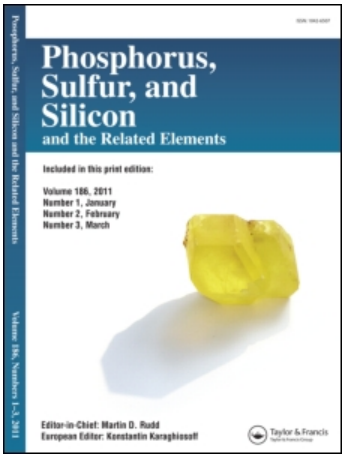


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# Counterion Size Versus Structure in Metal-Chalcogenide Salts

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# COUNTERION SIZE VERSUS STRUCTURE IN METAL-CHALCOGENIDE SALTS

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Abstract The effect of counterion on the structure of several anionic metal-chalcogenide complexes is discussed. Examples of compounds which show these dramatic effects are presented and some conclusions are made regarding our ability to predict the dimensionality of a structure.



## INTRODUCTION

Despite the abundance of molecular metal polychalcogenide complexes, analogs with extended solid state structures include only a few notable examples. These include the alkali metal salts of α- and β-$KCuQ_4$ (Q=S, Se)[1], $K_2PdSe_{10}$[2], $KAuQ_5$ (Q= S, Se)[3], $K_3AuSe_{13}$[3] and $K_2Sn_2S_8$[4]. Polymeric structures with organic counterions are even fewer, $(Ph_4P)AgSe_4$[5], $(Me_4N)AgQ_5$ (Q=S[6], Se[7]), $(H_3NCH_2CH_2NH_3)Cu_2S_{10}$[8] and $(Ph_4P)MSe_{12}$ (M =Ga, In and Tl)[9]. Polymeric metal polytellurides are scarcer. Examples include $K_4M_3Te_{17}$[10] (M=Zr, Hf) and the binary compound $CrTe_3$[11] and $(Me_4N)[M(Te_4)]$ (M=Cu, Ag)[12]. Based on the information available todate, it is apparent that in certain cases counterions influence the final structure in ways not well understood. These steric effects are dominant enough that seem to overcome any underlying electronic effects that may also be there. Systems that submit to counterion influence on structure are those which contain relatively labile anions which can quickly change their structure to respond to changes in counterion. In this paper we will present several polychalcogenide systems which strongly exhibit such steric effects. We note that some of the points that will be made here will apply to other non-chalcogenide systems as well, and thus, may be useful in either rationalizing existing results in the literature or predicting new compounds. In the case of polychalcogenides, it is interesting to view each $Q_x^{2-}$ fragment as a building block in the construction of two- and three-dimensional metal containing frameworks, especially ones with open structures. Therefore, it would very useful if we developed some intuitive understanding of how organic counterions influence the crystallization and structure of these systems. Results obtained in several laboratories suggest that identification of valuable trends in this important but complicated issue may be possible.

## DISCUSSION

Before we begin this qualitative discussion we clarify that in comparing the various systems we assume the stoichiometry of the anion to be invariant (or almost invariant) and that the most important parameters are the structure (i.e. connectivity in one, two and three dimensions) and in some systems (e.g. group 11 compounds) the metal coordination number. In this context, we will attempt to rationalize structural changes occuring as the countercation varies in size. For the purposes of this discussion, the countercations are thought to be non-interacting (other than coulombically) with the anions.

### Coordination Number and Counterion Size

The set of compounds in which we first identified a correlation between metal coordination geometry an counterion size and between structure an counterion size were the series $(Ph_4P)Ag(Se_4)$, $(Me_4N)Ag(Se_5)$, $\alpha$-$KCuS_4$, $CsCuS_6$[13], $[(Et_4N)Ag(Se_4)]_4$ and $(Me_4N)[M(Te_4)]$ (M=Cu, Ag). The common thread that joins these compounds is the similar stoichiometry of the metal polychalcogenide part. Except in $[(Et_4N)Ag(Se_4)]_4$, the anions in these compounds are polymeric possessing one- or two-dimensional structures.

Each $[Ag(Se_4)]_n^{n-}$ chain is a corrugated ribbon with the basic repeat unit five-membered $AgSe_4$ ring, see Figure 1. The $AgSe_4$ unit polymerizes via the bridging action of a terminal selenium atom in the chelating $Se_4^{2-}$ ligand on a second Ag atom of a neighboring five-membered $AgSe_4$ unit. The coordination geometry of the Ag atoms is distorted trigonal planar. The Se(1)-Ag-Se(4) inter-ring angle of 138.8 deg is unusually large indicating a slight departure from the ideal trigonal planar coordination geometry around the Ag atom towards linear geometry.

