Se_5$ in DMF according to Eq. (4):

$$AgNO_3 + Na_2Se_5 + R_4NCl \longrightarrow [(R_4N)Ag(Se_x)]_n + NaCl + NaNO_3 \; (x = 4, n = 4; x = 5, n = \infty) \qquad (4)$$

The structures of (IV) and (V) are one-dimensional and are shown in Figs. 6 and 7. The structure of (IV) contains polymerized $AgSe_4$ five membered rings. The $Ag^+$ coordination sphere is trigonal planar. The $Ph_4P^+$ cations act as non-interacting spacers between the parallel $[Ag(Se_4)]_n^{n-}$ chains. The chains are somewhat flat, resembling corrugated ribbons as shown in Fig. 6. The bridging mode of the $Se_4^{2-}$ ligand in this compound occurs in the molecular clusters $[Ag(Se_4)]_4^{4-}$ and $[Cu(S_4)]_3^{3-}$.[35] The Ag–Ag distance is very long at 4.52 Å with the corresponding Ag–Se(1)–Ag angle relatively large at 119.7°. This precludes any significant orbital overlap along the chain and thus broad bands do not occur along the chain axis.[36] The large $Ph_4P^+$ ion holds the $[Ag(Se_4)]_n^{n-}$ chains approximately 12.5 Å apart, making any possibility of interchain communication unlikely.

The structure of (V) consists of non-interacting $Me_4N^+$ cations and one-dimensional, non-centrosymmetric $[Ag(Se_5)]_n^{n-}$ macroanions, Fig. 7. The structure of $[Ag(Se_5)]_n^{n-}$ differs from that of $[Ag(Se_4)]_n^{n-}$ in two ways. First, in (V), $Se_5^{2-}$ instead of $Se_4^{2-}$ ligands are present with a distinct mode of ligation compared to those in (IV); second, the Ag atom in (V) assumes tetrahedral

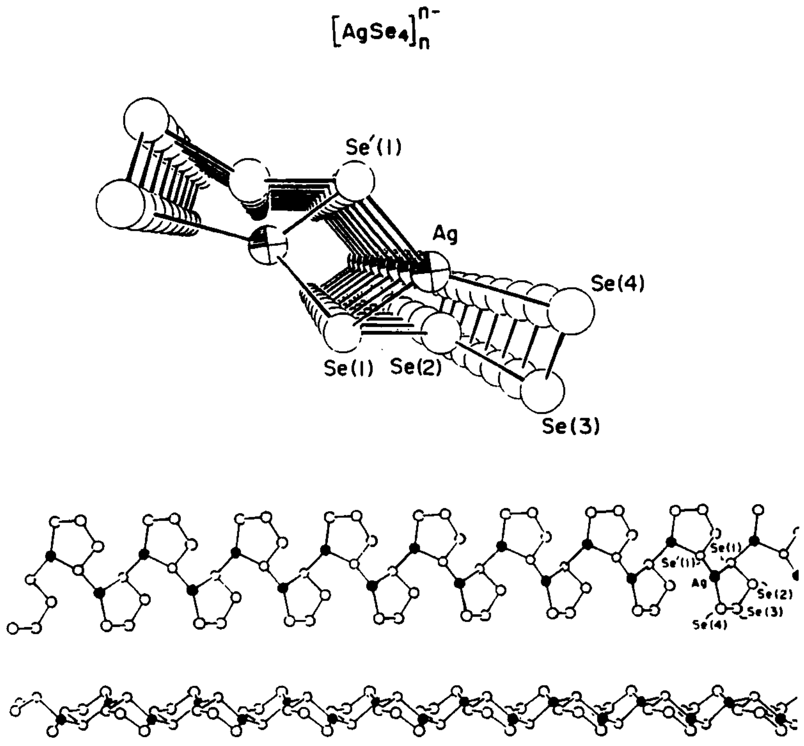


FIGURE 6 Three views of the one-dimensional structure of $[Ag(Se_4)]_n^{n-}$.

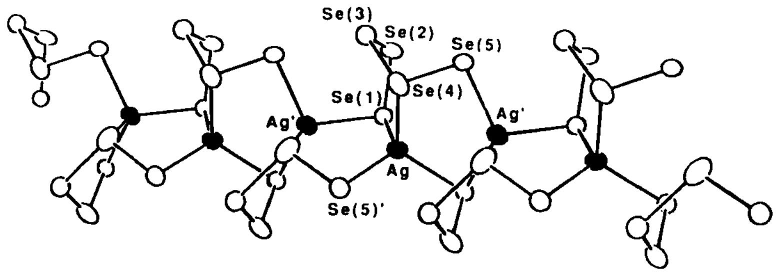
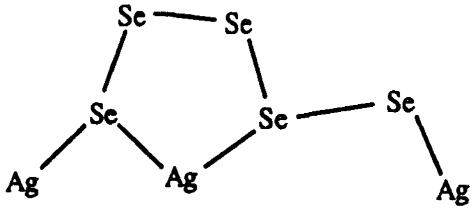


FIGURE 7 The one-dimensional structure of $[Ag(Se_5)]_n^{n-}$ chain.

geometry *vis a vis* trigonal planar in (IV). The $Se_5^{2-}$ ligands bridge three Ag atoms in an unprecedented fashion shown below.



In this bonding mode, the chelation of the $Se_5^{2-}$ ligand occurs through the first and the fourth Se atoms forming a five-membered ring. The fifth terminal Se atom is then bonded to a neighboring Ag atom. The entire $[Ag(Se_5)]_n^{n-}$ chain can be viewed as being made of fused five-membered $AgSe_4$ and $Ag_2Se_3$ rings. The structure of $[Ag(Se_5)]_n^{n-}$ is also different from the recently reported insoluble α- and β-$[Cu(S_4)]_n^{n-}$ [37] and represents a new structural motif for a one-dimensional material. (IV) and (V) dissolve in DMF to yield $Ag^+$, $Se_x^-\cdot$ and $Se_x^{2-}$ species. During the preparation of this manuscript the structure of the $\{(Me_4N)[Ag(S_5)]\}_n$ was reported.[38] With minor differences this material is isostructural to (V).

