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The chemistry of mixed 15/16 main group clusters

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ABSTRACT

This review describes the chemistry of anionic mixed 15/16 clusters and their coordination chemistry with transition metals. The focus is on the heavier elements such as sulfides and selenides of phosphorus, arsenic and antimony. A brief introduction with a historical perspective is followed by the chemistry of soluble anionic clusters, including preparative methods and structural characteristics. Solids containing recognizable anionic fragments (Zintl phases) are also described. Bonding is mentioned briefly. Transition metal complexes of these clusters are discussed in some detail and structures and bonding are highlighted. Neglected areas and future prospects are mentioned.

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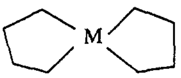
1. INTRODUCTION AND SCOPE OF REVIEW

The chemistry of mixed 15/16 clusters has a long and venerable history. Alchemists were first attracted to the bright golden yellow color of realgar (As_4S_4) and orpiment (As_2S_3), and combined them with cheaper metals such as lead to form gold. While these reactions probably do not work entirely as envisioned, they are responsible for another type of riches, namely the extensive class of structurally fascinating compounds known as the sulfosalts [1]. This class of compounds is well known in the mineralogical literature, and consists of a large number of solid state compounds made up of heavy metals such as silver or lead usually linked by trivalent or pentavalent arsenic or antimony sulfides.

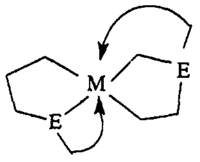
The parent mixed 15/16 clusters have some interesting chemical properties in their own right. For example, realgar is possibly the only mineral which is truly molecular. In addition, like the homonuclear chalcogens and pnicogens, the mixed element cages are readily reduced to form anionic clusters. The anions can form complexes in the solid state with softer elements such as lead, silver and mercury. The high degree of connectivity possible with these clusters leads to tightly linked, extended arrays in the solid state, usually with very complex structures. This extensive bonding leads to very stable solids which accounts for the importance of these compounds in mineralogy. However, investigation of the molecular chemistry of 15/16 clusters and their coordination complexes has only recently been undertaken in anything resembling a systematic manner. Judging by the progress in the last few years, this area will prove to be both chemically rich and structurally fascinating. In this review we attempt to introduce the chemistry of mixed 15/16 anions and describe their role as ligands toward a variety of metals.

The chemistry of the mixed 15/16 anions can perhaps best be conceptualized by relating them to their simpler and better understood counterparts, the polychalcogenide anions. The extensive chemistry of the polychalcogenides is due, in a large part, to the variability of the chain length [2]. Chain lengths for the chalcogenides can range from one to as high as nine. In addition, since each member of the chain contains at least two lone pairs of electrons, one or all of the members of a polychalcogenide chain can ligate to a metal. However, with only a few exceptions, the chalcogenide atoms are divalent. This reduces the connectivity and decreases the potential for formation of closed cages and clusters. In contrast, the presence of a trivalent group 15 element dramatically increases the potential connectivity of the cluster, and leads to many more possible permutations in terms of ligand binding to transition metals. Whereas a metal polychalcogenide is somewhat limited topologically (A), a trivalent group 15 element adds another degree of structural freedom, and can lead to cage formation (B) or polymerization (C).

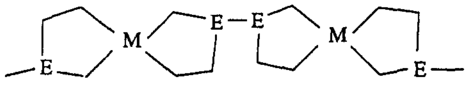


MS_8^{2-}

A



B



C

Despite the vastly greater potential for structural variations, the chemistry of the mixed 15/16 clusters has not been as intensely investigated as that of the pure group 16 clusters. Nevertheless, substantial progress has been made, and in this review we wish to describe some of these results as well as highlight some of the potential of this exciting class of compounds.

The review focuses predominantly on the anionic molecular clusters of the heavier group 15/16 elements. Though we attempt to highlight most of the significant areas, we apologize if we are not fully comprehensive. Compounds containing second row elements, such as phosphates [3] and sulfur–nitrogen compounds [4], are not dealt with, as they are beyond the scope of this review and have their own extensive literature. Neutral compounds such as the phosphorus sulfides and realgar are mentioned but only as they provide an initial reference point for further expansion of the chemistry. These neutral cages have also been the subject of a number of excellent reviews [5,6]. Similarly, predominantly organic derivatives of mixed 15/16 clusters, such as Lawesson's reagent ($(CH_3OC_6H_4)_2P_2S_4$) are mentioned only to provide perspective. Anions receive substantial attention in this article, not because of any inherent prejudice, but because most of the reaction chemistry of mixed 15/16 clusters involves anions. They are generally soluble, stable and relatively easily prepared. Neutral species are well known and have been more thoroughly studied, but are often not soluble in common solvents which limits their chemistry. In addition, the neutral cages are somewhat less inclined to remain intact on reaction with metals, but often either fragment or serve as simple sulfur transfer reagents. Cations, in contrast, are very rare species and very little of their chemistry has been reported [7].

Recently the structures of a large number of solid state compounds containing both group 15 and 16 elements have been reported, especially alkali metal derivatives containing anionic chains, layers and clusters. Many of these so-called Zintl phases have been featured in several excellent recent reviews [8], but they often possess structural and bonding properties reminiscent of their molecular analogs. As such, they are mentioned in the appropriate context. It should also be noted that the earlier main group elements such as tin, germanium and indium also form a beautiful series of anionic chalcogen containing clusters, and these have been thoroughly described in the definitive and now classic review article by Krebs [9]

2. SOLUBLE MIXED 15/16 ANIONIC CLUSTERS

There are a variety of synthetic entries to the mixed anionic clusters, although most involve some kind of a nucleophilic attack on a mixed 15/16 solid. The nucleophiles come in a variety of guises, but the successful reactions usually depend on the formation of an anionic chalcogenide at some point. Some of the more interesting compounds have been prepared by somewhat esoteric methods, and these are highlighted where appropriate.

2.1. Attack of chalcogenide anions on neutral binary solids

The attack of chalcogen anions on electrophilic 15/16 binary compounds is perhaps the oldest and most fundamental reaction type, as well as one of the most versatile. Its success hinges on the fact that both sulfur and selenium react readily with almost all of the group 15 elements to form a series of binary compounds of various stoichiometries, and these binaries are susceptible to nucleophilic attack. These mixed 15/16 clusters can be viewed as the formal oxidation products of the group 15 element [5,10]:

$$P + xsS \rightarrow P_4S_{10}$$

$$4\ As + 4S \rightarrow As_4S_4$$

Binary group 15 sulfides also form conveniently on reaction of group 15 halide or oxide with H_2S, usually under aqueous acidic conditions [11]. The driving force for these reactions is the formation of water or the hydrohalic acid:

$$2\ AsCl_3 + 3\ H_2S \rightarrow As_2S_3$$

$$2\ H_3SbO_4 + xsH_2S \rightarrow Sb_2S_5 + 8\ H_2O$$

It is our qualitative observation that freshly precipitated binary solids are often considerably more reactive toward nucleophiles than are older, more thermally stable forms of the solids. These compounds are quite susceptible to nucleophilic attack at the group 15 element, and almost any sulfide or selenide source will lead to soluble group 15/16 anions.

2.1.1. ES_4^{3-} (E = P, As, Sb) salts

The oldest and conceptually simplest examples of mixed 15/16 anions are the tetrahedral ES_4^{3-} salts. These are easily prepared by the reaction of a trivalent binary sulfide with an aqueous base solution saturated with H_2S and sulfur. For example, in the reaction below, the sulfide anion is generated by deprotonation of H_2S with base and the elemental sulfur serves to oxidize the As(III) to As(V) [12]:

$$3\,Na_2S + As_2S_3 + 2\,S \rightarrow Na_3AsS_4$$

Alternatively these salts can be prepared by reacting a sulfide source directly with pentavalent binary sulfide. This usually involves reactions in the melt or use of a soluble sulfide source, such as the commercially available $Na_2S{\cdot}9H_2O$ [13]:

$$Na_2S{\cdot}9H_2O + P_2S_5 \rightarrow Na_3PS_4{\cdot}8H_2O$$

One of the earliest variations of this technique was the preparation of $Na_3SbS_4{\cdot}9H_2O$, better known as Schlippe's salt [14]. Since these compounds are often prepared under aqueous conditions, the salts are usually heavily hydrated [15]. Use of anhydrous sources of sulfide, or extensive drying of salts prepared from basic sulfide solutions, can lead to anhydrous tetrathiopnictates such as Na_3SbS_4 [16]. Many of these are often extremely sensitive to hydrolysis. It has recently been demonstrated that Na_3PS_4 prepared carefully from the melt displays remarkable ionic conductivity [16c]. Ammonium salts such as $(NH_4)_3(AsS_4)$ can be prepared as well [11,16b], and they are somewhat soluble in hot alcohol. In general, however, these salts are not as synthetically useful as it might appear, since they are not soluble in organic solvents. To our knowledge, there have been no reports of the preparation of salts of ES_4^{3-} using quaternary ammonium or phosphonium cations as counterions. If salts of ES_4^{3-} could be developed which are soluble in non-aqueous solvents, their further coordination chemistry would probably develop quickly. There is also no evidence that a bismuth derivative BiS_4^{3-} can be prepared in solution, probably owing to the reluctance of Bi to assume the 5+ oxidation state, coupled with the inherent weakness of the Bi=S double bond.

In addition, the tetraselenide analogs are not very well known. Several derivatives including $Na_3AsSe_4{\cdot}9H_2O$ [17], K_3SbSe_4 [18a], and K_3AsSe_4 [18b] have been isolated recently, but little systematic development has taken place. Workers in our laboratories have also obtained NMR evidence for the formation of PSe_4^{3-} in solution but have been unable to isolate a product [19]. In addition a number of solids containing compositions related to these empirical formulas have been prepared such as Cu_3PSe_4 [20]. However, these compounds are dense solids, and generally do not contain recognizable molecular fragments. To our knowledge, no telluride derivatives have been reported.

2.1.2. Synthesis of other anions

The reaction of sulfide sources with other binary compounds leads to a variety of new anionic salts. For example, reaction of a trivalent group 15 sulfide with S^{2-}

leads to the formation of ES_3^{3-}

$As_2S_3 + Na_2S \rightarrow Na_3AsS_3$

These thioarsenites and thioantimonites were probably first prepared by Berzelius [21], but were well characterized in the 1970s [22]. Rauchfuss has succeeded in preparing the PPN^+ salt of the AsS_3^{3-} anion from ethanol and water, and states that it is more stable than the ammonium salt and is soluble in polar organic solvents [23]. He has used it to prepare several Ti and Mo complexes (vide infra), but further reaction chemistry of this promising reagent has not been reported.

Polysulfides and polyselenides are also soluble in polar aprotic solvents [24], and readily attack mixed 15/16 binary compounds. For example, polyselenides readily react with P_4Se_4 leading to the first example of a structurally characterized phosphorus selenide anion. This was isolated from DMF using a quaternary phosphonium counterion [25] (Fig. 1):

$P_4Se_4 + 3\ Se_4^{2-} \rightarrow 2\ P_2Se_8^{2-}$

Salts of other mixed cages, such as arsenic selenides, can be prepared in the same way [26] (Fig. 2):

$As_4Se_4 + Se_4^{2-} \xrightarrow{DMF/PPh_4Br} As_4Se_6^{2-}$

Further systematic work in this area is badly needed. For example, the use of

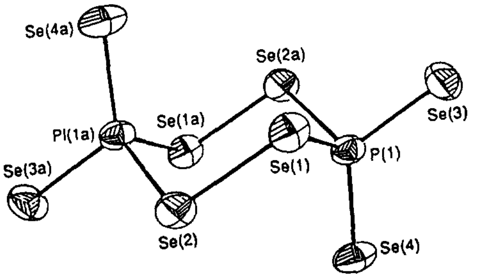


Fig. 1. Thermal ellipsoid plot of $P_2Se_8^{2-}$ (reprinted from ref. 25).

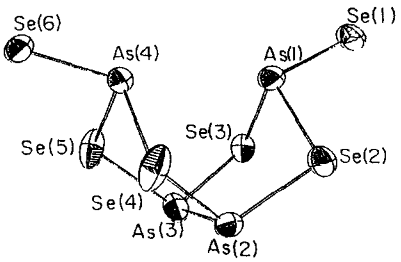


Fig. 2. Thermal ellipsoid plot of $As_4Se_6^{2-}$ (reprinted from ref. 26).

polytellurides to produce 15/16 molecules containing tellurium has been achieved only recently in our laboratories [27]. The nucleophilic attack of polytelluride on arsenic telluride glass leads to the formation of $As_2Te_6^{2-}$ in good yield (Fig. 3). This compound has been reported previously [28], but this procedure is considerably simpler and cheaper to carry out:

$$\text{“}As_4Te_4\text{”} + Te_4^{2-} \xrightarrow{DMF+PPh_4Br} As_2Te_6^{2-}$$

There is one other category of mixed 15/16 anions which deserves mention. This is the group of phosphorus sulfide anions which contain one organic group appended to the phosphorus atoms. Much of the developmental work involving these molecules has been performed by Hahn and co-workers [29]. These organo-functionalized anions are not strictly within the scope of this review, but they are prepared in the same manner as the soluble anions:

$$({}^tBuPS_2)_2 + Na + S_8 \rightarrow {}^{2t}BuPS_3^{2-}$$

$${}^{2t}BuPS_3^{2-} + 2\ Me_3SiCl \rightarrow {}^tBuP(S)(SSiMe_3)_2$$

In addition they provide a useful and practical link between the well known dithiophosphonates and the binary anions. It is anticipated that the organic group will impart substantial stability to these anions and make them considerably more useful in terms of further chemistry. The organic group serves to lower the overall charge, as well as provide some steric hindrance to prevent bulk polymerization and precipitation. Thus these organo-functionalized anions should find use as synthetic reagents in the near future.

2.1.3. *Attack of sulfides on element halides*

The chalcogenide anions will also induce metathesis reactions with element halides to afford a number of unusual salts such as $Bi_2S_{34}^{4-}$ [30] (Fig. 4):

$$BiCl_3 + S_n^{2-} \rightarrow Bi_2S_{34}^{4-}$$

It was recently found that polychalcogenide dianions will also induce nucleophilic

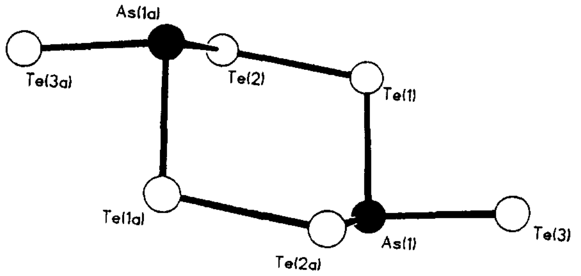


Fig. 3. Thermal ellipsoid plot of $As_2Te_6^{2-}$.