The $[Ag(Se_4)]_n^{n-}$ chain bears a structural relationship to the $\alpha$-$[Cu(Se_4)]_n^{n-}$,[1b] chain, as both chains are composed of $MQ_4$ five-membered rings. Yet, the coordination geometries of the metal ions in these two structures exhibit a significant difference which is caused by the different size of counterion in each structure. The $\alpha$-$[Cu(Se_4)]_n^{n-}$ chain contains tetrahedral copper atoms. One can view the $[Ag(Se_4)]_n^{n-}$ chain as being formed by "stretching" a hypothetical $\alpha$-$[Ag(Se_4)]_n^{n-}$ chain isostructural to $\alpha$-$[Cu(Se_4)]_n^{n-}$ along the chain direction. Conversely, by "compressing" the $[Ag(Se_4)]_n^{n-}$ along the chain direction will expand the Ag coordination sphere from three to four by bringing the Se(2) atom close to Ag, see Figure 2. The "stretching" effect results from the replacement of $K^+$ for $Ph_4P^+$ since the substitution of large cation for small one must cause the expansion of the overall structure in all directions, including the chain direction which breaks the "bond" between Se(2) and Ag'. Based on this argument, it is predicted that

$KAg(Se_4)$ will also be polymeric . Conversely, larger cations, such as $Ph_3PNPPh_3^+$, should reduce the metal coordination number in the $[Ag(Se_4)]_n^{n-}$ species to two.

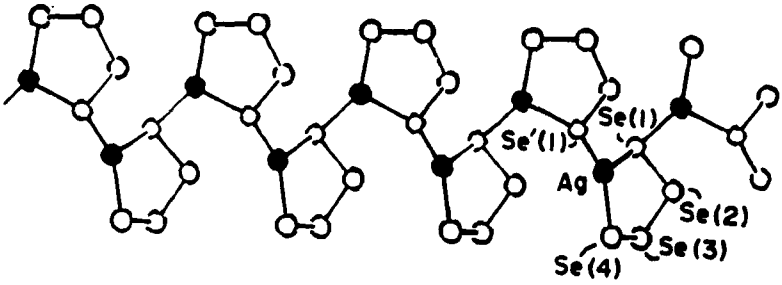



FIGURE 1. The structure of a $[Ag(Se_4)]_n^{n-}$ chain.

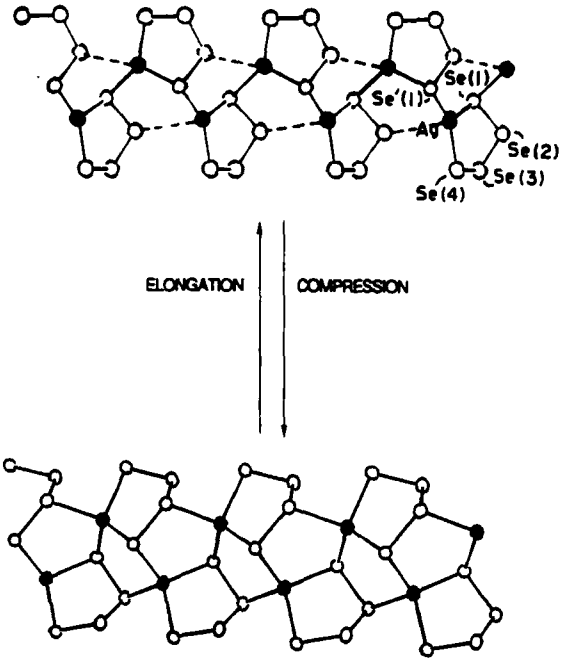



FIGURE 2. Structural relationship of $\alpha$-$[Cu(Se_4)]_n^{n-}$ and $[Ag(Se_4)]_n^{n-}$. Elongation of the $\alpha$-$[Cu(Se_4)]_n^{n-}$ structure along the chain axis results in the $[Ag(Se_4)]_n^{n-}$ structure and in reduction of the coordination number of the metal atom.

The related $[Ag(Se_5)]_n^{n-}$ crystallizes as the $Me_4N^+$ salt. The coordination geometry of the Ag atom is now tetrahedral, see Figure 3. Despite the six-member atom repeat unit occurring in the chains, the structure contains only five-membered $AgSe_4$ and $Ag_2Se_3$ rings. The ligation mode of the $Se_5^{2-}$ ligands in the compound differs from that of the $Se_4^{2-}$ ligands present in $[Ag(Se_4)]_n^{n-}$. Each $Se_5^{2-}$ ligand chelates a Ag atom via

Se(1) and Se(4) to form a $AgSe_4$ ring. The terminal atoms Se(1) and Se(5) bridge to coordinate other Ag atoms.

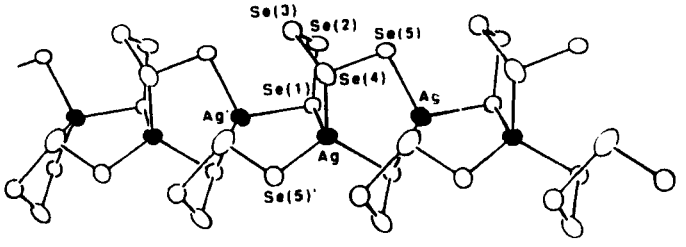



FIGURE 3. The structure of a $[Ag(Se_5)]_n^{n-}$ chain.