The structure of $[Ag(Se_4)]_4^{4-}$ is shown in Fig. 8(A). This is a discrete tetramer featuring two different kinds of $Ag^+$ coordination. A planar rhombus of four silver atoms, symmetrically disposed around a crystallographic inversion center, is "glued" together by four $Se_4^{2-}$ ligands. Two of the silver atoms Ag(1) and Ag(1)′ are tetrahedrally coordinated while the other two Ag(2) and Ag(2)′ possess a trigonal planar coordination. The bridging $Se_4^{2-}$ ligands are not equivalent and are divided into two sets. In one set, two $Se_4^{2-}$ ligands are bridging three silver atoms, Ag(1), Ag(1)′ and Ag(2) with atoms Se(1) and Se(4) being $\mu_2$ type. In the other set the two $Se_4^{2-}$ ligands are bridging two silver atoms with only one terminal atom, Se(8) being $\mu_2$ type. The tetrahedral geometry around Ag(1) is highly distorted with one very long "bond," Ag(1)–Se(1) at 2.901(1) Å, a long Ag(1)–Se(1)′ bond at 2.708(1) Å and two normal bonds Ag(1)–Se(8) and Ag(1)–Se(4)

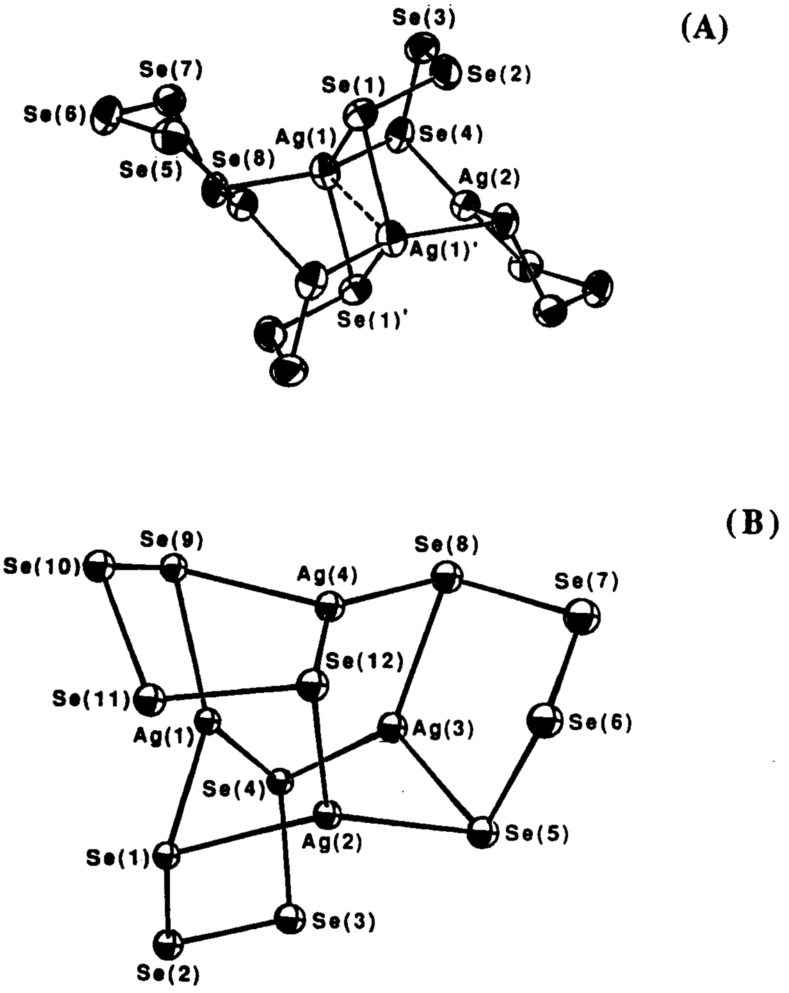
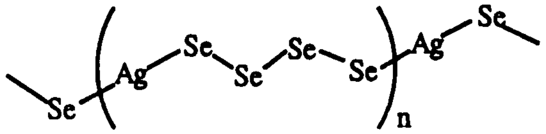


FIGURE 8 (A) The structure of $[Ag(Se_4)]_4^{4-}$; (B) the structure of $[Ag_4(Se_4)_3]^{2-}$.

at 2.641(1) and 2.644(1) Å, respectively. The Ag(1) atom is displaced from the center of the Se(1)/Se(4)/Se(8)/Se(1)′ tetrahedron towards the Se(1)/Se(4)/Se(8) face. The angles around Ag(1) deviate dramatically from the ideal tetrahedral angles. The Ag(1) atom lies 1.868(1) Å above the Se(1)′/Se(4)/Se(8) plane. The geometry around Ag(1) is best described as intermediate between trigonal planar and tetrahedral. The Ag–Ag distances in this cluster are, Ag(1)–Ag(1)′ 2.917(1) Å, Ag(1)–Ag(2) 3.178(1) Å, Ag(1)–Ag(2)′ 3.482(1) Å.

Interestingly when the counterion was changed to $Pr_4N^+$, a different stoichiometry was adopted to yield $[Ag_4(Se_4)_3]^{2-}$. This cluster features a tetrahedral array of silver atoms held together by three $Se_4^{2-}$ ligands forming a highly distorted $Ag_4Se_6$ central adamantane-like core in which all $Ag^+$ ions assume a trigonal planar coordination, Fig. 8(B). The chelating mode of the $Se_4^{2-}$ ligands is similar to that found in the isostructural series $[M_4(Q_4)_x(Q_5)_{3-x}]^{2-}$ (M = Cu, Q = S,[39] Se[40]; M = Ag, Q = Se[40]). Contrary to the structural disorder encountered in the polyselenide ligands in $[Ag_4(Se_4)_x(Se_5)_{3-x}]^{2-}$ (which crystallizes with $Ph_4P^+$), (VII) crystallizes with only $Se_4^{2-}$ ligands and no disorder.

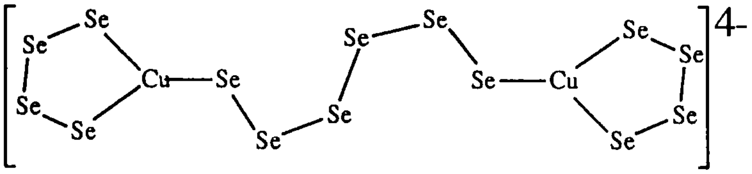
The above findings reveal a trend in the dependence of the $Ag^+$ coordination sphere on the size of the counterion appears to emerge. Large cations such as $Ph_4P^+$ and $Pr_4N^+$ effect lower $Ag^+$ coordination number while smaller ones such as $Me_4N^+$ favor higher coordination numbers. Intermediate size counterions such as $Et_4N^+$ can stabilize intermediate average coordination number of 3.5 (both trigonal planar and tetrahedral). Certainly the metal coordination numbers (CN) found in $\alpha$-, $\beta$-$KCuS_4$[37] (CN = 4), $(Ph_4P)_2(NH_4)[Cu_3(S_4)_3]$[35] (CN = 3), $(Ph_4P)_2[Au_2S_8]$[41] (CN = 2), $(Ph_4P)_4[M_2S_{20}]$ (M = Cu,[42] Ag[43]) (CN = 3), $(Ph_4P)_2[Ag_2(S_6)_2]$[44] (CN = 2), $[(Ph_3P)_2N][Ag(S_9)]\cdot S_8$[42] (CN = 2) and $(Ph_4As)[Au(S_9)]$[45] (CN = 2) are consistent with this contention. These effects probably are not limited to the $Ag^+/Se_x^{2-}$ system. A similar trend is expected with other congeners in this system (i.e., $Cu^+$, $Au^+$ and $S_x^{2-}$, $Te_x^{2-}$) and possibly even in $Tl^+/Q_x^{2-}$ chemistry.[46] It would be interesting to explore the effect of other small and intermediate size counterions on the structure of the $[Ag(Se_x)_m]^{n-}$ anion, such as $NH_4^+$, $Cs^+$, $EtMe_3N^+$, $Et_2Me_2N^+$, $Me_3NH^+$, etc. with the prospect of isolating large oligomeric or extended structures. Conversely, the use of very large cations like $[(Ph_3P)_2N]^+$ could result in 2-coordinate one-dimensional or discrete $Ag^+$ compounds such as:



or $[Ag(Se_x)]^-$. The latter would be analogous to $[Ag(S_9)]^-$.[44] The one-dimensional structure finds precedence in $[Au(Se_5)]_n^{n-}$ which was prepared by molten salt techniques.[47]

In solution, (DMF, acetonitrile) dissociation of these complexes results in loss of their structural identity with formation of free $Se_x^{2-}$ species. The latter may be involved in complex equilibria between themselves and $Ag^+$ ions as evidenced by (i) the UV/vis spectra of these solutions which are very similar to those of pure $Se_x^{2-}$ species and (ii) the total absence of $^{77}Se$ NMR signals.