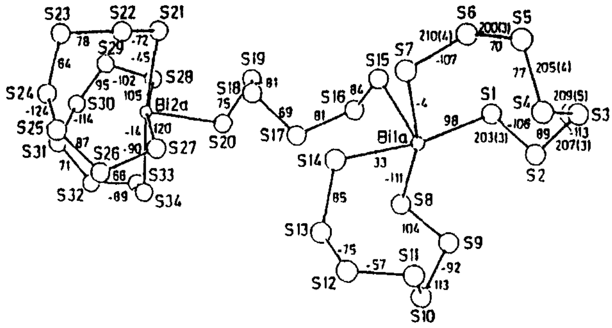


Fig. 4. Thermal ellipsoid plot of $Bi_2S_{34}^{4-}$ (reprinted from ref. 30).

substitution on haloanions as well leading to several novel binary anions such as $[SAsS_5]^-$ [31]. However, substitution is often incomplete and this reaction type usually leads to some very interesting mixed group 15 halosulfide anions such as $[As_2SCl_5]^-$:

$$[As_2Cl_8]^{2-} + S_5^{2-} \rightarrow [SAsS_5]^- + [As_2SCl_5]^-$$

An unusual reaction of sulfide with PCl_3 leads not only to displacement of halide by sulfide, but reduction of phosphorus with the formation of P–P bonds as well [32a]:

$$PCl_3 + Na_2S{\cdot}9H_2O \rightarrow Na_4P_2S_6$$

$$PCl_3 + HS^- \rightarrow HP_2S_5^{3-}$$

Under appropriate conditions, a protonated mixed valent species can be isolated [32b]. The metathesis reaction type has generally not been used extensively, presumably because it usually leads to rapid precipitation of amorphous binary solids. However, the presence of such fascinating compounds as $Bi_2S_{34}^{4-}$ implies that there is a large number of exciting compounds awaiting isolation and characterization. Once again the use of non-aqueous solvents seems very important to any successful further exploration of this reaction type.

2.2. *Base induced disproportionation*

Like homonuclear compounds possessing strained rings, the neutral binary cages are susceptible to base induced disproportionation. The first reported example of this type of reaction involving 15/16 compounds was probably the work of Behrens and Glasser, involving the disproportionation of As_2S_3 in liquid ammonia [33]:

$$As_2S_3 + NH_3 \rightarrow (NH_4)_3AsS_3 + As_4S_5NH$$

A number of new anions have been isolated by reacting mixed cages with moderate bases. For example, pyridine attacks P_4S_{10} to induce disproportionation to $P_2S_8^{2-}$ and several unidentified products [34]. Similarly, piperidine attacks As_4S_4 to form the arsenic sulfide anion $As_4S_6^{2-}$ [35] (Fig. 5):

$$py + P_4S_{10} \rightarrow [py_2H]_2[P_2S_8]$$

$$pip + As_4S_4 \rightarrow [C_5H_{12})]_2[As_4S_6]$$

Other bases such as ethylenediamine also induce the same types of disproportionation reactions [36] (Fig. 6):

$$en + As_2S_3 \rightarrow [enH_2]_3[As_3S_6]\cdot 6en$$

It should be noted that in each case the counterion is the protonated form of the original nitrogenous base. The source of the proton is not clear. It is postulated that in some cases it arises form adventitious water in the basic solvent, but this is far from certain. The protons may also arise form the decomposition of the nitrogenous base on attack of the main group cage. This would be directly analogous to the formation of ammonium polysulfide salts on base induced attack of ammonia on elemental sulfur in liquid ammonia [37]. Other bases such as azide, may induce

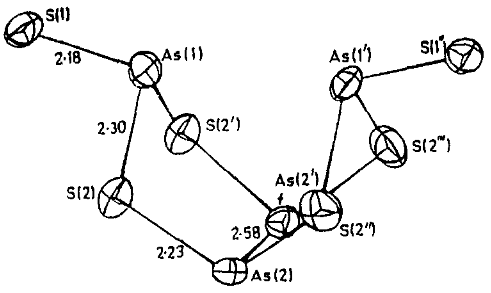


Fig. 5. Thermal ellipsoid plot of $As_4S_6^{2-}$ (reprinted from ref. 35).

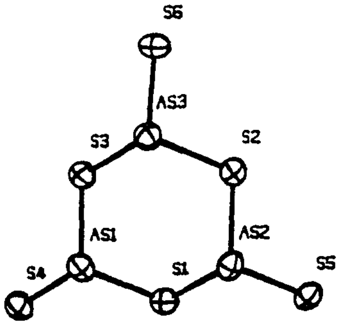


Fig. 6. Thermal ellipsoid plot of $As_3S_6^{2-}$ (reprinted from ref. 36).

disproportionation as well [38]:

$$P_4S_{10}+N_{3-}\rightarrow P_2S_{10}^{2-}+N_2$$

The use of simple reduction of mixed phases also shows great promise. This route has not been extensively explored, but recent results suggest that it may be a useful synthetic pathway to new mixed clusters. Several years ago Haushalter demonstrated the effectiveness of this method with the isolation of $As_{10}Te_3^{2-}$ as its PPh_4^+ salt [39] (Fig. 7):

$$As_2Te_3+K\xrightarrow{en+PPh_4Br}[PPh_4]_2[As_{10}Te_3]$$

Similarly, reduction of As_2Se_3 with elemental potassium leads to the formation of $As_2Se_6^{2-}$ simply, and in good yield [26]. We have recently found that simple reduction of antimony selenide in DMF leads to formation of a salt with the formula $[PPh_4]_4[Sb_{12}Se_{20}]$ [40] (Fig. 8):

$$2\,K+Sb_2Se_3\xrightarrow{DMF+PPh_4Br}[PPh_4]_4[Sb_{12}Se_{20}]$$

By the classical definition, this is the largest molecular Zintl ion characterized.

Haushalter and co-workers have reopened a major route to soluble anions by using electrochemical reduction of an Sb_2Te_3 alloy cathode to generate $[Sb_4Te_4]^{4-}$ and $[Sb_9Te_6]^{3-}$ [41]. The cathodic dissolution of a main group electrode is the original method used by Zintl to make main group polyanions [42], and has now been resurrected to make novel mixed element clusters. Once again, it is likely that a very large of number of other exciting molecules can be isolated via reduction of binary phases, depending on factors such as solvent, reducing agent and counterion.

A very unusual compound containing a P–P bonded square has been isolated from a reaction involving attack of a polysulfide solution on white phosphorus [43] (Fig. 9):

$$P_4+4(Et_3NH)HS_{2.5}\rightarrow(Et_3NH)_4(P_4S_8)$$

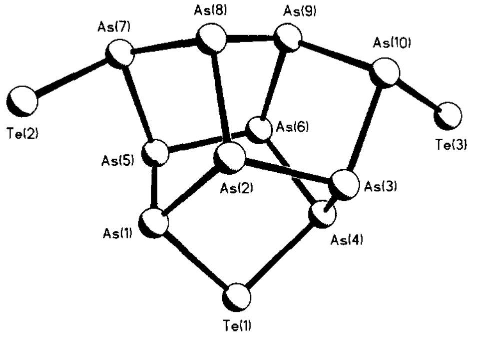


Fig. 7. Thermal ellipsoid plot of $As_{10}Te_3^{2-}$.

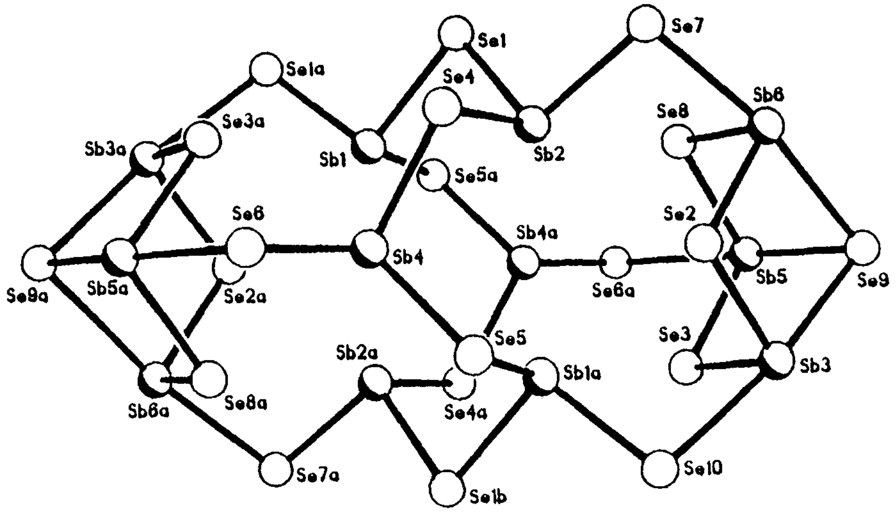


Fig. 8. Thermal ellipsoid plot of $Sb_{12}Se_{20}^{4-}$ [40].

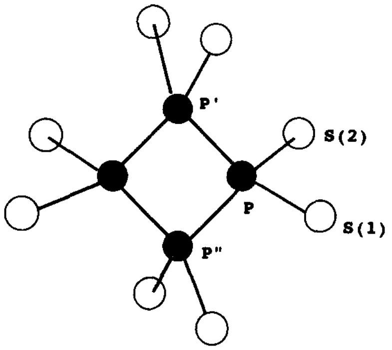


Fig. 9. Thermal ellipsoid plot of $P_4S_8^{4-}$.

To our knowledge the reaction of polychalcogenides on other pure group 15 elements has not been further explored, but the potential for success may be lessened owing to the decreased reactivity of the heavier group 15 elements.

Finally, Rauchfuss and co-workers have applied an unusual twist to this kind of reaction by isolating $Sb_2S_{15}^{2-}$ in good yield via the reaction of antimony metal with sulfur powder and magnesium metal in a strongly coordinating solvent such as *N*-methylimidazole [44] (Fig. 10).

$$Sb + xsS + Mg \xrightarrow{N\text{-MeIm}} [Mg(N\text{-MeIm})_6][Sb_2S_{15}]$$

It is postulated that some of the sulfur dissolves in the basic solvent and attacks the antimony to form Sb_2S_3 in situ. At the same time the magnesium reduces more of the sulfur which attacks the Sb_2S_3. This methodology is quite new, and has been

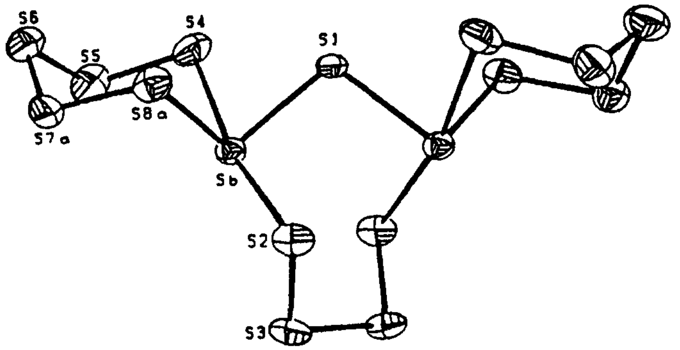


Fig. 10. Thermal ellipsoid plot of $Sb_2S_{15}^{2-}$ (reprinted from ref. 42).

shown to be effective with a number of other main group metals, so further new 15/16 clusters may be anticipated.

2.3. Extraction of Zintl anions

A number of unusual mixed 15/16 anions have been prepared by the extraction of pre-made anions from Zintl phases. The Zintl phases are a fascinating class of solids which are usually prepared by the high temperature reaction of a post-transition element with an alkali metal [45]. There is complete electron transfer from the electropositive alkali metal to the more electronegative main group element, resulting in the formation of a salt-like phase containing an alkali metal cation and an anionic main group cluster. These clusters can be extracted into strongly basic solvent such as ethylenediamine (en), and isolated using a suitable sequestering agent for the alkali metal countercation [45b]. The most common countercation is an alkali metal complex of 2,2,2 crypt, and this has lead to the formation of a number of novel mixed 15/16 anions. Belin and co-workers have exploited this technique to extract a number of arsenic selenides into en and crystallize them using either crypt or quaternary counterions [46] (Fig. 11):

$$K_xAs_ySe_z \xrightarrow{\text{en}+\text{PPh}_4^+} As_{10}Se_3^{2-}$$

$$K_xAs_ySe_z \xrightarrow[\text{2,2,2 crypt}]{\text{en}} As_2Se_6^{2-}$$

This method seems very well suited for the preparation of heavy post-transition element clusters, since a large number of Zintl phases involving these elements have been prepared (vide infra). However, there are some experimental limitations. Many Zintl phases consist of extended solids and would not be expected to be very soluble. In most of the phases which do contain discrete anions, the clusters have very high charge densities, and hence would be either insoluble or unstable in solution.

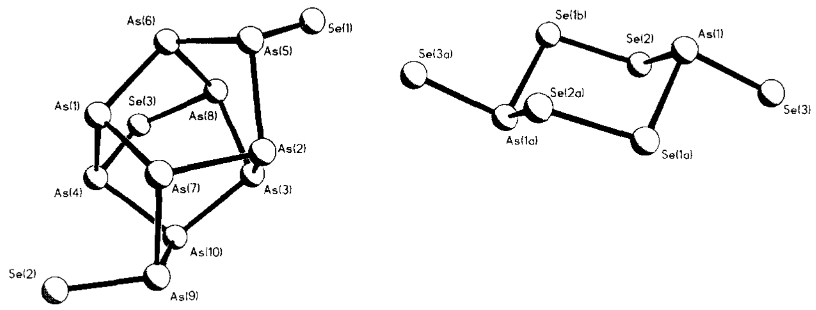


Fig. 11. Thermal ellipsoid plots of $As_{10}Se_3^{2-}$ and $As_2Se_6^{2-}$.

Nevertheless, there are a number of salts which appear to be very suitable for use as soluble reagents.

3. SOLID STATE PHASES

Without question, the most extensive and systematic synthetic work involving mixed 15/16 compounds has been done involving compounds in the solid state. The predominant chemical type is anionic chains or clusters of group 15 and 16 elements with alkali metal counterions. These are generally considered a subset of the broader class of Zintl phases. There are two significant synthetic entries to this chemistry. The more traditional and fully developed method involves melting a combination of an alkali metal with the appropriate amount of group 15 and 16 elements. The other method involves the synthesis of new ternary 1/15/16 phases in superheated solvents. This method is newer and less well developed, but in many ways has greater potential for chemical variation.