Interestingly, the $[(Et_4N)Ag(Se_4)]_4$ is a discrete tetrameric cluster molecule composed of five-membered ring $AgSe_4$ rings and featuring two different kinds of Ag coordination, see Figure 4. The four Ag atoms in the cluster are divided into two different pairs according to their coordination environments. One pair containing Ag(1) and Ag'(1), possesses a very distorted tetrahedral coordination. The other group containing Ag(2) and Ag'(2), shows a trigonal-planar coordination. The four bridging $Se_4^{2-}$ ligands are not equivalent and split in two sets. In one set, two $Se_4^{2-}$ ligands bridge 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, two $Se_4^{2-}$ ligands are bridging two silver atoms Ag(1) and Ag(2) each with only one terminal atom, Se(8), being $\mu_2$ type.

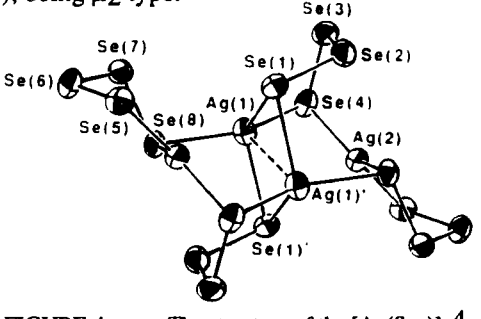



FIGURE 4. The structure of the $[Ag(Se_4)]_4^{4-}$ cluster.

Comparing the coordination geometries of the metal atoms in the above complexes, it is clear that the metal coordination sphere in each compound depends to a large extent upon the size of the counterion. For large cations such as $Ph_4P^+$, the metal atoms assume the lower coordination number of three while a small cation such as $K^+$ or $Me_4N^+$ favors the higher coordination number of four. Interestingly, an intermediate size cation, such as $Et_4N^+$, results in two types of coordination geometries of Ag atoms

distorted tetrahedral and trigonal planar in $[Ag(Se_5)]_4^{4-}$. The average coordination number therefore can be regarded as 3.5. A literature review for similar counterion-dependent trends in other known metal polychalcogenides show that most $Cu^+$, $Ag^+$ and $Au^+/Q_x^{2-}$ systems follow this correlation as well. For example, the $Cu^+$ coordination number (CN) in $(Ph_4P)_2(NH_4)[Cu_3(S_4)_3]$[14] and $(Ph_4P)_4[Cu_2S_{20}]$[15] is 3 as both compounds contain the large cation $Ph_4P^+$. Several known $Ag^+$ polysulfide compounds have been isolated with various organic cations. These are $(Ph_4P)_4[Ag_2S_{20}]$ (CN=3)[16], $(Ph_4P)_2[Ag_2(S_6)_2]$ (CN=3)[17], $(Ph_3PNPPh_3)$-$[Ag(S_9)]\cdot S_8$ (CN=2)[17]. For $Au^+$, there are two complexes, $(Ph_4P)_2[Au_2S_8]$ (CN=2)[17] and $(Ph_4As)[Au(S_9)]$ (CN=2)[18]. Notice that the largest cation, $Ph_3PNPPh_3^+$ favors the smallest CN.

This correlation of counterion size vs. CN can be rationalized based on packing considerations. In any salt lattice the packing of cation and anions must be such that effective screening can be achieved for all species. Therefore, the screening of anions must be sufficient with a certain range of cation sizes, but with cations much smaller or much larger than the correct size range proper screening of anions would not be possible. With ineffective screening of anions, repulsive coulombic forces will become operative. If the anions, or anionic framework possesses some elasticity in the form of being able to change its volume, then it could respond to a change in counterion size to maintain the necessary screening. This, for example, may be achieved by adjusting the metal coordination number. Another way may be through folding and unfolding of the polychalcogenide chains. Of course, high coordination numbers will produce compact structures while small coordination numbers will result in expanded structures. This is schematically shown in two different ways in Figure 5.



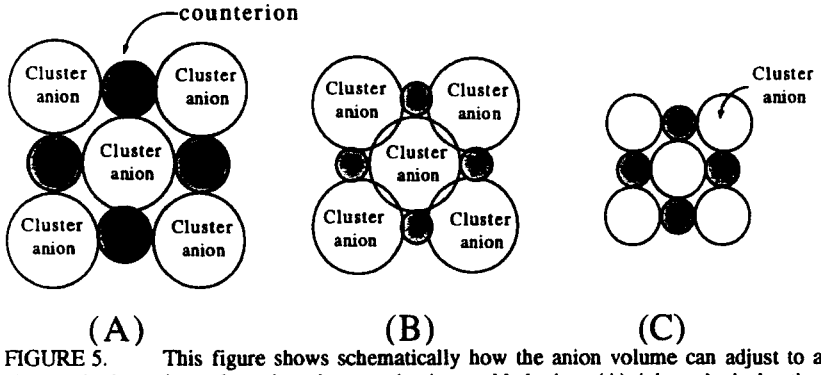



FIGURE 5. This figure shows schematically how the anion volume can adjust to accommodate changes in the cation volume in order to maintain a stable lattice. (A) A hypothetical cation-anion stable crystalline assembly. (B) substitution of the cation in (A) with a smaller cation causes poor anion screening. That is it brings the anions too close together (see anion sphere overlap) which experience destabilizing anion-anion repulsions. (C) the anion responds by decreasing its volume (e.g. by increasing intra-atomic bonding), achieving again a stable packing with the smaller cation.