The chemistry of the $Cu^+/Se_x^{2-}$ system has been examined to a lesser extent. For example, the analogous reaction to prepare a $Cu^+$ compound isostructural to (III) did not yield the desired product. Instead, the $(Ph_4P)_4[Cu_2Se_{14}]$ structure (shown below) was isolated and found to be severely disordered at the anion site. No accurate metric parameters could be extracted. The growth of better quality crystals is currently being pursued.[48] This complex is related to that of $[Ag_2S_{20}]^{4-}$ which also crystallizes with $Ph_4P^+$.[43]



The counterion dependence on the $Cu/Se_x$ products is expected to be significant.

In the gold system we encountered redox phenomena. The familiar interconversion of $Au^+$ and $Au^{3+}$ highlights the chemistry of this metal with $Se_x^{2-}$ ligands. The reaction of $AuCl_3$ with $Na_2Se_5$

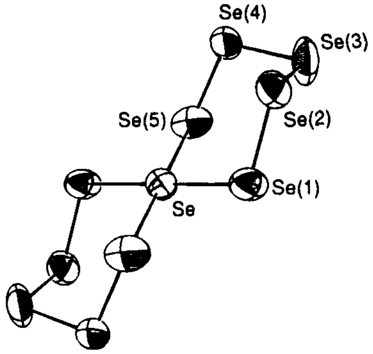


FIGURE 9 The structure of $[Se_{11}]^{2-}$.

results in the isolation of a product with the stoichiometry $(Ph_4P)_2[Se_{11}]$ **(IX)**.[49] The formation of $[Se_{11}]^{2-}$ is a product of oxidation of the pentaselenide ligand by $Au^{3+}$ ions. The structure of (IX) is identical to that reported by Böttcher[50] and is shown in Fig. 9. Given the existence of various $Se_x^{2-}$ species ($x$ = 3,[51] 4,[52] 5,[51] 6,[52]), all of which have helical chain structures, the structure of $[Se_{11}]^{2-}$ is intriguing. (IX) consists of a central Se atom (situated at an inversion center) chelated by two $Se_5^{2-}$ ligands. Formally the central four-coordinate selenium atom can be regarded as a $Se^{2+}$ center. This explains its square-planar geometry and the very long bonds to the ligated pentaselenide ligands. These bonds are Se–Se(1) 2.659(2) Å and Se–Se(5) 2.680(3) Å (see Fig. 9). The square-planar 32e $SeSe_4$ fragment of (IX) is isoelectronic to analogous $[TeTe_4]^{2-}$ fragments found in solid-state alkali metal polytellurides.[53-55] $[Se_{11}]^{2-}$ forms in good yield by the oxidation of $[Se_5]^{2-}$ with other oxidants such as iodine.

Surprisingly the use of AuCN as a $Au^+$ source results in $[Au_2Se_2(Se_4)_2]^{2-}$ **(X)**, a $Au^{3+}$ polyselenide. Although this behavior is not presently understood, it is analogous to the $Tl^+/I_3^-$ system in which $Tl^{3+}$ is susceptible to rapid and complete reduction to $Tl^+$ by $I^-$ solution.[56] Curiously the reaction of $Tl^+$ with excess $I_3^-$ results in the tetrahedral $[TlI_4]^-$. The structure of (X) is shown in Fig. 10 and consists of a rare[57] planar $[Au_2Se_2]^{2+}$ core with a nonbonding Au–Au distance of 3.660(1) Å and Au–Se–Au angle

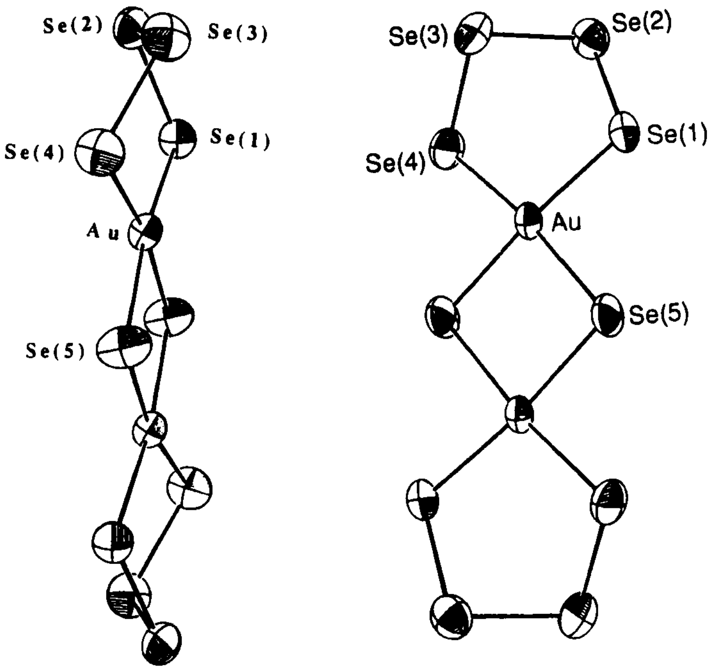
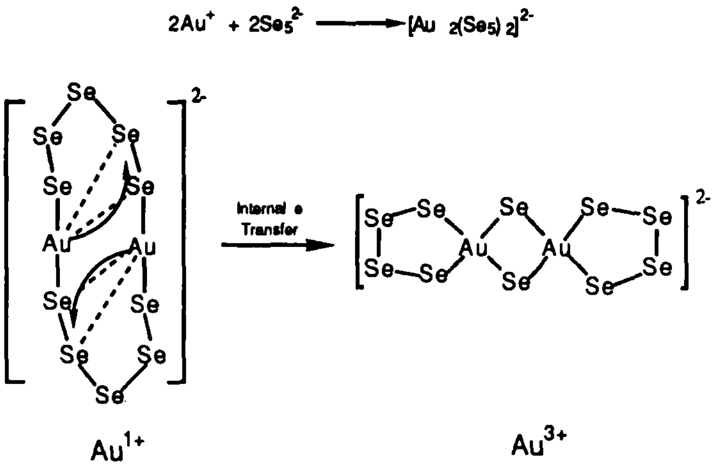


FIGURE 10 The structure of $[Au_2Se_2(Se)_2]^{2-}$.

of 96.70(1)°. The average intracore Au–Se bond length is 2.446(2) Å. The $Au^{3+}$ centers show the expected ($d^8$ configuration) square-planar geometry.[58] Two chelating $Se_4^{2-}$ ligands complete the coordination of the $[Au_2Se_2]^{2+}$ core.