3.1. *Zintl phases from the melt*

The use of melts to prepare new solids is a useful and versatile synthetic method. It is especially useful for the s-block metal derivatives of the Zintl ions since the ternary mixtures tend to have relatively low melting points (often between 200 and 700°C). This allows reactions to be performed conveniently in quartz ampoules using either an intimate mixture of the pure elements, or a mixture of an alkali metal chalcogenide and a binary 15/16 solid [47]:

$$K_2S + Sb_2S_3 \xrightarrow{120^\circ C} K_2Sb_4Se_7 \ [47a]$$

$$K + Sb + 2Se \xrightarrow{650^\circ C} KSbSe_2 \ [47b]$$

$$2Ba + 2As + 5Se \xrightarrow{700^\circ C} Ba_2As_2Se_5 \ [47c]$$

The relatively low reaction temperatures also inhibit the formation of thermodynamically stable dense phases. Thus an enormous variety of new compounds has been isolated and characterized through the years by varying systematically the stoichiometry and identity of the three components [8]. This method is particularly well suited for combinations involving heavy elements, such as bismuth and tellurium [48], as ions containing these elements are often unstable in solution. Recently this method was extended to include ternary fluxes such as $A_xP_yS_z$ which provide both a reactant and a solvent medium for the formation of novel quaternary species [49]:

$$A_xP_yS_z + Bi \rightarrow ABiP_2S_7 \qquad A = K, Rb$$

The large number of ternary compounds prepared in the melt generally fall into two categories. One group is those which contain infinite chains or layers of the 15 and 16 elements, with the s-block metal cations occupying spaces between the layers or chains (Fig. 12). The other class is made up of those compounds which contain discrete molecules of mixed 15/16 anions along with alkali metal cations occupying holes in the lattice, stabilizing the anionic clusters through extensive ion pairing (Fig. 13). The extended chains usually consist of various 15/16 polyhedra which are corner or edge bridged by a chalcogenide atom. In general the compounds containing the discrete molecules contain a considerably higher percentage of s-block metal, which leads to more reduced anions. The molecules are discrete because the additional electrons have served to reduce 15–16 or 16–16 bonds. Thus, $BaSb_2Se_4$ consists of infinite one-dimensional double chains of edge and corner sharing $SbSe_3$ and $SbSe_4$ groups [50] (Fig. 14), while $Ba_4Sb_4Se_{11}$ is made up of well separated $SbSe_3^{3-}$ pyramids, $Sb_2Se_4^{2-}$ dimers and Se_2^{2-} dumbbells [51] (Fig. 15).

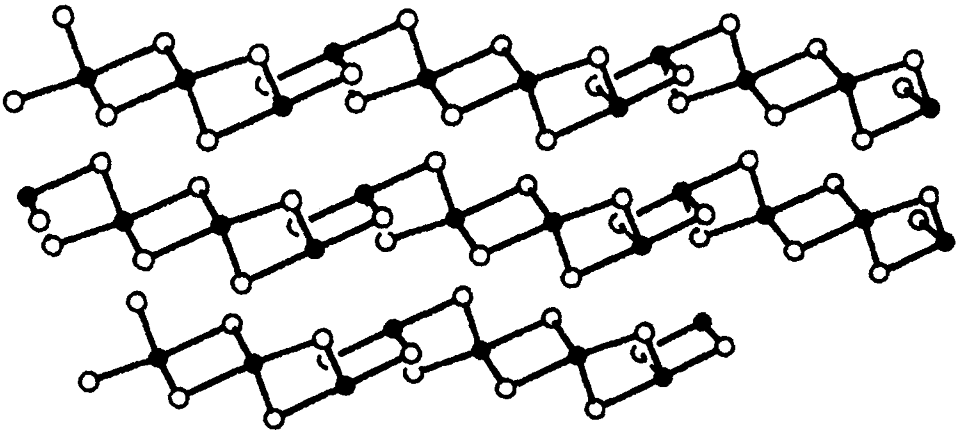


Fig. 12. Computer drawing of $KSbSe_2$ [47b], showing the infinite chains of antimony selenide between which reside the K^+ ions (○, selenium atoms; ●, antimony atoms, potassium ions not shown).

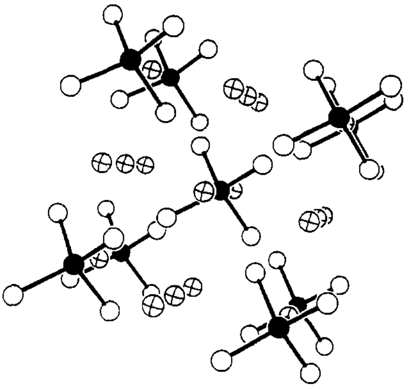


Fig. 13. Computer drawing of K_3SbS_4 [16b] highlighting the large amount of ion pairing between the highly charged anionic clusters and the large number of countercations.

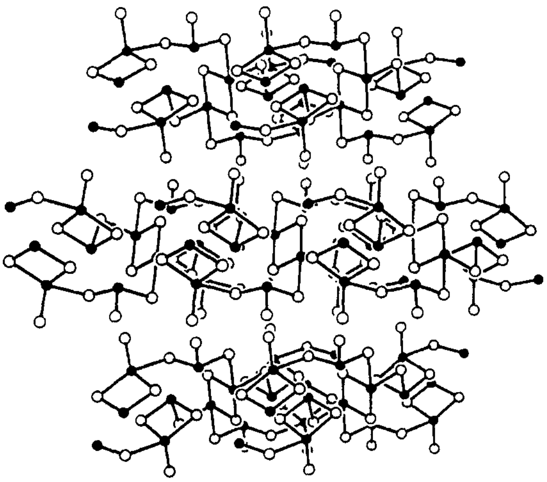


Fig. 14. Computer drawing of the anionic chains of $BaSb_2Se_4$ showing the edge and corner sharing $SbSe_3$ and $SbSe_4$ groups linking together to form an infinite chain [50] (○, selenium atoms; ●, antimony atoms; barium atoms not shown).

3.2. Covalent metal containing solids

There are a large number of solids which contain 15/16 compounds along with another metal, either a transition metal or a heavy post-transition metal. These compounds do not contain the clear charge separation of the s-block metals, and the bonding is considerably more covalent, leading to solids which are often more densely packed phases. However, they often contain recognizable fragments of 15/16 clusters and, in that context, are mentioned here.

Unquestionably, the largest class of compounds of this type is the sulfosalt minerals [1]. These are very stable minerals which consist of heavy metal, usually

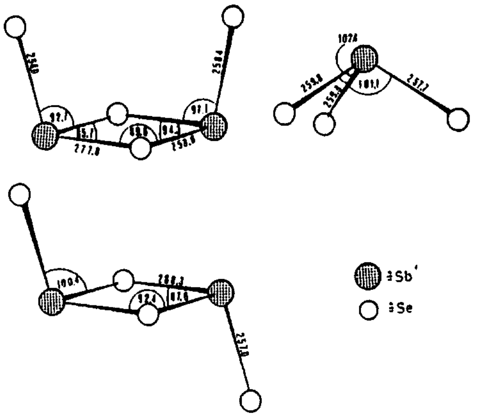


Fig. 15. Computer drawing of the anionic portions of $Ba_4Sb_4Se_{11}$. Note the well separated anionic fragments with no interaction between them [51].

Ag, Cu, Hg or Pb, complexes of φ-tetrahedra of trivalent ES_3^{3-} (E=As, Sb, Bi). Examples of these formulas include $Cu_{12}Sb_4S_{13}$ (tetrahedrite), $Pb_2Bi_2S_5$ (cosalite) and $HgSb_4S_8$ (livingstonite). Most of these are true minerals, formed in the earth, most probably by direct reaction of the metal sulfide with a mixed 15/16 sulfide or oxide at elevated temperatures. Alternatively, they may have been formed through hydrothermal reaction in superheated water, probably with acid as a mineralizer [52]. There are an enormous number of these sulfosalt minerals which generally have very complex structures [53] (Fig. 16). Several schemes to classify these structures systematically have been reported. However, very few attempts to systematize and extend further the synthesis of these compounds to new species have been described. This area may be of interest from the point of view of artificial or cultured minerals. This would be particularly significant if any sulfosalts were found to have commercial interest, since naturally occuring sulfosalt crystals are often not of good quality.

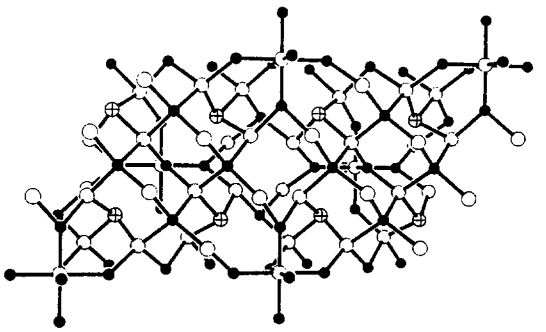


Fig. 16. Computer drawing of several repeat units of $Cu_{12}Sb_4S_{13}$ (tetrahedrite). Note the φ-pyramidal SbS_3^{3-} groups linking the Cu(I) groups. Note also the lone S^{2-} group surrounded by an octahedron of Cu(I) atoms (○, sulfur atoms; ●, copper atoms; ⊕, antimony atoms). Coordinates taken from ref. 53.

Another class of solid state compounds is the transition metal phosphorus sulfides. There are many derivatives of these compounds and some have quite fascinating structural and electronic properties. There are a number of early transition metal (V, Nb, Ta) phosphorus sulfides which are usually prepared by reaction of the elements at high temperature. These products generally consist of a series of face-sharing trigonal prismatic dimers of formula M_2S_8, linked by various phosphorus sulfide anions [54]. The biprisms tend to link together forming one-dimensional chains, and the crosslinking by the phosphorus sulfide groups leads to the formation of channels and layers in the solid (Fig. 17). The anions range from PS_3^{3-} to $P_4S_{13}^{6-}$, depending on the identity and ratio of the transition metal [55] (Fig. 18). Typifying the fascinating characteristics of this class of compounds is the structure of $Ta_4P_4S_{29}$ [55c]. The unit cell of this structure contains four tantalum sulfide face-sharing biprisms bridged by PS_4^{3-} groups. This connectivity pattern creates a large ring, which is an infinite open channel passing through the center of the unit cell. However, this channel is filled with an infinite helical spiral of elemental sulfur, having an S_{10} repeat unit (Fig. 19). The electronic and bonding properties of this class of compounds have been investigated in considerable detail [56].

One interesting subgroup of the M/P/E system is the metal containing phosphorus chalcogenide glasses, which are under investigation as ionic conductors [57]. These glasses usually contain an alkali metal such as Li^+ but can often remain Ag^+. The glasses are prepared by quenching the melts leading to solids having formulas like $Ag_4P_2S_7$ and $Ag_7P_3S_{11}$. They usually have only short-range order and are characterized by careful solid state NMR studies [57b]. However, a number of single-crystal X-ray studies have been carried out indicating the formation of solids containing various combinations of phosphorus chalcogenide fragments such as PE_4^{3-} and $P_2E_7^{4-}$ (E = S, Se) [57c].

Finally there is an extensive and well known group of solids which are obtained from the heating of almost any first row transition metal with elemental phosphorus and sulfur having the formula MPS_3. The first members of this class of compounds

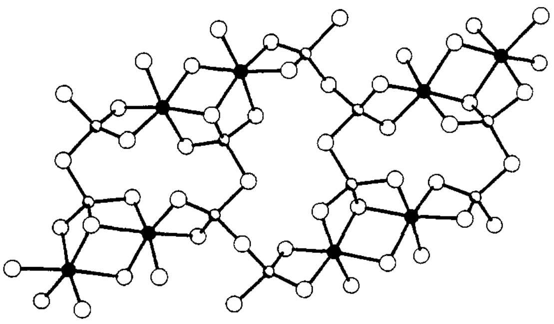


Fig. 17. Computer generated drawing of $V_2P_4S_{13}$ (○, sulfur atoms; ●, vanadium atoms; ◐, phosphorus atoms). Note the bridging $P_3S_{10}^{5-}$ groups linking the metal centers together [55b].

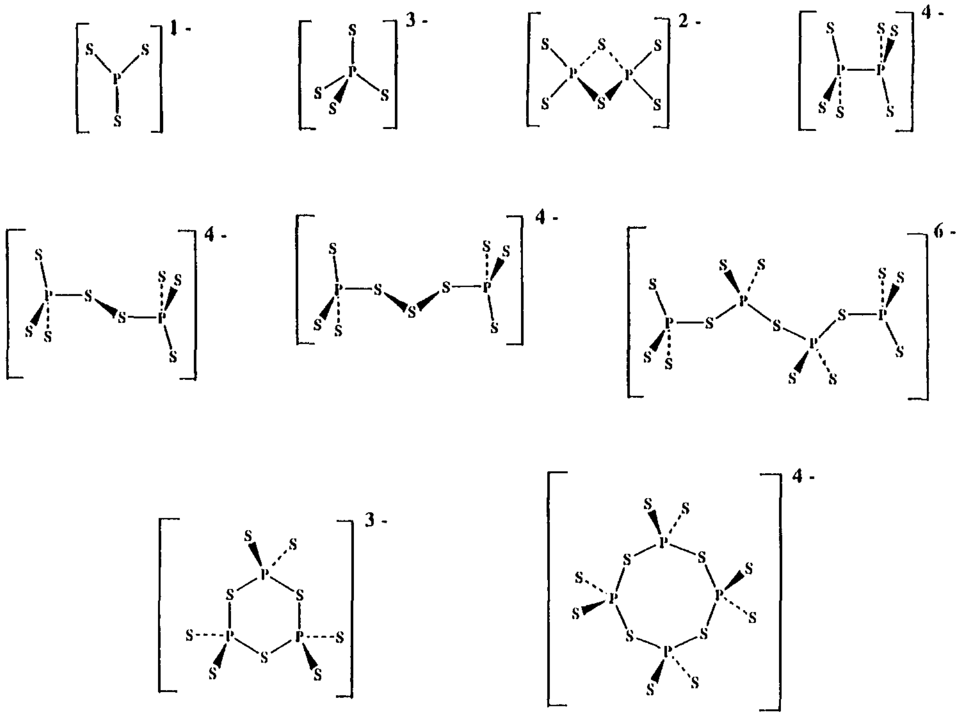


Fig. 18. Some of the known anionic phosphorus sulfide structures.

were prepared and characterized in 1965 [58]. They all contain M^{2+} ions surrounded by $P_2S_6^{4-}$ groups arranged in such a fashion as to provide an octahedral coordination environment around the metal center (Fig. 20). The net effect is to create a layered compound not unlike MoS_2. Accordingly, this structural property has been exploited to great advantage by Brec and co-workers who have successfully altered the chemical and electronic properties of the solids by the use of extensive intercalation chemistry. These low dimensional compounds have some very unusual physical properties and may ultimately find a number of practical uses, such as ionic conductors [59]. It should be noted that reactions of later d-block metals and f-block metals often lead to formation of dense phases with PS_4^{3-} groups [60]:

$$Ln+P+xsS \xrightarrow{900°C} LnPS_4 \quad Ln=La,\ Ce\ Pr,\ Y,\ Gd,\ Tb,\ Yb\ etc.$$

These compounds are probably best treated as substituted metal sulfides.