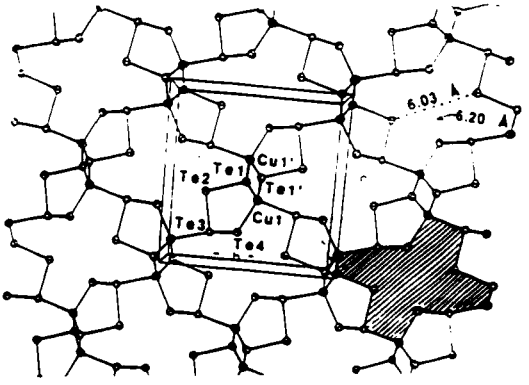
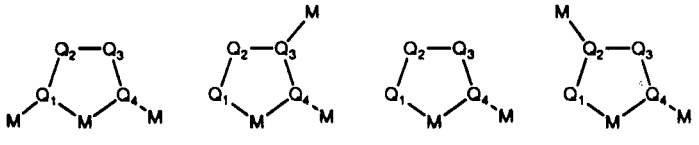



FIGURE 6. (A) The structure of $[Cu(Te_4)]^-$ layer viewed along the a-axis. The shaded area indicates the presence of 14-member ring holes in the layers.



The polytelluride analogs $(Me_4N)[M(Te_4)]$ (M=Cu, Ag) contain anionic layers and non-interacting $Me_4N^+$ cations situated between, see Figure 6. The layers form by interconnection of five-membered $MTe_4$ rings via a new bridging mode for a $Te_4^{2-}$ ligand which holds three Cu atoms together. Scheme (A) shows the four different bridging modes of a $Q_4^{2-}$ ligand known to result in polymeric $[M(Q_4)]^-$ structures. Variations in connectivity of $Q_4^{2-}$ and $M^+$ atoms determines the dimensionality of the structures.




Scheme (A)

The most interesting feature of the layers are the large holes made of 14-membered rings. The dimensions of the rings, are 6.034(2) Å and 6.195(3) Å, respectively. The layered structural motif is retained even with $EtMe_3N^+$ as the counter ion, suggesting the possible existence of a whole family of isostructural lamellar $(RMe_3N)[M(Te_4)]$ materials.[12] In these compounds, which contain relatively small organic cations, the metal coordination number is four. It is noteworthy that when larger cations such as $Ph_4P^+$ and $Et_4N^+$ are employed the $[M(Te_4)]$ stoichiometry is not maintained but the resulting complex $[M_2(Te_4)_2(Te_4)]^{4-}$ (M=Cu, Ag) contains trigonal planar metal centers.[19]

It is interesting that the compounds $KAuQ_5$ (Q=S or Se)[3] seem to violate the above correlation. These compounds are made of linearly-coordinated $Au^+$ ions bridged by $Q_5^{2-}$ chains. In spite of the small $K^+$ cation in the structures, the $Au^+$ does not adopt the higher coordination number as expected. All the Au atoms, however, are found to participate in interchain Au···Au interactions which, in combination with the well known

strong preference of $Au^+$ for linear coordination, may account for this deviation. In this case electronic effects appear to play a dominant role. The attractive Au···Au interactions between $[AuQ5]_n^{n-}$ chains would tend to compensate foe any coulombic repulsions that might develop due to poor screening of the chains.

Two sets of monochalcogenide compounds NaCuTe and KCuTe and NaAuTe, KAuTe and CsAuTe also show a trend in metal coordination number as a function of alkali ion size.[20,21] Thus, while the NaCuTe possesses an anti-PbO type $[CuTe]^-$ layered structure, the $K^+$ salt exhibits $[CuTe]^-$ layers in the boron nitride structure type. In the former the coordination number of copper is four while in the latter is three. Similarly, in the gold system the NaAuTe and KAuTe are isostructural to KCuTe (i.e. Au has coordination number of three) while the CsAuTe compound shows $[AuTe]^-$ chains with Au in linear coordination. Figure 7 schematically shows how both, the coordination number and dimensionality of a system can change with shrinking countercation. Such trends are numerous in the literature and can be found in even non-chalcogenide systems such as the ternary Cation/Cu/halide and Cation/Ag/halide systems.[22]