Assuming that the initial step in the reaction of AuCN with $Se_5^{2-}$ is simple coordination, to form a $Au^+$ intermediate (e.g., $[Au_2(Se_5)_2]^{2-}$), the formation of $Au^{3+}$ can be envisioned via internal two electron transfer from the gold atom to the terminal Se–Se bond of the $Se_5^{2-}$ ligand. Such a process would not demand extensive structural rearrangement. This will result in the splitting of the Se–Se bond creating $Se^{2-}$ and $Se_4^{2-}$ ligands. Scheme (A) illustrates a possible pathway for the formation of (X).

The species on the left is a reasonable intermediate because a close structural sulfur analog, $[Au_2(S_4)_2]^{2-}$ exists, with linear $Au^+$



SCHEME A

centers.[41] It is more difficult to reductively cleave the Se–Se bond than it is to cleave the S–S bond, and thus one would expect $[Au_2S_2(S_4)_2]^{2-}$ to be stable. Although $Au^{3+}$ square-planar complexes with all-sulfur coordination are known (e.g., $Au(S_2C_2(CN)_2)_2^{1-}$ [59]), no analogous $Au^{3+}$/polysulfide compounds have been reported thus far. Other structurally characterized binary anionic gold polychalcogenides include $[Au(S_9)]^-$ and $[Au_2(Te_2)_2]^{2-}$,[12] with linear gold geometry.

We found that (IX) and (X) are best prepared when $Se_5^{2-}$ is used. The use of $Se_4^{2-}$ and $CH_3CN$ (instead of DMF) in the synthetic procedure yields $Au^+$/polyselenides. Yellow microcrystals of $[Au(Se_x)]^-$ have been obtained from DMF solutions by fast crystallization. They convert to $[Au_2Se_2(Se_4)_2]^{2-}$ upon standing in solution, and thus isolation of single crystals has not been possible. Soluble $Au^+/Se_x^{2-}$ complexes, however, should be stable in view of the fact that such analogous polysulfide complexes exist.[40,43] Less polar solvents (e.g., $CH_3CN$, $CH_3NO_2$) and the use of shorter $Se_x^{2-}$ ligands should slow down the ensuing redox transformations (due to their more negative oxidation potentials) and allow isolation of $Au^+/Se_x^{2-}$ complexes.

It would be useful to mention the non-soluble polymeric

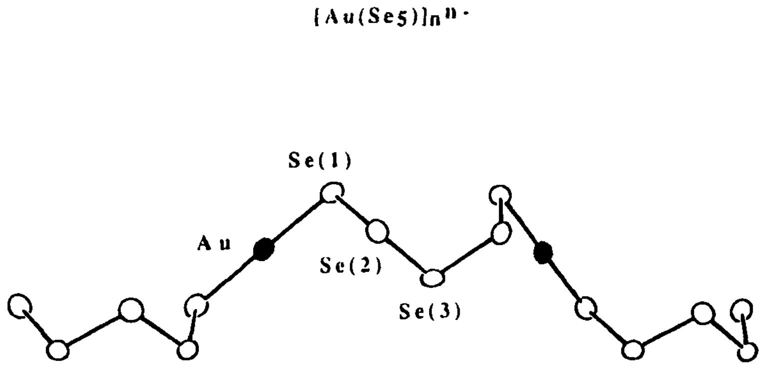


FIGURE 11 The structure of the one-dimensional $[Au(Se_5)]_n^{n-}$ chain.

$[Au(Se_5)]_n^{n-}$.[47] The structure of this material is shown in Fig. 11. One-dimensional chains are formed by bridging linearly coordinated $Au^+$ atoms with $Se_5^{2-}$ ligands. The cation in this compound is $K^+$, and thus the linear $Au^+$ coordination is not consistent with the counterion size/metal coordination trend. However, the exceptional stability of the linear geometry in $Au^+$ systems compared to other possible geometries, and Au–Au interactions in this material may account for this deviation.

### 3.3. Group 12 Chemistry

In this group analogies between the sulfur, selenium and tellurium compounds are the rule rather than the exception. Isostructural compounds with Zn, Cd and Hg and $Q_4^{2-}$ ligands of the general formula $[M(Q_4)_2]^{2-}$ have been prepared.[60] The series $[(15\text{-Crown-}5)Na]_2[M(Se_4)_2]$ (M = Zn, Cd, Hg) feature two chelating $Se_4^{2-}$ ligands providing a tetrahedral coordination geometry around the metal. We have prepared and structurally characterized $(Ph_4P)_2[Hg(Se_4)_2]$ **(XI)**, $[(Ph_3P)_2N]_2[Hg(Te_4)_2]$ **(XII)** and $(Ph_4P)_2[Cd(Te_4)_2]$ **(XIII)**. (XI) and (XIII) are not X-ray isomorphous. The structures of $[Hg(Se_4)_2]^{2-}$ and $[Hg(Te_4)_2]^{2-}$ are similar and are shown in Figs. 12 and 13. The average Hg–Se distance in (XI) is 2.649(10) Å, in good agreement with that reported for $[(15\text{-Crown-}5)Na]_2[Hg(Se_4)_2]$ and for (XI) which has been reported independently.[28] The average Hg–Te distances in (XII) is 2.829(3) Å. This is in the same range found in Haushalter's remarkable

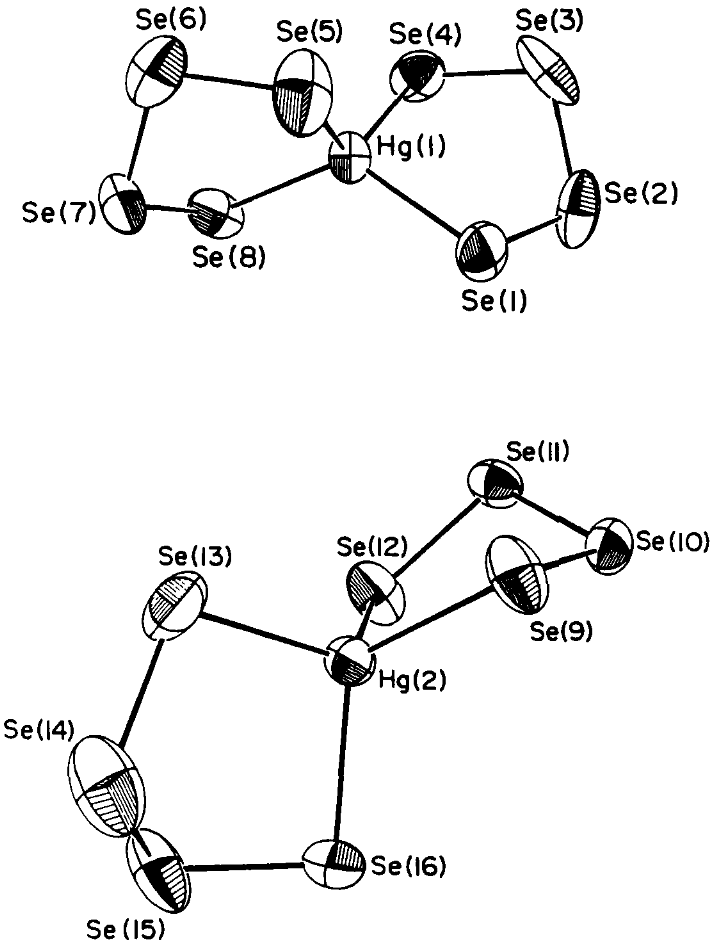


FIGURE 12 The structures of the two crystallographically independent ions of $[Hg(Se_4)_2]^{2-}$