3.3. *Solids from superheated fluids*

A synthetic method which is somewhat newer involves the reaction of appropriate starting materials in superheated fluids. Superheated fluids are those which

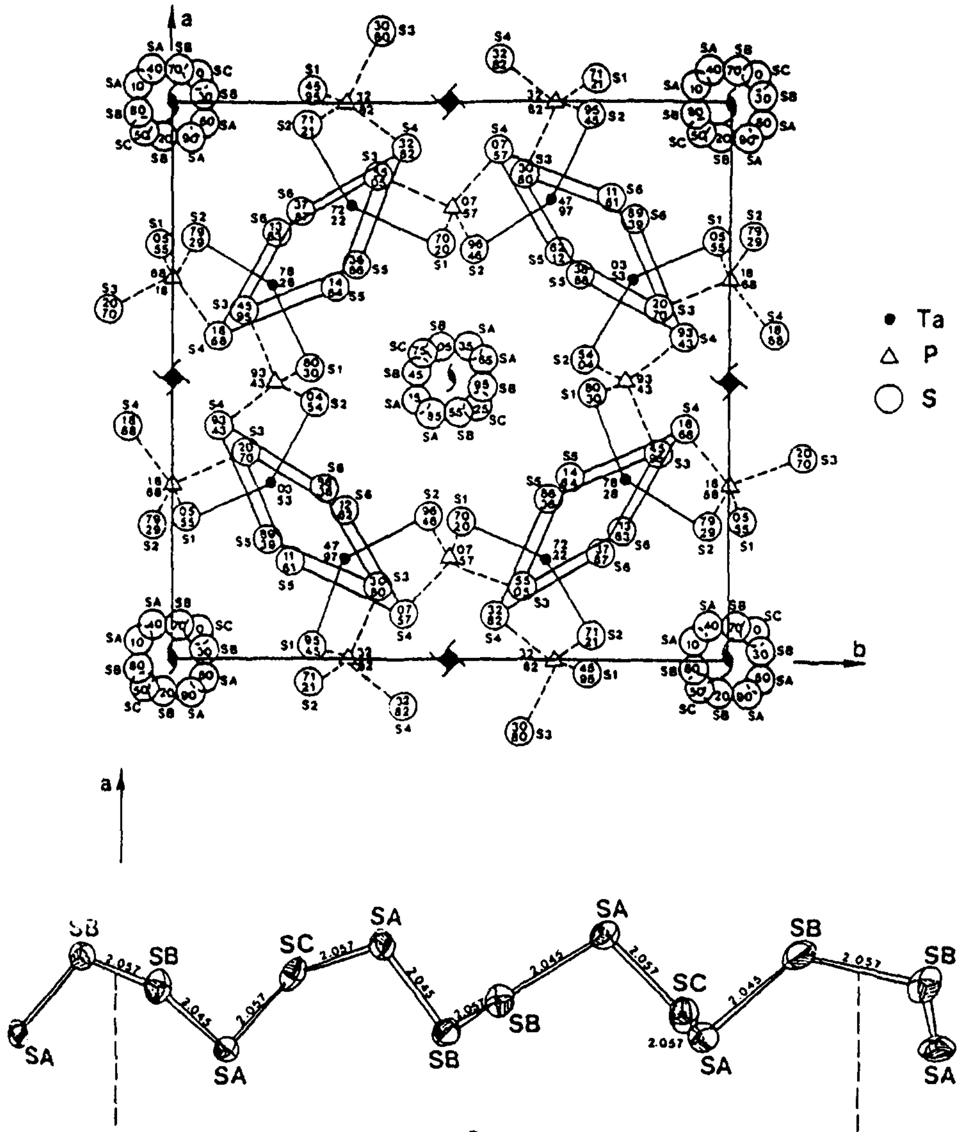


Fig. 19. Schematic view of the structure of $Ta_4P_4S_{29}$. Note the tantalum–phosphorus sulfide framework which generates an open channel which is occupied by the infinite spiral of polymeric sulfur (reprinted from ref. 56).

are heated above their boiling point, with sufficient pressure applied to contain the solvent in a fluid state. The superheated fluids have a number of unusual properties which render them different from the normal liquid phase. They also offer a number of advantages for crystal growth, and provide a medium for the synthesis of solids

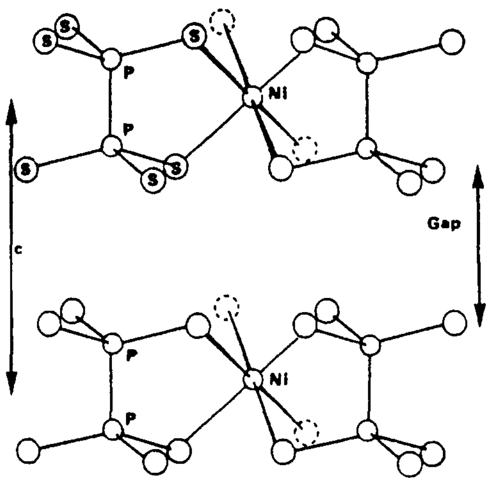


Fig. 20. View of $NiPS_3$ showing how the $P_2S_6^{4-}$ groups are side bonded to the Ni^{2+} centers creating an infinite slab which is responsible for the laminar structure and properties of this structural type (reprinted from ref. 59).

at temperatures considerably below that of conventional solid state melt reactions [61]. The lower reaction temperatures gives access to a new thermal regime where directional covalent bonding still predominates. In addition, the fact the chemistry is done essentially in the solution phase allows all of the experimental flexibility available to the traditional solution chemist. Thus polarity, temperature, stoichiometry, counterion and any other parameter can be varied as the situation demands. This methodology has seen the most development using superheated water, but recently a variety of other solvents has been used successfully as well. Indeed, once techniques have been developed to contain the fluids under the appropriate pressure, there is no limit to the solvent system which may be used. This synthetic technique is poised for rapid expansion in the next few years.

For the synthesis of mixed 15/16 compounds, dramatic results have been achieved using superheated water or methanol as the solvent medium. Water was probably the first superheated solvent used to prepare alkali metal salts of mixed 15/16 anions [62]. More recently, Sheldrick and co-workers have shown that a large number of ternary phases can be prepared easily by the simple reaction of an alkali metal carbonate with a binary 15/16 phase [63]:

$$Rb_2CO_3 + Sb_2Se_3 \xrightarrow{175°C,\ MeOH} RbSb_3Se_5$$

$$M_2CO_3 + As_2Se_3 \xrightarrow{130°C,\ MeOH} MAsSe_2 \qquad M = K, Rb, Cs$$

The carbonate serves as a convenient reducing agent leading to the formation of a mixed 15/16 anion and main group element oxides upon heating. This technique has led to a wide variety of new ternary phases, which are mostly infinite anionic chains of 15/16 fragments of varying degrees of connectivity, with alkali metal cations occupying spaces between the chains (Fig. 21). If a countercation other than an alkali metal is present, such as Me_4N^+, then more open frameworks can be attained, with the larger counterions occupying the open sites [64] (Fig. 22). These may ultimately serve as forerunners to a new class of microporous solids:

$$Me_4NSH + Sb_2S_3 \xrightarrow{180°C,\ H_2O} [Me_4N][Sb_3S_5]$$

We have recently demonstrated that superheated ethylenediamine is also a suitable medium for synthesis of new 15/16 compounds [65]. It was found that reaction of potassium selenides with a As_2Se_3 leads to the formation of several ternary arsenic selenides such as K_3AsSe_4 and $K_4As_2Se_5$:

$$3\ K_2Se_3 + As_2Se_3 \xrightarrow{300°C\ en} 2\ K_3AsSe_4$$

However, if an alkaline earth metal is used as the reducing agent, en chelates to the

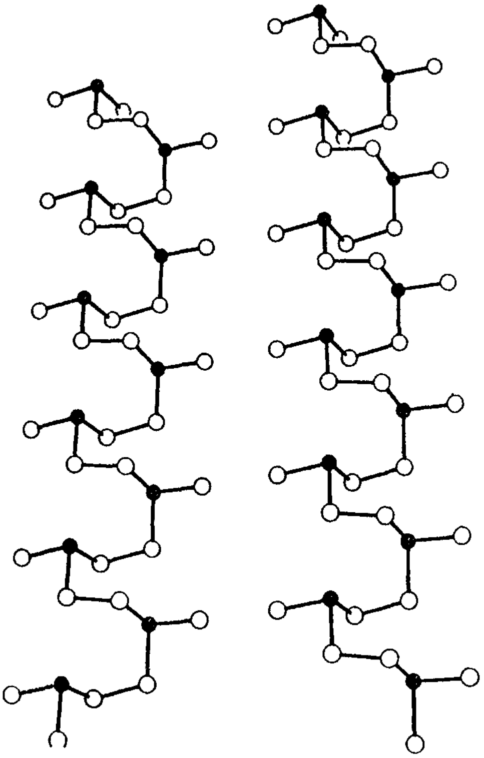


Fig. 21. Computer generated drawing of the anionic portion of $KAsSe_3$ showing the double-stranded infinite chains created by the Se–Se bond formation (○, selenium atoms; ●, arsenic atoms; potassium ions not shown) [63f].

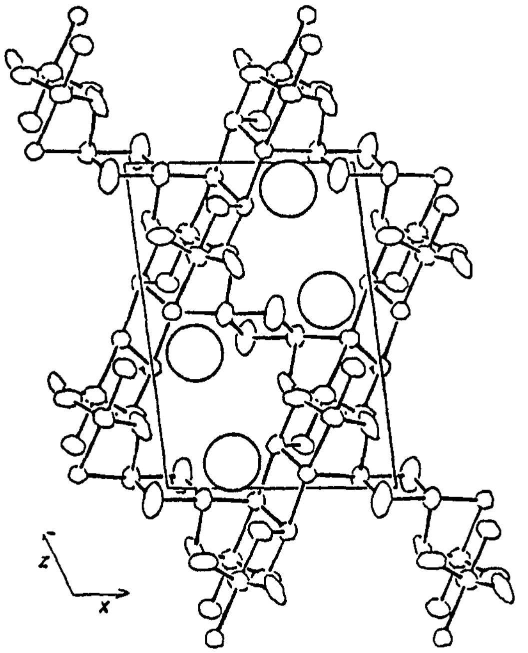


Fig. 22. View of the anionic framework portion of $(Me_4N)(Sb_3S_5)$ showing the microporous voids occupied by the quaternary ammonium cations (large circles) (reprinted from ref. 64a).

divalent cation, generating a large doubly charged counterion. Variation of stoichiometry and reaction conditions leads to the formation of new arsenic selenides which are molecular in nature, like $[Ca(en)_4]_2[As_4Se_6]$ and $[Ca(en)_4]_2[As_2Se_7]$ (Fig. 23):

$$2\,Ca + As_2Se_3 + 5\,Se \xrightarrow{300^\circ C\ en} [Ca(en)_4]_2[As_2Se_7]$$

We have also been successful in incorporating transition metals into mixed 15/16 containing solids using supercritical fluids. Recently workers in our laboratories discovered that soluble arsenic sulfides react with copper powder in supercritical ethylenediamine to produce two new quaternary phases containing Cu(I) linked by AsS_3^{3-} groups and sulfides. This connectivity pattern produces one compound which is a layered species and another containing a complex three-dimensional net. Both are anionic, with alkali metal cations located between the layers (Fig. 24), or in infinite channels passing through the nets [66] (Fig. 25):

$$Cu + KAsS_2 \xrightarrow{300^\circ C\ en} KCu_2AsS_3 + KCu_4AsS_4$$

Preliminary results indicate that many other metals and mixed 15/16 combinations also react to form new quaternary phases in superheated amines. It is hoped that this technique, which is only in its infancy, may lead to new structures inspired by the enormous variety of sulfosalts reported in the literature.

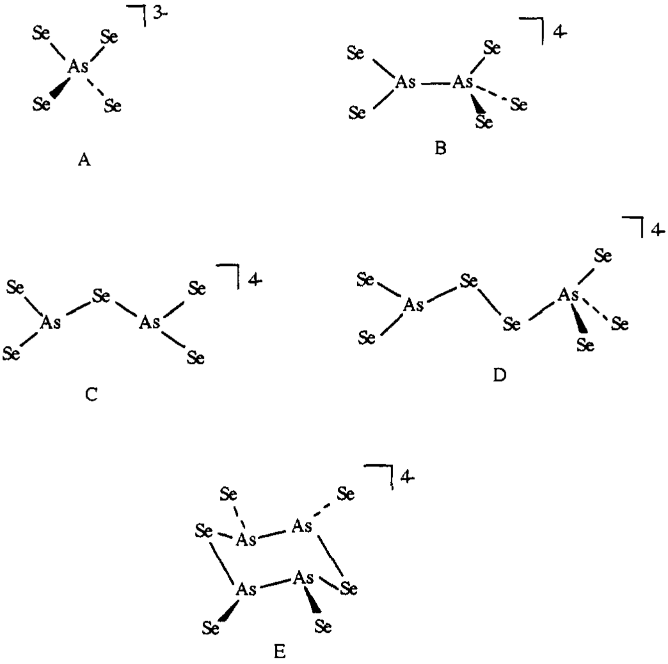


Fig. 23. Schematic drawing of some of the arsenic selenide anions which can be prepared in supercritical ethylenediamine: A, $AsSe_4^{3-}$; B, $As_2Se_5^{4-}$; C, another structural isomer of $As_2Se_5^{4-}$, D, $As_2Se_7^{4-}$; E, $As_4Se_6^{4-}$.

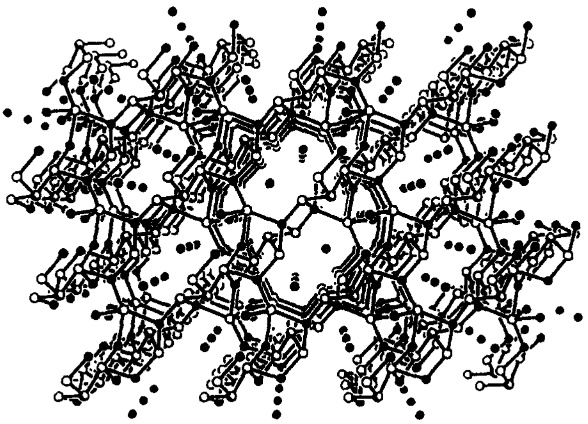


Fig. 24. View of KCu_4AsS_4 showing the linking of Cu(I) ions by AsS_3^{3-} groups as well as S^{2-} groups which serve to create a complex channeled structure, with the K^+ ions located in the channels (○, sulfur atoms; ●, copper atoms; ◐, arsenic atoms; filled circles in channels, potassium ions) (reprinted from ref. 66).

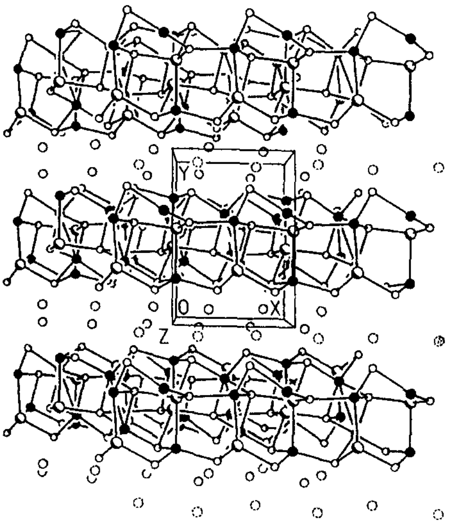
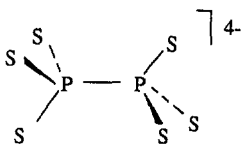


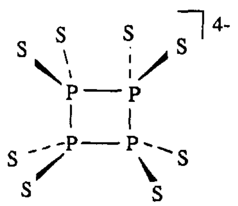
Fig. 25. View of the layered structure of KCu_2AsS_3, showing the AsS_3^{3-} groups linking Cu(I) ions to form layers with K^+ located between the layers (atoms denoted as in Fig. 24). (reprinted from ref. 66).