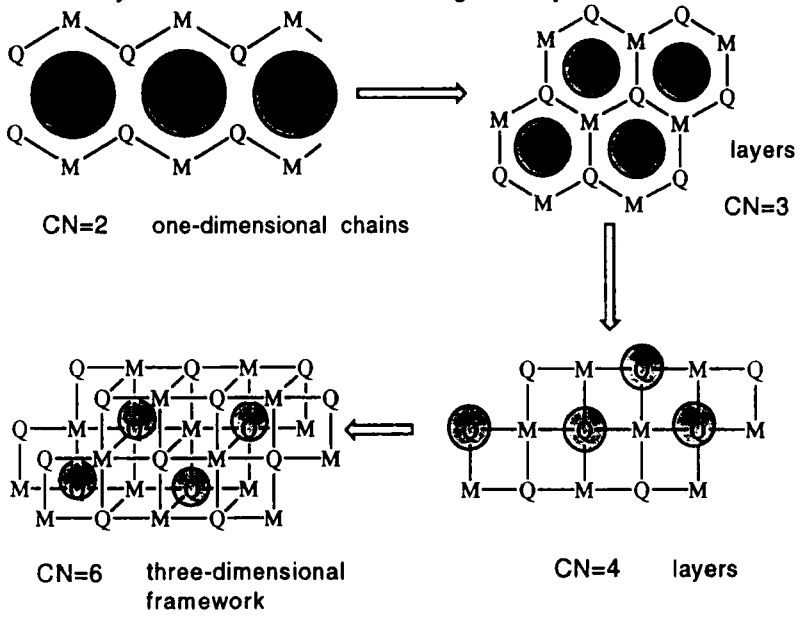



FIGURE 7. Illustration of how the countercation size can dictate the structure of an anionic covalent framework. The smallest cation could stabilize a three-dimensional framework. For simplicity only the NaCl type (with CN=6) is shown as an example of a three-dimensional framework but one may imagine other frameworks such as a ZnS type etc. In the case of ACuTe, for example, the LiCuTe phase is not known, but based on the arguments presented here it may crystallize in a three-dimensional structure where the $[CuTe]^-$ part is isostructural to ZnS. This in fact happens in the isoelectronic LiZnP.

Dimensionality of Anion vs. Counterion Size

An interesting set of compounds that illustrate the role of counterion in stabilizing molecular vs. extended structures is $(Ph_4P)_2Pd(Se_4)_2$[22], $K_4[Pd(Se_4)_2][Pd(Se_6)_2]$[2], $[MeN(CH_2CH_2)_3N]_2[Pd(Se_6)_2]$[23], $(Ph_4P)_2Au_2(Se_x)_2$ (x=2,3,4) $Cs_2Au_2(Se_3)_2$[1b] and $(Ph_4P)M(Se_6)_2$ M=Ga, In, Tl.[9] These complexes have similar stoichiometries but dramatically different structures.

$K_2[PdSe_{10}]$ is a metal polychalcogenide compound featuring interpenetrating frameworks. The spectacular structure of $K_2[PdSe_{10}]$ is composed of $K^+$ ions and two remarkable macroanions of $[Pd(Se_4)_2]^{2-}$ (Ia) and $[Pd(Se_6)_2]^{2-}$ (Ib). Therefore, $K_4[Pd(Se_4)_2][Pd(Se_6)_2]$ is a more descriptive formulation. Both (Ia) and (Ib) resemble diamond-like frameworks having the intriguing property of existing one inside the other. Polyselenide ligands $Se_4^{2-}$ and $Se_6^{2-}$ serve as long bridges between square-planar Pd metal centers. Shown in Figure 8A, the individual $[Pd(Se_x)_2]^{2-}$, are topologically equivalent to the structure of cristobalite $SiO_2$ ($Pd^{2+}$ atoms occupy the Si sites and $Se_x^{2-}$ ligands occupy the O sites). The average distance between Pd metal centers in both frameworks is 8.577(6) Å. The interpenetrating behavior of (Ia) and (Ib) is shown in Figure 8B. There are no covalent or ionic bonds between these two remarkeable frameworks and thus one can never cross, through bonds, from one to the other.

When considered alone, framework (Ia) is perforated with mutually perpendicular large tunnels running parallel to both the a- and b-axes. These tunnels are large enough to fit small organic molecules. The tunnels of (Ia) are shown in Figure 9A. Framework (Ib) is also perforated with mutually perpendicular large tunnels running parallel to both the a- and b-axes. The tunnels of (Ib) are shown in Figure 9B.