basket-like $[Hg_4Te_{12}]^{4-}$.[6] The intrachelate Q–Hg–Q angles for (XI) and (XII) are 102° and 106°, respectively. The interchelate Q–Hg–Q angles are 120° and 116°, respectively. Alternation in Q–Q bond lengths similar to those observed for $[Pd(Te_4)_2]^{2-}$ is not observed in $[Hg(Q_4)_2]^{2-}$. The various conformations of the $HgQ_4$ five-membered rings interconvert in solution at room temperature. This is common in complexes containing $Se_4^{2-}$ ligands,

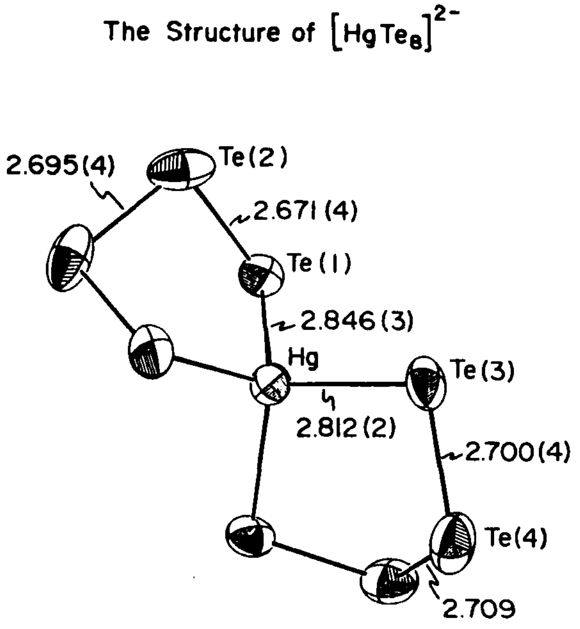


FIGURE 13 The structure of $[Hg(Te_4)_2]^{2-}$.

as in the series $[MQ(Se_4)_2]^{2-}$ (Q = O, S, Se)[61] where the fluxional behavior persists to −60°C as determined by $^{77}Se$ NMR spectroscopy.

A change in the stoichiometry of the reactants, in the Hg system resulted in the dimeric $(Ph_4P)_2[Hg_2(Se_4)_3]$ according to Eq. (5). The structure of $[Hg_2(Se_4)_3]^{2-}$ **(XIV)** is shown in Fig. 14, and can be viewed as a coordination complex of the $[Hg(Se_4)_2]^{2-}$ ligand with the $Hg^{2+}$ center of a $HgSe_4$ moiety.

$$2Hg^{2+} + 3Na_2Se_4 \longrightarrow [Hg_2(Se_4)_3]^{2-} \qquad (5)$$

$$[Hg(Se_4)_2]^{2-} + Hg^{2+} + Se_4^{2-} \longrightarrow [Hg_2(Se_4)_3]^{2-} \qquad (6)$$

The Hg–Hg distance in (XIV) is 3.754(1) Å. Upon coordination of the $[Hg(Se_4)_2]^{2-}$ anion to the second Hg atom a structural distortion occurs in which the Se–Hg–Se angle involving the bridging selenium atoms decreases dramatically by 25° to 93°, while the opposite Se–Hg–Se angle adjusts by increasing from 120° to 130°.

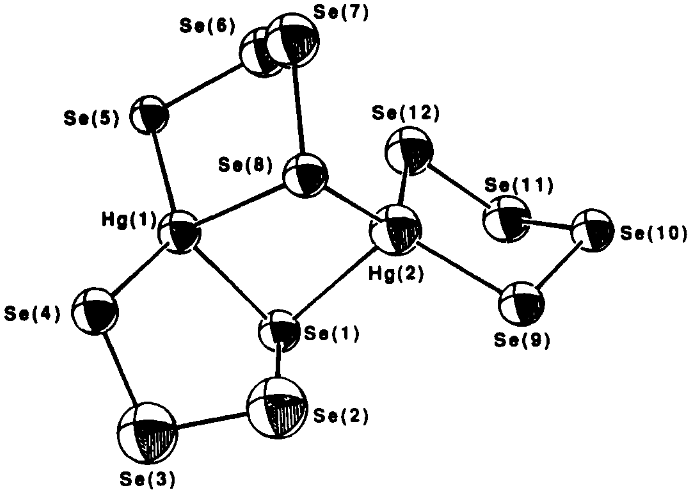
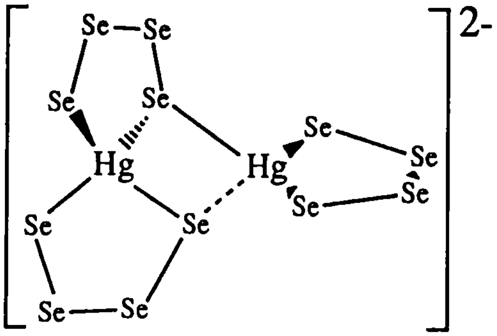


FIGURE 14 The structure of $[Hg_2(Se_4)_3]^{2-}$.

The bridging effected by Se(1) and Se(8) is highly asymmetric with long and short Hg–Se bonds, respectively. For example, in the Hg(1)Se(4)Hg(2)Se(8) core fragment the Hg–Se distances are as follows: Hg(1)–Se(1) 2.670(4) Å, Hg(1)–Se(8) 2.888(4) Å, Hg(2)–Se(1) 2.910(4) Å and Hg(2)–Se(8) 2.571(5) Å. The coordination around the Hg atoms is very distorted and it is best described as trigonal planar with weak ternary interactions. Hg(1) and Hg(2) are only 0.29 Å displaced from the Se(1)Se(4)Se(5) and Se(8)Se(9)Se(12) planes, respectively. Considering the long bonds as weaker interactions, the structure of (XIV) can be schematically represented as follows:



with the dotted lines implying weak bonds.

The $^{77}$Se NMR spectra of (XI) and (XIV) in DMF are identical, showing two peaks at 604 and 86 ppm. This suggests that $[Hg_2(Se_4)_3]^{2-}$ dissociates into $[Hg(Se_4)_2]^{2-}$ and other species.