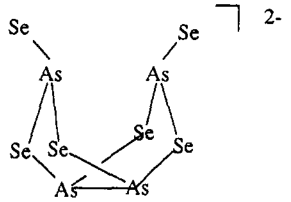
4. STRUCTURE AND BONDING

The structures of most of the reported anionic 15/16 compounds are well known because they are invariably accompanied by a single-crystal X-ray study. This has become de rigueur for any new compound in this field. Vibrational spectra usually contain bands at very low wavenumbers which can be assigned for relatively simple high symmetry systems, but are less informative for more complex systems. Multinuclear NMR can sometimes supply a great deal of structural information in the appropriate system, as phosphorus, selenium and tellurium all have $S = 1/2$ nuclei in significant natural abundance. Surprisingly, however, the solution study of mixed phosphorus selenides and phosphorus tellurides has not been undertaken in any detail. In fact, to our knowledge, the first phosphorus selenide anion was prepared only recently [25], and no phosphorus tellurides have been reported. Some of the other elements such as sulfur and arsenic possess NMR active nuclei but they are either quadrupolar or so low in natural abundance as to render them practically worthless for routine characterization purposes. Thus single-crystal X-ray diffraction is the most common and informative method of characterization.

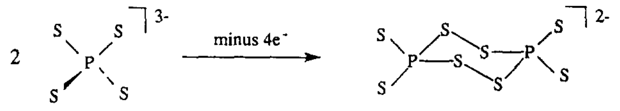
The known anionic 15/16 clusters can be divided into three structural categories. There are those containing 15–15 bonds, those containing 16–16 bonds, and those involving single chalcogenide atoms bridging between pnictide centers. There are several examples of cages containing group 15–15 bonds as part of the framework, such as $P_2S_6^{4-}$ [31], $P_4S_8^{4-}$ [41], and $As_4Se_6^{4-}$ [65].

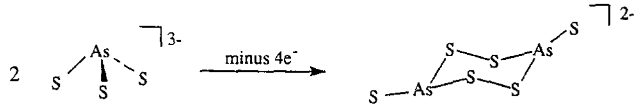






Many of the larger, pnictide rich clusters, such as $As_{10}Te_3^{2-}$ [39] and As_7Se_4- [45c] also contain As–As bonds building up the cage framework. In addition there are a number of species containing 16–16 bonds. Most compounds containing 16–16 bonds can be envisioned as oxidation products of simpler anions, such as $As_2Se_6^{2-}$ and $P_2S_8^{2-}$, which can be viewed as four-electron oxidation products of $AsSe_3^{3-}$ and PS_4^{3-} respectively:





Examples of this behavior occur in solid state compounds as well. Thus $KAsSe_2$ consists of infinite single chains of $ArSe_2-$ [63c] (Fig. 26), whereas $KAsSe_3$ contains arsenic selenide chains linked through Se–Se bonds, forming double-stranded infinite chains [63f] (Fig. 21). However, there are few examples of compounds containing traditional coordination-type structures with a polychalcogenide chain chelating to a central pnictide. One interesting example of this type of structure is $[SAsS_7]^-$, prepared from the reaction of $[As_2SCl_5]^-$ and S_5^{2-} [67] (Fig. 27). The eight-membered crown shaped ring compound is isoelectronic with S_8. Compounds such as $Bi_2S_{34}^{4-}$ and $Sb_2S_{15}^{2-}$ also have this type of structure, but they are far from common. The reluctance of polychalcogenides to form chelating complexes with group 15 elements is, of course, quite different from their behavior toward transition metals

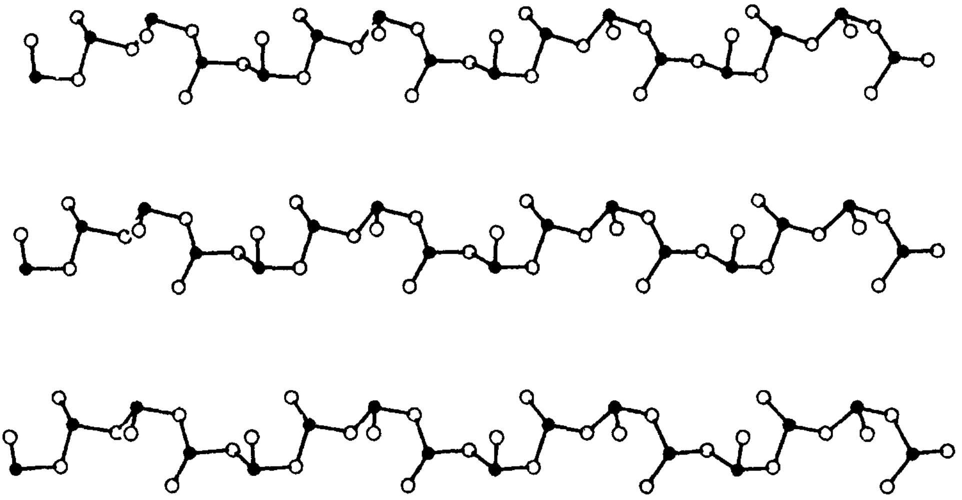


Fig. 26. Computer generated drawing of the anionic portion of $KAsSe_2$. Note the infinite chains created by the corner linking $AsSe_3^{3-}$ groups (○, selenium atoms; ●, arsenic atoms; potassium ions not shown) [63c].

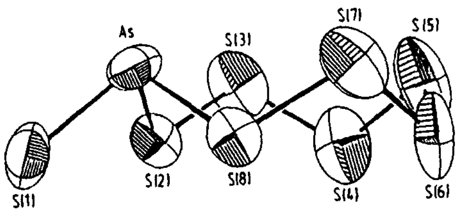


Fig. 27. Thermal ellipsoid plot of $[SAsS_7]^-$ (reprinted from ref. 67).

[2]. This difference in behavior may be due to the similarity in electronegativity of the group 15 and 16 elements, making the donor–acceptor relationship of traditional coordination compounds less favorable between phosphorus and selenium, for example. This postulate is supported by the observation that this type of chelating coordination of polychalcogenides is well known for the earlier, more metallic, main group elements such as Sn and In [68].

The most common structural motif of 15/16 anions in the solid state involves monochalcogenides bridging between trivalent or pentavalent pnictide centers. Phosphorus complexes usually adopt a four coordinate, pentavalent state, while arsenic and antimony show a reduced tendency to assume the pentavalent state and are often only trivalent. Arsenic and antimony also show an increased tendency to expand their coordination sphere and often assume a mixture of trigonal pyramidal (φ-tetrahedral) or SF_4 type coordination environments[1]. These φ-tetrahedra and φ-trigonal bipyramids can share edges or corners in a variety of orientations to generate an almost infinite variety of possible shapes, both in molecular and solid state compounds. In particular, the Zintl phases are replete with examples of this kind of structure. Most of the chains and layers can be characterized as a series of repeat units of one or more φ-tetrahedra and φ-trigonal bipyramids sharing edges and corners. As an illustration of some of the incredible structural diversity possible in these compounds, the compound $Cs_2As_8S_{13}$ consists of infinite chains of sulfide bridged, eight-membered rings formed by edge-sharing φ-AsS_3 tetrahedra [69] (Fig. 28). However, the related compound $[NH_4]_2[Sb_4S_7]$ is made of infinite chains of similar eight-membered rings but is bridged by other φ-SbS_3 tetrahedra instead of sulfide [70] (Fig. 29). Alternatively, the isoelectronic compound $K_2Sb_4S_7$ consists of φ-SbS_3 tetrahedra and φ-SbS_4 trigonal bipyramids which are edge sharing in a complicated fashion to form a three-dimensional net, with the alkali metal cations located in channels running through the nets [47a] (Fig. 30). In general antimony shows a greater tendency to expand its coordination sphere than arsenic. Thus φ-pyramids are more common for arsenic whereas antimony more often adopts a φ-trigonal bipyramidal coordination environment.

This structural flexibility is quite promising in terms of future applications, particularly in terms of specialized structural applications. For example, $RbSb_3Se_5$ consists of infinite sheets created by the edge- and corner-sharing of one φ-tetrahedron and two φ-trigonal bipyramids, to form the two-dimensional slabs [63a] (Fig. 31). However, replacing the Rb^+ cation with MeN^+ leads to an entirely different struc-

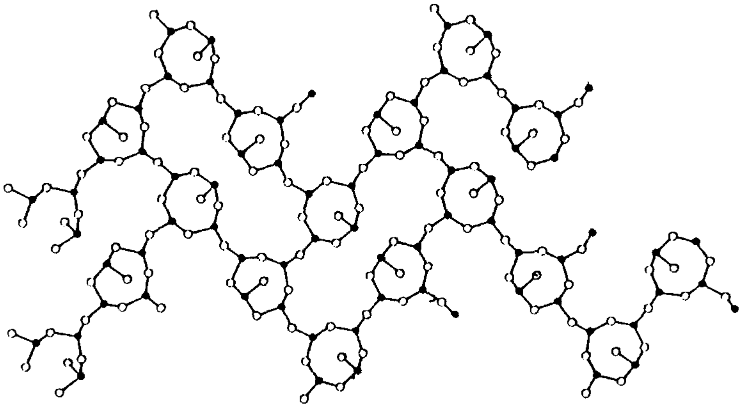


Fig. 28. View of anionic portion of $Cs_2As_8S_{13}$, showing the linked eight-membered rings created by edge-sharing φ-AsS_3 tetrahedra (○, sulfur atoms; ●, arsenic atoms; cesium atoms not shown) [69].

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[1] In this paper we adopt the convention used frequently by European workers in this area, whereby a φ-prefix before a structural descriptor delineates the geometrial shape with a stereochemically active lone pair included. Thus pyramidal NH_3 is said to have the φ-tetrahedral structure, see-saw SF_4 has a φ-trigonal bipyramidal structure, and square pyramidal IF_5 has a φ-octahedral structure, see [62].

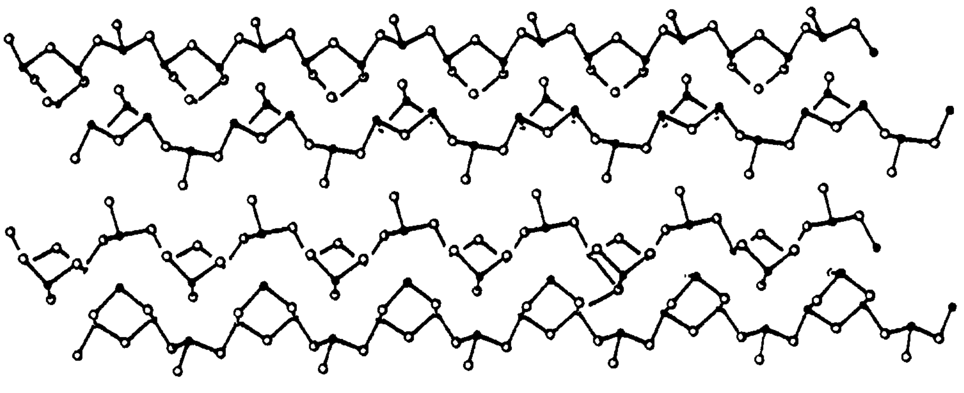

Fig. 29. Computer generated view of the anionic portion of $[NH_4]_2[Sb_4S_7]$. Note the similarity of the eight-membered rings to those in $Cs_2As_8S_{13}$. However, they are bridged by φ-SbS_3 tetrahedra instead of sulfide, creating an entirely different solid state structure (○, sulfur atoms; ●, antimony atoms; ammonium ions not shown) [70].

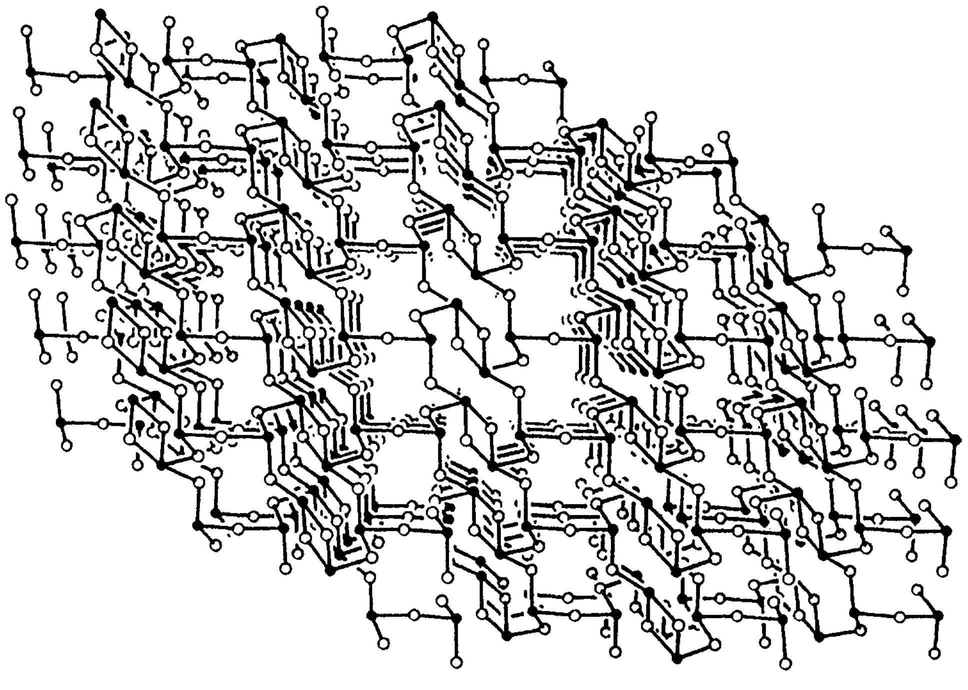

Fig. 30. Computer generated view of the anionic portion of $K_2Sb_4S_7$. Despite having the same anionic formula as $[NH_4]_2[Sb_4S_7]$, the structure consists of a complicated three-dimensional net with the alkali metal cations occupying channels running through the network (○, sulfur atoms; ●, antimony atoms; potassium ions not shown) [47a].