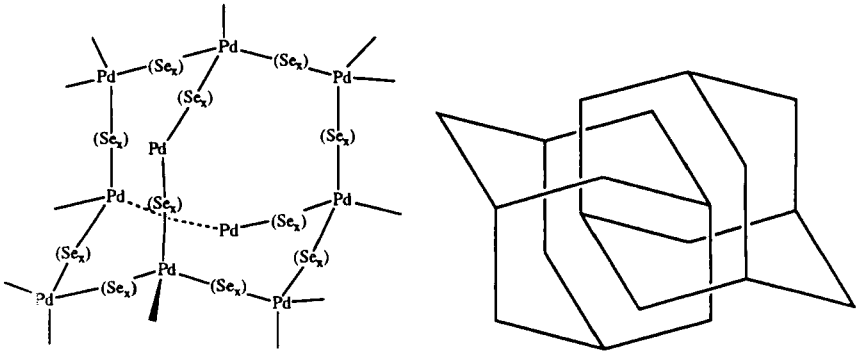



FIGURE 8. (A) Schematic representation of a single 3D framework of $[Pd(Se_x)_2]^{2-}$. The tetrahedral depiction of Pd atoms signifies the disposition and connectivity pattern of the $Se_x^{2-}$ ligands, not their actual coordination geometry. (B) schematic view of the interpenetrating behavior of $[Pd(Se_4)_2]^{2-}$ and $[Pd(Se_6)_2]^{2-}$ frameworks.

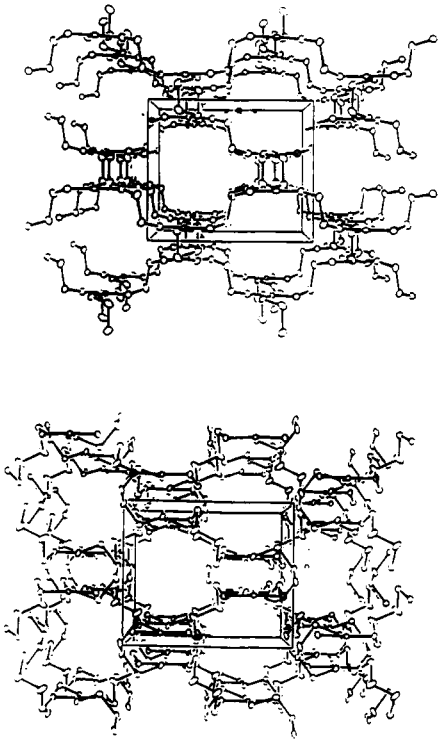
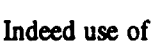
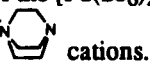


FIGURE 9. **(A) View of the $[Pd(Se_4)_2]^{2-}$ substructure looking down the a-axis and (B) View of the $[Pd(Se_6)_2]^{2-}$ substructure looking down the a-axis, illustrating the large one-dimensional channels.**

The distance between Pd atoms in the 3D diamond-like framework structure determine the size of adamantane cage. In order to avoid the disadvantage of creating too much empty space in the structure, two frameworks come together and coexist in such a way as to fill each other's empty cages and tunnels. Alternatively, each individual framework can be viewed as a host framework, raising the intriguing possibility of microporosity in this type of frameworks. Since the $K^+$ ion is too small to fit inside the adamantane cage and separately stabilize each framework it would be more appropriate to use larger cations as templating agents. Indeed use of the  cation resulted in a two-dimensional framework with the stoichiometry $[Pd(Se_6)_2]^{2-}$, see Figure 10. Essentially, this represents an isolation of the $[Pd(Se_6)_2]^{2-}$ part of $K_2PdSe_{10}$ by filling the $[Pd(Se_4)_2]^{2-}$ part of the lattice with  cations. The fact that the dimensionality dropped from three to two probably reflects the fact that this cation may be larger than the optimum needed to fill the void space occupied by the $[Pd(Se_4)_2]^{2-}$ framework in $K_2PdSe_{10}$.

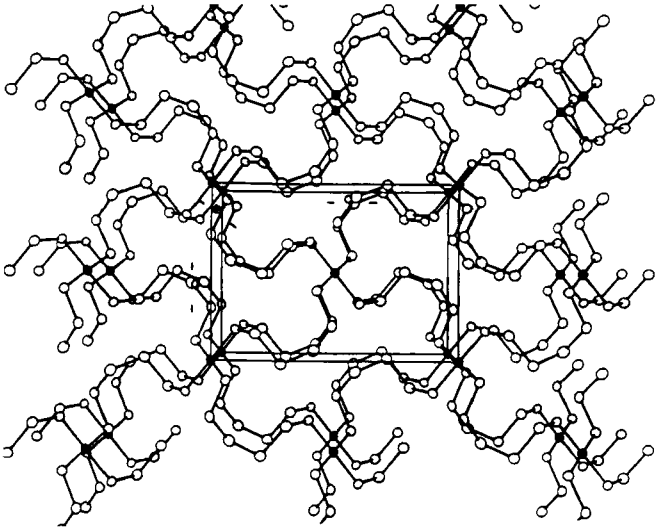


FIGURE 10. The structure of the two-dimensional layers $[MeN(CH_2CH_2)_3N]_2[Pd(Se_6)_2]$. Thje cations have been omitted for clarity.