Equation (6) implies that heterobimetallic complexes should be possible by using different metals. If both metals prefer tetrahedral geometry, scrambling among the different metal sites may occur. However, if metals with different coordination preferences are used, e.g., square-planar geometry (Ni, Pd, Pt), ordered complexes could be obtained. To date no heterometallic complexes exist in which both metals are coordinated to polychalcogenide ligands.[62]

## 3.4. Group 13 Chemistry

Prior to our work there were no reports of complexes of polychalcogenide ligands with Ga, In and Tl. Recently we reported the synthesis of the first polyselenide of indium,[63] $[In_2Se_{21}]^{4-}$ **(XV)**, which was found to have the remarkable dimeric structure shown in Fig. 15. The structure consists of two $[In(Se_4)_2]^-$ units bridged by a $Se_5^{2-}$ chain. The $In^{3+}$ center is chelated by two $Se_4^{2-}$ ligands. The geometry around the indium atom can be described as trigonal bipyramidal with two axial Se(4) and Se(8) atoms and three equatorial ones, Se(1), Se(5) and Se(9). The trigonal bipyramidal geometry is unusual among idium/chalcogenide compounds in which indium is normally found as tetrahedral or octahedral.[64] The structure of (XV) is reminiscent of that of $[Bi_2S_{34}]^{4-}$ which is composed of two $[Bi(S_7)_2]^-$ units bridged by a $S_6^{2-}$ chain.[65] The $Bi^{3+}$ atom, however, adopts a tetragonal pyramidal geometry. The average In–Se distance in this complex is 2.67(1) Å.

Unlike the extreme sensitivity of the group 11 products on the accompanying counterion, the group 13 products are relatively insensitive to counterion effects. Thus the $[In_2Se_{21}]^{4-}$ ion was isolated and structurally characterized from DMF as its $Et_4N^+$, $Pr_4N^+$ and $Ph_4P^+$ salts. There is, however, a dependence on solvent. When the reaction of $InCl_3$ and $Na_2Se_5$ is carried out in $CH_3CN$, the new trimeric $(Et_4N)_3[In_3Se_{15}]$ **(XVI)** can be isolated in excellent yield. Its structure is shown in Fig. 16. In the same solvent, but

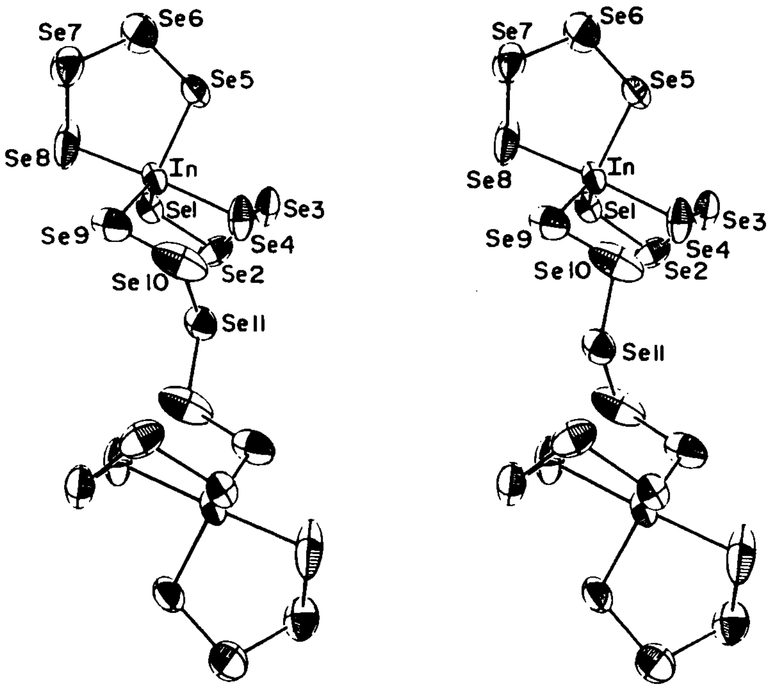
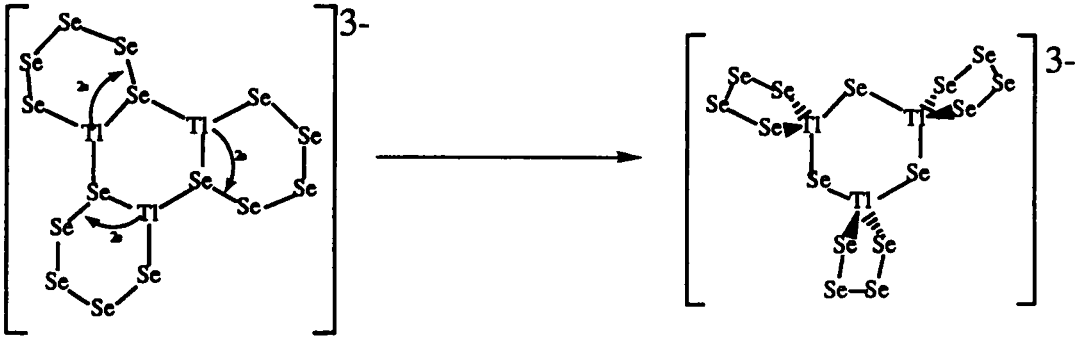


FIGURE 15 The structure of $[In_2(Se_4)_4(Se_5)]^{4-}$. The anion is located on a crystallographic inversion center, resulting in positional disorder of Se11.

using TlCl as starting material the X-ray isomorphous $(Et_4N)_3[Tl_3Se_{15}]$ **(XVIII)**, a $Tl^{3+}$ compound is obtained.[66] The formation of a $Tl^{3+}$ compound from $Tl^{+}$ is similar to the redox reaction found in the $Au/Se_x^{2-}$ case and it probably occurs in a similar fashion. Though there is no experimental evidence, it is reasonable to envision formation of a precursor $Tl^{+}$ complex followed by internal 2e electron transfer from $Tl^{+}$ to $Se_x^{2-}$ to split a proximal Se–Se bond and thus generate the $Se^{2-}$ ion. This is shown in Scheme (B). The precursor trimeric $Tl^{+}$ complex (i) is analogous to the known $[Cu(S_6)]_3^{3-}$ and it is related to a homologous dimeric $Tl^{+}$/tetrasulfide complex.[46] Since it is easier to reductively cleave $Se_5^{2-}$ than $Se_4^{2-}$, it may be possible to isolate a $Tl^{+}$/polyselenide complex similar to (i) (Scheme (B)) by using a shorter polyselenide in the synthesis.