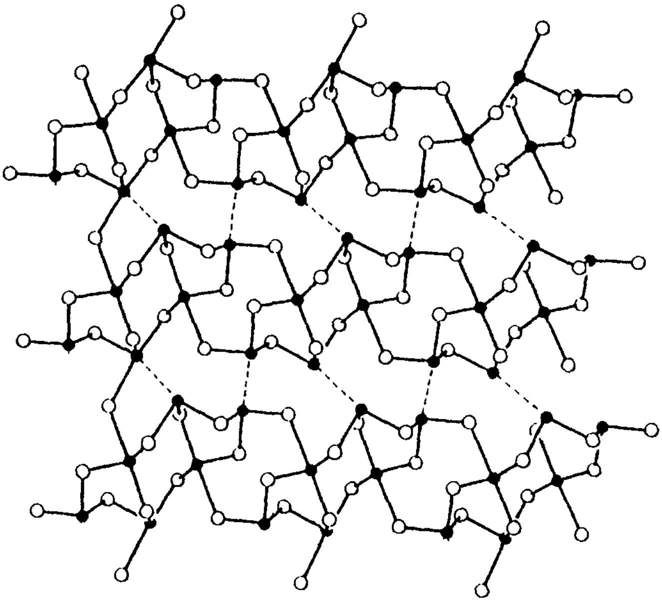

Fig. 31. Computer generated structure of the anionic portion of $RbSb_3Se_5$ showing the infinite slabs created by the linking of one φ-tetrahedron and two φ-trigonal bipyramids (○, selenium atoms; ●, antimony atoms; rubidium ions not shown) [63a].

ture, namely a three-dimensional solid formed by the edge sharing of all φ-trigonal bipyramids [64a] (Fig. 22). The cations are located in intersecting channels passing in two dimensions through the structure. The ability to control the structure of compounds with related formulas, by varying preparative conditions and counterions, suggests that this class of compounds may yield rationally designed solids in much the same way as low valent metal phosphates have done, using the highly successful methods of Haushalter [71].

The bonding in the 15/16 anions has not received a great deal of intensive investigation. One reason for this apparent lack of interest is that the bonding in most of these compounds appears to be decidedly straightforward. Many of the homoatomic cationic clusters, such as Te_6^{4+} [72] and Bi_9^{5+} [73], and the soluble Zintl anions of the more metallic p-block elements, such as Sn_9^{4-}, clearly possess delocalized cluster bonding [45b,74,75]. However, the same does not appear to be true for most of the mixed 15/16 anions. They generally appear to be valence precise molecules, with all of the valence electrons readily accounted for as bonding or lone pairs. There do not appear to be very many examples of delocalized bonds or multiple bonds, excluding some conventional terminal P=S or As=Se groups. In addition, nearly all lone pairs seem to be sterochemically active, appearing as vertices in pyramidal centers, or in an equatorial position of a trigonal bipyramid, as predicted by VSEPR theory. The bonding in these complexes can be explained using two-electron single bonds, and no theories of electron deficient bonding need be invoked.

One particular exception to all this is the series $BaBiSe_3$ and $BaSbTe_3$ [49b]. These compounds contain edge shared octahedra of EQ_6 forming tetrameric chains, which are linked by planar polychalcogenide chains (Fig. 32). The bonding in these compounds clearly cannot be explained using valence precise 8-N explanations, and delocalized arguments must be invoked. In support of this observation, these compounds have a metallic luster. Perhaps as the area expands and heavier, more metallic elements are investigated, delocalized bonding may be observed more frequently. There is also evidence that transition metal complexes will also not be so straightforward. However, for the moment, most of the mixed 15/16 anionic compounds are best described as classical species.

5. TRANSITION METAL COMPLEXES

The structural diversity, high charge density, large number of electron lone pairs, and topological complexity make the mixed 15/16 anionic clusters seem almost ideal ligands toward transition metals. Indeed, all these factors combine to render the related light element compounds such as phosphates excellent ligands, and useful building blocks for an enormous variety of complexes and solids. The conceptual link between soluble 15/16 anionic clusters and polychalcogenides generates a powerful allure, and there should be considerable potential payback for the successful development of the coordination chemistry of such versatile ligands of the formual $Q_xE_y^{z-}$. However, the heavier 15/16 polyanions have not enjoyed the same degree of extensive development as either the phosphates or the polychalcogenides. Some of

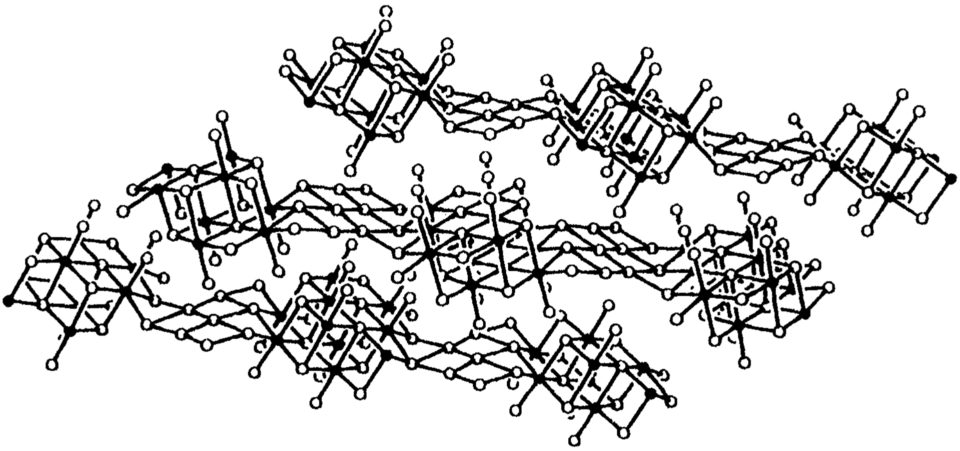

Fig. 32. Computer generated structure of $BaBiSe_3$ showing the tetramers of edge sharing $BiSe_6$ octahedra which form infinite chains, and are connected by layers of planar polyselenides (○, selenium atoms; ●, bismuth atoms; barium atoms not shown) [49b].

this limited development is because this very exciting and potentially enormous field of chemistry has been somewhat neglected. However, there are several legitimate limitations to the full-fledged exploitation of these compounds as ligands.

The high charge density of the simple building blocks such as ES_4^{3-} and ES_3^{3-} (E = P–Bi) leads to a decrease in solubility of both the reagents and the resultant products. Since many of these simple building blocks have only been prepared as alkali metal salts, their solubility in polar organic solvents is low, limiting their potential as ligands to a number of different classes of transition metal starting materials, such as organometallics. Several quaternary ammonium and phosphonium salts of anionic clusters have recently been prepared conveniently, and are already finding use as reagents towards transition metal complexes. Another concern is the instability of the parent acids of the mixed anions. Obviously H_3PO_4 and its partially deprotonated analogs are very stable, and the pH of the reaction solution can be used to control the concentration of charge in solution. However, protonation of PS_4^{3-}, or any of the anionic mixed 15/16 clusters, leads to rapid decomposition to H_2S and neutral binary solids, meaning that only the parent trianions can be used as starting material. This high charge density, and the ability of such building blocks to bridge several metal centers, often means that complexation to a cationic metal center is rapid and uncontrollable, leading to precipitation of insoluble powders. This suggests that ideal metal starting materials should contain several coordination sites which are blocked by ligands stronger than the 15/16 cages. In addition, we have found that the reaction of the traditional building blocks, such as PS_4^{3-} or Schlippe's salt ($Na_3SbS_4{\cdot}9H_2O$), with cationic transition metals suffers from the limitation that metal sulfide bonds are often more stable than main group sulfides. Thus combination of a pentavalent anionic ligand such as PS_4^{3-} with metal salts, often leads to abstraction of sulfide from the ligands. This results in the formation of a trivalent species and precipitation of bulk powders which are predominantly binary metal sulfides. Since the most straightforward reactions, namely those involving alkali metal salts of EQ_4^{3-}, do not appear to provide convenient entry to this field, other more subtle approaches must be sought. Despite the limitations some progress has been made particularly in recent years. A number of novel transition metal complexes containing recognizable 15/16 fragments have been isolated, and the area was briefly reviewed several years ago [76].

5.1. Early transition metal complexes

Many of the most exciting results in this field have been achieved using transition metals on the left side of the d-block. In his seminal paper. Rauchfuss and co-workers demonstrated that the coordination chemistry of polychalcogenides could be extended to three dimensions with the incorporation of a group 15 element [23]. They reported the isolation of a $Cp'_3Ti_2O(AsS_3)$ containing bridging AsS_3^{3-} group starting with solubilized AsS_3^{3-} (Fig. 33):

$$AsS_3^{3-} + 4\ Cp'_2TiCl_2 \xrightarrow{H_2O + \text{acetone}} Cp'_3Ti_2O(AsS_3) \qquad C' = (CH_3)C_5H_4^-$$

This compound contains AsS_3^{3-} bridging across Ti centers using all three sulfides, with the lone pair on the arsenic not involved. It also contains an oxo bridge which could have arisen from the aqueous conditions or silica gel workup. The same product could be obtained in lower yield from the reaction of $Cp'_2Ti(CO)_2$ and As_4S_4. This is an important compound because it demonstrated for the first time that mixed 15/16 anionic molecules could be used as ligands toward transition metals.

In the same paper, these workers were able to show that the neutral cages such as As_4S_4 are also susceptible to attack by metal sulfide anions, just as they are by ordinary sulfides. Thus they found that MoS_4^{2-} readily serves as a nucleophile toward As_4S_4 leading to the formation of a complex structure having the formula $[Mo_2O_2As_4S_{14}]^{2-}$. (Fig. 34):

$$MoS_4^{2-} + As_4S_4 \rightarrow [PPh_4]_2[Mo_2O_2As_4S_{14}]$$

Once again the origin of the oxo group is probably due to adventious water in the workup. This compound, which contains the highly unusual $+As_4S_{12}^{4-}$ chelate, can be obtained in reasonable yield and foretells some of the fascinating chemistry that these ligands can provide.

Recently workers in our laboratories have been able to extend this concept of

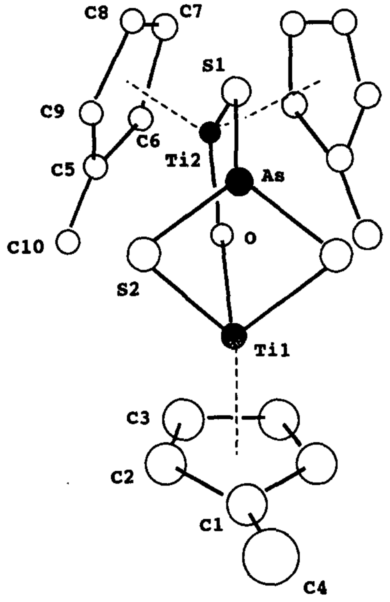

Fig. 33. Thermal ellipsoid view of $Cp'_3Ti_2O(AsS_3)$ showing the bridging AsS_3^{3-} group.

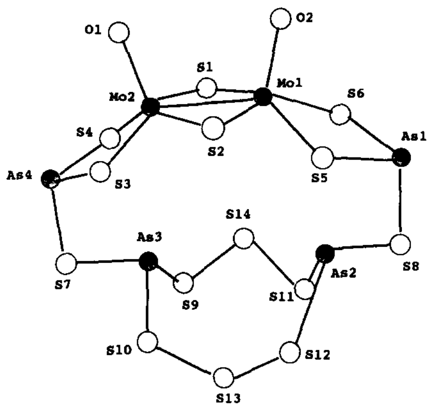

Fig. 34. Thermal ellipsoid view of $[Mo_2O_2As_4S_{14}]^{2-}$ Showing the novel $As_4S_{12}^{4-}$ chelating ligand.

metal centered nucleophiles to reactions involving cages of the heavier main group elements. It was found that WSe_4^{2-} readily attacks P_4Se_4 glass to form the first metal phosphorus selenide complex (Fig. 35) [77]:

$$[PPh_4]_2[WSe_4] + P_4Se_4 \xrightarrow{DMF} [PPh4]_2[Se{=}W(PSe_4)(PSe_2)]$$

This complex can be prepared in very good yield and contains the first reported example of a coordinated PSe_4^{3-} ligand. It also contains the highly unusual side-bonded PSe_2^- group, which is the first heavy element analog to nitrite. Related reactions of $MoSe_4^{2-}$ and WSe_4^{2-} with arsenic selenide cages also lead to a series of novel clusters [78] (Figs. 36 and 37):

$$[PPh_4]_2[WSe_4] + As_4Se_4 \xrightarrow{DMF} [PPh_4]_2[W_2(\mu-Se)_3(AsSe_5)_2]$$

$$[PPh_4]_2[MoSe_4] + As_4Se_4 \xrightarrow{DMF} [PPh_4]_2[Mo(AsSe_5)_2]$$

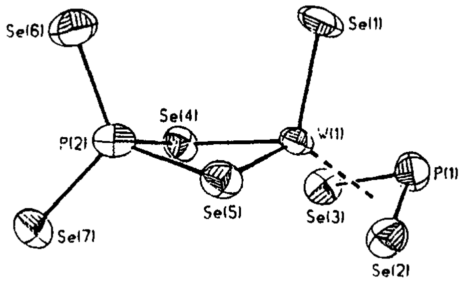

Fig. 35. Thermal ellipsoid view of $[Se{=}W(PSe_4)(PSe_2)]^{2-}$ (reprinted from ref. 77).

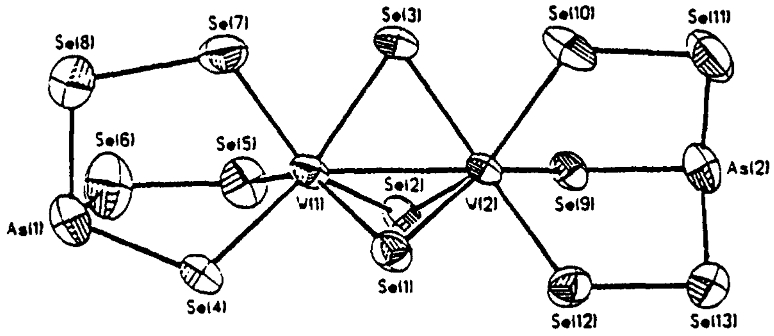

Fig. 36. Thermal ellipsoid view of $[W_2(\mu\text{-Se})_3(AsSe_5)_2]^{2-}$ (reprinted from ref. 78).

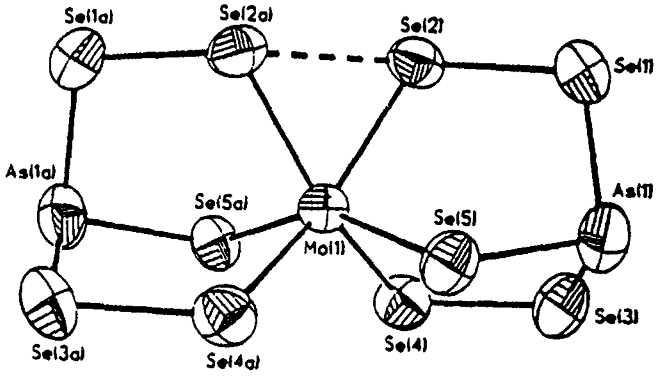

Fig. 37. Thermal ellipsoid view of $[Mo(AsSe_5)_2]^{2-}$ showing the metal coordinated by two $AsSe_5^{3-}$ groups. Note the similarity of the ligands to those in $[W_2(\mu\text{-Se})_3(AsSe_5)_2]^{2-}$ (reprinted from ref. 78).