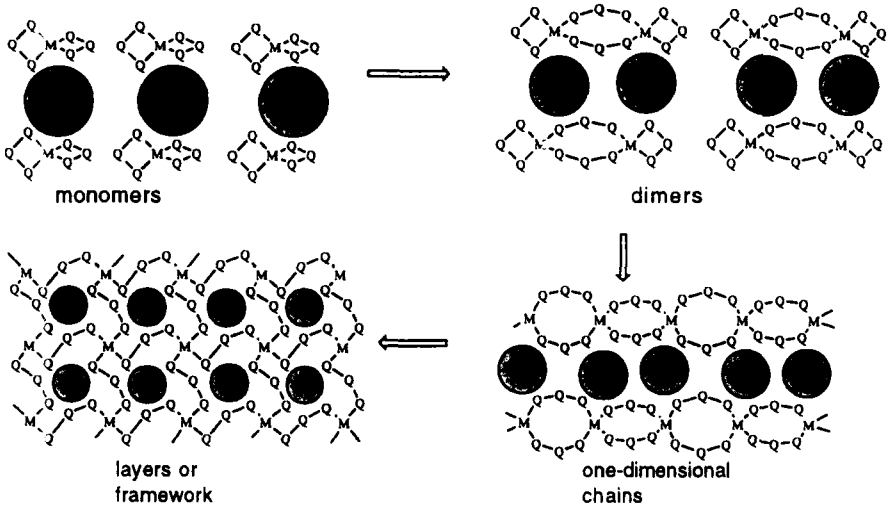



FIGURE 11. Schematic illustrating a possible structural evolution from a hypothetical mononuclear $[M(Q_3)_2]^{z-}$ polychalcogenide crystallized with large counterions to a dimeric complex and a one-dimensional chain as the counterion shrinks in size (the gray circles represent cations). Finally further reduction in cation size can lead to layered or even three-dimensional assemblies. Every time a transition occurs from one structure to the next there is a change in the binding mode of the ligand from chelating to bridging. This eliminates the repulsive interactions which develop with reduction in cation volume and leads to extended structures of lower lattice energy.

In contrast to the potassium salt, the $Ph_4P^+$ salt of $[Pd(Se_4)_2]^{2-}$ features discrete molecular anions where two $Se_4^{2-}$ ligands chelate to a single Pd atom. Naively, one may expect the structure of the anion to remain unchanged from counterion to counterion. To

explain the observed differences one must consider the packing arrangement of anions and cations. In the molecular $(Ph_4P)_2[Pd(Se_4)_2]$, it is obvious that the anions and cations pack in such a way as to screen each other. When the large $Ph_4P^+$ cation is changed to the drastically smaller $K^+$ the $[Pd(Se_4)_2]^{2-}$ anions can no longer be effectively screened, resulting in destabilizing repulsions. If the stoichiometry is to remain the same, the system must respond and avoid these destabilizing repulsions. It does this by converting the $Se_4^{2-}$ ligands from chelating on Pd atom to bridging two neighboring Pd atoms. In this fashion the number and type (i.e. metal-Se, Se-Se) of bonds remains constant, with no cost in enthalpy. However, the repulsive interactions transform into attractive ones leading to a lattice energy gain. This is shown schematically for a hypothetical system in Figure 11.

Related to $(Ph_4P)_2[Pd(Se_4)_2]$ are the $(Ph_4P)_2[M(Se_4)_2]$ (M=Hg, Cd, Zn, Mn)[23] which are all molecular tetrahedral complexes. One may wonder, in a gedanken experiment, whether the molecular structure of $[M(Se_4)_2]^{2-}$ can survive in the solid state if one half of the $Ph_4P^+$ cations were removed from the lattice. We might expect that with this substantial cation volume reduction the $[M(Se_4)_2]^{2-}$ anions to be inadequately screened. Such a system can be achieved either by replacing the $Ph_4P^+$ with an isostructural dication or if M is a trivalent metal with tetrahedral coordination preference. The closest we can come to the hypothetical situation above is $(Ph_4P)[In(Se_6)_2]$. In this compound one $Ph_4P^+$ cation is missing relative to $(Ph_4P)_2[M(Se_4)_2]$ but also the $Se_x^{2-}$ ligands are longer. The $(Ph_4P)[In(Se_6)_2]$ represents a dramatic decrease in cation/anion volume ratio with respect to $(Ph_4P)_2[M(Se_4)_2]$. As expected, the structure of the anionic $[In(Se_6)_2]_n^{n-}$ is a two-dimensional framework polymer, see Figure 12. The layers stack perfectly one on top of the other giving rise to one-dimensional channels running down the crystallographic *c-axis*. The channels are filled with $Ph_4P^+$ cations. Surprisingly, these cations are not situated between the layers but lie within them. Therefore, they can be viewed as *templates*, helping to stabilize the structure. The notion that the cation plays a role of a template comes from our failure to stabilize this same framework with other cations of the type $R_4N^+$ (R=Me, Et, Pr, Bu). The $Ph_4P^+$ cation appears to be an exact fit in the 28-member $[M_4(Se_6)_4]^{4+}$ ring. The transition of the molecular structure of $(Ph_4P)_2[M(Se_4)_2]$ to the extended structure of $(Ph_4P)[In(Se_6)_2]$ is described conceptually in Figure 11. The intermediate hypothetical structures shown in this Figure may be isolated through the use of proper intermediate size counterions.