(i)

SCHEME B

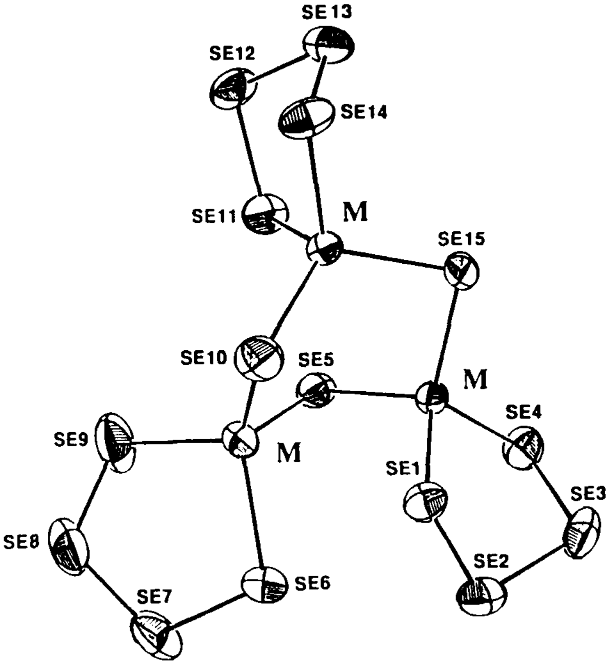


FIGURE 16 The structure of $[M_3Se_3(Se_4)_3]^{3-}$ (M = In, Tl).

In the structure of $(Et_4N)_3[M_3Se_{15}]$ the $In^{3+}$ and $Tl^{3+}$ are tetrahedral and they are part of a rather stable $M_3Se_3$ six-membered ring. The average M–M distance in these rings is 3.664(2) and 3.682(2) Å, respectively, for In and Tl. The average M–Se distances are 2.59 Å and 2.64 Å, respectively. The $[M_3Se_3]^{3+}$ six-membered ring core assumes a boat conformation in the solid state. The average M–Se–M angle for both complexes is 92°.

UV/vis and $^{77}Se$ NMR spectroscopic data indicate that $[In_2Se_{21}]^{4-}$ does not exist as such in DMF solution. The presence of a band in the region 610–650 nm (it is not observed in the solid state) suggests the presence of dissociated $Se_x^{2-}$ chains. This is also supported by cyclic voltammetric data for (XV) which are very similar to those obtained from pure $Se_5^{2-}$ in DMF solutions. In contrast, the featureless UV/vis spectra of DMF solutions of $(Et_4N)_3[In_3Se_{15}]$ suggest that they do not contain dissociated $Se_x^{2-}$ chains. This is in concert with the $^{77}Se$ NMR data which show three peaks as expected at 643, 197 and −244 ppm. The former two peaks are due to the chelating $Se_4^{2-}$ ligands in (XVI), while the latter originates from the bridging $Se^{2-}$ unit. Surprisingly, the NMR spectra of (XV) and (XVI) are identical, indicating that $[In_2Se_{21}]^{4-}$ converts to (or is in equilibrium with) $[In_3Se_{15}]^{3-}$ in DMF. Reaction of $[In_3Se_{15}]^{3-}$ with $Se_x^{2-}$ results in $[In_2Se_{21}]^{4-}$.

In the Ga/Se system we have isolated $(Ph_4P)_2Ga_2Se_{12}$ **(XVIII)** which is isostructural to $(Ph_4P)_2Fe_2Se_{12}$.[67]

### 3.5. Group 14 Chemistry

Polychalcogenide chemistry in this group is scarce as well, with the polysulfide complex(es) $[Sn(S_4)_2(S_6)]^{2-}/[Sn(S_4)_3]^{2-}$ being the only structurally characterized compounds.

$(Ph_4P)_2[Sn(Se_4)_3]$ **(XIX)** can be prepared[68,69] by reacting $SnCl_4$ with $Na_2Se_5$ in DMF in the presence of $Ph_4P^+$. Interestingly the same compound can be obtained by using $SnCl_2{\cdot}2H_2O$ as starting material which indicates that possible $Sn^{2+}$–$Se_x^{2-}$ ($x > 1$) complexes are unstable towards internal redox chemistry yielding $Sn^{4+}$ species. This is similar to the behavior of the corresponding $Fe^{2+}/Se_x^{2-}$,[67] $Au^+/Se_x^{2-}$ [49] and $Tl^+/Se_x^{2-}$ [66] systems from which only $Fe^{3+}$, $Au^{3+}$ and $Tl^{3+}$ complexes have been isolated.

The absence of a band around 650 nm in the UV/vis spectrum suggests that the complex (XIX) does not dissociate in this solvent to form $Se_x^{2-}$ anions. The $^{77}Se$ NMR spectrum of (XIX) in DMF solution at room temperature, shows two peaks at 618 and 459 ppm, respectively, indicating that all three $Se_4^{2-}$ ligands in the complex are equivalent.

The $^{119}Sn$ NMR spectrum of $[Sn(Se_4)_3]^{2-}$ in DMF solution at room temperature shows a single peak at −723 ppm as expected. The observed $^{119}Sn$ NMR chemical shift for $[Sn(Se_4)_3]^{2-}$ correlates well with those of $[SnSe_3]^{2-}$ and $[SnSe_4]^{4-}$ anions[70] which occur at −264.3 and −476.6 ppm, respectively, and reflects the increased shielding of the Sn nucleus upon expansion of its coordination sphere by negatively charged ligands.

The structure of (XIX) is similar to $[Pt(Se_4)_3]^{2-}$ [31] and $[Sn(S_4)_3]^{2-}$.[42] The latter was found cocrystallized with $[Sn(S_4)_2(S_6)]^{2-}$. The structure of the $[Sn(Se_4)_3]^{2-}$ anion is shown in Fig. 17, and consists of three four-membered selenium chains chelated to a central $Sn^{4+}$. The coordination geometry of the $Sn^{4+}$ is octahedral, approaching $D_3$ symmetry, with an average Sn–Se

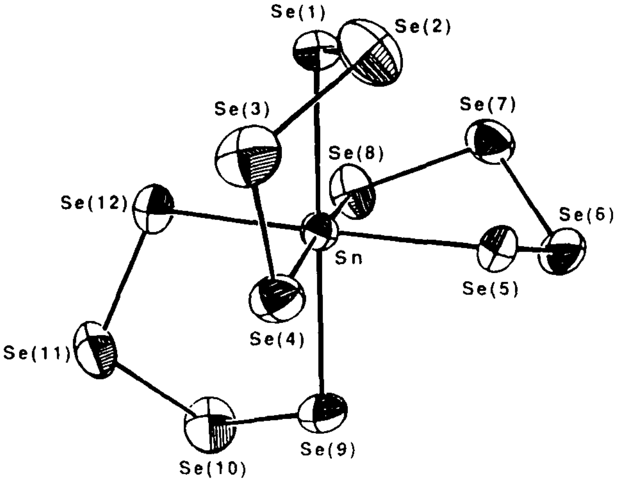
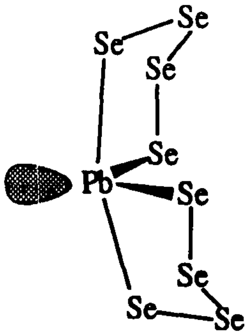


FIGURE 17 The structure of $[Sn(Se_4)_3]^{2-}$.

bond distance of 2.709(13) Å and a Se–Sn–Se angle of roughly 90°. The observed Se–Se bonds are in the normal range of single Se–Se bond distances reported for other metal–polyselenide compounds. The SnSe(1)Se(2)Se(3)Se(4) ring adopts the envelope conformation while the other two SnSe(5)Se(6)Se(7)Se(8) and SnSe(9)Se(10)Se(11)Se(12) adopt puckered conformations. Both of these conformations are common in $Q_4^{2-}$ chemistry. For example, the envelop conformation is notable in the series $[M(Se_4)_2]^{2-}$ [60] (M = Zn, Cd, Hg) while the puckered one is characteristic in the $[MQ(Se_4)_2]^{2-}$ (Q = O, S, Se) series.[7,8,61]

Recently the structure of the $[Pb(Se_4)_2]^{2-}$ was reported.[28] The Pb compound is schematically shown below:



It features an irregular coordination around the Pb center. The approximate geometry around the Pb atom can be described as trigonal bipyramidal with one vacant equatorial position as expected from VSEPR considerations.