Both compounds contain two tridentate $AsSe_5^{3-}$ groups as capping ligands. The molybdenum is a monomer with the metal in the 4+ state. However, the tungsten complex is a dimer bridged by three selenides and contains a W(V)–W(V) bond. The W(V) oxidation state presumably reflects the greater tendency of third row elements to achieve a higher valence. All these molecules can be prepared relatively straightforwardly, and there are presumably many such compounds which can be made by related methods.

It was also found that many of the anionic clusters, particularly those whose salts are soluble in polar organic solvents, will react with metal carbonyls to form novel hybrid transition metal main group cage complexes. Most of these complexes are not merely adducts but rather are the result of oxidation of the metal center with concomitant reduction of the main group cage. This oxidative decarbonylation reaction is well known for polychalcogenide chains and metal carbonyls, and has led to an extensive amount of reaction chemistry [79]. It was of interest to see whether this reaction could be extended to main group anions other than polychalcogenides. Indeed it was found that this was the case and a number of new and unusual clusters have been isolated. For example $P_2Se_8^{2-}$ reacts with iron carbonyl to form a dimer containing a bridging PSe_5^{3-} unit [25] (Fig. 38):

$$3Fe(CO)_5 + P_2Se_8^{2-} \xrightarrow{DMF + PPh_4Br} [PPh_4]_2[Fe_2(CO)_4(PSe_5)_2]$$

The PSe_5^{3-} groups bridge across two Fe(II) centers and contain pentavalent phosphorus and, as such, are heavy element analogs of peroxyphosphate. Note that the PSe_5^{3-} has a different structure from that of $AsSe_5^{3-}$, reflecting the increased tendency of P to assume a pentavalent state.

Anionic arsenic selenide cages will also induce oxidative decarbonylation in transition metal carbonyls. It was found that the nature of the arsenic selenide cage directly affects the identity of the product. Thus $As_2Se_6^{2-}$ reacts with $M(CO)_6$ to form $[M(AsSe_5)_2]^{2-}$, which is the same compound obtained from $MoSe_4^{2-}$ and As_4Se_4 (Fig. 37). In this case the metal center has been clearly oxidized from a zero valent state to M(IV) [80]. In contrast, $As_4Se_6^{2-}$ leads to the formation of $[M(CO)_2(As_3Se_3)_2]^{2-}$ in good yield (Fig. 39). This product contains a metal center coordinated by two As_3Se_3 fragments as well as two CO ligands:

$$M(CO)_6 + As_2Se_6^{2-} \xrightarrow{DMF + PPh_4Br} [PPh_4]_2[M(AsSe_5)_2] \qquad M = Mo, W$$

$$M(CO)_6 + As_4Se_6^{2-} \xrightarrow{DMF + PPh_4Br} [PPh_4]_2[M(CO)_2(As_3Se_3)_2] \qquad M = Mo, W$$

The metal centers are in an eight-coordinate face-capped trigonal prismatic coordina-

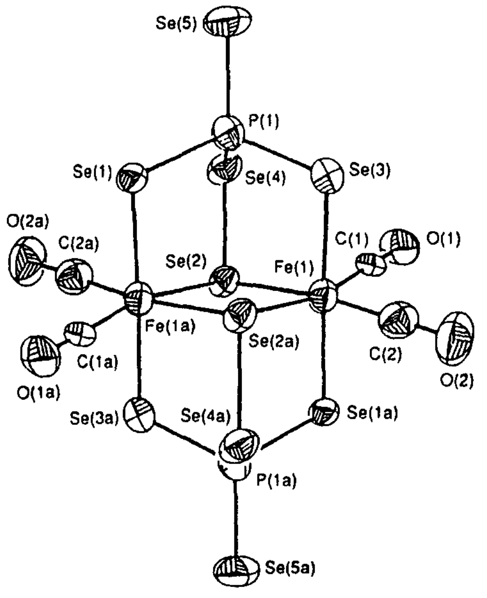

Fig. 38. Thermal ellipsoid view of $[Fe_2(CO)_4(PSe_5)_2]^{2-}$ highlighting the two bridging PSe_5^{3-} units (reprinted from ref. 25).

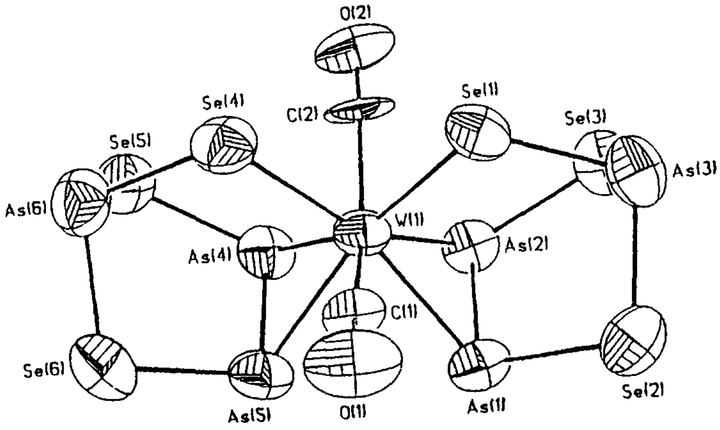

Fig. 39. Thermal ellipsoid view of $[M(CO)_2(As_3Se_3)_2]^{2-}$ showing the transition metal replacing a basal As vertex of the birdcage structure (reprinted from ref. 80).

tion environment, with the two CO ligands serving as face-capping ligands. In this case the formal oxidation states are not so easily defined, and the metal can best be thought of as a vertex of a main group bird cage. In addition, the carbonyl-containing product can be converted quantitatively to $[M(AsSe_5)_2]^{2-}$ on reaction with red selenium.

Recently we have extended the oxidative decarbonylation reaction of arsenic selenide cages to iron carbonyl as well. It was found that $As_4Se_6^{2-}$ reacts cleanly with $Fe(CO)_5$ to form a monomer containing a seven coordinate iron center bound to two As_3Se_3 fragments and a CO ligand [81] (Fig. 40):

$$Fe(CO)_5 + As_4Se_6^{2-} \xrightarrow{DMF+PPh_4Br} [PPh_4]_2[Fe(CO)As_3Se_3)_2]$$

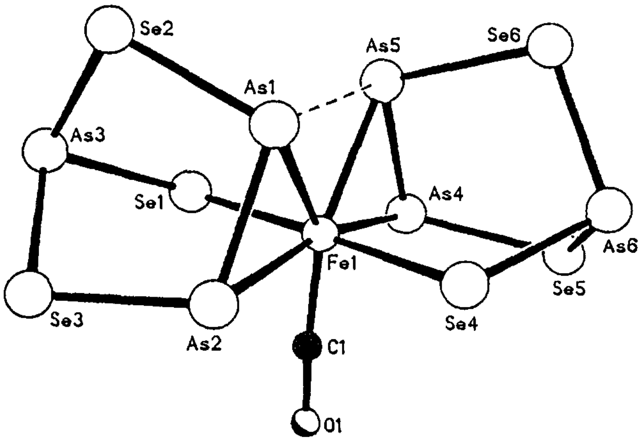

Fig. 40. Thermal ellipsoid view of $[Fe(CO)(As_3Se_3)_2]^{2-}$ [81].

Thus metal carbonyls have demonstrated their willingness to form novel cage structures with the mixed 15/16 cluster anions. We think it is important that the anionic starting materials be soluble and stable in solvents that are compatible with organometallic complexes, namely polar aprotic solvents such as DMF. Since the preparative routes to such anionic salts have been increasing recently, this opens the door for further exploration of transition metal mixed cage chemistry. Given the precedence of the rich chemistry of the metal carbonyls and polychalcogenides, the reaction of main group anions and metal carbonyls should be a major source of new clusters in the near future.

There have also been several interesting metal complexes containing organo-functionalized 15/16 fragments. For example, WS_4^{2-} reacts with $PhPCl_2$ to form $[W_2S_4(S_2(S)PPh)_2]^{2-}$ containing two $PhPS_3^{2-}$ groups [82] (Fig. 41). This type of ligand is intermediate between the very common $R_2PS_2^-$ and the surprisingly rare PS_4^{3-} group. Similarly the reaction of perthiophosphinic anhydride, $R_2P_2S_4$, with neutral Cp titanium compounds yields compounds with coordinated RPS_3^{2-} groups [83] (Fig. 42):

$$Cp_2Ti(CO)_2 + R_2P_2S_4 \rightarrow Cp_2Ti(S_3PR) + Cp_2Ti(R_2P_2S_4)$$

DiMaio and Rheingold were able to extend their work with homoarsenacycles to organo-functionalized heterocycles, leading to several novel molybdenum complexes [84] (Figs. 43 and 44):

$$\textit{cyclo}\text{-}(CH_3As)_5 + S_8 + Mo(CO)_6 \xrightarrow{\text{toluene, 110°C}} [Mo(CO)_3(CH_3As)_6S_3]$$

$$(CH_3AsS)_n + Cp_2Mo_2(CO)_6 \xrightarrow{\text{toluene, 125°C}} Cp_2Mo_2As_4S \qquad n = 3,4$$

The carbonyl compound contains an unusual nine-membered arsenic sulfide ring coordinated to the $Mo(CO)_3$ fragment through the arsenic rather than the sulfur atoms. The Cp compound is a dimer bridged by an As_3 group as well as a side-bonded AsS group. Both ligands have lost all of their alkyl groups during the reaction. This suggests that neutral organo-functionalized complexes could be suitable starting materials for formation of hybrid main group–transition metal com-

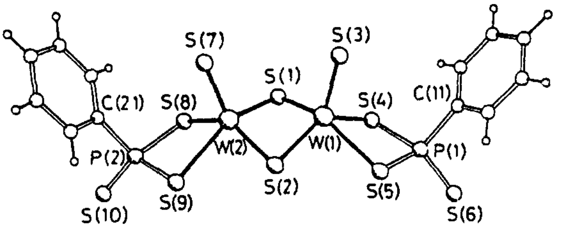

Fig. 41. Thermal ellipsoid view of $[W_2S_4(S_2(S)PPh)_2]^{2-}$ showing the two chelating $PhPS_3^{2-}$ groups (reprinted from ref. 82).

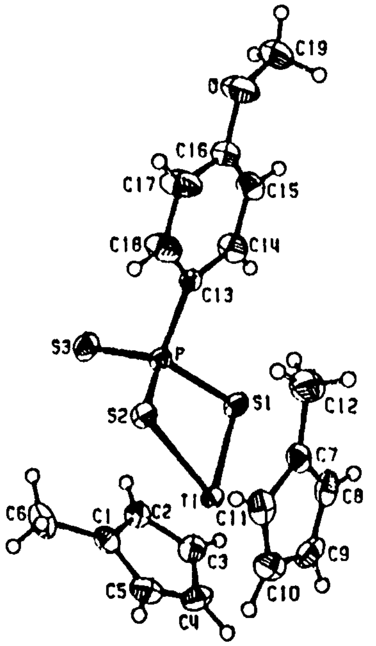

Fig. 42. Thermal ellipsoid view of $Cp_2Ti(S_3PR)$ (reprinted from ref. 83).

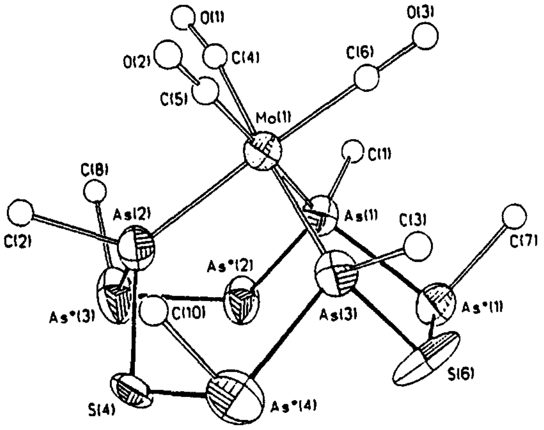

Fig. 43. Thermal ellipsoid view of $[Mo(CO)_3(CH_3As)_6S_3]$ (reprinted from ref. 84).

plexes. This is an enticing prospect since there are a large number of stable organofunctionalized 15/16 complexes and the synthetic routes to such species are well known. The neutral species are often reasonably stable and soluble in a variety of solvents eliminating many of the potential shortcomings of the anionic clusters (vide supra).

Most of the remainder of the known transition metal complexes of mixed 15/16

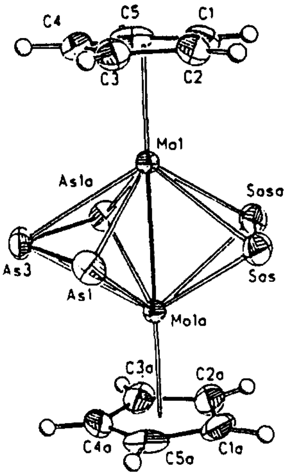

Fig. 44. Thermal ellipsoid view of $Cp_2Mo_2As_4S$ (reprinted from ref. 84).

cages can best be considered as adducts of neutral parent cages such as P_4S_3. Thus one of the first papers in this area reports the formation of a metal carbonyl complex with two intact P_4S_3 cages as ligands [85]:

$$C_7H_8M(CO)_4 + P_4S_3 \rightarrow (CO)_4M(P_4S_3)_2 \qquad M = Cr, Mo, W$$

This reaction was later extended to include the complexes containing only one cage ligand using a similar synthetic pathway [86] (Fig. 45):

$$Mo(CO)_6 + P_4S_3 \xrightarrow{\Delta} (CO)_5Mo(P_4S_3)$$

Both complexes contain the intact cage coordinated through the apical phosphorus atom. No further reaction chemistry was reported with these molecules, but their robustness suggests that they may be useful precursors to other metal main group hybrid clusters. In contrast to the above behavior, reaction of neutral As_4S_4 with unsaturated $Cp^*_2Mo_2(CO)_4$ leads to fragmentation of the main group cage and isolation of a number of arsenic sulfide metal complexes [87]:

$$Cp^*_2Mo_2(CO)_4 + As_4S_4 \rightarrow Cp^*_2Mo_2(CO)_4(As_2)$$
$$+ Cp^*Mo(CO)(As_3) + Cp^*_2Mo_2(As_2S)(S_2)$$

This is a mixture of complexes which must be separated and this type of fragmentation reaction is much more typical of the reaction chemistry of these neutral cages.