Another interesting pair of related compounds is $(Ph_4P)_2Au_2(Se_x)_2$ (x=2,3,4) $Cs_2Au_2(Se_3)_2$. The $Ph_4P^+$ salt crystallizes as discrete cyclic dimers while the $Cs^+$ salt stabilizes extended one-dimensional chains, see Figure 13. Presumably, screening of the $[Au_2(Se_x)_2]^{2-}$ dimers with Cs ions is not possible.

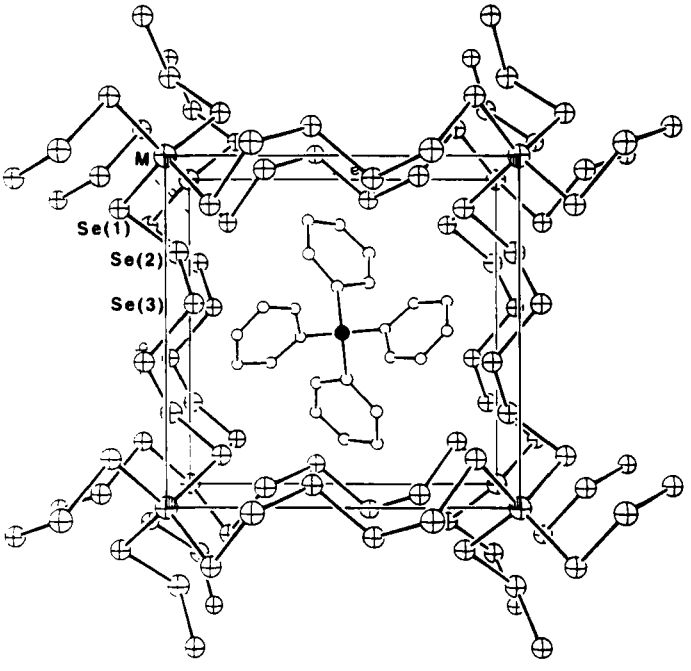



FIGURE 12. (a) View of a single unit cell of $(Ph_4P)[In(Se_6)_2]$ along the crystallographic ab plane. The shaded circles are M atoms; the crossed circles are Se atoms; the black circles are P atoms; the open circles are carbon atoms.

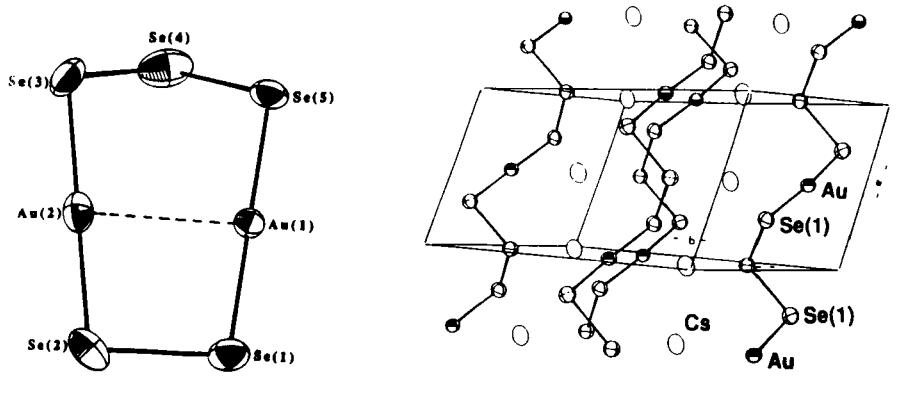



FIGURE 13. The structures of the homologous $[Au_2(Se_2)(Se_3)]^{2-}$ and $[Au_2(Se_3)_2]^{2-}$

At this point we should contrast the one-dimensional structure of $(Me_4N)Ag(Se_5)$ with the lamellar structure of $(Me_4N)[M(Te_4)]$. Although a change in counterion has not occurred, the substitution of the larger Te for Se creates a larger anion and achieves essentially the same effect as when decreasing the size of the cation. Qualitatively then, one could rationalize that the chains of $[M(Te_4)]^-$ are not effectively screened by $Me_4N^+$

and thus they associate into layers to avoid the expected repulsive interactions. Of course, the one-dimensional structure of $KCuSe_4$ would seem to be a discrepancy since the $K^+$ ion is even smaller than the $Me_4N^+$ ion. Here one has to evaluate the importance of ionic $K^+$-Se contacts in the lattice in order to be able to correctly explain the difference in structure. There is no doubt that the behavior of anions in the presence of cations is a lot more enigmatic than perhaps is projected here, but it is also clear that the trends identified thus far are real and that the, admittedly rather crude, packing arguments are reasonable. It would be very desirable if proper computer modeling of these packing interactions could be worked out so that this counterion effect could be evaluated at a more quantitative level. Deeper understanding of these interactions will help us design and predict interesting new materials not only for chalcogenides but for other compounds with main group elements.

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