## 4. THERMAL DECOMPOSITION STUDIES

We are devoting considerable effort to evaluate the molecular chalcogenides as convenient precursors to form solid-state electronic materials such as binary and ternary chalcogenides: CdSe, ZnSe, $CuInSe_2$, $Hg_xCd_{1-x}Te$, etc. Although it is beyond the scope of this article to elaborate on these studies, some preliminary but important decomposition characteristics of these materials will be given.

We have carried out preliminary thermal decompositions by thermal gravimetric analysis, TGA (under nitrogen or argon), to determine the nature of the final decomposition products and their formation temperatures. Not all complexes show clean decomposition characteristics.

The Cd and Zn complexes decompose to the corresponding binary chalcogenides (Eq. (7)).

$$(R_4N)_2[Cd(Se_4)_2] \longrightarrow CdSe + R_2Se_x + 2R_3N \qquad (7)$$

Also solid solutions of various binaries can be prepared (Eq. (8)):

$$(R_4N)_2[Cd(Se_4)_2] + (R_4N)_2[Cd(Te_4)_2] \longrightarrow CdSe_{1-x}Te_x + R_2Se_n + R_2Te_m + Se + Te + 2R_3N \qquad (8)$$

The mercury compounds release Hg vapor and chalcogen upon heating and thus do not yield any solid decomposition products (i.e., HgSe, HgTe). β-$(Ph_4P)_2Pd(Te_4)_2$ decomposed, yielding a complex mixture of $PdTe_x$ products.

The silver–polyselenide compounds decomposed by degradation of the organic cation to yield $Ag_2Se$ and Se, releasing $R_3N$ and $R_2Se$. Pure $Ag_2Se$ (Naumannite) phase was obtained at 400°C. $(Ph_4P)_4[Cu_2Se_{14}]$ decomposes to $Cu_2Se$. The decomposition temperatures in these materials depend heavily on the nature of the counterion and reflect the decomposition of the individual $R_4N^+$ cations via nucleophilic attack of an R group by a polyselenide fragment to form volatile $R_2Se$ and $R_2Se_2$ species. In the Ag/Se system it was found that the stability order is $Me_4N^+ < Et_4N^+ < Pr_4N^+ < Ph_4P^+$.

The compounds $(Ph_4P)_4In_2Se_{21}$ and $(Et_4N)_3In_3Se_3(Se_4)_3$ thermally decompose in a clean way to the corresponding β-$In_2Se_3$ at 510 and 440°C, respectively. $(Et_4N)_3Tl_3Se_3(Se_4)_3$ decomposes at 240°C to a mixture of $Tl_2Se$ and Se. Typical TGA diagrams for (XV) and (XVI) are shown in Fig. 18. Interestingly co-thermolysis of $(Ph_4P)_4Cu_2Se_{14}$ and $(Ph_4P)_4In_2Se_{21}$ mixtures in a (1:1) ratio yielded crystalline films of the important photoconductor $CuInSe_2$ at ~530°C.[71]

Preliminary TGA examination of the thermolysis of $(Ph_4P)_2[Sn(Se_4)_3]$ under flowing nitrogen shows that the compound begins to decompose at ~335°C. Following a smooth and contin-

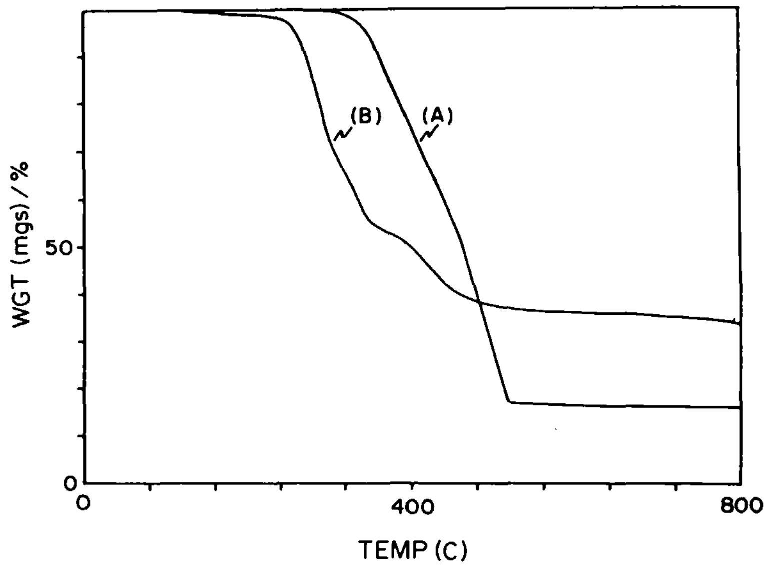


FIGURE 18 TGA diagrams under flowing nitrogen of (A) $(Ph_4P)_4[In_2(Se_4)_4(Se_5)]$ and (B) $(Et_4N)_3[In_3Se_3(Se_4)_3]$. The final thermolysis product is β-$In_2Se_3$.

uous weight loss, its decomposition ends at 520°C with formation of SnSe.

In the cases where the decomposition characteristics of these complexes are well defined, their uses as precursors to useful semiconducting solids are being explored. For example, we have grown films of CdSe, β-$In_2Se_3$, $CuInSe_2$ and $Cu_2Se$ from the pyrolysis of "green" film of DMF solutions of the corresponding complexes.

## 5. SUMMARY

Our results outlined above show that the chemistry of the late transition and main group metals with heavier polychalcogenides is fascinating, diverse and significant, and warrants further investigation. Interesting new polychalcogenide molecules demonstrate that the structural possibilities accessible by these ligands are intriguing and that a great deal awaits to be learned about the behavior of the various $Q_x^{2-}$ species in solution and in the solid state. The reactivity of such ligands with organic substrates and the potential for new organoselenium and organotellurium chemistry have not even begun to be investigated.[72] Furthermore, this class of compounds will provide a useful compound pool from which to draw suitable precursors for the synthesis of solid-state chalcogenide semiconductors. The fundamental chemistry of polychalcogenides is still in its infancy. Therefore interest in it is expected to grow.

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