5.2. Late transition metal complexes

The predominant reaction type of main group clusters and the later transition metals is the combination of neutral cages with unsaturated metal complexes. This

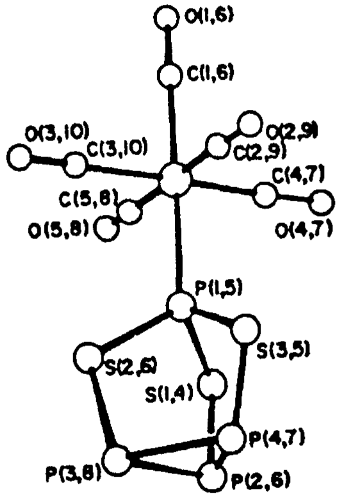

Fig. 45. Thermal ellipsoid view of $(CO)_5Mo(P_4S_3)$ highlighting the P_4S_3 cage coordinated through the apical P atom (reprinted from ref. 86).

usually results in substantial fragmentation of the main group cage with stabilization of smaller fragments by the metal center. However, these complexes often contain recognizable mixed 15/16 fragments. The majority of work done in this field was performed by DiVaira and co-workers who have fully explored reactions involving P_4X_3 ($X = S$, Se) and low valent, later transition metals. They exploited the technique of blocking most of the available coordination sites of the metal using a bulky tridentate ligand such as triphos (p3) or *tris*(2-diphenylphosphinoethyl)amine (np3) [88]. By inhibiting runaway polymerization reactions, they were able to isolate a number of very interesting metal main group hybrid cages. Reaction of $np3Ni^{2+}$ with P_4X_3 leads to isolation of a simple metal complex $np3Ni(P_4X_3)^{2+}$ containing an intact P_4X_3 group coordinated through the apical phosphorus atom, as expected [89]. However, when the reaction is extended to Co(II) salts in the presence of various tripodal ligands, the product is invariably the result of fragmentation of the cage with stabilization of a tri-coordinated three-membered heterometallic ring [90] (Fig. 46):

$$Co(BF_4)_2{\cdot}6H_2O + \text{triphos} + P_4X_3 \rightarrow [(p3)Co(\eta^3 - P_2X)]^+ \qquad X = S, Se$$

$$Co(BF_4)_2{\cdot}6H_2O + \text{triphos} + As_2X_3 \rightarrow [(p3)Co(\eta^3 - As_2X)]^+ \qquad X = S, Se, Te$$

Each of these complexes is a monocation with the three-membered ring bound symmetrically to the metal center, and is usually disordered. Since the tridentate phosphine ligands are invariably neutral, the Co center can be formally assigned to Co(III) state with the ligand assigned a dianonic charge, making it an electron precise six-electron donor. These coordinated three-membered rings can still undergo

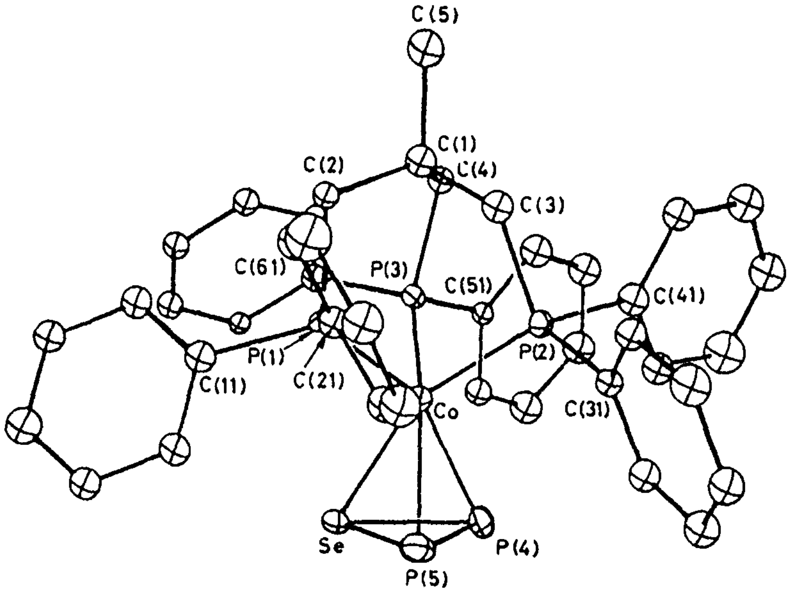

Fig. 46. Thermal ellipsoid view of $[(p3)Co(\eta^3-P_2X)]^+$ (X=S, Se) (reprinted from ref. 90).

further complexation in the presence of other cationic metal centers [91] (Fig. 47):

$[(p3)Co(P_2S)]^+ + [Rh(p3)]^+ \rightarrow [(p3)Co(P_2S)Rh(p3)]^{2+}$

If metal complexes other than those containing tripodal ligands are used, the chemistry changes dramatically. The metal centers tend to insert into the cage framework creating unusual new metal-containing hybrid clusters. For example, if Vaska's complex or $Pt(C_2H_4)(PPh_3)_2$ is reacted with P_4S_3, dimers can be isolated which contain P_4S_3 bridging groups [92,93] (Fig. 48):

$Ir(CO)Cl(PPh_3)_2 + P_4S_3 \rightarrow [Ir(CO)Cl(PPh_3)(\mu\text{-}P_4S_3)]_2$

$Pt(C_2H_4)(PPh_3)_2 + P_4S_3 \rightarrow [Pt(PPh_3)_2(\mu\text{-}P_4S_3)]_2$

However, in each of the above molecules, the metal center has effectively inserted into a basal P–P bond. Thus an oxidative addition has taken place at the metal center, which of course is not unexpected for these metal complexes. One of the coordinated phosphorus atoms also has a lone pair coordinated to another metal center, creating the bridging interaction. When P_4S_3 is reacted with unsaturated Rh(I) complexes in the presence of triphos, a vertex replacement reaction is observed [94] (Fig. 49).

$P_4S_3 + RhCl(COD) + p3 \rightarrow p3Rh(P_3S_3)$

In this case, the main group birdcage structure essentially remains intact, but the transition metal center has replaced one of the basal phosphorus atoms and inserted

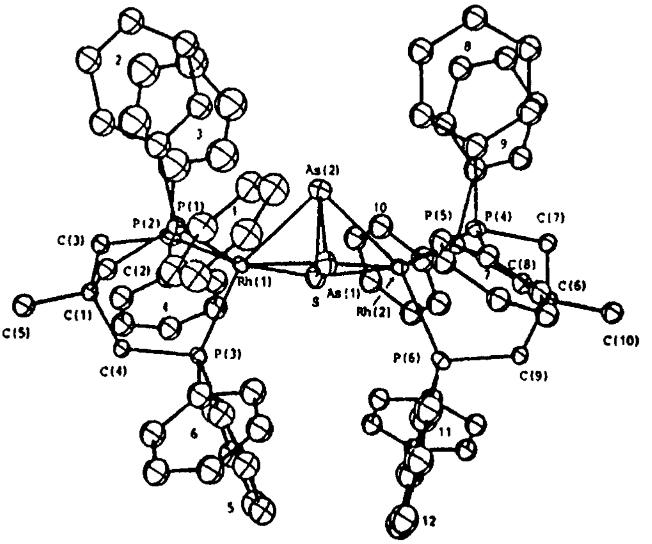

Fig. 47. Thermal ellipsoid view of $[(p3)Co(P_2S)Rh(p3)]^{2+}$ showing the P_2S group acting a ligand toward two metal centers (reprinted from ref. 91).

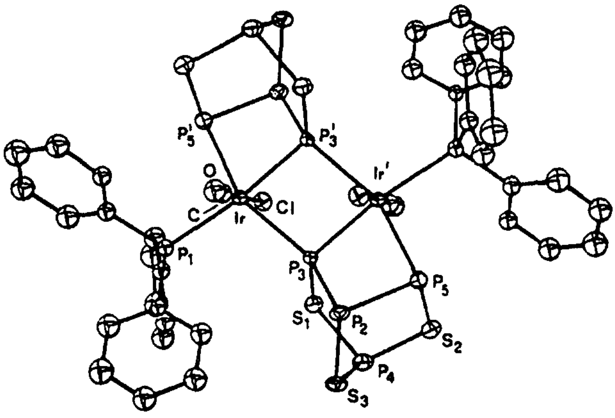

Fig. 48. Thermal ellipsoid view of $[Ir(CO)Cl(PPh_3)(\mu\text{-}P_4S_3)]_2$ highlighting the bridging P_4S_3 group. Note the insertion of the transition metal center into a basal P–P bond (reprinted from ref. 92).

itself into the main group cage. Note that this framework is similar to the metal arsenic selenide cage in $[M(CO)_2(As_3Se_3)_2]^{2-}$ mentioned previously. This sort of behavior, whereby the main group cage largely stays intact but acts as a non-innocent ligand, is reminiscent of the polychalcogenide anions, implying that a large amount of exciting chemistry awaits discovery in these systems.

There are several examples of a neutral binary reacting with an unsaturated late transition metal complex. Probably the first report was that of Nixon and

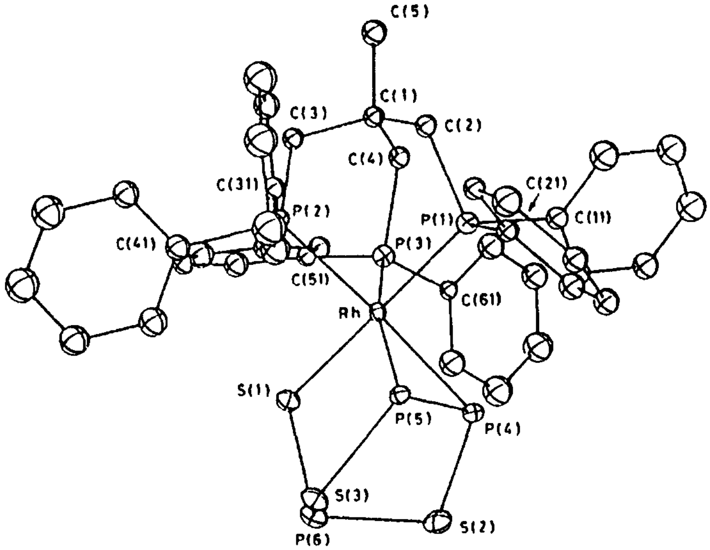

Fig. 49. Thermal ellipsoid view of p3Rh(P_3S_3) showing the replacement of one of the basal phosphorus vertices with a transition metal center (reprinted from ref. 94).

co-workers who briefly described a nickel complex [85]:

$$Ni(C_3H_5)_2 + P_4S_3 \rightarrow Ni(P_4S_3)_4$$

Later, a number of unsaturated metal Cp complexes were prepared using As_4S_4, and a Cp cobalt was fully characterized [95] (Fig. 50):

$$Cp^*{}_2Co_2(CO)_4 + As_4S_4 \rightarrow Cp^*{}_2Co_2As_2S_3$$

The cobalt complex was activated by photolysis and the formally unsaturated Co=Co complex reacted with As_4S_4 to generate a cage linked by an As_2S_3 group.

The more straightforward reactions involving simple alkali metal salts of anionic clusters have not proven to be a satisfactory route to soluble late metal complexes thus far. The high charge density and multitudinous coordination sites of the clusters generally lead to insoluble bulk solids on direct reaction. Sometimes this results in the formation of useful products as shown below [96]:

$$M^{2+} + \tfrac{1}{2}P_2S_6^{4-} \rightarrow NiPS_3 \qquad M = Ni, Zn, Co, Pb \text{ etc.}$$

However, without other ligands to block some of the coordination sites, uncontrolled polymerization is the most common reaction. Another problem which plagues this type of reaction is that the late transition metals also tend to abstract sulfides or selenides from the main group cluster, leading to simple metal sulfides. These problems are certainly solvable with some ingenuity on the part of the synthetic chemist, and the rewards should be substantial, particularly given the enormous chemistry of the late metal sulfides and selenides as precedent.

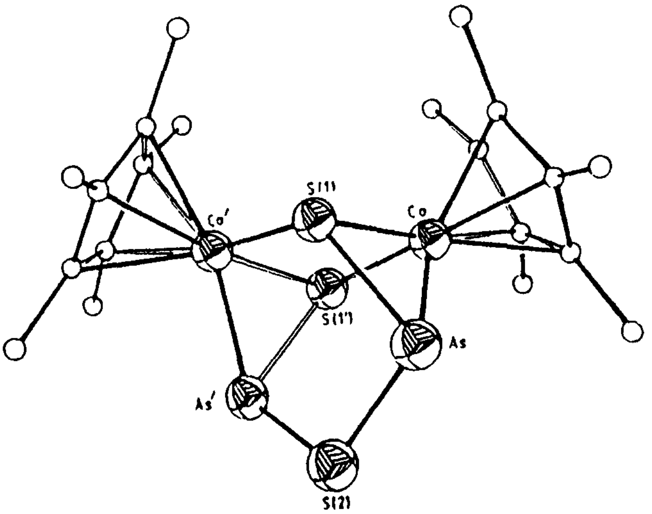

Fig. 50. Thermal ellipsoid view of $Cp^*_2Co_2As_2S_3$ showing the As_2S_3 chain chelating to two Cp*Co centers (reprinted from ref. 95).

6. SUMMARY AND OUTLOOK

The mixed 15/16 anionic clusters have a very long history. For example Schlippe's salt ($Na_3SbS_4{\cdot}9H_2O$) was first reported in 1821 [14]. However, their subsequent reaction chemistry has been largely ignored. One reason for this lack of attention has been a certain amount of experimental difficulty in working with these compounds, but for the most part this class of compounds simply has not received a great deal of attention. This is unfortunate as the anionic 15/16 clusters are fascinating compounds which can be prepared and handled quite easily. The alkali metal salts of the simple building blocks, such as the tetrahedral thioanions, can be made by a number of simple routes, but are not really convenient reagents for a number of reasons described in this review. However, these difficulties can be overcome with some experimental creativity. New synthetic routes to soluble anions are emerging, providing new starting materials for exploration. In particular, the new preparations of salts which are soluble in polar organic solvents is beginning to allow for the systematic development of reaction chemistry. Despite some of the exciting results highlighted in this article, the surface has been barely scratched. Many of the most fundamental reactions involving the soluble molecular anions have not been carried out.

The solid state area has seen substantial progress in the last few years. The melt reactions involving s-block elements and various group 15 and 16 elements have been systematically and completely investigated, particularly by the workers at Darmstadt, with an enormous volume of elegant results. Low temperature reaction techniques have proven to be a boon for this area. By performing the same reactions in superheated solvents rather than the melt, entirely new classes of compounds have been reported in the last several years. These superheated solvents show enormous promise since they provide the experimental variability of solution chemistry in the production of solid state compounds. Thus new electronic materials, such as ionic conductors, and structural materials, such as microporous solids, can be systematically synthesized and investigated. Finally, the last ten years has seen the beginnings of the use of these 15/16 anions as ligands towards a number of transitional metal complexes. The incorporation of transition metals into metal frameworks has led to some potentially useful new solids, as well as some very exciting structures which strain current concepts of structure and bonding. The synthetic approaches must be somewhat subtle, but a number of new reaction types are emerging. The use of soluble main group clusters with low valent metal complexes such as organometallics is particularly promising, and initial results are very exciting. Similarly, the use of nucleophilic transition metal centers with neutral main group cages has yielded some very exciting results. We feel that both of these pathways are ripe for further development and have in no way been fully exploited. Thus it is felt that these exciting anionic 15/16 clusters are laden with potential for new chemistry both in solution and in the solid state.

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